STARTUP CHARACTERISTICS OF POLYMER ELECTROLYTE FUEL CELLS UNDER SUBZERO TEMPERATURES

A Dissertation in
Mechanical Engineering

by

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Abstract

Cold start capability and survivability of polymer electrolyte fuel cells (PEFCs) in a subzero temperature environment remain a challenge for automotive applications. Fundamental mechanisms governing cold start are not fully understood, although it is recognized that product water becomes ice or frost upon startup when PEFC internal temperature is below the freezing point of water. If the local pore volume of the cathode catalyst layer (CL) is insufficient to contain all of the accumulated water before cell operating temperature rises above freezing, ice may plug the CL and stop the electrochemical reaction by starving it of the reactant gases.

In this dissertation the characteristics of PEFC cold start are experimentally studied in three parts, as follows. In part one the cold start capability and characteristics of the PEFC are investigated, introducing the concept of isothermal cold start. For this study two methods of gas purge are used to generate the initial conditions prior to cold start. The first method is to precisely control the cell internal condition to examine the intrinsic capability of the membrane and electrode assembly (MEA), although the purge procedure to generate this condition is not practical for vehicular application. The second is designed to simulate realistic operation in a fuel cell vehicle, but is less controllable, and less efficient with respect to cold start performance. In both cases, it is found that the membrane water absorption during cold start is important for better cold start performance, and therefore the initial condition with low membrane water content is crucial.
In part two, the gas purge process is elucidated. Gas purge is an integral part of the PEFC shutdown process, and this process determines the initial conditions of the eventual cold start. To investigate purge effectiveness, the experimental procedure to provide excellent repeatability is first developed. Introducing two characteristic parameters for purge effectiveness which represent the through-plane diffusive flux of water vapor from the CL to gas channels, and the in-plane convective flux of water vapor through the gas channels, respectively, it is found that the cell high frequency resistance after 60 second purge can be uniquely determined by these two parameters.

Part three provides a method to measure the time- and space-resolved water distribution along the gas channels. Purge effectiveness decreases as the purge gas flows down the channel because of the increasing water vapor pressure. Therefore, in order to develop a time-saving, energy-efficient purge protocol for vehicular applications, it becomes imperative to capture the spatial distribution of purge effectiveness. Measurement of local high frequency resistance (HFR) is non-trivial, because the imposed AC current can travel in-plane through the gas diffusion layers (GDLs) and pass across the membrane in the adjacent regions. In this study, we developed a novel method to estimate the local HFR during gas purge, and obtained the transient local HFR distribution data during gas purge.

These three sections form a comprehensive study of cold start capability and provide a route to prediction of cold start performance.
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List of Symbols

\( A \)  fuel cell active area
\( a \)  activity
\( c_{f,dry} \)  molar concentration of electrolyte phase
\( D \)  diffusion coefficient
\( E_h \)  thermodynamic equilibrium potential
\( F \)  Faraday’s constant
\( I \)  current
\( M_{H_2O} \)  molecular weight of water
\( m_{CL} \)  weight of water in catalyst layer
\( m_{H_2O} \)  weight of product water
\( p_{v,inlet} \)  inlet vapor pressure
\( p_{v,sat} \)  saturation vapor pressure
\( Q \)  volumetric flow rate
\( R \)  universal gas constant
\( T \)  temperature
\( V \)  cell voltage

**Greek Letters**

\( \Delta \lambda \)  membrane water uptake potential, \( \lambda_{sat} - \lambda_i \)
\( \delta_{CL} \)  catalyst layer thickness
\( \delta_{GDL} \)  gas diffusion layer thickness
\( \epsilon \)  porosity
\( \epsilon_e \)  porosity of electrolyte phase
\( \zeta_c \)  convective flux of water vapor
\( \zeta_d \)  diffusive flux of water vapor
\( \kappa_c \) membrane proton conductivity

\( \lambda \) water content in membrane

\( \lambda_{\text{sat}} \) water content of a fully hydrated membrane

\( \lambda_i \) initial water content

\( \rho_{\text{ice}} \) ice density

**Acronyms**

BP bipolar plate

CC current collector

CCM catalyst coated membrane

CFD computational fluid dynamics

CL catalyst layer

DSC differential scanning calorimeter

ECA electrochemical active area

EIS electrochemical impedance spectroscopy

EOD electro-osmotic drag

FCV fuel cell vehicle

FRP fast rise period

GDL gas diffusion layer

HFR high frequency resistance

MEA membrane and electrode assembly

MEP membrane equilibration period

MPL microporous layer

NMR nuclear magnetic resonance

OCV open circuit voltage

ORR oxygen reduction reaction

PEFC polymer electrolyte fuel cell

PFSA perfluorosulfonic acid

RH relative humidity

SRP slow rise period
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A special thanks is given to my wife for all her love, support, and encouragement, and finally, great thanks are given to my son who has brought extra joy into my life.
1.1 Cold Start of Polymer Electrolyte Fuel Cells

Polymer electrolyte fuel cell (PEFC) systems are considered a favorite among alternative automotive power sources, and have been studied extensively in the past 20 years. For automotive applications, however, an intrinsic problem remains to be solved, which is the cold-start capability, or startup of the fuel cell system under very low ambient temperature such as -20 or $-30^\circ$C. Arita (1) reported the technical difficulties of the fuel cell vehicle (FCV), including cold start.

In the discharge operation of PEFCs, the following reactions occur in the anode and cathode electrodes, respectively.

\[ \text{H}_2 \rightarrow 2\text{H}^+ + 2e^- \quad (1.1) \]

\[ 2\text{H}^+ + 2e^- + \frac{1}{2}\text{O}_2 \rightarrow \text{H}_2\text{O} \quad (1.2) \]

Thus, water is produced by this operation. If the produced water remains in the cathode catalyst layer (CL), it blocks oxygen transport from the gas channel to the catalyst, and cell operation stops. Therefore, the unnecessary water must be removed from the catalyst layer in order to secure the oxygen transport. Under ordinary operating temperature ($\sim 80^\circ$C) the water is removed in the vapor phase, and in the liquid phase because
of capillary forces. However, at subfreezing temperatures, vapor phase transport is not
effective because of small saturation vapor pressure, and liquid phase removal is negligible
because the liquid water immediately changes to ice. As a result, most of the produced
water remains in the catalyst layer and terminates cell operation.

1.2 Literature Review

1.2.1 Studies on PEMFC at normal temperature

A large number of studies have reported on the PEFC at temperatures above the
freezing point and the number of publications increases yearly. From this wide range of
research, that most closely related to PEFC cold start will be reviewed here.

1.2.1.1 Early research on PEFC

One of the earliest studies in modern fuel cell research was reported by Ticianelli
et al. (99). They developed an advanced method to fabricate the MEA with very low
platinum loading of $\sim 0.4\text{mg/cm}^2$, and analyzed cell performance with polarization
curves as well as cyclic voltammetry. This report can be considered a milestone among
modern PEFC studies, and has often been used as benchmark data for later studies.

Parthasarathy et al. investigated the oxygen reduction reaction (ORR) in the
cathode CL experimentally in their series of studies (74)(75)(76)(77). First they mea-
sured the concentration and diffusion coefficient of oxygen in Nafion, and the electrode
kinetic parameters for the ORR (75). In this report they discussed the two-section Tafel
plot with slopes of $\sim 60\text{mV/decade}$ and $\sim 120\text{mV/decade}$. Second, they studied the
ORR characteristics under low humidification using electrochemical impedance spectroscopy (EIS) (74). Third, they studied temperature effect on the ORR in the range of 30°C to 80°C to find that while the Tafel slope linearly increased with temperature increase in the low current density region, the slope was independent in the high current density region (77). Then, they investigated the dependence of ORR kinetics on oxygen pressure, and found that the reaction order with respect to oxygen was unity at both high and low current densities (76).

Bernardi and Verbrugge (4) developed a one-dimensional mathematical model to simulate the cathode electrode, focusing on the cell polarization characteristics, water transport, and catalyst utilization, and evaluated the contribution of ohmic loss and cathode activation loss. Next, they extended their model to include the anode catalyst layer (5). With this model they calculated the O₂ limiting current density as a function of cathode gas porosity, concentration distribution in the through-plane direction, and compared the model results with the experiment reported by Ticianelli et al. (99).

Springer et al. (88) developed an isothermal, one-dimensional, steady-state model. With this model they estimated net water flux was 0.2H₂O/H⁺, much less than the measured electro-osmotic drag coefficient. It is considered that the most important contribution of this study is the measurement of Nafion membrane properties such as water uptake and proton conductivity, which have been utilized in many later studies.

\[
\lambda = \begin{cases} 
0.043 + 17.81a - 39.85a^2 + 36.0a^3 & \text{for } 0 < a \leq 1 \\
14 + 1.4(a - 1) & \text{for } 1 \leq a \leq 3 
\end{cases} \quad (1.3)
\]
\[ \kappa_e = \exp \left[ 1268 \left( \frac{1}{303} - \frac{1}{T} \right) \right] (0.005139 \lambda - 0.00326) \]  

(1.4)

where \( \lambda \) is a water content in the membrane, \( a \) is water activity, \( \kappa_e \) is a membrane proton conductivity in S/cm, and \( T \) is temperature in Kelvin. In a later study (87) they extended the model to include the losses caused by the interfacial kinetics at the Pt-ionomer interface, mass transport limitation in CL, and gas transport limitation in the gas diffusion layer (GDL). Comparison of model experimental results shows that their model predicted the effect of cathode gas composition well.

### 1.2.1.2 Water and thermal management

Because perfluorosulfonic acid (PFSA) membrane needs water to transport the proton, the membrane must be in a wet condition during operation as well as during storage. On the other hand, when excess liquid water exists in the cathode CL, the oxygen transport is blocked, although water is always produced by ORR. Thus, it is critical to maintain the optimal condition in terms of water amount and distribution in the fuel cell, termed water management. The issue of water management is inevitable in PEFC operation. In addition, since the saturation vapor pressure and other physical/chemical properties are functions of temperature, the thermal management and water management cannot be decoupled. For those reasons, numerous studies are reported on these subjects.

Ren et al. (80) experimentally determined the electro-osmotic drag (EOD) coefficient, using a direct methanol fuel cell. The measured EOD coefficient increased with temperature, from \( 2.0 \text{H}_2\text{O}/\text{H}^+ \) at \( 15^\circ \text{C} \) to \( 5.1 \text{H}_2\text{O}/\text{H}^+ \) at \( 130^\circ \text{C} \).
Buchi and Srinivasan (9) explored the possibility of fuel cell operation without external humidification. With the counter flow configuration for \( \text{H}_2 \) and air, the experiments showed that up to 60\(^\circ\)C the cell endured long-term operation with dry gases with 20 to 40\% lower current density at 0.6V, compared to performance with fully humidified gases.

Wood et al. (117) studied a fuel cell with interdigitated flow field and direct liquid water injection to the anode. In the interdigitated flow field the gas inlet channels and the outlet channels are not directly connected, and the reactant gases are forced to flow through the GDL. Therefore, the diffusion distance becomes shorter than the conventional flow field, which is expected to improve the performance. In this study they used the interdigitated flow field in conjunction with direct liquid water injection instead of humidifying the gases, and verified the performance improvement.

Bellows et al. (3) used neutron radiography to measure the through-plane water distribution in the membrane. The results showed qualitative agreement with the expected response against the changes of feed gas humidification and current density. However, the quantitative interpretation was limited in the neutron radiographic measurement at this time.

Buchi and Scherer (8) measured the transversal water distribution in the Nafion membrane by combining several Nafion membranes and inserting Pt-wire electrodes between the membranes. The results showed that membrane resistance was high at the anode side and the anode side resistance increased with current density, whereas the other region (center and cathode side) had no significant change.
Yang et al. (119) and Zhang et al. (128) visualized liquid water movement in the cathode gas channels using a transparent cell. They observed the emergence of droplets from the GDL surface only at preferential locations, and two modes of water removal from the GDL surface: droplet detachment by the shear force of the core gas flow, and capillary wicking onto the more hydrophilic channel walls.

1.2.1.3 Membrane characterization

The Nafion membranes (PFSA membrane produced by the E. I. DuPont company) are often used as an electrolyte for PEFC. However, this is not the only application of Nafion. In fact, it has been widely used for membrane chlor-alkali cells or water electrolyzers (27), and a literature search by DuPont library estimated that more than 30,000 papers and patents exist (61). In this section recent studies specifically for PEFC application at normal temperatures (above freezing point) are reviewed. The characteristics of PFSA membranes at subzero temperatures will reviewed later in this chapter.

Zawodzinski et al. (124)(125)(126)(127) measured various properties of PFSA membranes such as Nafion and Dow membranes. They measured the membrane water uptake, diffusion coefficient, conductivity, and EOD coefficient at 30°C as functions of membrane water content, and found from the contact angle measurement that the surface of PFSA membrane was quite hydrophobic even when exposed to saturated water vapor. In addition, they found the EOD coefficient was $2.5\text{H}_2\text{O}/\text{H}^+$ for liquid-equilibrated membranes and $1.0\text{H}_2\text{O}/\text{H}^+$ for vapor-equilibrated membranes, independent of the membrane water content. Their Nafion property data have been widely used in later studies.
Hinatsu et al. (28) measured the water uptake of PFSA membranes from liquid water at the temperature range 25 to 130°C, and from water vapor at 80°C. The uptake from liquid water increased with temperature, while the uptake from water vapor at 80°C was less than that for the lower temperature.

Motupally et al. (68) measured the water diffusivity in Nafion 115 and obtained the following expressions for the Fickian diffusion coefficient,

\[
D_{W,F} = \begin{cases} 
3.10 \times 10^{-3} \lambda (-1 + e^{0.28\lambda}) \exp(-2436/T) & \text{(for } 0 < \lambda \leq 3) \\
4.17 \times 10^{-4} \lambda (1 + 161e^{-\lambda}) \exp(-2436/T) & \text{(for } 3 \leq \lambda < 17) 
\end{cases}
\]

where \(\lambda\) is water content and \(T\) is temperature in Kelvin.

The studies on the ionic conductivity of the Nafion membrane were reviewed by Slade et al. (86).

1.2.1.4 Fuel cell diagnostics

In-plane current distribution. — In order to investigate the in-plane distribution of the various parameters, a segmented cell or similar method is often used, and several techniques are proposed to measure the local current. Cleghorn et al. (17) used a printed circuit board technique to segment the current collector and flow field of a 100cm² cell. With this configuration of the segmented cell they studied the effects of gas humidity and the flow rate of air on the current density. Stumper et al. (91) compared three different techniques to measure the current density distribution: the partial MEA method, subcell method, and current mapping method. Wieser et al. (116) proposed a method of using a
magnetic loop array to measure current distribution in a 600cm\(^2\) cell, but no investigation of the fuel cell was presented in this paper.

Mench et al. (63)(64)(65) measured current distribution using a multichannel potentiostat, and also the species distribution in the flow channel using a gas chromatograph, simultaneously. These detailed data were not only helpful for fundamental understanding, but are also useful for verification of the analytical/numerical models. Yang et al. (120) used the same technique to determine the current and species distributions in low humidity operation of a fuel cell. With a simple mass balance analysis, they showed that the net water transport coefficient ranged between 0.05 and 0.3 even under very dry cathode conditions.

Mass transfer limitation. — Decomposition of overpotentials is a useful method widely used to analyze FC performance. The losses of fuel cells can be broken down into roughly three components: ohmic overpotential, activation overpotential, and concentration overpotential. Determination of each component is reviewed by Kocha (45) and Gasteiger et al. (21).

On the mass transport phenomena there are several reports proposing methods to determine the mass transport limitation, especially in the cathode electrode. Perry et al. (79) developed a porous catalyst agglomerate model for both liquid electrolyte and polymer electrolyte. They derived asymptotic solutions for their model in four different regimes and concluded that two distinct double Tafel slopes result from mass transport restrictions. Based on their model result they suggested that the use of cathode gas with different oxygen concentration would help to determine the limiting factors of mass transport.
Makharia et al. (58) reported a method to measure the catalyst layer electrolyte resistance using electrochemical impedance spectroscopy and data fitting to the model. They also reported that although the 1kHz high frequency impedance was interpreted as membrane resistance, the resistance could include contribution from the electrolyte in the catalyst layer.

Stumper et al. (92)(93) developed a method to measure oxygen diffusivity in the catalyst layer. In their method the fuel cell under galvanostatic discharge operation experienced an abrupt cessation of oxygen gas supply by shutting off the inlet and outlet valves, and the resulting potential profile was used to estimate the diffusivity.

Lindbergh’s group has reported a series of studies on mass transport (35)(37)(38)(39). Jaouen et al. first developed a steady state, one-dimensional, isothermal, single phase, agglomerate model for the cathode catalyst layer and GDL to simulate the oxygen diffusion and proton migration (38), and this model is validated with experimental results (35). Then, Jaouen et al. modified their model to the transient version (37). The transient model is used to simulate the response to the current interruption and EIS, and also validated with the experimental results (39).

Electrochemical Impedance Spectroscopy. — Electrochemical impedance spectroscopy (EIS) is a method widely used to characterize electrochemical systems, including fuel cells (2). Wagner et al. (101) used EIS to determine the anode and cathode transfer functions independently using a symmetric cell, where the H₂ or O₂ are supplied to both anode and cathode electrode.
1.2.1.5 Fuel cell modeling

A large number of studies have reported on the modeling and computation of PEFCs, from the molecular dynamics level to industrial-size fuel cell stack simulations.

Nguyen and his colleagues published several papers on the computation of millimeter scale. Yi and Nguyen first developed an along-the-channel model including both convective water transport across the membrane and temperature distribution in the solid phase (121), and then developed a two-dimensional, multicomponent model of the cathode electrode (122). He et al. (26) studied the interdigitated flow field using a two-dimensional, two-phase, multi-component transport model. Natarajan and Nguyen developed a two-dimensional, two-phase, multicomponent, transient model for conventional flow channels (70), and expanded it to a three-dimensional version (71). Lin et al. focused on CL modeling, using a thin film-agglomerate approach, first one-dimensional (56), and then enhanced to two-dimensional (57). Kulikovsky et al., focusing more on the analytical aspect, developed a two-dimensional model of cathode compartment, including the gas channel, and examined the effect of carbon phase conductivity (49). In his study (46) he focused on water transport in the membrane, and reproduced the experimental result measured by Buchi and Scherer (8). Then he developed a simple analytical model of water transport (47), the laws of the fuel consumption in analytical form (50), an approach to analyze the experimental voltage-current curves (51), and the general relation for voltage loss in the bipolar plates (48).
Weber and Newman developed a one-dimensional, two-phase model to describe PEFCs (109). They first developed a physical model of water transport in the membrane which took into account Schroeder’s paradox (111), next developed a mathematical model based on the physical model (112), and then validated this in a fuel cell model (113). They also developed a model to describe the change in the maximum power of PEFCs as a function of the structural properties of the GDL (110), a model of the microporous layers (114), and a nonisothermal model (115).

Wang and his colleagues reported many modeling studies from the microscale simulation in the catalyst layer pores (69)(103)(104) to the industrial scale (∼200cm²) single cell (108). Special features of their model include a single set of conservation equations valid for flow channels, GDL, CL, and membrane (100), two-phase analytical (78) and numerical models (67), non-isothermal model (41)(42)(43)(107), and transient model (106). Recent progress in the modeling of fuel cells and experimental results used for the validation were reviewed by Wang (102).

1.2.2 PEFC at subzero temperatures

In this section the studies on PEFC at subzero temperatures are reviewed, and classified into three areas: membrane characteristics at low temperatures, effect of freeze/thaw cycles on the components or on the normal temperature performance, and startup at subzero temperatures.
1.2.2.1 Membrane characteristics at low temperature

There are a substantial number of studies on the characteristics of the membrane at low temperatures compared to the latter two areas. This may be because Nafion membrane has long been used for many industrial and research applications, for instance in electrolysis and sensors (27).

Sivashinsky and Tanny (85) studied the state of water as a function of temperature in the various ionomers including Nafion, using proton nuclear magnetic resonance (NMR) and the differential scanning calorimeter (DSC), and found only a part of the water in Nafion froze.

The studies utilizing NMR include the following. Boyle et al. (6) used proton NMR with neutron-scattering and dielectric data to detect a glass transition temperature. Fontanella et al. (12)(13)(19)(20) used NMR and impedance spectroscopy to investigate the effects of high pressure, equivalent weight, and different molecular weight of acid form Nafion on the proton conductivity.

DSCs were also used in many studies to measure the thermodynamic properties of Nafion under low temperatures. With DSC data, Yoshida and Miura (123) classified water molecules in the membrane into three types: non-freezing, freezing bound, and free water. Saito et al. (81)(82) measured the ionic conductivity, water self-diffusion coefficient, and DSC as functions of temperature, and found a part of water in the membrane froze around $-20^\circ$C, but nonfreezing water remained. Corti et al. (18) also used DSC to detect the glass transition temperature of polymers equilibrated with water. Most of the DSC measurements revealed that the water in the membrane showed no
significant phase transition in the temperature range of interest for cold start ($T \geq -40\,^\circ C$) when the membrane water content is low, and that some water remains unfrozen when the water content is large.

Cappadonia et al. (10)(11) measured proton conductivity with impedance spectroscopy between 140K and room temperature in the membrane form and in the MEA form with hot-pressing of Nafion. Arrhenius-type analysis of conductance showed two regimes of the activation energy, in which transition occurred at a temperature between 225 and 260K, depending on the water content. Thompson et al. (96) used a direct current to measure the proton conductivity at low temperature. In conjunction with the DSC data, they found the dependency of crossover temperature (temperature where the activation energy changes) on the water content, and the hysteresis between the freezing and melting.

1.2.2.2 Freeze/thaw cycle effect

The second area of concern at low temperature is the effect of freeze/thaw cycles on the durability of fuel cell components or on degradation in fuel cell performance at normal temperature. A critical difference between this area and the next area, cold start, is that here, no electrochemical reaction or water production occurs at subzero temperatures. In most cases the gas lines of the fuel cell are closed at the inlet and outlet and the cell internal compartments are isolated from the environment. Therefore, interaction between the system inside the cell and the environment is heat transfer only.

Cho et al. (14) studied the effect of thermal cycling between 80 and $-10\,^\circ C$ on a wet polymer membrane, evaluating the polarization curves, pore diameter distribution,
cyclic voltammogram, and AC impedance measurement. They found that cell performance drastically degraded after only four cycles, and that various characteristics of the membrane-electrode assembly (MEA), such as its pore size distribution and cyclic voltammograms, were changed, but the OCV and the membrane proton conductivity were not. In a later study, Cho et al. (15) observed that purging the cell with dry gas or filling the cell compartments with an anti-freeze solution before the cell temperature drops below 0°C could prevent MEA degradation.

McDonald et al. (62) also found that temperature dependence of the proton conductivity of Nafion 112 membrane did not change in slope, indicating that no phase transition of water within the membrane and no catalyst layer degradation occurred, for dry MEA subject to freeze/thaw cycling between -40 and 80°C.

Guo and Qi (25) investigated the effect of freeze-thaw cycles between 20 and −30°C on freestanding MEA and on MEA assembled in a cell. They found that the SEM image of freestanding MEA fully hydrated in water at 80°C showed severe cracks and segregation of catalyst layers, but the images of dry MEA did not. In addition, the fully humidified MEA assembled in a cell showed the electrochemical active area (ECA) decreased after the freeze-thaw cycles, but the short-term fuel cell performance did not change. When the MEA was dehydrated with gas purge before the freezing process, the SEM images of the MEA did not show the catalyst layer crack, and the cell performance did not change.

Hou et al. (31)(32)(33)(34) conducted intensive research on PEFC degradation due to freeze-thaw cycling. First they reported the PEFC degradation due to 20 freeze-thaw cycles between 60°C and −20°C. Before freezing, one cell was purged with 16.6%
RH at 50°C, and the other cell with 18% before the first cycle and 12.9% RH for the rest of the cycles at 50°C, both for 5 minutes. After 20 cycles of freeze-thaw, the former MEA did not show performance degradation in polarization curves, and the proton conductivity and interfacial charge transfer resistance did not change. The latter MEA became easily flooded after the first freeze-thaw cycle, but did not show further degradation after the rest of the cycles (34). Then, they compared the former MEA with freeze-thaw cycles to the one without temperature cycles. Using polarization curves, ECA, and EIS, they concluded no performance decay was observed with the freeze-thaw cycles in this condition (33). Next, they prepared four fuel cells with different amounts of residual water and investigated the effect of freezing on the ohmic resistance, charge transfer process, and oxygen transport using EIS. The conclusions drawn from this study were: (a) the ohmic resistance did not change, (b) the ORR mechanism remained the same, and (c) slower oxygen diffusion within CL was the main contributor to performance loss (32). Most recently they reported the change of ionic resistance in the CL after eight freeze-thaw cycles. With the EIS measurements and equivalent circuit study, they observed nonuniform change of the ionic resistance profile in the through-plane direction of the CL (31).

Lee and Mérida (52) reported on GDL durability under temperature cycling between -35 and 20°C. In their study no change was observed in the GDL properties, such as in-plane electrical resistivity, bending stiffness, surface contact angle, porosity, or water vapor diffusion after 50 cycles.

As reviewed here, the consensus of most temperature-cycle studies is that the MEA is not likely damaged by freezing when the MEA is dehydrated.
1.2.2.3 Cold start

Only a few years ago very little was known about the physical nature of PEFC cold start, and despite its importance to fuel cell deployment, there was limited active research in this area (albeit there existed a large number of system-based patents that do not necessarily address fundamental questions). Recently, however, an increasing number of the studies has been reported, mainly from automotive industries.

Kagami et al. (44) and Hishinuma et al. (29) explored the cold-start performance of a 104cm$^2$ single cell both experimentally and numerically. In their cold-start experiment, they varied several operating parameters such as current density, startup temperature, and gas pressure, and recorded the voltage change with time. In their numerical model, the CL and GDL were treated as an interfacial layer between the membrane and the bipolar plate with zero thickness. Furthermore, the water storage role of the membrane was neglected, which is quite important for cold start as shown later. Finally they concluded that from the steady-state water balance between the water production rate and the water vapor removal rate, self-startup was possible at $-5^\circ$C or higher but impossible at lower temperature without external heat assist.

Oszcipok et al. (72) conducted cold-start experiments and the statistical analysis of the experimental results. Notable features of their experiments are as follows. First, they began cold start from very low proton conductivity initial condition (1kHz AC impedance of $\sim 15\Omega$cm$^2$). Second, they used constant voltage operation not common in the practical FC operational mode. Because of these two features, their fuel cell could survive a very long period of cold start ($\sim 30$min). They defined the cumulative charge
transfer density as a measure of cold-start capability, and fitted it statistically with the
air flow rate during startup, membrane water content prior to startup, and cell discharge
current density at cell voltage of 0.45V at 30°C prior to cold start. With their fitting
data it may be possible to predict the cumulative charge transfer density from the initial
and operating conditions, but this method does not help the understanding of cold start
mechanisms. Subsequently, Oszcipok et al. (73) experimentally studied the effects of
membrane thickness, types of GDL, and gas flow rates on the cumulative charge transfer
density, and developed a similar empirical-based statistical relation to the previous study.

Hottinen et al. (30) used a planar air-breathing PEFC to study operation at
subzero temperatures and cold-start capability. Initially, they cooled down the operat-
ing fuel cell from room temperature to subzero temperatures and observed the voltage
change, resistance change, cell temperature, and ice/frost formation on the cathode-side
openings for air. It should be noted that cell temperature was mostly above zero or
at lowest about −3°C during the subzero temperature operation. In this method, they
found higher current density was required at lower temperature in order to generate
more heat. Finally, the air-breathing cell was started at −5°C and −10°C. When the
cold start succeeded, the cell temperature increased above zero regardless of the ambient
temperature.

Yan et al. (118) experimentally investigated the effect of subzero temperatures on
PEFC performance and cold-start capability. They cooled down the cell temperature
during operation, measured polarization curves at subzero temperatures, and found that
when the environmental temperature was −15°C the cell cathode temperature was below
zero and cell operation stopped. For the study of cold-start capability, they varied the
startup temperature, gas purge process, cell insulation, air stoichiometry, and preheat of the reactant gas and tested whether startup succeeded or failed. In this study, they concluded the preheat of reactant gas also affected the results because the hotter gases could remove more water vapor from the cell. However, it is unlikely because the specific heat of the dry gas is so small. The gas is cooled down to cell temperature as soon as it enters the cell, no matter how much the gas is preheated.

Ge and Wang also visualized the fuel cell cathode during cold start (22). Using a silver mesh as cathode GDL, they observed that when the product water was less than 0.56mg/cm² the water was not seen on the catalyst layer surface, and that when it reached 1.12mg/cm² the liquid water emerged from the catalyst layer surface. This is consistent with the roughly estimated value of cathode catalyst layer water storage capacity of ~ 0.4mg/cm². They also estimated from their experiment the freezing-point depression of water in the catalyst layer was at most 2°C. Then, they made the fuel cell optical configuration more realistic using carbon paper GDL punched with microholes instead of silver mesh (23). In this paper they reported the importance of the purge duration prior to cool down such that the most useful purge duration is between 90 and 120 seconds, and that cell HFR relaxation occurs after purge because of water redistribution. Subsequently, they used a cyclic voltammetry technique to examine the ECA change due to the cold start (24). It was found that the Pt area decreases as the product water increases during cold start, and that the Pt area loss substantially recovers with the higher temperature operations. However, permanent loss in the active Pt area and cell performance degradation are observed and become more severe as the cold start temperature decreases, or as the number of the cold start increases.
Ishikawa et al. (36) used a transparent cell to observe the behavior of product water during cold start, and to measure the temperatures of GDL surface and water using thermograph simultaneously. From their cold-start experiment at $-10^\circ$C, they concluded that the product water was in a super-cooled liquid phase, and that the water temperature increased to $0^\circ$C when it solidified. The physical origin of the super-cooled liquid water was not discussed.

Thompson et al. reported the study of ORR kinetics under subfreezing temperature (97). They used thick membranes and short-duration testing for maximum control of the membrane water content, and found that, as observed at above-freezing temperatures, the ORR kinetics decreased with decreasing water content at subfreezing temperatures, which was attributed to the effect of reduced proton activity. The kinetic parameters, such as the exchange current density, specific activity, and Tafel slope, were found to be consistent with the kinetics observed at above-freezing temperatures, and the activation energies were found to be constant within the temperature range of $-40$ to $55^\circ$C, indicating no change in the fundamental reaction mechanisms. They subsequently studied the water storage characteristics of membrane and catalyst layer during cold start using galvanostatic discharge operation and cryo-scanning electron microscopy (98). At low current densities the membrane absorbed product water to fully utilize its capacity, and the catalyst layer pores were completely filled with product water. With increasing current density, the fraction of water storage utilization in the membrane, as well as the fraction of water-filled CL pores, decreased. They concluded that water storage utilization was mainly controlled by current density, and less dependent on the initial water content or electrode thickness.
Li et al. visualized ice formation and distribution in the catalyst layer during cold start process using a cryo-scanning electron microscope (55). The fuel cell was operated to control the amount of product water during cold start, and then cooled down to −75°C immediately for the sample preparation. SEM images were taken at −170°C environment. They observed that even after the purge process 75% of the cathode catalyst layer pores were filled with ice. After cold start the porosity decreased from 65% in its dry condition to 13% after cold start with ~0.3mg/cm² product water, and to 8% with ~0.6mg/cm² product water, which caused the cell shutdown. They also observed that after ~0.6mg/cm² water production operation, ~0.25mg/cm² of product water remained in ice phase in the catalyst layer and in the microporous layer, and the remaining product water was thought to be absorbed in the membrane.

For the computational study of the cold start with transient, gas-solid two phase model, Mao and Wang (59) first developed an analytical model, and others followed. The first model developed by Mao and Wang (59) described heat balance, ice formation, water transport, and voltage change during cold start. The ice fraction in the catalyst layer is modeled to affect cold start in two ways: one is the blockage of oxygen diffusion, and the other is the surface coverage of the catalyst. With this model they identified the key parameters controlling cold-start performance as the initial membrane water content and the thermal mass of the bipolar plates. Then, Mao et al. (60) developed a multiphase, transient computational model on commercial CFD code to describe the cold start phenomena, including the transport, electrochemistry, and ice formation. The results were validated with experimental data, and the effects of startup current density and membrane thickness were numerically explored.
Wang (105) investigated the heat and mass transport and electrochemical kinetics in the cathode catalyst layer during cold start, and identified the key parameters which characterized the cold start performance. They found the the spatial variation of temperature was small under low current density cold start and thereby developed the lumped thermal model. A dimensionless parameter, defined as ratio of the time constant of cell warmup to that of ice volume growth was found to be important for successful self cold start.

Jiang et al. (40) developed a multiphase, three-dimensional model to describe the non-isothermal cold start and to study the effect of temperature rise. Due to the temperature rise during cold start, more water was transported into the membrane and less ice formation occurred in the catalyst layer. It was also found that a lumped thermal analysis significantly overestimated the overall thermal requirement for the success of self cold start. In addition, the pre-startup conditions had significant impact on the cold start which implied the importance of the shutdown process, such as gas purge.

Recently Meng (66) developed a transient, multiphase, multi-dimensional PEFC model to elucidate the fundamental physics of cold start. The results showed the importance of the water vapor concentration in the gas channels, which implies that the large gas flow rates benefit cold start performance. They also found that ice growth in the cathode catalyst layer during cold start was faster under the land than under the gas channels, and accumulated more at the interface between the cathode catalyst layer and GDL.
1.3 Motivations

Clearly, much remains to be done to establish engineering fundamentals of PEFC startup from subzero temperatures. Furthermore, the existing research on cold start is mostly of applied nature and lacks fundamental impact due to two apparent deficiencies.

1. The cell shutdown procedure before cool down is not well defined. Cold start highly depends on the initial condition of the cell, such as the membrane water content or the presence of liquid water in the CL pores. But the existing studies did not pay attention to that process, or used unrealistically dry conditions.

2. In fuel cell operation, a part of the energy is converted to electricity and the rest is converted into heat. Therefore, the cell temperature increases as the cell operates, and the rate of temperature increase depends on the heat capacity of the cell, that is, the cell configuration. This temperature increase affects many factors in fuel cell operation, for example, the activation energy of reactions, the proton conductivity in the membrane, and the saturation vapor pressure of water. Hence, most of the cold start studies reported are not reproducible with different cell configurations.

Paying attention to the above two factors, this dissertation study consists of the four following chapters. In Chapter 2, the cold start capability and characteristics of the PEFC are investigated, introducing the concept of isothermal cold start. For this study two methods of gas purge are used to generate the initial conditions prior to cold start, and the transport of product water during the cold start is carefully examined. Next, in Chapter 3, water removal from the PEFC during the gas purge process is studied. For vehicular application, the gas purge should be of short-duration, at most
one minute, and must still remove the water effectively. Hence, the key factors controlling purge effectiveness are studied and the method to predict the purge effectiveness is identified. Chapter 4 describes a novel method to measure the time- and space-resolved water distribution along the gas channels. The capability of water removal decreases as the purge gas flows through the gas channel, and therefore the gas purge produces nonuniform distribution of water along the gas channel. This measurement method provides a way to determine the transient, local water content in the membrane. Finally, the conclusions drawn from this study are summarized and future work is recommended in Chapter 5.
Chapter 2

ISOTHERMAL COLD START

In this chapter the cold start capability and characteristics of the PEFC are discussed under isothermal condition, with two different methods to build up the initial conditions. The first method, *equilibrium purge*, can precisely control the cell internal condition and is therefore suitable to investigate the MEA cold start capability. The second one, *short purge*, was designed to simulate realistic operation in a fuel cell vehicle, but is less controllable, or less efficient with respect to the cold start performance.

2.1 Equilibrium Purge Cold Start

2.1.1 Equilibrium Purge

This section describes a set of novel experimental protocols for cold start research using laboratory-scale single cells. Aimed at generating reproducible and consistent data that are indicative of intrinsic cold-start capability of MEA and other key components rather than highly dependent on cell fixtures, the present experimental procedures consist of equilibrium gas purge and isothermal cold start till cell shutdown, as will be elaborated below.

*Equilibrium Purge.* — Gas purge is a common and integral part of PEFC cold start in the industry. The primary purpose of gas purge is to remove residual water from a PEFC prior to cell shutdown and cool down. The gas purge process thus defines
the initial condition of water distribution throughout a cell and plays a crucial role in
cold start. While gas purge is commonly conducted using dry nitrogen/air for durations
ranging from tens of seconds to a few minutes, in this work we introduce a method
using partially humidified gas with well-controlled relative humidity (RH) to purge for
extended periods of time (of the order of several hours). After this purge, all liquid
water should be evaporated away from all components of the cell, and the membrane
water content reaches thermodynamic equilibrium with the RH of purge gas (thus termed
equilibrium purge). Equilibrium purge permits the initial water content in the membrane
to be precisely controlled and well defined (through the RH control in purge gas) and
hence, the important effect of the initial water distribution on cold start performance
can be investigated, as will be illustrated in this study.

 Isothermal cold start. — In practice, cold start of a PEFC stack is inherently
non-isothermal, as power generation produces waste heat that causes the cell tempera-
ture to rise. However, non-isothermal cold start data vary greatly from one system to
another and strongly depend on the thermal mass of the test cell/stack. In order to de-
termine key MEA characteristics to ensure self-startup of an automotive PEFC from, for
example, −30°C and ultimately to relate these characteristics to materials and control
requirements, isothermal cold start is uniquely useful as proposed here. Isothermal cold
start can be easily realized in laboratories by using a single cell fixture with sufficiently
large thermal mass. While isothermal cells are bound to shut down (the cell tempera-
ture is always kept constant at the ambient temperature of startup), the product water
so measured before cell shutdown is a quantitative measure of the intrinsic cold-start
capability of a MEA that is completely independent of the thermal mass of a specific
cell. Such experimental data are therefore of benchmark quality, highly reproducible in laboratories (independent of cell fixtures), and practically useful for stack design as the amount of product water also roughly corresponds to the amount of waste heat able to be generated. Lastly, isothermal cold start provides the most conservative scenario to examine the impact of MEA material and design on performance of PEFC cold start.

Intuitively, the performance of PEFC cold start is measured by how long a cell can operate before it is shut down by ice filling in the cathode CL. However, we propose to use the total product water (in the unit of mg/cm$^2$) to quantify cold start performance for reasons that product water: (1) combines the effects of current density and operational time; (2) allows direct comparison with water accumulation in various components such as the membrane, CL and GDL; and (3) is indicative of the amount of waste heat generated from the cell according to the following derivation:

\[
\text{Heat generation (J/cm}^2\text{)} = \int (E_h - V_{\text{cell}})Idt \\
\sim (E_h - V_{\text{cell}}) \int Idt \\
= \frac{2F(E_h - V_{\text{cell}})}{M_{H_2O}} m_{H_2O} \quad (2.1)
\]

where $E_h$ is the thermal potential ($= \Delta h/2F \sim 1.48V$ for H$_2$ – O$_2$ reaction), $V_{\text{cell}}$ the operating cell voltage in cold start (assumed to be roughly constant, for example, at 0.6V), $M_{H_2O}$ the molecular weight of water, and $m_{H_2O}$ the total product water in mg/cm$^2$ generated from cold start. That is,

\[
m_{H_2O} = \frac{M_{H_2O}}{2F} \int Idt \quad (2.2)
\]
From Eq. (2.1), the amount of waste heat capable of generating from a cell during cold start can be easily estimated from the product water, and subsequently the stack temperature rise can be computed by dividing the waste heat by the thermal mass of the stack.

2.1.2 Experimental

2.1.2.1 Experimental setup

The test cell used in this study has 25 cm$^2$ active area with both anode and cathode flowfields consisting of straight, parallel channels (Figures 2.1-2.3). The bipolar plates (BP) are made of graphite with the total thickness of 15 mm. Two pairs of gold-plated copper current collectors of 4 mm thickness and stainless steel end plates of 15 mm thickness are placed outside the two graphite BPs. The heat capacitance of these components per unit active area is about 20 J/cm$^2$K, resulting in a maximum temperature increase of $\sim 0.1^\circ$C for one minute of operation at 0.5 V and 40 mA/cm$^2$, if in the absence of any heat loss to the ambient. The MEAs used in this study are commercially available Japan Gore-Tex MEAs with 30 $\mu$m-thick membrane and CL with Pt loading of 0.4 mg/cm$^2$ on each electrode. Toray carbon paper coated with a microporous layer is used as the gas diffusion layer (GDL).

The experimental setup is shown schematically in Figures 2.4 and 2.5. For all experiments carried out at temperatures above the freezing point, Arbin fuel cell test system (Arbin Instruments, College Station, TX) is used to control the load, cell temperature, and anode and cathode gas parameters such as flow rate, dew point, and back
pressure (see Figure 2.4). For cold start experiments performed inside a subzero environmental chamber as shown in Figure 2.5, dry hydrogen and air directly from gas bottles are fed into the cell with separate rotameters to control their flow rates in order to avoid entrainment of any water vapor from humidifiers of the fuel cell test station.

To simulate the cold ambient temperature, the test cell is placed in a Tenney environmental chamber (model T10C; Lunaire Limited, Williamsport, PA). The chamber is pre-cooled from room temperature to a prescribed startup temperature such as −30°C, and about two hours are required for the test cell to reach −30°C after being placed in the chamber.

In addition to recording voltage-time curves during constant current density startup, cell resistance is measured and monitored by a Tsuruga milliohm meter (model 3566; Osaka, Japan). The meter is operated at 7.4mA of AC current with 1kHz frequency. The high-frequency resistance (HFR) data, along with cell temperature measured by thermocouples, are logged by an Agilent 34970A data acquisition unit (Agilent Technologies, Inc., Loveland, CO) on a PC.

2.1.2.2 Procedure

The procedure for all cold start experiments reported in this work consists of four steps: cell conditioning, gas purge, cool down, and startup, as described in detail below.

The test cell is first conditioned by operation at the current density of 500mA/cm² and 55°C for 30 minutes. Both anode and cathode gases are kept at 100% RH, and the \( \text{H}_2 \) and air flowrates are 1.57 and 4.48L/min, respectively.
As mentioned earlier, the method of equilibrium purge is developed in this experimental work to initialize the cell internal condition before each cold start experiment. In this process the fuel cell temperature and the gas dew point are set to prescribed values, and nitrogen gases are supplied to both anode and cathode channels. The purge process continues until the cell HFR measured by the milliohm meter reaches a final, stabilized value. At this point in time it is considered that the MEA reaches equilibrium with the purge gas RH and residual liquid water in the CL and GDL pores or gas channels is completely removed. Under this condition the water content of the MEA can be easily calculated from the purge gas RH via the membrane water uptake curve such as (88)

\[
\lambda = 0.043 + 17.81a - 39.85a^2 + 36.0a^3
\]  

(2.3)

where \(\lambda\) is water content in the membrane and \(a\) is the relative humidity of purge gas. Typically the equilibrium purge takes two to three hours to complete.

In this study the dew point of the purge gas is fixed at 30\(^{\circ}\)C while the cell temperature during purge varies at 30, 35, 50, and 60\(^{\circ}\)C so as to create a RH range of 21% to 100% and corresponding water content in the membrane at 2.4, 2.9, 6.2 and 14. All equilibrium purge cases and their conditions are summarized in Table 2.1.

The third step in a cold start experiment is cool down of the fuel cell. Once equilibrium purge is concluded, the inlet and outlet gas lines are closed for both anode and cathode in order to keep the cell internal condition unchanged, and the cell is then moved inside the environmental chamber. In the chamber the fuel cell temperature and the cell resistance are simultaneously measured during cool down. When the cell
temperature reaches a specified startup temperature, the cell is left at that temperature for more than one hour before proceeding to the next step in order to ensure that the entire cell becomes isothermal at the ambient temperature. In the present work the test cell is cooled down and started up at $-30^\circ$C as this is the most challenging startup temperature required for automotive application.

During cool down, water content in the membrane can be safely assumed to remain constant or locked in place. This assumption can be justified by the fact that the cell compartment on each side has about 2cm$^3$ and its filling gas at the dew point of $30^\circ$C after equilibrium purge contains $\sim 0.06$mg of water, equivalent to an increase in membrane water content of $\Delta \lambda = 0.02$. Thus the change in membrane water content during cool down is negligible, making it possible to predetermine the membrane water content at the beginning of cold start.

The final step involves operating the test cell under a subfreezing temperature. After dry reactant gases are supplied to the cell and the open-circuit voltage rises, a given current density is applied from the Arbin fuel cell test system. The current density applied increases linearly from zero at the rate of 0.5mA/cm$^2$/sec for 80 seconds and then is kept constant at 40mA/cm$^2$, unless otherwise specified. When the voltage drops below a preset cutoff voltage (i.e. 0.3V in the present study), the load is released and the cold start experiment is terminated. The total product water from each cold start experiment can be calculated from the total operational time and the applied current density via Eq. 2.2.
2.1.3 Results and Discussion

2.1.3.1 Typical equilibrium purge cold start

The change in cell resistance during equilibrium purge is displayed in Figure 2.6 for Case 1 listed in Table 2.1. The cell temperature and purge gas dew point are 60°C and 30°C, respectively, resulting in purge gas RH of \( \sim 21\% \) and water content of 2.4 in the membrane at the end of equilibrium purge. It is seen from Figure 2.6 that the membrane resistance rapidly rises in the first ten minutes and then slowly increases for the next two hours. This behavior is consistent with the most recent measurements of liquid water removal from GDL by purge gas using X-ray microtomography (83). It was found that the water saturation in GDL decreases rapidly in the first six minutes by purge gas, after which this decrease slows substantially between 6 and 25 minutes.

The final stage of removing all liquid water trapped in small pores of CL, MPL and GDL takes much longer because there is high tortuosity for purge gas to reach these sites for evaporation. This time-consuming stage is required before the membrane fully reaches equilibrium with water vapor in the purge gas, as any small amount of liquid water remaining in porous components will serve as a water reservoir to re-hydrate the electrolyte in the CL and membrane. For all cases of equilibrium purge listed in Table 2.1, the overall trend and time scale of HFR vs. time curves remain similar.

The cool down process also provides an opportunity to obtain the membrane proton conductivity as a function of temperature at known water content. Note that the temperature dependence of proton conductivity with low membrane water content is of particular interest here as PEFC cold start rarely involves fully hydrated membranes.
after gas purge. In addition, unlike PEFCs operated under normal temperatures, the membrane resistance under low water content and low temperature typical of cold start conditions is much greater than the contact resistance, thus making in-situ measurements of the membrane proton conductivity in a PEFC a simple but accurate method.

Figure 2.7 shows the proton conductivity variation with temperature for varying membrane water content. In the Arrhenius form the lines displayed in Figure 2.7 are nearly straight and parallel to each other, indicating no noticeable phase transition of water occurring in the membrane in this temperature range between room temperature and $-30^\circ$C and water content range from 2.4 to 14. This finding is in good agreement with observations of McDonald et al. (62) for partially hydrated Nafion 112-based MEAs. For $\lambda_i = 14$ case, the conductivity curve shown in Figure 2.7 is slightly convex. This may be because the 100% RH purge gas used in equilibrium purge could not remove all liquid water by evaporation from the interfaces between GDL and current-collecting lands, or between CL and GDL, resulting in water freezing at these interfaces during cool down and hence a change in contact resistance.

The conductivity data measured in-situ in this work are within the temperature range from room temperature ($27^\circ$C) to $-30^\circ$C. In contrast, Cleghorn et al. reported the proton conductivity for Gore-Select membranes in the temperature range of 40 – 100$^\circ$C (16). Extrapolating the correlation of Cleghorn et al. to $27^\circ$C and at 100% relative humidity, the membrane conductivity is calculated to be 0.027S/cm, which is in reasonable agreement with our in-situ measurement of 0.021S/cm.

Figure 2.8 shows the evolution of cell voltage and resistance with time during cold start from $-30^\circ$C for Case 1 of equilibrium purge listed in Table 2.1. The applied
current density is an initial ramp of 0.5mA/cm²/sec for 80 seconds followed by constant 40mA/cm². The cell voltage initially decreases under the load and as the applied current density increases, then slightly rises until about 3.5 minutes, after which voltage drop-down is evident till the cutoff voltage of 0.3V. The cell resistance is seen to decrease during both the initial current-ramp and the full load periods, dropping from an initially 6000mΩcm² to 800mΩcm² at the final stage of cold start. This resistance decrease is direct evidence of gradual absorption of product water generated from CL into the membrane. Owing to membrane re-hydration during cold start, the cell voltage recovers a little between 90 and 210 seconds into the cold start, as can be seen from Figure 2.8. The iR-free voltage is computed to change from 650mV to 710mV in this voltage recovery period, which indicates that there may also be a slight improvement in activation besides the membrane resistance reduction. The rapid voltage drop in the final stage of cold start is apparently due to hindrance of oxygen transport into an ice-filled CL. The product water generated from oxygen reduction reaction (ORR) is difficult to remove from CL via vapor phase transport because of the very low saturation vapor pressure ($P_{v, \text{sat}} = 40\text{Pa at } -30^\circ\text{C}$). Consequently, product water accumulates in the cathode CL unless it partially diffuses into the membrane. Notice also that water existing in CL under isothermal cold start from $-30^\circ\text{C}$, as involved in the present experiments, must be in the form of ice or frost according to the freezing-point depression observations made by Ge and Wang (22).

2.1.3.2 Effect of initial membrane water content

The effect of initial membrane water content prior to cold start on the voltage curve during cold start is shown in Figure 2.9. During the initial current ramp period
the cell voltage is higher as the initial membrane water content increases, as expected. In the voltage recovery period two characteristics can be noticed. First, the voltage recovery due to membrane re-hydration decreases as the initial membrane water content increases. Secondly, the duration of this period is greater for lower initial water content. For $\lambda_i = 14$ case the voltage recovery is hardly seen and the profile moves directly from the initial period to the final voltage drop-down stage. This is because the membrane is already nearly saturated at the beginning of cold start and hence no room remains to accommodate product water diffusion. Consequently, the total operational time of cold-start discharge increases as the initial membrane water content decreases, demonstrating the profound significance of gas purge.

In light of the importance of water storage in partially dry membranes, it is instructive to correlate the cold start performance quantified by product water ($m_{H_2O}$, mg/cm$^2$) with the membrane water uptake potential ($\Delta \lambda$) defined as:

$$\Delta \lambda = \lambda_{sat} - \lambda_i$$

(2.4)

where $\lambda_{sat}$ denotes the water content of a fully hydrated membrane (taken to be 14 in this study) and $\lambda_i$ the initial membrane water content prior to cold start. If a membrane is initially fully hydrated prior to cold start, i.e. $\lambda_i = \lambda_{sat}$, then the water uptake potential in the membrane is zero, and all product water must accumulate in the CL at the startup temperature of $-30^\circ C$. In the other extreme, if gas purge is highly effective and the membrane is dry initially, then the water uptake potential reaches the maximum, thus resulting in more product water. Figure 2.10 displays such an experimental relationship.
between product water and membrane water uptake potential. It can be said that in the case of \( \Delta \lambda = 0 \) (i.e. \( \lambda_i = 14 \)) the majority of product water resides in the cathode CL. Thus, the measured product water (i.e. \( \sim 0.5\text{mg/cm}^2 \)) in this condition is indicative of the water storage capacity in the CL. One can quickly estimate the latter by the following equation:

\[
m_{\text{CL}} = \delta_{\text{CL}} (\epsilon \rho_{\text{ice}} + \epsilon_e c_{e,\text{dry}} \Delta \lambda M_{\text{H}_2\text{O}})
\]

where the first term on the right hand side accounts for ice storage in open pores of the CL and the second term for water storage in the electrolyte phase. Assuming typical CL properties (\( \delta_{\text{CL}} = 12\mu\text{m} \), \( \epsilon = 0.5 \), \( \rho_{\text{ice}} = 0.9\text{g/cm}^3 \), \( \epsilon_e = 0.2 \), and \( c_{e,\text{dry}} = 1.818 \times 10^{-3}\text{mol/cm}^3 \)), the CL water storage capacity is estimated to be \( 0.54\text{mg/cm}^2 \) for \( \Delta \lambda = 0 \), which is in good agreement with the measured product water. This analysis further suggests that the vapor phase transport of product water out of CL into GDL is indeed negligible at the startup temperature of \( -30^\circ\text{C} \).

Figure 2.10 also shows that the total product water can be separated into the CL and membrane contributions for each water uptake potential in the membrane. While the CL contribution depends mainly on the CL pore volume and weakly on the water uptake potential \( \Delta \lambda \) as indicated in Eq. (2.5), the membrane contribution varies nonlinearly with \( \Delta \lambda \). This is because longer CL operation before ice filling and shutdown allows more membrane water uptake.

A fundamental map like Figure 2.10 is useful for developing novel MEA materials and designs in order to enhance the intrinsic capability of PEFC cold start. For example, in order to earn more time for product water diffusion into the membrane, low water
production rate or current density is preferred for isothermal cold start from startup temperatures as low as −20°C or −30°C. This conclusion implied from Figure 2.10 can be experimentally verified as discussed below.

2.1.3.3 Effect of startup current density

To see the effect of the startup current density, the current density profile applied to the cell is doubled. As seen from Figure 2.11, the current density is initially increased from 0 to 80mA/cm\(^2\) with the scan rate of 1mA/cm\(^2\)/sec for 80 seconds, and then kept constant at 80mA/cm\(^2\) until the voltage drops below the cutoff voltage of 0.3V. The condition of equilibrium purge for this experiment is Case 3, i.e. cell temperature and purge gas dew point are 35 and 30°C, respectively. For the higher current density case the cell voltage drops gradually in the first one minute and then falls into the voltage drop-down period quickly. Soon after the current density reaches 80mA/cm\(^2\), the voltage drops below 0.3V and the cold start operation stops. Thus, only two stages of voltage evolution are evident at this higher current density, as compared to the three stages experienced in the lower current density case shown in Figure 2.11.

In Figure 2.12 the iR-free voltage is plotted against the applied current density during the initial current ramp period of the startup for both current densities. This plot can be viewed as a polarization curve under linear current scan. For the low current density case the iR-free voltage decreases nearly linearly with log\(i\), indicative a typical Tafel kinetic behavior of ORR. However, for the higher current density this linear relationship persists only up to ~ 55mA/cm\(^2\), and beyond this threshold current density there is appreciable mass transport loss, implying that the limiting step has shifted from
the charge transfer kinetics to mass transport. At this transition point the cumulative product water is found to be 0.15mg/cm². At the same cumulative product water of 0.15mg/cm², the low current density startup has just reached 40mA/cm² and the cell voltage begins to slightly increase (see Figure 2.11). This demonstrates that the cumulative product water of 0.15mg/cm² has not resulted in mass transport limitation in the CL due to ice formation in the low current density case. The cumulative product water at cell shutdown is 0.32 and 0.53mg/cm² for the high and low current densities, respectively. Mass transport limitation in CL with lower product water at higher current density can be explained by the water distribution in CL as schematically shown in Figure 2.13. For the low current density case (Figure 2.13a), the reaction current distribution is more uniform and product water has sufficient time to redistribute uniformly throughout the pores in CL. Thus, the CL water storage capacity can be fully utilized. On the other hand, in the high current density case (Figure 2.13b), the reaction current is non-uniform and is determined by a delicate balance between proton conduction through ionomers and O₂ transport through pores of the catalyst layer. Further, the dominance between the two resistances changes with time during cold start; the proton resistance continues to decreases with more water production but ice formation exacerbates the O₂ transport. As a result, the peak reaction current tends to shift toward the CL/GDL interface in favor of O₂ transport, which leads to even more ice formation and aggravated mass transport limitation in that region. In addition, product water formed in the CL near the CL/membrane interface is likely to be absorbed in the membrane, leaving less water to precipitate as ice in CL pores. That is, product water may concentrate in the front portion of the electrode interfacing with GDL and form an ice sheet there to block
oxygen transport into the CL before all pores are occupied by product water. Thus the water storage capacity in CL cannot be fully utilized and CL is prematurely shut down under the high current density. The differing utilization in the CL water storage capacity is responsible for ~ 60% reduction in cold start product water between the high and low current densities.

2.1.3.4 Effect of startup temperature

The effect of the startup temperature was studied by starting the cell at ambient temperatures of -3, -10, -20, and -30°C. The initial water content in the membrane prior to cold start was fixed at $\lambda_i = 6.2$ for all startup temperatures. Figure 2.14 shows the time evolution of current density and cell voltage during each startup. It can be seen that as the startup temperature increases, the fuel cell can operate much longer. At -3°C the cell shows no significant voltage drop-down and is able to operate indefinitely.

In these startup experiments the initial current linear scan (0.5mA/cm$^2$/sec, 0 to 80 seconds) can be viewed as a fast-scan polarization curve. The iR-free voltage during the initial current ramp is plotted with the current density in the logarithmic scale in Figure 2.15 for four startup temperatures. Two remarkable features can be observed in Figure 2.15. First, the lower the startup temperature, the lower the iR-free voltage becomes. This is mainly because of the slow ORR kinetics at low temperature. Second, the slope of the lines (i.e. the Tafel slope of ORR) increases as the startup temperature decreases. The change of Tafel slope with temperature is plotted in Figure 2.16. Note that the V-I curve for -30°C in Figure 2.15 bends downward, indicating the onset of the mass transport loss around 25mA/cm$^2$. Therefore, in the -30°C case, only the I-V
data between 10 and 25mA/cm² were taken to calculate the Tafel slope in Figure 2.16. Figure 2.16 clearly shows that the Tafel slope increases from typically $\sim 66\text{mV/decade}$ under room temperature to $\sim 105\text{mV/decade}$ at $-30^\circ\text{C}$.

We use the cumulative product water till cell shutdown to quantify the cold-start performance. Figure 2.17 depicts a strongly nonlinear relationship between the product water and the startup temperature. Primary reasons for large product water at high temperatures include the high proton conductivity, large water diffusivity in the membrane, facile ORR kinetics, and high saturation vapor pressure.

As mentioned earlier, at $-3^\circ\text{C}$ the cell can operate indefinitely at steady state. Then, how is the water production rate of $0.0037\text{mg/cm}^2/\text{sec}$ balanced by the water removal rate from the cathode CL? Assuming the exhaust gases from the cell are fully saturated with water vapor at the cell temperature of $-3^\circ\text{C}$, $0.0012\text{mg/cm}^2/\text{sec}$ of water vapor can be removed from the cell which is only 30% of the production rate. Therefore, to achieve the steady state operation at $-3^\circ\text{C}$, $0.0025\text{mg/cm}^2/\text{sec}$ of water must be removed out of the cathode CL either in liquid or vapor. Indeed, Ge and Wang (22) observed that liquid water emerges from the CL surface at the cell plate temperature of $-3^\circ\text{C}$, implying that the CL temperature is slightly higher than the ambient temperature because of the thermal gradient in GDL resulting from heat generation. Thus, it is likely that the water produced in the cathode CL is transported to the GDL in liquid phase by capillary forces and may freeze in the GDL pores or be further transported to the gas channels.
In Figure 2.18 the product water is plotted versus the membrane water uptake potential \( \Delta \lambda \) for two startup temperatures, -20 and \(-30^\circ C\). The membrane water uptake potential \( \Delta \lambda \) is defined as \( \Delta \lambda = 14 - \lambda_i \), where 14 denotes the water content for saturated Nafion membranes and \( \lambda_i \) is the initial membrane water content prior to startup as controlled by changing the purge gas RH. As \( \Delta \lambda \) increases, that is, when the initial membrane is dry, the product water during cold start increases, because more water from the CL can be absorbed and stored in the membrane. As indicated in section 2.1.3.2, when \( \Delta \lambda \) approaches zero (i.e. the initial membrane prior to cold start is fully hydrated), no water can be transported into the membrane and therefore the product water measured reflects the storage capacity in the cathode CL under very low temperatures such as \(-20^\circ C\). When \( \Delta \lambda > 0 \), the product water can either accumulate in the cathode CL or transport into a partially hydrated membrane, thereby increasing the cumulative product water. At low temperatures such as \(-20^\circ C\) or \(-30^\circ C\), no water can transport from the CL into the GDL either in the liquid or vapor phase. The liquid phase transport is ruled out based on the recent visualization study (22), while the vapor phase transport should be negligible since the saturation vapor pressure is exceedingly low in this temperature range, e.g. \( p_{\text{sat}} \sim 100\text{Pa} \) at \(-20^\circ C\) and \(~ 40\text{Pa} \) at \(-30^\circ C\).

It can be seen from Figure 2.18 that the gap in the product water between -20 and \(-30^\circ C\) amounts to about 0.3 – 0.4mg/cm\(^2\) for partially dry membranes. The larger product water at \(-20^\circ C\) is attributed mainly to the higher water diffusivity in the membrane and hence higher water storage in it. If the initial membrane is fully hydrated (i.e. \( \Delta \lambda \to 0 \)), the difference in the cumulative product water diminishes between \(-20^\circ C\)
and \(-30^\circ C\) because the product water primarily accumulates in the CL pores in this situation.

### 2.2 Short Purge Cold Start

The second purge method, *short purge*, was designed to simulate the realistic operation in a fuel cell vehicle. Similar to the equilibrium purge, the short purge cold start experiment consists of four steps:

1. The cell is operated with 500mA/cm\(^2\) discharge current density for 15 minutes with both fully humidified 1.57L/min H\(_2\) and 4.48L/min air at 55\(^\circ\)C;

2. The cell is purged at 55\(^\circ\)C with 2L/min and 4.48L/min of dry N\(_2\) for anode and cathode, respectively, and the purge duration is varied from 15 to 90 seconds as one of the operating parameters for study;

3. The cell is cooled down in the environmental chamber, in the same manner as in the equilibrium purge case, and the membrane water content is estimated by measuring the cell HFR at 10\(^\circ\)C during cool down via the proton conductivity and membrane water content relationship;

4. A current density of 100mA/cm\(^2\) is applied for cold start. Each experiment is terminated when the cell voltage drops to the cutoff voltage of 0.3V.

In short purge experiments, the initial membrane water content can be controlled by purge duration. Figure 2.19 shows the time evolution of cell voltage during startup from \(-20^\circ C\) with three different short purge durations of 15, 30, or 60 seconds at the cell
temperature of 55° C. The corresponding initial membrane water content was $\lambda_i = 6.4$, 3.4, and 2.9, respectively. Two remarkable characteristics in the voltage curves can be seen in Figure 2.19 under the current density of 100mA/cm$^2$. First, the initial cell voltage is lower for longer purge duration that corresponds to the lower membrane water content. This is mainly because the drier membrane exhibits lower proton conductivity and therefore higher ohmic drop under the load. Secondly, the cold start operation lasts longer if the purge duration is longer. Again, this is because the drier membrane can take up more product water, and therefore the ice accumulation rate is lower within the cathode CL and cell shutdown is delayed. Another possible reason is that longer purge duration results in less residual water in the CL or more open pores.

Figure 2.20 shows the short purge cold start results from −30° C with two different purge durations. The short purge of 60 and 90 seconds at 55° C yields the membrane water content of $\lambda_i = 3.4$ and 1.9, respectively. Similar to the −20° C startup cases shown in Figure 2.19, the lower initial membrane water content gives rise to lower cell voltage. However, the operation time remains nearly the same for the two different initial water contents, implying that the limiting factor in the startup from −30° C is not the membrane water uptake potential, but the residual water within the CL pores.

Figure 2.21 compares the cumulative product water for cold start after short purge for two startup temperatures, −20° C and −30° C. This map shows a similar trend to the equilibrium purge cold start displayed in Figure 2.18, except for two major differences. First, the product water is smaller at the $\Delta \lambda \rightarrow 0$ limit than that after equilibrium purge. This clearly indicates existence of residual water in the cathode CL after short purge, whereas the CL is free of water after equilibrium purge. Secondly, the product water
difference between $-20^\circ\text{C}$ and $-30^\circ\text{C}$ is smaller ($0.15 - 0.3\text{mg/cm}^2$) than the equilibrium purge case ($0.3 - 0.4\text{mg/cm}^2$) shown in Figure 2.18. This can be explained by the different current densities applied in short purge ($100\text{mA/cm}^2$) versus equilibrium purge ($40\text{mA/cm}^2$). Higher current density applied in the short purge experiments diminishes the role of the membrane in storing product water and accelerates the shutdown of CL by ice.

Experimental results on the current density effect under short purge are shown in Figure 2.22, along with the corresponding model predictions made earlier by Mao et al. (60) Here the cell was operated at $-20^\circ\text{C}$ with current density of either $40\text{mA/cm}^2$ (with current ramp) or $100\text{mA/cm}^2$ (without current ramp) for various membrane water uptake potential $\Delta\lambda$. This figure clearly demonstrates that the low current density operation results in high product water during cold start. The computational results of Mao et al. agree well with the experimental data.

The cold start performance for two different purge modes are directly compared in Figures 2.23 and 2.24 for $-20$ and $-30^\circ\text{C}$ startup, respectively. It should be noted that two parameters differ between these two experimental sets: the purge method as well as the startup current density (see Table 2.2). Therefore, the difference in product water shown in Figures 2.23 and 2.24 is contributed by both factors.

Generally, the product water is seen to increase with the membrane water uptake potential $\Delta\lambda$. Furthermore, the equilibrium purge startup has roughly $0.5\text{mg/cm}^2$ and $0.3\text{mg/cm}^2$ higher product water than that of the short purge startup at $-20^\circ\text{C}$ (Figure 2.23) and $-30^\circ\text{C}$ (Figure 2.24), respectively. The reasons for lower product water in
short purge startup are the higher current density and the presence of residual water in
the CL pores.
<table>
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<th>Case Number</th>
<th>Cell Temperature ($^\circ$C)</th>
<th>Gas Dew Point ($^\circ$C)</th>
<th>Relative Humidity (%)</th>
<th>Membrane Water Content</th>
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<tr>
<td>4</td>
<td>30</td>
<td>30</td>
<td>100</td>
<td>14.0</td>
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</table>
Table 2.2: Experimental conditions for two purge modes

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<th>equilibrium purge</th>
<th>short purge</th>
</tr>
</thead>
<tbody>
<tr>
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<td>55°C</td>
</tr>
<tr>
<td>purge gas dew point</td>
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<td>dry</td>
</tr>
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<td>anode purge gas flow rate</td>
<td>1L/min</td>
<td>2L/min</td>
</tr>
<tr>
<td>cathode purge gas flow rate</td>
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<td>4.48L/min</td>
</tr>
<tr>
<td>purge duration</td>
<td>&gt; 2 hours</td>
<td>15-90 seconds</td>
</tr>
<tr>
<td>cold start current density</td>
<td>40mA/cm² with initial ramp</td>
<td>100mA/cm²</td>
</tr>
<tr>
<td></td>
<td>of 0.5mA/cm²/sec</td>
<td></td>
</tr>
<tr>
<td>controlling parameter</td>
<td>purge cell temperature (purge gas relative humidity)</td>
<td>purge duration</td>
</tr>
</tbody>
</table>
Figure 2.1: Sketch of laboratory-scale single cell assembly used in this study.
Figure 2.2: Exploded view of the cell.
Figure 2.3: Gas channels machined on the bipolar plates.
Figure 2.4: Experimental setup for operation above the freezing temperature.
Figure 2.5: Experimental setup for startup from a sub-freezing temperature.
Figure 2.6: Cell resistance change with time during equilibrium purge at the cell temperature and purge gas dew point of 60°C and 30°C, respectively (case 1).
Figure 2.7: Proton conductivity as a function of temperature for various membrane water content $\lambda$ between the room temperature and $-30^\circ C$. 
Figure 2.8: Time evolution of applied current density, cell voltage, and cell resistance during startup from $-30^\circ$C for case 1 of equilibrium purge.
Figure 2.9: Effect of initial water content $\lambda$ in the membrane on cold start performance. The environmental temperature is $-3{0}^\circ\text{C}$. Data were recorded at 1Hz.
Figure 2.10: Relation between product water and membrane water uptake potential for startup from \(-30^\circ\text{C}\). The dashed line indicates the amount of water stored in the catalyst layer and the extra portion above it denotes the amount of water diffused into the membrane.
Figure 2.11: Effect of current density on voltage evolution during cold start from $-30^\circ C$ in case 3 of equilibrium purge.
Figure 2.12: Current-voltage curves with linear scan in current at $-30^\circ$C for case 3 of equilibrium purge.
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Figure 2.14: Time evolution of current density and cell voltage at various startup temperatures after equilibrium purge ($\lambda_i = 6.2$). Data were recorded at 1Hz.
Figure 2.15: Current-voltage relations during linear current ramp at various startup temperatures after equilibrium purge ($\lambda_i = 6.2$).
Figure 2.16: Effect of startup temperature on Tafel slope of oxygen reduction reaction ($\lambda_i = 6.2$).
Figure 2.17: Relation between product water and startup temperature under equilibrium purge ($\lambda_i = 6.2$) and current density of 40mA/cm$^2$. 
Figure 2.18: Relation between product water and membrane water uptake potential for startup from -20 and -30°C after equilibrium purge.
Figure 2.19: Time evolution of current density and cell voltage during startup from $-20^\circ C$ for different short purge durations. Data were recorded at 1Hz.
Figure 2.20: Time evolution of current density and cell voltage during startup from $-30^\circ C$ for different short purge durations. Data were recorded at 1Hz.
Figure 2.21: Relation between product water and membrane water uptake potential for startup from -20 and −30°C under short purge and 100mA/cm²
Figure 2.22: Relation between product water and membrane water uptake potential for startup from $-20^\circ\text{C}$ under short purge for different current densities. The simulation results are reproduced here from Mao et al. (60)
Figure 2.23: Relation between product water and membrane water uptake potential for startup from $-20^\circ$C for different purge methods.
Figure 2.24: Relation between product water and membrane water uptake potential for startup from $-30^\circ$C for different purge methods.
Chapter 3

WATER REMOVAL DURING GAS PURGE

3.1 Introduction

Gas purge is an integral part of the frequent shutdown process of polymer electrolyte fuel cells (PEFC) as a fuel cell vehicle (FCV) typically goes through a large number of start and stop cycles. In some situations, gas purge serves to avoid or minimize various types of material degradation in a fuel cell stack, some of which are permanent and catastrophic. In others, gas purge is intended to remove water from the fuel cell, thus avoiding ice formation and blockage when exposed to sub-freezing temperatures.

Much research has reported the possible carbon corrosion on the air electrode due to residual hydrogen in the anode during idle state. This degradation is primarily caused by the presence of a H₂/O₂ front in the anode along with the high cathode voltage (∼ open circuit voltage), and can be prevented by fully removing the hydrogen from the anode compartment. Lee et al. studied the effect of the residual hydrogen in the anode compartment during the idle using polarization measurement, cyclic voltammetry and electron microscopy, and found that hydrogen removal from the anode channels by gas purge helps prevent fuel cell degradation (53).

In the cathode side, on the other hand, the primary purpose of gas purge is to remove water from the cathode compartment, particularly in preparation for cold start from subzero temperatures. As gas purge defines the initial condition of water
distribution in a cell, it is a crucial step in the PEFC cold start. Recent experimental studies have amply shown that not only performance but also material durability of PEFC hinges strongly upon the gas purge process prior to cool-down and cold start as reviewed in Section 1.2.2. This is because an effective gas purge can remove water from the catalyst layer and membrane, thereby creating space for water produced in cold start to be stored.

In Chapter 2 we developed a method of equilibrium purge, in which a cell is purged with partially humidified gas for an extended period of time (typically three hours or more) so as to remove all the liquid water in the cell as well as to equilibrate the proton exchange membrane and ionomer in the catalyst layer (CL) with the purge gas relative humidity (RH). The distribution of water in the cell is well controlled in equilibrium purge, thus providing an excellent experimental technique for fundamental research of PEFC cold start and other problems requiring highly reproducible gas purge practice. Whereas the equilibrium purge is useful for laboratory experiments, practical gas purge for FCVs requires much shorter duration, preferably less than 60 seconds, and high efficiency. Therefore, a fundamental understanding of water removal during practical gas purge is necessary. Unfortunately, very little is known in the literature on purge mechanisms for automotive application. St-Pierre et al. (90) showed that cool purge at 20°C is better than hot purge at 85°C. Performance losses were not observed in a cell purged with dry gas at 20°C after the freeze / thaw cycling. Bradean et al. (7) touched upon the purge effectiveness using one section of their paper to briefly present a one-dimensional model and experimental results, and concluded that the purge cell
temperature is the most critical parameter for an effective purge. However, they did not seek a fundamental understanding of purge mechanisms.

Ge and Wang (23) measured the cell high-frequency resistance (HFR) during gas purge with various purge durations, and demonstrated that the cell HFR directly impacts the amount of product water generated or cell operational time in isothermal cold start. Sinha et al. (83) used X-ray microtomography to dynamically visualize the liquid water in the gas diffusion layer (GDL) and calculated the variation of liquid saturation with time during room-temperature purge. St-Pierre et al. (89) applied a residence time distribution method and demonstrated its potential to detect the amount of liquid water in the gas channels and the gas diffusion electrodes. Lee et al. (54) studied the water removal characteristics during gas purge, where the residual water in a fuel cell after gas purge was forced to evaporate under low pressure and the gaseous pressure was measured to estimate the amount of residual water. They reported the general trend of the water removal with various parameters such as the flow rate and purge temperature, but not much discussion was found about the water removal mechanisms. Most recently, Sinha and Wang (84) presented a comprehensive theoretical description of water removal phenomena during gas purge, classifying the process into four stages, through-plane drying, in-plane drying, vapor transport and membrane equilibrium stages. The theoretical predictions further concluded that the high cell temperature and low RH and high flow rate of purge gas facilitates water removal.

The present work concerns experimental characterization of gas purge typical of automotive applications. In the next section, we describe a new experimental method, setup, and procedure to characterize gas purge of short duration. Much attention has
been paid to finding a procedure to achieve reproducible purge experiments. A purge curve is defined and stages of gas purge are elaborated. Then, we introduce two characteristic parameters to describe the purge performance. Finally, we present a comprehensive set of experimental results characterizing automotive gas purge for the first time.

3.2 Experimental Methods

We note that the purpose of gas purge is not to address how much water is removed from the cell, or how thoroughly the GDL is dried. Instead, gas purge is ultimately to remove water from the catalyst layer and membrane, thereby creating space for water produced in cold start to be stored. Thus, we propose to use the membrane HFR (or more conveniently cell HFR) as the indicator to measure effectiveness of gas purge. A purge curve is thus defined as the cell HFR versus purge time in this work. An effective purge protocol is the one that reaches a certain HFR within the shortest purge time (with least energy consumption as well).

3.2.1 Experimental setup

The fuel cell used in this study (Figures 2.1-2.3) has straight, parallel flow channels with the dimensions of 54mm length, 1mm width, 0.6mm depth, and 1mm land width. The number of channels is 24, with total active area of 25cm$^2$. The membrane electrode assemblies (MEAs) used are commercially available from Japan Gore-Tex Inc. with 30µm thick membrane and catalyst layer of 0.4mg/cm$^2$ Pt on each electrode. Toray carbon paper coated with a microporous layer (MPL) was used as the GDL.
The fuel cell discharge and gas purge operation is carried out and controlled by a fuel cell test station (Arbin Instruments, College Station, TX), and the cell temperature is controlled with a heat transfer fluid passing through the coolant channels located in the stainless steel end plates. During gas purge, the cell HFR is measured at 1 kHz using an AC milliohm meter (Tsuruga model 3566, Osaka, Japan).

### 3.2.2 Experimental procedure

The practical, short-duration gas purge of a fuel cell is inherently transient and extremely sensitive to the initial water distribution inside the cell. Therefore, controlling the initial conditions prior to gas purge is of paramount importance to ensure reproducibility and consistency of purge results. Extreme care must be taken to establish a controllable pre-purge condition and demonstrate the repeatability of purge data. Our procedure, after extensive trial-and-error, is described below.

First, the fuel cell is operated at a discharge current density of 0.5A/cm$^2$ for one hour with fully humidified H$_2$ and air at 30°C. This step is to ensure that the membrane is identically in the fully hydrated state in all experiments. Then, an equilibrium purge is carried out for the cell, that is, the cell is purged with partially humidified nitrogen for a sufficiently long period (typically 3 to 4 hours). In this study the cell temperature is fixed at 35°C while the purge gas dew point is controlled at 30°C, which corresponds to 75% relative humidity. At the end of this step liquid water in the cell is expected to be completely removed and the membrane is in equilibrium with the 75% RH gas. At this point it is assumed that all the history of the cell is totally erased and the cell is in the identical condition of every experiment.
The next step is to create a controllable pre-purge condition by mimicking the FCV situations prior to shutdown and gas purge, that is, to generate some liquid water in the cell. By changing operating conditions of this step, it is possible to control the amount of liquid water in the cell. In the present study, we discharge the cell at 0.5A/cm² for 10 minutes with cell temperature of 55°C and stoichiometry of 18 and 21.6 for H₂ and air, respectively, both fully humidified and at ambient pressure. Although we cannot quantify the amount of liquid water present in the cell prior to purge, we can reproduce the same initial condition under which a comparative study becomes possible.

Then, the cell is gas-purged under various conditions to be described in detail in the next section. For all cases the gas-purge was conducted for both electrodes independently without circulation. Once a gas purge is completed, the valves at the cell inlet and outlet are closed and the cell temperature is maintained constant to monitor any HFR change after purge. The membrane HFR typically decreases over the time scale of one to two hours, a phenomenon called HFR relaxation after purge in this work.

### 3.2.3 Two characteristic parameters for water removal

To better analyze and understand gas purge, we propose two characteristic parameters based on a simplified schematic of purge physics, as shown in Figure 3.1. Although the figure only shows the cathode side of the fuel cell from the polymer electrolyte membrane to the gas channel, the same conceptual depiction is applicable to the anode side. Prior to gas purge, CL and GDL are partially saturated with liquid water. We assume that water removal during gas purge is primarily a vapor-phase transport process, because liquid water residing in gas channels is swept away typically within the
very first seconds of purge operation and the liquid water motion inside CL and GDL is sufficiently slow to be considered quasi-stationary in the time scale of a gas purge. Thus, the water is removed from the liquid surfaces residing within CL/GDL to the gas channel by through-plane vapor diffusion. Subsequently, the water is removed by the down-the-channel convection by purge gas. Mathematically, the first process of water vapor removal can be characterized by the through-plane diffusive flux between a liquid surface in CL/GDL to the gas channel, i.e. \( D(p_{v,\text{sat}} - p_{v,\text{inlet}})/RT/\delta_{\text{GDL}} \). Here \( D \) stands for the diffusion coefficient of water in purge gas, and \( p_{v,\text{sat}} \) and \( p_{v,\text{inlet}} \) the saturation vapor pressure at the purge temperature and the water vapor partial pressure in the purge gas at the inlet, respectively. \( R \) is the universal gas constant, \( T \) the purge cell temperature, and \( \delta_{\text{GDL}} \) an effective diffusion length for water vapor from the membrane surface to the gas channel, which should scale mainly with the GDL thickness but could also contain effects of CL and MPL thickness and porosity, as well as the effects of the land-to-channel width ratio to account for in-plane transport effects.

The second process of water vapor removal down the channel can be described by the convective flux, \( Q(p_{v,\text{sat}} - p_{v,\text{inlet}})/RT/A \), representing the maximum amount of water vapor removed with the purge gas when the exit purge gas is fully saturated with vapor. In the above definition \( Q \) is the purge gas volumetric flow rate and \( A \) the active area of the fuel cell. Both parameters defined above have the unit of \( \text{mol/s per unit of the fuel cell active area} \). It follows that the net rate of water removal during gas purge is determined by the two characteristic parameters and their relative magnitudes.
To study the effects of these characteristic parameters as well as the direct operating parameters, such as the purge cell temperature and purge gas flow rate, we have taken the following approach in carrying out experiments.

1. To examine the effect of the vapor diffusion coefficient $D$, $N_2$ and He are used as the purge gas in this study. The diffusion coefficient of water vapor in He is roughly three times that in $N_2$. While impractical for vehicle application, He gas is used here solely as a diagnostic tool.

2. The purge gas RH in the vast majority of our experiments has been controlled at higher than 40% in order to avoid the regime of very low membrane water content where there is a large uncertainty in our knowledge of the membrane behavior.

3. The duration of gas purge is 60 seconds in most experiments (except section 3.3.1), and experimental data include the profiles of HFR evolution with time during purge and the final HFR values at the end of purge.

All purge conditions in this study are tabulated in Table 3.1 along with the calculated two characteristic parameters. Two purge gases, $N_2$ and He, are used with four different flow rates for $N_2$ (1.0, 3.0, 4.5, and 9.0 L/min) and two flow rates for He (1.0 and 4.5 L/min). The cell temperatures at purge are 42, 55, and 75°C, respectively, and for all temperatures the RH of the purge gas is controlled at no less than 40% based on the purge cell temperature. The case 1 condition, for example, gives the diffusive flux and the convective flux of $2.96 \times 10^{-5} \text{mol/cm}^2/\text{s}$ and $1.43 \times 10^{-6} \text{mol/cm}^2/\text{s}$, respectively, using the following values: $D = 0.318 \text{cm}^2/\text{s}$, $p_{v,\text{sat}} = 8132 \text{Pa}$, $p_{v,\text{inlet}} = 3253 \text{Pa}$, $T = 315.2\text{K}$, $\delta_{\text{GDL}} = 0.02\text{cm}$, $Q = 19.2 \text{cm}^3/\text{s}$ (= 1 L/min at 0°C), and $A = 25 \text{cm}^2$. 
Furthermore, because the cell HFR or membrane proton conductivity is also a function of temperature, we convert the raw HFR data at different purge temperatures to the single reference temperature of 30°C via the following temperature-dependent correlation obtained empirically as described in the next subsection:

\[
T\text{-compensated HFR} = \exp\left[1455\left(\frac{1}{303} - \frac{1}{T}\right)\right]HFR_{\text{purge}}
\]

(3.1)

The temperature-compensated HFR is then essentially indicative of membrane water content only, and the temperature dependence is removed from actually measured HFR data. All HFR results shown in the following sections are the T-compensated values, unless otherwise noted.

### 3.2.4 Proton Conductivity Measurement for Japan Gore-Tex Membrane

Because Japan Gore-Tex membrane has different proton conductivity dependency on temperature and on water content from that of Nafion membrane, the equations 1.3 and 1.4 proposed by Springer et al. (88) cannot be used to estimate the HFR at 30°C for Japan Gore-Tex membrane. Therefore, the proton conductivity of Japan Gore-Tex membrane was measured at various temperatures and water vapor activities, and an expression was developed as function of these parameters as described below.

During the equilibrium purge the purge gas dew point was set to 30°C and the cell temperature was set to the various values, which are equivalent to the purge gas relative humidity of 0.3, 0.45, 0.6, 0.76, and 0.9. When the cell HFR reaches the steady state, the valves upstream and downstream of the cell were closed and the cell temperature was
varied between 10 and 55°C to obtain the HFR change with temperature. Figure 3.2 shows the HFR change with temperature for various water activity.

The measured overall cell HFR consists of the resistance of the cell components, such as the current collectors (CC) and the bipolar plates (BPP) and various contact resistances between two components (Figure 3.3a), and is expressed algebraically as follows.

\[
HFR_{\text{cell}} = 2R_{\text{CC}} + 2R_{\text{CC-BPP}} + 2R_{\text{BPP}} + 2R_{\text{BPP-GDL}} + 2R_{\text{GDL}} + 2R_{\text{GDL-CCM}} + R_{\text{CCM}} \tag{3.2}
\]

In order to eliminate the unnecessary resistance components and extract the pure CCM resistance, a dummy cell resistance was measured. The dummy cell was assembled without the CCM (Figure 3.3b), and its resistance consists of the following components.

\[
HFR_{\text{dummy}} = 2R_{\text{CC}} + 2R_{\text{CC-BPP}} + 2R_{\text{BPP}} + 2R_{\text{BPP-GDL}} + 2R_{\text{GDL}} + R_{\text{GDL-GDL}} \tag{3.3}
\]

Finally, subtracting the equation 3.3 from the equation 3.2 yields the CCM resistance \(R_{\text{CCM}}\) and two contact resistances.

\[
HFR_{\text{cell}} - HFR_{\text{dummy}} = R_{\text{CCM}} + (2R_{\text{GDL-CCM}} - R_{\text{GDL-GDL}}) \tag{3.4}
\]

Assuming these remaining contact resistances are negligible and every resistance component is independent of the temperature, the pure CCM resistance can be estimated.
The actual resistance of the dummy cell was measured about 11mΩcm$^2$.

Figures 3.4 and 3.5 show the conductivity of Japan Gore-Tex CCM with 30 µm thickness as function of temperature and water activity, respectively. The CCM resistance was first calculated using the equation 3.4 and converted to the form of conductivity.

Using the numerical data listed in Table 3.2, and assuming the similar form of expression to the Springer’s one, the following correlation is obtained.

$$\kappa_e = \exp \left[ 1455 \left( \frac{1}{303} - \frac{1}{T} \right) \right] \left( 0.06756a^3 - 0.09007a^2 + 0.06799a - 0.01104 \right) \quad (3.5)$$

3.3 Results and Discussion

3.3.1 Verification of repeatability

As explained earlier, realizing consistent and reproducible purge experiments is a critical step towards the development of a reliable purge database and hence a fundamental understanding of purge mechanisms. Here, we verify the experimental repeatability through multiple purge experiments of various duration performed under identical purge conditions. Figure 3.6 shows the time evolution of cell HFR during gas purge for four experiments with different purge duration. The purge cell temperature is 55°C and the purge gas is dry N$_2$ with the flow rate of 4.5 L/min. We use the dry purge gas in this set of experiments, unlike all other experiments of this study, in order to provide the most severe condition to verify the experimental repeatability. It should also be mentioned that the cell HFR shown in this figure is not compensated for temperature, but raw data
at the cell temperature of 55°C. The excellent repeatability is evident by the fact that purge curves of longer duration closely overlap those of short durations, under otherwise identical purge conditions. We recommend that the type of repeatability tests as shown in Figure 3.6 be carried out as a standard procedure in all purge experiments before reporting meaningful results.

### 3.3.2 Stages of purge

Figure 3.6 also reveal general characteristics of a purge curve, consistent with the model prediction of Sinha and Wang (84). Several stages of gas purge are evident from the 60-second purge case shown in Figure 3.6. The first stage (between 0 and ~20 sec) can be called the slow rise period (SRP) where the membrane HFR does not rise substantially. This stage can be subdivided into SRP1 (0 to ~10 sec) and SRP2 (10 to ~20 sec). Physically, SRP1 coincides with the through-plane drying where liquid water is evaporated from CL/GDL underneath the channel area. This is then followed by SRP2 where the drying front propagates along the in-plane direction into the land area. During SRP1 and SRP2, the CL/GDL remains saturated with water vapor and hence the membrane remains nearly fully hydrated. We define the end of SRP as the critical point, at which contiguous clusters of liquid water have completely disappeared in CL/GDL. While the SRP seems ineffective to increase the membrane HFR, it is a required step of gas purge to clear liquid water from CL/GDL and every gas purge must go beyond the critical point to be effective. Thus, the critical point also defines the minimum of purge duration. A residence time distribution method may be applicable to detect the liquid
water saturation in the GDLs during SRP, although several issues have to be solved such as the treatment of dynamic saturation change during the measurement (89).

After the critical point, purge enters the fast rise period (FRP) (between 20 and \(\sim 45\) sec in Figure 3.6), where the membrane HFR is seen to rise substantially. Physically, the FRP coincides with the vapor diffusion process with the entire membrane subject to water desorption by dry gas. The FRP is finally followed by a membrane equilibration period (MEP) where water content in the membrane gradually reaches equilibrium with the relative humidity of purge gas. As a consequence, HFR asymptotically approaches the theoretical value corresponding to the equilibrium water content. In Figure 3.6, due to the short duration of purge, the MEP is not clearly visible. A schematic illustration of all stages of gas purge is provided in Figure 3.7. Evidently, the FRP is the most efficient period of gas purge. Hence, an optimized gas purge should pass beyond the critical point, take full advantage of the FRP, but not dwell on the MEP.

### 3.3.3 Effect of purge cell temperature

Based on our afore-mentioned hypothesis that the primary mechanism of water removal during gas purge is by the vapor phase, the purge performance is expected to strongly depend on the saturation vapor pressure or equivalently, the purge cell temperature. Figures 3.8-3.10 show the purge curves and the final HFR after 60-second purge for various purge cell temperatures. The purge curves plotted in Figure 3.8 correspond to three cell temperatures and two purge gases, respectively, with a constant flow rate of 4.5 L/min for each side. Two observations can be made. First, as the purge cell temperature increases, the HFR rise becomes faster and the final value at 60 seconds is
higher. Second, at all temperatures the He purge is more effective than \(N_2\). The final HFR value depends primarily on the slope of the FRP (between 5 and 10 second in He, 75\(^\circ\)C purge case, for instance) and this slope is related to the through-plane diffusive flux of water vapor. Furthermore, at 75\(^\circ\)C with He, the HFR approaches a constant asymptote of \(\sim 650 \text{m}\Omega \text{cm}^2\) already in less than 60 seconds, signifying the attainment of MEP of gas purge. From this result it can be expected that if all purge experiments continue for a sufficiently long period, the final temperature-compensated HFR values all approach \(\sim 650 \text{m}\Omega \text{cm}^2\).

In Figure 3.9 the T-compensated HFR after 60 second purge is plotted as a function of temperature for two purge gases with two flow rates. At every temperature or flow rate, the He gas purge (open symbols) yields higher HFR than \(N_2\) (solid symbols), due to its high water vapor diffusivity. However, with 1 L/min flow rate the advantage of He almost vanishes at 75\(^\circ\)C, as the water removal in this case is limited by the convective flux down the channel and the enhanced diffusion does not help.

Figure 3.10 displays the T-compensated HFR as a function of the through-plane vapor diffusion flux. If there is sufficiently large flow rate, the resulting HFR should no longer be affected by the convective flux of water vapor down the channel, and hence the HFR would be determined only by the diffusive flux. In Figure 3.10 it is seen that the purge curves for \(N_2\), 1.0 L/min and He, 1.0 L/min deviate from each other even at the same diffusive flux (e.g. \(1 \times 10^{-4} \text{mol/cm}^2/\text{s}\)). This is because the flow rate in this case is not large enough to eliminate the effect of convective flux. Similarly, the purge curves for \(N_2\), 4.5 L/min and He, 4.5 L/min differ, although the difference becomes smaller than the 1.0 L/min case, indicating that the contribution of convective flux becomes weaker
at the higher flow rate. It is expected that if we further increase the flow rate, the purge curves for N$_2$ and He will collapse together over an entire range of the diffusive flux, indicative of a diffusion-controlled regime free of the convection effect down the channel.

3.3.4 Effect of purge gas flow rate

Next, the effect of the purge gas flow rate is studied and displayed in Figures 3.11-3.13. The flow rate, or equivalently gas velocity, affects not only the vapor capacity rate of the channel flow but also the residence time of purge gas through the channels. The higher flow rate gas stays for a shorter time in the channel, allowing less vapor diffusion into the channel and reaching the exit with lower relative humidity, and vice versa. Therefore, even in the diffusion-dominated regime the purge curve is partly controlled by the purge gas flow rate.

Figure 3.11 shows the purge curves for various flow rates at 55°C purge cell temperature. At a certain temperature (55°C in this case) the slope of the HFR curve in the in-plane drying stage (i.e. SRP2) becomes larger, and the transition to the FRP takes place sooner for He than N$_2$. Larger flow rate results in the higher HFR rise for the aforementioned reasons. In Figure 3.12 the T-compensated HFR is plotted as a function of purge gas flow rate for three different temperatures. In most cases the final HFR increases with the flow rate, but at 75°C the final HFR of N$_2$ purge begins to level off at the flowrate of $\sim$4 L/min and further increase in flowrate does not increase the HFR. It is believed that a regime controlled by through-plane vapor diffusion has been reached at this high temperature and high flowrate. Under the same conditions, the He gas purge is seen to yield higher HFR than N$_2$ because of its higher water diffusivity. In
the diffusion-dominated regime or at the limit of sufficiently large flow rate, the rate of water removal is only determined by the diffusion parameter; as such, and the resulting HFR is higher for He purge than $N_2$.

It should be noted that the advantage of He gas purge diminishes with the increasing temperature, as can be seen from the purge curves displayed in Figure 3.8. At high temperature such as $75^\circ$C, the HFR evolution nearly reaches the equilibrium stage, in other words, the membrane is nearly equilibrated with the 40%RH purge gas after 60 second purge both in He and $N_2$ cases. However, the transition from FRP to MEP occurs much earlier for He gas purge (about 10 second at $75^\circ$C) than for $N_2$ (about 20 second at $75^\circ$C). Therefore, when the system requires the shorter purge duration such as 15 seconds, the advantage of He gas purge is still significant.

Next, the T-compensated HFR is plotted in Figure 3.13 as function of the convective flux of water vapor down the channel, where the data points for the same diffusive flux are connected by a dashed line. It can be seen that all dashed lines corresponding to various diffusive fluxes do not cross each other and that at a certain convective flux the resulting T-compensated HFR value after 60 second purge monotonically increases with the diffusive flux. For instance, at the convective flux of $1 \times 10^{-5}$ mol/cm$^2$/s, the T-compensated HFR increases from 300mΩcm$^2$ at $\zeta_d = 3.0$ to 620mΩcm$^2$ at $\zeta_d = 45.7$. Thus, we conclude that the T-compensated HFR after 60 second purge may be expressed as a unique function of these two parameters only, namely:

$$T\text{-compensated HFR} = f\left(\frac{D(p_{v,sat} - p_{v,inlet})}{RT\delta_{GDL}}, \frac{Q(p_{v,sat} - p_{v,inlet})}{RTA}\right)$$ (3.6)
Equation (3.6) is significant in that the HFR after purge becomes predictable based on calculations of the through-plane diffusive flux and convective flux down the channel.

3.3.5 Matching two parameters

To further test the hypothesis that the HFR after purge is uniquely determined by the two characteristic parameters defined above, two additional purge experiments were conducted as tabulated in Table 3.1 (case # 19 and 20). In these experiments, both diffusive and convective fluxes are matched while the purge cell temperature is varied. Case # 2 (N\textsubscript{2}, 55\textdegree C, 1L/min) has the parameters \((\zeta_d, \zeta_c) = (5.9, 2.8)\) while Case # 19 (He, 42\textdegree C, 2L/min) has the parameters of \((9.2, 2.9)\) which closely match Case #2. Similarly, # 3 (N\textsubscript{2}, 75\textdegree C, 1L/min) and #20 (He, 55\textdegree C, 2.5L/min) share the nearly identical diffusive and convective fluxes. The purge curves for these four cases with the diffusive and convective fluxes closely matched are displayed in Figure 3.14. It is interesting to note that if the two characteristic parameters are matched, the HFR evolution indeed exhibits a similar pattern, and the resulting T-compensated HFR after 60 second purge is nearly equal. Figure 3.14 strongly suggests that a purge curve can be adequately described by the diffusive and convective fluxes developed in this work.

3.3.6 HFR relaxation

Another interesting phenomenon observed in this work is that after purge the cell HFR gradually decreases in a time scale of hours, which we call HFR relaxation after purge. Typical results of HFR relaxation are shown in Figure 3.15. The purge conditions prior to the relaxation correspond to three different purge temperatures (42,
55, or $75^\circ$C) with 4.5L/min $N_2$ (cases #7, 8, and 9 in Table 3.1). When the 60 second purge is completed, the valves at the inlet and outlet of the cell for both anode and cathode gas lines are closed and the cell temperatures are maintained constant at the purge cell temperature during the whole relaxation process.

Fundamental mechanisms of this relaxation phenomenon remain unknown and need future investigation. However, correlating the T-compensated HFR after relaxation with that after purge is of practical interest, because the initial membrane water content critically important for PEFC cold start performance corresponds to the HFR after relaxation (during cool-down), not the HFR immediately after purge. For this reason, we attempt an empirical correlation between the HFR after purge and that after relaxation, as shown in Figure 3.16. It can be seen that a reasonable correlation exists over a range of HFR, or equivalently membrane water content, that ranges from full humidification to that corresponding to 40% RH. It is clear from Figure 3.16 that the extent of HFR relaxation after purge increases with lowering membrane water content. Beyond the HFR corresponding to 40% RH, we do not include any data in Figure 3.16 as they become widely scattered and somewhat chaotic. We note that HFR relaxation after purge becomes stochastically random as soon as the membrane becomes drier than that corresponding to 40% RH.

The correlation shown in Figure 3.16 provides a practical means to estimate the HFR or membrane water content as the important input to evaluate cold-start performance as described in the previous chapter (94)(95). That is, one can estimate the HFR after purge from equation (3.6) based on the purge conditions, and subsequently correct for HFR relaxation using Figure 3.16. Based on the HFR value after relaxation or
prior to cold start, one can use the analytical models and performance data developed in previous work to estimate the cold start performance.
Table 3.1: Purge conditions and HFR values after 60 seconds of purge.

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<td>cell temperature (°C)</td>
<td>55</td>
<td>75</td>
<td>42</td>
<td>55</td>
<td>75</td>
<td>42</td>
<td>55</td>
<td>75</td>
<td>42</td>
<td>55</td>
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<tr>
<td>purge gas dew point (°C)</td>
<td>37</td>
<td>55</td>
<td>26</td>
<td>37</td>
<td>55</td>
<td>26</td>
<td>37</td>
<td>55</td>
<td>26</td>
<td>37</td>
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<tr>
<td>purge gas flow rate (at 0°C) (L/min)</td>
<td>9</td>
<td>9</td>
<td>1</td>
<td>1</td>
<td>1</td>
<td>1</td>
<td>4.5</td>
<td>4.5</td>
<td>4.5</td>
<td>2</td>
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<td>purge gas species</td>
<td>N₂</td>
<td>N₂</td>
<td>He</td>
<td>He</td>
<td>He</td>
<td>He</td>
<td>He</td>
<td>He</td>
<td>He</td>
<td>He</td>
</tr>
<tr>
<td>convective flux (×10⁶) (mol/cm²/s)</td>
<td>24.92</td>
<td>60.98</td>
<td>1.43</td>
<td>2.77</td>
<td>6.78</td>
<td>6.45</td>
<td>12.46</td>
<td>30.49</td>
<td>2.86</td>
<td>6.92</td>
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<td>post-purge HFR (mΩcm²)</td>
<td>410</td>
<td>340</td>
<td>252</td>
<td>335</td>
<td>306</td>
<td>361</td>
<td>399</td>
<td>366</td>
<td>305</td>
<td>383</td>
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<tr>
<td>T-compensated HFR (mΩcm²)</td>
<td>591</td>
<td>633</td>
<td>303</td>
<td>483</td>
<td>569</td>
<td>433</td>
<td>575</td>
<td>681</td>
<td>366</td>
<td>552</td>
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<td>relaxed HFR (mΩcm²)</td>
<td>135</td>
<td>180</td>
<td>165</td>
<td>148</td>
<td>160</td>
<td>173</td>
<td>210</td>
<td>131</td>
<td>143</td>
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<tr>
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<td>195</td>
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<td>156</td>
<td>238</td>
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<td>391</td>
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Table 3.2: Conductivity data of Japan Gore-Tex MEA. Water content is calculated using the Springer’s correlation (equation 2.3).

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<th>Water activity</th>
<th>0.30</th>
<th>0.45</th>
<th>0.60</th>
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<td></td>
<td></td>
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<tr>
<td>50°C</td>
<td>$3.98 \times 10^{-3}$</td>
<td>$9.87 \times 10^{-3}$</td>
<td>$1.61 \times 10^{-2}$</td>
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<td>$9.22 \times 10^{-3}$</td>
<td>$1.51 \times 10^{-2}$</td>
<td>$2.16 \times 10^{-2}$</td>
<td>$3.16 \times 10^{-2}$</td>
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<td>40°C</td>
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<td>$8.68 \times 10^{-3}$</td>
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<td>$2.07 \times 10^{-2}$</td>
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<td>35°C</td>
<td>$3.38 \times 10^{-3}$</td>
<td>$8.15 \times 10^{-3}$</td>
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<td>$1.99 \times 10^{-2}$</td>
<td>$2.78 \times 10^{-2}$</td>
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<tr>
<td>30°C</td>
<td>$3.16 \times 10^{-3}$</td>
<td>$7.46 \times 10^{-3}$</td>
<td>$1.20 \times 10^{-2}$</td>
<td>$1.84 \times 10^{-2}$</td>
<td>$2.64 \times 10^{-2}$</td>
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<tr>
<td>25°C</td>
<td>$2.86 \times 10^{-3}$</td>
<td>$6.81 \times 10^{-3}$</td>
<td>$1.09 \times 10^{-2}$</td>
<td>$1.71 \times 10^{-2}$</td>
<td>$2.47 \times 10^{-2}$</td>
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<tr>
<td>20°C</td>
<td>$2.61 \times 10^{-3}$</td>
<td>$6.21 \times 10^{-3}$</td>
<td>$9.95 \times 10^{-3}$</td>
<td>$1.57 \times 10^{-2}$</td>
<td>$2.30 \times 10^{-2}$</td>
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<td>15°C</td>
<td>$2.31 \times 10^{-3}$</td>
<td>$5.53 \times 10^{-3}$</td>
<td>$9.02 \times 10^{-3}$</td>
<td>$1.42 \times 10^{-2}$</td>
<td>$2.10 \times 10^{-2}$</td>
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<td>10°C</td>
<td>$2.08 \times 10^{-3}$</td>
<td>$4.99 \times 10^{-3}$</td>
<td>$8.08 \times 10^{-3}$</td>
<td>$1.27 \times 10^{-2}$</td>
<td>$1.89 \times 10^{-2}$</td>
</tr>
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</table>
Figure 3.1: Schematic diagram of two limiting stages of water removal during gas purge.
Figure 3.2: HFR change of the test cell with Japan Gore-Tex 30μm CCM with temperature
Figure 3.3: Components of cell HFR resistance.
Figure 3.4: Japan Gore-Tex 30µm CCM conductivity change with temperature.
Figure 3.5: Japan Gore-Tex 30µm CCM conductivity change with activity.
Figure 3.6: Time evolution of cell HFR for four experiments with different purge durations. Data were recorded at 1Hz.
Figure 3.7: Stages of purge curve.
Figure 3.8: Time evolution of cell HFR at different cell temperatures and for various purge gases. Data were recorded at 1Hz.
Figure 3.9: Cell HFR after 60 second purge as a function of purge cell temperature.
Figure 3.10: Cell HFR after 60 second purge as a function of diffusive flux of water vapor.
Figure 3.11: Time evolution of cell HFR during purge at 55°C cell temperature. Data were recorded at 1Hz.
Figure 3.12: Cell HFR after 60 second purge as function of purge gas flow rate.
Figure 3.13: Cell HFR after 60 second purge as function of convective flux of water vapor.
Figure 3.14: Time evolution of cell HFR with matched parameters. Data were recorded at 1Hz.
Figure 3.15: HFR relaxation after purge. Data were recorded at every minute.
Figure 3.16: Relation between HFR after relaxation and HFR after 60 second purge with purge gas RH greater than 40%. The dashed line symbolizes no HFR relaxation.
Chapter 4

TIME- AND SPACE-RESOLVED HFR MEASUREMENTS DURING GAS PURGE

Chapter 3 discussed fundamentals of gas purge with a differential cell which had relatively short channel length and high flow rate, and therefore had negligibly small along-the-channel variation of some parameters. However, one can expect that the purge effectiveness decreases as the purge gas flows down the channel because of the increasing water vapor pressure. Therefore, in order to develop a time-saving, energy-efficient purge protocol for vehicular applications, it becomes important to capture the spatial distribution of purge effectiveness.

4.1 Experimental

4.1.1 Segmented cell

Figure 4.1 shows the sketch of the segmented cell used to investigate the along-the-channel variation, and its photograph is in Figure 4.2. The active area is 6mm width \( \times \) 100mm length = 6cm\(^2\), with 3 parallel, straight channels. The channel cross-sectional dimensions are 1mm width, 0.5mm depth, and 1mm land width. The 100mm length is divided into 10 segments. Each segment of bipolar plate is made of stainless steel with gold plating, and inserted to the polycarbonate plate. Since the number of the channels is decreased from 24 in the 25cm\(^2\) cell used in Chapters 2 and 3 to 3 in the segmented cell, the flow rates were also reduced to 1/8 of the values for the 25cm\(^2\) cells.
For example, to compare the purge results with 4.48 L/min purge gas flow rate for 25 cm$^2$, 4.48/8 = 0.56 L/min was used for the segmented cell.

Figure 4.3 schematically displays the diagram of e-load connections and the high frequency resistance (HFR) measurement method. For simplicity, this figure only shows four segments and e-loads, but in reality 10 segments are individually connected to 10 independent e-loads. When the Tsuruga milliohm meter is used for HFR measurement, a manual rotary switch is used to switch the connection from the milliohm meter to the targeted segment. Meanwhile, the Arbin fuel cell test station also has HFR measurement function with 1.5 kHz frequency, and this function was used to obtain the segment local HFR during the short purge process. When the Arbin HFR was used, the Tsuruga milliohm meter was disconnected to avoid interference with the measurement. A photograph of the experimental setup with the cable connections in the segmented cell experiment is shown in Figure 4.4 to visualize the difficulty of this experiment.

### 4.1.2 Difficulties in local HFR measurement

Figure 4.5 illustrates three major factors which make local HFR measurement difficult in the segmented cell.

The first factor is compression non-uniformity. This non-uniformity generates the contact resistance variation from segment to segment. Since the measured HFR includes the contact resistance, the actual measurement does not provide directly the proton conductivity in the membrane, which is what we really want to measure. The contact resistance uniformity can be evaluated by measuring the resistance between two segments in anode or in cathode, and plotting the resistance versus the distance.
between the segments, as shown in Figure 4.6. In this figure the resistance between two segments were measured, such as segments #1 and #2, #1 and #3, #1 and #4, and so on, and the resistances were plotted with the distance, for example (distance = 1) for segments #1 and #2, (distance = 2) for #1 and #3. Each measured resistance includes two contact resistances between segmented bipolar plates and GDL and GDL in-plane electric resistance. GDL in-plane electric resistance is expected to be proportional to the distance, and therefore, when the contact resistances are uniform for all segments, the plots should be linear. From the results shown in Figure 4.6, it is reasonable to consider the contact is uniform for both anode and cathode sides. It should be noted that the slight difference between anode and cathode is due to the difference of physical contact.

The second factor in Figure 4.5 is a cross-talk of imposed AC current to the adjacent segments. Because the electric conductivity in GDL in-plane direction is relatively good, the imposed current scatters from the targeted segment to the other segments and passes through the membrane in more than one segment. This causes the measured local HFR to appear lower than the actual local HFR in area-specific terms. This effect is calibrated and compensated in the following purge results, and the method of calibration is explained in detail in Section 4.2.1.

The third factor in Figure 4.5 is interference between the multiple, simultaneous HFR measurements. If we impose two or more AC currents from distinct sources to measure the local HFR, then the currents interfere and the resulting AC voltage measurements are ruined. To avoid this interference we must ensure the HFR measurement one segment at a time. For this reason, the moment of the local HFR measurement, such as shown in Figure 4.10, were shifted in time from segment to segment.
4.2 Results and discussion

4.2.1 Local HFR calibration

As mentioned earlier (Section 4.1.2), the cross-talk current for local HFR measurement in the segmented cell results in the lowered HFR and must be calibrated. In this section the calibration method is explained.

The calibration was performed using the equilibrium purge technique. First the equilibrium purge was carried out with known RH (say, 75%RH). At the end of the equilibrium purge, it is considered that the membrane is uniformly equilibrated with 75%RH gas from segment 1 to 10. At this moment we measure the overall cell resistance by bundling all segment cables into one and connecting this to the milliohm meter. This value exhibits real HFR at this RH, and the cell overall HFR should be equal to the cell local HFR in the area-specific wise (with the unit of mΩcm²). Thus, this value is called the actual local HFR.

Then we measure the local HFR using Arbin HFR measurement function, and call it the measured local HFR. Now we have one-to-one correspondence from the measured local HFR to the actual local HFR at 75%RH for each segment. Repeating this measurement for various RH, we have ten conversion correlations from the measured local HFR to the actual local HFR, one for each segment. We can apply these correlations to the measured local HFRs obtained during the purge and estimate the actual local HFR. This calibration method assumes the uniform water content everywhere in the membrane, and this is not true during the gas purge. However, the effect of non-uniformity in water content is neglected here.
The measured local HFRs are shown in Figure 4.7 at 55°C with five distinct relative humidities (30, 45, 60, 75, and 90%RH). We could predict that the segments near inlet or outlet had larger measured local HFR values than the middle segments because the middle ones have two ways (upstream side and downstream side) for the imposed current to spread out which makes the effective area larger. The results proved the prediction was true.

With this measurement, the conversion correlations were obtained using the second order polynomials as shown in Figure 4.8 for segments #1 to #5, and in Figure 4.9 for segments #6 to #10. These are tabulated in Table 4.1.

The limitation of this calibration method should be clarified. This conversion method uses the calibration data ranging from 30% to 90%RH, which corresponds to 200mΩcm² to 1700mΩcm² in the actual local HFR. Therefore, the actual local HFR values outside of this range are not quantitatively true. In particular, at the beginning of the purge it is likely that liquid water exists in the catalyst layer and that the actual local HFR is less than 200mΩcm². But the actual local HFR value less than 200mΩcm² only implies that the HFR is lower than 200mΩcm².

4.2.2 Along-the-channel variation

Figures 4.10-4.13 show the actual local HFR evolution and distribution during a short purge experiment. Note that the HFR values in these figures are not T-compensated HFR, but the values at 55°C. The purge conditions are: 55°C cell temperature, 0.56L/min (equivalent to 4.48L/min for 25cm² cell) purge gas flow rates with
40%RH, with pre-purge operation for 10 minutes at 30°C with 0.5A/cm². The experiments were conducted twice under identical conditions, first to measure the local HFR at odd number segments, and then for the even number segments. The purpose of this double experiments is to increase the time resolution, because if we measure the HFRs for all ten segments at once, the obtained data will be too coarse to draw the HFR evolution profiles.

The HFR evolutions are plotted in Figure 4.10 for even number segments. As explained, the values below 200mΩcm² are inconclusive, but still the result shows a clear trend in local HFR increase. Segment #2, closest to the inlet, shows quickest HFR increase and reaches the highest final value. As the segment moves downward, the rate of HFR increase becomes slow and the final value small. The local HFR distribution at particular moments (0 to 60 seconds with 10 second increment) for the same experiment is plotted in Figure 4.11. The HFR values at such particular moments are linearly interpolated (or extrapolated) from the obtained data.

The combined results of HFR evolution and HFR distribution from two identical experiments are plotted in Figure 4.12 and Figure 4.13, respectively. However, because of the experimental error, the HFR at segment #3 and segment #7 could not be properly obtained. Therefore these figures show the data for only 8 segments. These results show the qualitative trend. For example, the upstream segments have quicker HFR increase and higher final HFR values. However, because of the difficulty of combining two different experiments, it is difficult to carry out the quantitative analysis with these combined results. In addition, Figure 4.12 also shows the HFR increase profile in 25cm² cell. The purge curve for 25cm² cell shows transition to the membrane equilibration
period (MEP) near the end of purge (\(\sim 40\) seconds), while the local HFR curves do not show transition to MEP. Because the channel length of 25cm\(^2\) cell is 54mm, the average of HFR in the first 5 segments should be close to the 25cm\(^2\) results, but the obtained HFR values from segments 1 to 5 are higher than that from the 25cm\(^2\) cell.

It is concluded that further improvements in both experimental procedure and the calibration method are required to better quantitatively analyze the along-the-channel variation during gas purge.
Table 4.1: Conversion correlations from the measured local HFR to the actual local HFR.

<table>
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<th>segment number</th>
<th>A</th>
<th>B</th>
<th>C</th>
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<tbody>
<tr>
<td>1</td>
<td>0.0138</td>
<td>2.2052</td>
<td>32.441</td>
</tr>
<tr>
<td>2</td>
<td>0.0102</td>
<td>4.584</td>
<td>-53.685</td>
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<td>3</td>
<td>0.0093</td>
<td>5.5133</td>
<td>-144.38</td>
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<td>4</td>
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<td>-168.7</td>
</tr>
<tr>
<td>5</td>
<td>0.0058</td>
<td>6.5311</td>
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</tr>
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<td>6</td>
<td>0.0044</td>
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<td>-224.03</td>
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<td>7</td>
<td>0.0012</td>
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<td>8</td>
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</tr>
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<td>3.9034</td>
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</tr>
<tr>
<td>10</td>
<td>0.0056</td>
<td>1.8554</td>
<td>54.557</td>
</tr>
</tbody>
</table>

Actual local HFR (mΩcm$^2$) = $Ax^2 + Bx + C$

where $x$ = measured local HFR (mΩcm$^2$)
Figure 4.1: Sketch of 6cm$^2$ segmented cell.
Figure 4.2: Photograph of 6cm² segmented cell.
Figure 4.3: Diagram of the segmented cell measurement. The figure shows 4 segments only for simplification.
Figure 4.4: Photograph of segmented cell cable connection.
1. compression nonuniformity

Segmented cell results don't represent the ordinary cell characteristics. Measured HFR doesn't directly reflect the membrane conductivity.

2. cross-talk of HFR current

Imposed AC for HFR measurement can flow GDL in-plane and pass through membrane in other segments. This effect is larger in the middle segments than end segments.

3. simultaneous measurement

HFR cannot be measured at two or more segments simultaneously because of interference.

Figure 4.5: Three major factors making local HFR measurement difficult.
Figure 4.6: Linearity of resistances between two segments shows the uniformity in contact resistance. The expressions and residuals for anode and cathode are, respectively, $y = 99.15x + 63.694$, $R^2 = 0.9976$, and $y = 92.45x + 62.639$, $R^2 = 0.9987$. The slight difference between anode and cathode is due to the difference of physical contact.
Figure 4.7: Measured local HFR after equilibrium purge at 55°C with five distinct water activities.
Figure 4.8: Calibration curves for local HFR for segments 1 to 5. Lines are the fitting curves with second order polynomials.
Figure 4.9: Calibration curves for local HFR for segments 6 to 10. Lines are the fitting curves with second order polynomials.
Figure 4.10: Time evolution of actual local HFR during 60 second purge for segments 2, 4, 6, 8, and 10.
Figure 4.11: Distribution of actual local HFR during 60 second purge for segments 2, 4, 6, 8, and 10.
Figure 4.12: Time evolution of actual local HFR in 6cm$^2$ segmented cell and of overall HFR for 25cm$^2$ cell during 60 second purge.
Figure 4.13: Distribution of actual local HFR during 60 second purge. Results of two experiments were merged to generate this figure (one for segments 2, 4, 6, 8, and 10; the other for segments 1, 5, and 9).
Chapter 5

CONCLUSIONS AND FUTURE WORK

5.1 Conclusions

We have introduced experimental methodologies of equilibrium purge to control initial water distribution inside a PEFC prior to cold start and isothermal cold start to evaluate the intrinsic startup capability of an MEA from subzero temperatures. Isothermal cold start also provides the most conservative scenario to study the impact of MEA material and design on PEFC cold start. Then, we have investigated the effects of various operating and design parameters on PEFC cold start performance under the isothermal boundary condition. The following conclusions can be drawn from this study:

1. Equilibrium purge can effectively control the cell internal condition before cold start, thereby making consistent and reproducible cold start experiments possible.

2. Proton conductivity in membranes with low water content, typical of cold start conditions, is measured in situ in an operating fuel cell under subzero temperatures. No slope change in the temperature dependence of proton conductivity is found between room temperature and $-30^\circ$C with water content between 2.4 and 14, indicative of no phase transition of water occurring in these membranes within the given temperature range.
3. During startup from $-30^\circ$C, a PEFC with low water content membrane experiences three stages of voltage evolution: an initial drop period under load, a recovery period owing to membrane rehydration by product water and hence lowered membrane resistance, and finally a voltage drop-down due to ice formation in the cathode CL.

4. The amount of product water can be used as a quantitative measure of cold start performance, and it exhibits a nonlinear relationship with the membrane water uptake potential ($\Delta \lambda$).

5. The product water in isothermal cold start from $-30^\circ$C can be divided into CL and membrane contributions, with the CL contribution principally depending on the CL pore volume and the membrane contribution on water transport through the membrane. Water accumulated in the CL is believed to be ice or frost, and water transport out of CL via vapor phase transport plays a negligible role for cold start from $-30^\circ$C. Therefore, the membrane is a key component to improve cell performance under isothermal cold start.

6. When the current density is high, the water storage capacity in CL is not fully utilized and, therefore, the total product water decreases.

7. The startup temperature strongly affects cold-start performance quantified by the cumulative product water. In cases of equilibrium purge, the product water increases drastically with the startup temperature, and at $-3^\circ$C the cell can operate indefinitely.
8. The startup current density strongly impacts the product water in both equilibrium purge and short purge. At high current density the product water becomes small, because less time is offered for the membrane to absorb and store product water.

9. In the case of short purge, the purge duration is a decisive operating parameter controlling the cold-start performance. As the purge duration increases, the membrane becomes drier and the residual water in the CL pores prior to cold start is reduced. As a result, the product water during cold start increases.

10. The equilibrium purge cold start has 0.5 and 0.3mg/cm$^2$ larger product water than the short purge cold start for -20 and $-30^\circ$C, respectively. Diminished product water in short purge cold start is due to the presence of the residual water in the CL pores, as well as the higher current density employed in short purge experiments. The smaller difference in $-30^\circ$C startup is due to the lower water diffusivity in the membrane.

In the latter part of this study we have described an experimental method to fundamentally investigate the performance of short-duration gas purge in PEFCs for the first time. This was made possible by development of a reliable purge experimental procedure with excellent repeatability. Specifically, the following conclusions are drawn from this study.

1. A novel experimental procedure for gas purge studies is developed and its excellent repeatability is confirmed.
2. A purge curve, defining the cell HFR versus purge time, can be generally categorized into the SRP controlled by through- and in-plane drying or liquid water removal from CL/GDL, the FRP characterized by vapor diffusion and significant membrane desorption of water, and the MEP where water content in the membrane asymptotically reaches equilibrium with relative humidity of purge gas.

3. The end of the SRP is called the critical point. An optimal gas purge should pass beyond the critical point, taking full advantage of the FRP, but not dwell on the MEP.

4. Purge performance can be described by two parameters: the through-plane vapor diffusion flux from the CL/GDL to the gas channel, and the convective flux of water vapor along the channel with purge gas. The temperature-compensated HFR after gas purge is found to be predictable solely by these two parameters.

5. There exists a unique correlation between HFR after relaxation and HFR after purge for the membrane water content down to that corresponding to 40% RH. This correlation thus enables the estimation of the membrane water content prior to cold start from the HFR after purge, which in turn can be calculated from the two characteristic parameters describing the purge process.

6. A novel method to determine the temporally and spatially resolved HFR was developed. However, further improvements are required in both experimental procedure and in the calibration method to quantitatively analyze along-the-channel variation.
5.2 Recommendations for Future Work

Based on the current investigation of the PEFC cold start characteristics, opportunities for future work exist.

The present study investigated cold start under isothermal condition with a broad range of initial and operating conditions. However, as a numerical investigation predicted (40), the non-isothermal condition drastically changes the mass transport process and improves the cold start performance. Although it is not an easy task to realize the non-isothermal condition in a laboratory scale, single cell configuration, it should be worthwhile to study the effect of temperature rise. In addition, the investigation of the phenomena near freezing point (\(\sim 0^\circ\text{C}\)) should be interesting. As soon as the temperature reaches the freezing point, the ice begins melting and the liquid water starts moving due to the capillary force, and as a result, unpredictable phenomena may be observed.

The spatially resolved purge effectiveness is also worth studying. In Chapter 4 a novel method to determine the local HFR and local membrane water content was developed, and the method was validated qualitatively. However, in order to analyze the results quantitatively, improvements are necessary both in the experimental procedure and in the calibration method. In particular, the current method cannot determine the water content when liquid water exists in the cell. This issue should be addressed in further investigation. It is expected that the experimental procedure and method of analysis developed in the purge study are also applicable to other problems involving water removal from a PEFC during operation.
Bibliography


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Education

The Pennsylvania State University University Park, Pennsylvania 2005–Present
Ph.D. in Mechanical Engineering, expected in August 2008

Georgia Institute of Technology Atlanta, Georgia 1999–2001
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Thesis Advisor: Prof. Chao-Yang Wang
PEFC diagnostics and rapid cold start.

Industrial Research Nissan Research Center, Nissan Motor Co., Ltd. 2001–2004
Supervisor: Dr. Kazuhiko Shinohara
Water and thermal management of PEFCs.

Graduate Research Georgia Institute of Technology 1999–2001
Research Advisor: Prof. Suresh Menon
2-D unsteady simulation of combustion dynamics in pulse combustor.

Undergraduate Research University of Tokyo 1993–1995
Research Advisor: Prof. Toshio Nagashima
Pressure distribution measurement in a centrifugal compressor.

Selected Publications


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