FINAL TECHNICAL REPORT

Visualization of Fuel Cell Water Transport and Performance Characterization under Freezing Conditions

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Submitted by

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EXECUTIVE SUMMARY

In this program, Rochester Institute of Technology (RIT), General Motors (GM) and Michigan Technological University (MTU) have focused on fundamental studies that address water transport, accumulation and mitigation processes in the gas diffusion layer and flow field channels of the bipolar plate. These studies have been conducted with a particular emphasis on understanding the key transport phenomena which control fuel cell operation under freezing conditions. The project was conducted in two phases over a period of three years. In Phase I of the project, the project team has defined a baseline system including GDL material set and bipolar plate channel design, and characterized its performance with ex-situ, in-situ and neutron radiography experiments. In Phase II, the research team implemented changes to the baseline GDL and flow channel, and explored various GDL/channel combinations with ex situ and in situ experiments. Liquid water transport in the GDL and the channels under normal and freezing conditions and during shutdown purge were mapped and quantified. Technical accomplishments during this period are listed below:

- Demonstrated that shutdown air purge is controlled predominantly by the water carrying capacity of the purge stream and the most practical means of reducing the purge time and energy is to reduce the volume of liquid water present in the fuel cell at shutdown. The GDL thermal conductivity has been identified as an important parameter to dictate water accumulation within a GDL.
- Found that under the normal shutdown conditions most of the GDL-level water accumulation occurs on the anode side and that the mass transport resistance of the membrane electrode assembly (MEA) thus plays a critically important role in understanding and optimizing purge.
- Developed a new method based on the entrance region pressure drop measurements to measure individual channel flow rates and characterize flow maldistribution during single- and two-phase flows.
- Identified two-phase flow patterns (slug, film and mist flow) in flow field channel, established the features of each pattern, and created a flow pattern map to characterize the two-phase flow in GDL/channel combination.
- Implemented changes to the baseline channel surface energy and GDL materials and evaluated their performance with the ex situ multi-channel experiments. It was found that the hydrophilic channel (contact angle $\theta \sim 10^\circ$) facilitates the removal of liquid water by capillary effects and by reducing water accumulation at the channel exit. It was also found that GDL without MPL promotes film flow and shifts the slug-to-film flow transition to lower air flow rates, compared with the case of GDL with MPL.
- Identified a new mechanism of water transport through GDLs based on Haines jump mechanism. The breakdown and redevelopment of the water paths in GDLs lead to an intermittent water drainage behavior, which is characterized by dynamic capillary pressure and changing of breakthrough location. MPL was found to not only limit the number of water entry locations into the GDL (thus drastically reducing water saturation), but also stabilizes the water paths (or morphology).
- Simultaneously visualized the water transport on cathode and anode channels of an operating fuel cell. It was found that under relatively dry hydrogen/air conditions at lower temperatures, the cathode channels display a similar flow pattern map to the ex-situ experiments under similar conditions. Liquid water on the anode side is more likely formed via condensation of water vapor which is transported through the anode GDL.
- Investigated the water percolation through the GDL with pseudo-Hele-Shaw experiments and simulated the capillary-driven two-phase flow inside gas diffusion media, with the pore size distributions being modeled by using Weibull distribution functions. The effect of the inclusion of the microporous layer in the fuel cell assembly was explored numerically.
- Developed and validated a simple, reliable computational tool for predicting liquid water transport in GDLs.

- Developed a new method of determining the pore size distribution in GDL using scanning electron microscope (SEM) image processing, which allows for separate characterization of GDL wetting properties and pore size distribution.
- Identified a drop size dependency of the static contact angle on GDL, which is measured using an adaptation of the classical sessile drop method and is calculated using an in-house code specially developed for measuring static contact angles on rough, porous substrates.
- Developed a unique SEM sample holder which allows for visualization of GDL material while under compression. The stress-strain behavior and SEM visualization of the GDL sample can thus be obtained simultaneously. This imaging technique reveals internal damage to the GDL due to compression.
- Developed a high-speed microscopy system to assess the role of surface wettability and channel geometry on two-phase flow in fuel cell channels.
- Determined the effect of surface wettability and channel cross section and bend dihedral on liquid holdup in fuel cell flow channels.

A major thrust of this research program has been the development of an optimal combination of materials, design features and cell operating conditions that achieve a water management strategy which facilitates fuel cell operation under freezing conditions. Based on our various findings, we have made the final recommendation relative to GDL materials, bipolar design and surface properties, and the combination of materials, design features and operating conditions:

- GDL materials: use lower thermal conductivity cathode GDL and decrease the anode GDL thickness.
- Bipolar plate design: use a channel geometry that can be produced using a high-speed manufacturing process, with a hydrophilic coating.
- Shutdown and gas purge protocol: incorporate above findings in developing cost effective and energy efficient shutdown purge protocol.

It should be noted that a comprehensive fuel cell operating strategy must consider the entire range of operating conditions under which the system needs to perform. Although the recommendations above will benefit fuel cell performance under conditions where liquid water is expected to be present, they must also be fully assessed to understand their impact under relatively dry conditions.

I. INTRODUCTION

Approximately 20 million barrels of oil are currently used daily in the United States, the majority of this amount coming from non-U.S. sources. Transportation accounts for nearly 70% of the oil end use, a figure that is not expected to change significantly as the total U.S. oil consumption increases to 28 million barrels per day by 2025 [1]. Hydrogen is a likely replacement for oil as an energy carrier because it can be produced from a wide variety of feedstocks and when supplied to a fuel cell can be converted to electricity with relatively high efficiency.

A particularly attractive feature of fuel cells is that, when using hydrogen as the fuel, the only reaction products are water and heat. One of the most significant challenges in designing robust hydrogen fuel cell systems, however, is managing the water introduced in the humidified reactant streams and that produced by the electrochemical reaction itself. While the proton conducting membrane (usually perfluorosulfonic acid) and electrode ionomer must be well hydrated to facilitate proton transfer, if excess water is present, reactant hydrogen and oxygen will be restricted from reaching catalytic sites at the electrode surfaces. The problem of water management is especially challenging under cold conditions because the water carrying capacity of the reactant streams is quite low and water may freeze within the fuel cell assembly. Additionally, many successive freeze-thaw cycles can lead to premature degradation of the bulk materials and surface treatments used on the various fuel cell components. All of those potential problems are magnified for automotive applications because the ancillary equipment available for thermal management and mitigation of water accumulation are limited by stringent requirements for volumetric and gravimetric power density. To be competitive with internal combustion engines (ICEs), a fuel cell vehicle must be able to start from -20 °C and drive away at 50% of rated power within 30 seconds [2].

In this project, Rochester Institute of Technology (RIT), General Motors (GM) and Michigan Technological University (MTU) are tightly focused on exploratory studies that address water transport, accumulation and mitigation processes in the gas diffusion layer (GDL) and flow field channels of the bipolar plate (BPP). The overall objective of the project is to deliver an optimized combination of GDL material, BPP design and surface treatment, and anode/cathode flow conditions that minimize fuel cell water accumulation and the attendant freeze damage while suppressing regions of dehumidification that also degrade performance and material durability. This has been accomplished by a systematic experimental and modeling program that begins at the component level, synthesizes this fundamental learning into combinatorial ex-situ experiments with nearly full visual access, and then progresses to increasingly more complex in-situ experiments that utilize advanced diagnostic methods such as current and high-frequency resistance (HFR) distribution and neutron radiography.

The research program described herein was executed to address the following specific objectives:

- Develop a fundamental understanding of the water transport processes in PEMFC gas diffusion layer and flow field channels as well as across their interface under normal operation, shutdown purge and freezing conditions.
- Optimize materials, design, and surface properties of gas diffusion layer and bipolar plate as well as anode/cathode flow conditions to ensure uniform water distribution, alleviate flooding and suppress regions of dehumidification.
- Develop a combinatorial approach to integrate new materials, improved design concepts and operating strategies into a robust and cost effective cell-level solution.
- Apply advanced diagnostic methods, experimental and modeling tools to evaluate ex-situ and in-situ performance of PEMFC stack components.
- Formulate handling, testing, and characterization protocols and techniques for component and stack properties before, during and after fuel cell operation.

This report presents a compilation of research accomplishments achieved as of February 28, 2010, at the end of our 3-year funding period.

II. BACKGROUND

Water management has been identified as one of the most critical issues in the performance and longevity of a proton exchange membrane fuel cell (PEMFC) [3]. Sufficient water, often controlled by externally humidified air and hydrogen gas streams, must be present within the fuel cell to maintain the proton conductivity of the polymer electrolyte membrane; however, excess water must be removed from the cell to avoid flooding. Flooding is a phenomenon in which liquid water accumulation inside a fuel cell blocks gas transport pathways in the catalyst layers, gas diffusion layer (GDL), and the gas channels, inducing large mass-transport voltage losses. Due to water condensation from the humidified gas streams and water product at the cathode side, two-phase flow commonly exists in various PEMFC components. The problem of water management is especially challenging under cold conditions because the water carrying capacity of the reactant streams is quite low and water may freeze within the fuel cell assembly. Additionally, many successive freeze-thaw cycles can lead to premature degradation of the bulk materials and surface treatments used on the various fuel cell components. All of these potential problems are magnified for automotive applications because the ancillary equipment available for thermal management and mitigation of water accumulation are limited by stringent requirements for volumetric and gravimetric power density. Therefore, it is of critical importance to address water transport, accumulation and mitigation processes in GDL and flow channels of the bipolar plate (BPP) as well as across their interfaces under normal and freezing conditions.

Many of the problems associated with fuel cell water management, especially under higher temperatures, have been investigated previously. For example, the works from Dr. Wang's group [4-7] as well as Dr. Mench's group [8-10] at Penn State University have established a good framework for the investigation of cathode (including catalyst layer, GDL and gas channel) two-phase flow and flooding phenomena at normal operation conditions.

Two-phase flow in a fuel cell could be considered in three sub-categories: catalyst layer flooding, GDL flooding, and two-phase flow in gas channels. A number of studies are reported on the investigation of water transport in the GDL, e.g. [11-15], and the catalyst layers [16-18]. Two-phase flow in gas channels is also very important and has recently received more attention with the application of several visualization techniques, such as optical and neutron imaging. Tuber et al. [19] was the first group to use optical visualization to study water buildup in a cathode gas channel at low temperatures. This technique was later widely used to study water transport in gas channels under various fuel cell operating conditions [20-26]. Neutron radiography provided another in-situ visualization technique and was utilized by a number of groups to visualize and quantify water retention in the GDL, under the lands, and in the gas channels [27-30]. Higher water retention was found at the U-bends and under the lands of the serpentine channels. In a recent publication, Owejan et al. [31] used this technique to study the effects of flow field and diffusion layer properties on water accumulation in a PEMFC and found that flow field channels with hydrophobic coating retain more water, but the distribution of a greater number of smaller slugs in the channel improves fuel cell performance. Water distribution in the anode side was also visualized in a few studies [24,26,32].

Two-phase flow in gas channels has been investigated through modeling and numerical simulation as well. Quan et al. [33] simulated the water flow behavior in a U-shaped channel using volume of fraction model and varying initial liquid water distribution. Jiao et al. [34] did similar work for fuel cell stacks with varying preset water distribution. Recently, Quan and Lai [35] studied the effects of channel surface hydrophilicity together with channel geometry and air inlet velocity on the water behavior in a serpentine channel, and they concluded that the hydrophilicity of flow channel surface plays an important role in water management of a reactant flow channel. However, a common problem faced in such models is that the liquid water must be placed a priori at certain locations in the channels, thus making the

simulation less physically realistic. Wang et al. [36] developed a two-phase flow model to estimate the liquid water saturation profiles along the axial flow direction.

Although most of these investigations focused on the behavior of liquid water in gas channels, the flow dynamics of the gas streams were largely neglected. Presence of liquid water has been found to influence the air flow and the two-phase flow pressure drop. In a few studies, the pressure drop across the channels was shown to be closely related to the PEMFC performance [25,37], and was therefore proposed to be a diagnostic tool for the detection of flooding [38-41]. Despite these studies, the relationship between pressure drop and water accumulation, in particular the effect of random droplet emergence and liquid water clogging, is not clearly understood. Part of the reason is that the pressure drop provides an overall measure across the entire flow field, while the water accumulation and water clogging may be highly localized to certain regions in specific channels. Conversely, the variation of individual channel air flow rates provides a sensitive measure of the liquid water in that channel. A real time monitoring of the instantaneous flow rate in individual channels can therefore provide important information with regards to water accumulation and two-phase behavior in PEMFC gas channels.

Improved transport of liquid water and reactant gases through GDL has recently been an active research area. Commonly used GDL materials for PEMFCs are carbon fiber based paper and cloth. These materials are highly porous (having porosities of about 80%) to allow reactant gas transport to the catalyst layer, as well as liquid water transport from the catalyst layer. In order to facilitate the removal of liquid water, GDLs are typically coated with a non-wetting polymer such as polytetrafluoroethylene (PTFE) to make them hydrophobic [42]. Additionally, a fine microporous layer (MPL), consisting mainly of carbon powder and PTFE particles, is generally applied to the GDL side facing the MEA (membrane-electrode assembly) to further increase cell performance [43,44]. The primary functions of a GDL are to supply reactant gases and remove product water from the catalyst layers, to conduct electricity and heat between adjacent components, and to provide mechanical support for the MEA. These functions impose stringent requirements on the electrical, transport, and mechanical properties of the GDL. The extreme structural and chemical heterogeneity of GDLs substantially complicates the studies of liquid water transport and associated mass transport losses [45,46].

The presence of a MPL on GDLs has been shown to improve fuel cell performance, but the roles of (or mechanisms within) MPL are not clearly understood. It has been postulated that the MPL improves the fuel cell water management and mass transport, avoiding fast dry-out of the PEM at low current densities and electrode flooding at high current densities. Several authors [43,47] have demonstrated that the MPL improves the humidification of the membrane at the anode side. Kong et al. [48] concluded that the MPL enhances oxygen diffusion by reducing flooding in the cathode. The critical role of MPL in reducing flooding is a result of the modification of the GDL pore structure (e.g., porosity, pore size distribution, hydrophobicity, and nonuniformity) has received wider acceptance in many recent studies [49-52]. Weber and Newmann [53] and Lin and Nguyen [54] explained the function of the MPL in reducing the cathode flooding as a capillary barrier, which prevents water from entering the cathode GDL and forces water to permeate from cathode to anode. However, recent experimental studies show that the MPL does not significantly influence the water back-diffusion rate [55,56]. Alternatively, the role of MPL in control of water distribution has been proposed in the theoretical treatment of water saturation distribution in multi-layer electrodes [15,57]. The authors suggest that the MPL reduces the water saturation in GDL near the catalyst layer and therefore improves the cell performance. In this way, the MPL enhances the cathode water transport rather than hindering it. Gostick et al. [58] measured the water saturation and associated capillary pressure at the point of water breakthrough in GDL samples with and without a MPL. Their data demonstrated that the GDL saturation at water breakthrough is drastically reduced in the presence of MPL, suggesting that the MPL restricts the number of points of entry of water into the GDL. However, pore scale phenomena associated with the movement of liquid water and its interplay with GDL pore structure and wettability warrant further investigation.

The characteristic scale of GDL and gas flow channels is small enough that capillary forces play a dominant role in the behavior of liquid water interfaces in these components. Capillary forces are also the likely mechanism for water holdup at the exit header. Two-phase flow in GDL and gas channels presents especially difficult problems since the passages are capillary-scale, non-circular geometries with variable contact angles and manifold flow paths. There have been numerous studies in which macroscale modeling has been applied to microscale two-phase flow, yet correlations developed by one research group are rarely repeatable by another research group [59]. Recent research has demonstrated that two-phase flow pressure drop through a microchannel is significantly influenced by the channel wall wettability, channel geometry, contact line dynamics, interfacial shear, gas phase inertia and density wave oscillations [60-63]. Water–nitrogen two-phase flow in circular capillary exhibits as much as 1.5 times greater pressure drop through a hydrophobic channel ($\theta_s = 110^\circ$) than through a hydrophilic channel ($\theta_s < 20^\circ$) for identical flow rates.

The dynamics of the liquid water transport through a GDL is of interest to understand the resistance of reactant gas transport due to water accumulation. However, this has barely been studied until recently due to the difficulties of observing water transport phenomena inside the GDLs. Nam et al. [57] and Nam and Kaviani [15] observed vapor condensation and liquid breakthrough in a GDL using an environmental scanning electron microscope, and proposed a tree-like transport mechanism in which micro-droplets condensed from vapor agglomerate to form macro-droplets which eventually flow preferentially toward larger pores and breakthrough. However, with this method is not possible to simulate fuel cell operating conditions due to the vacuum requirements. Pasaogullari and Wang [64] also hypothesized a tree-like water transport behavior in GDLs in their two-phase flow model. Litster et al. [11] visualized liquid water flow as it emerged from the surface and a few micrometers below the surface of a GDL using a fluorescence microscope. They observed that water emerges from preferential pathways and suggested a “fingering and channeling” mechanism for water transport in GDL pores. Bazylak et al. [65] found that the preferential water pathways coincided with the compression areas in the GDL, which they accounted for by a loss of GDL hydrophobicity due to the fiber breakup and PTFE coating deterioration caused by compression. In a later study, Bazylak et al. [66] observed the dynamic changes in breakthrough locations for water transport through a GDL and explained it using a dynamic and interconnected network of water pathways within the GDL. Gao et al.’s [67] confocal microscope visualization revealed an unstable “column flow” in GDLs, which is similar to Litster et al.’s fingering model [11], except that wider flow paths spanning several pores are observed. Manke et al. [68,69] and Hartnig et al. [70] investigated the in-situ liquid water evolution and transport in an operating fuel cell with synchrotron X-ray radiography. They observed an “eruptive transport” mechanism in GDL pores near the channels, which they describe as the quick ejection of droplets from the GDL into the gas channels. However, water fills continuously in the GDL pores under the central land following a capillary tree-like process [15,64]. Both the ex-situ and in-situ experiments have clearly demonstrated that there exist fast “water transport channels” within a GDL and that the water transport and breakthrough are dynamic processes. However, the morphology of transport channels and the dynamics of water transport in these channels need further investigation.

Theoretical treatment of water transport in a GDL has been the focus of several models. A large number of works are based on the continuum two-phase flow model [15,64,71-73], which describes the flow and transport on the basis of Darcy’s law. Unfortunately, GDL-specific experimental data on many of the necessary relationships and parameters, such as the water saturation dependent relative permeability, effective diffusivity, and air-water capillary pressure, are scarce, making the application of these models to GDL materials questionable. As an alternative approach, a pore-network model, which has a long history in the study of porous media such as soils and rocks [74], has recently been used in modeling water transport in GDL materials [75-78]. The pore-network model maps a complex pore space continuum onto a regular and irregular network of pore bodies and pore throats. Several works have shown that invasion-percolation process, which is a strongly capillary-driven process at the limiting case

of zero fluid velocity, may be an important mechanism for water transport in GDL. However, most of the pore-network models [76,78] focus on the numerical determination of the macroscopic two-phase properties, such as the capillary pressure versus saturation correlation (P_c - S_w curve) and the relative phase permeability as a function of S_w , and little work has been done to clearly understand the mechanism of water transport through a GDL.

The transport of liquid water through a GDL is a drainage process in which water, as a non-wetting fluid, displaces the wetting fluid, air. When water is injected at a low constant rate (thus negligible viscous forces), the displacement will be dominated by capillary forces. Notably, at normal fuel cell operating conditions, the capillary number ($Ca = \frac{u\mu_{nw}}{\sigma}$, in the range of $10^{-8} - 10^{-5}$, where u , μ_{nw} and σ are the velocity, viscosity and surface tension respectively of non-wetting fluid) and viscosity ratio ($M = \frac{\mu_{water}}{\mu_{air}}$, 17.5) produce capillary-driven water flow [79,80]. One of the critical constitutive relationships for describing capillary flow in a porous material is capillary pressure versus liquid water saturation (P_c vs. S_w). This has been the focus of several recent investigations [81-83]. A permanent capillary pressure hysteresis between liquid water injection and withdrawal is generally observed. Gostick et al. [82] accounted for the capillary hysteresis in terms of the contact angle hysteresis and the pore geometric effects. It should be noted that all these works measured the GDL saturation up to 1, which may be correlated to the GDL under the ribs where the drainage of water is restricted and water remains confined in the GDL. However, for the GDL under the channels, water drainage is quite different because water in this area can be easily removed in the form of droplets and films as well as slugs causing a lower saturation in the GDL. Because of this fact, the GDL saturation in an operating fuel cell is non-uniformly distributed [84,85].

In a fuel cell stack, the cell components are assembled together under a compressive load to prevent gas leakage and to reduce the contact resistance between the GDL and the bipolar plate. However, over-compression of the GDL leads to poor cell performance. Many researchers have studied the effect of compressive stresses on fuel cell performance. Lee et al. [86] studied the influence of compression on PEMFC performance with different types of GDLs and found that the performance was a function of the compression pressure and GDL materials. Ge et al. [87] and Escibano et al. [88] also studied the effect of GDL compression on PEMFC performance. Both of their results showed that the fuel cell performance at high current densities decreased with the increase in compression force. Zhou and Wu [89] numerically simulated the effect of the GDL compression deformation on the performance of PEMFCs. Their results show that the fuel cell performance decreases with increasing compression. The performance loss caused by the compression was primarily ascribed to the increase in mass transport loss due to the reduction of GDL porosity and gas permeability. A GDL has a characteristically soft and brittle structure, which readily leads to deformation or damage when compressed. As a consequence, the microstructure and the physical properties of the GDL, e.g., porosity, diffusivity, electrical conductivity, etc., are drastically changed under compression. Nitta et al. [90,91] extensively investigated the effects of compression (in terms of compressed GDL thickness) on gas permeability, in-plane and through-plane electric conductivities, and contact resistances at interfaces. They found that the compression of GDL reduces gas permeability and contact resistance, while improving bulk conductivity. Feser et al. [92] measured the GDL in-plane permeability under various compressions and found an approximate linear decrease of in-plane permeability with compression. The influence of compressing a GDL on liquid water transport behavior as well as on the GDL microstructure morphology was studied by Bazylak et al. [65]. The compression of the GDL was found to cause fibers to breakup and deterioration of the hydrophobic coating, which contributes to the formation of preferential pathways for liquid water transport in the GDL.

It is particularly worth noting that most papers on fuel cell compression and its effect on PEMFC performance considered a homogeneous GDL compression. In reality, the deformation of the GDL in a

PEMFC is not homogeneous due to the flow field structure. The parts of the GDL under the lands of the flow field plate are significantly more compressed than the parts under the channel. This phenomenon has not received much attention until recently. Hottinen and Himanen [93] and Hottinen et al. [94] numerically investigated the effect of inhomogeneous compression of GDL on the temperature distribution and mass and charge transfer in a PEMFC. They concluded that the inhomogeneous compression causes a variety of contact resistances between the GDL and electrodes, resulting in significant effects on the temperature and current density distribution. The inhomogeneous problem is compounded by GDL intrusion into the channels. The high compression pressure pushes the softer GDL material into the channel, partially blocking the gas flow. GDL intrusion may lead to significant local variations of mass (both gas reactants and product water) transport in the channels and GDL. Nitta et al. [90] and Lai et al. [95] experimentally determined the GDL intrusion by using a floating bar technique. It was found that the GDL is compressed very little under the channel whereas GDL under the land is compressed to gasket thickness. Basu et al. [96] developed a complete PEMFC two-phase flow model which included two-phase flow in both anode and cathode channels and the specific effect of GDL intrusion in the edge channels on channel flooding was numerically studied. Severe flow and liquid water maldistribution were found in the intruded channels due to the increased flow resistance. GDL intrusion reduced flow through the intruded channel, making it more difficult to flush liquid water out of the channel. They further pointed out that innovative flow field designs are needed to mitigate flow maldistribution and ensuing adverse impact on cell performance and durability.

Even though GDL intrusion was determined in a few studies [90,95], only a simple case with a single channel was studied. A real PEMFC usually implements a large active area and contains large number of parallel channels. The local compression force derived from the location distribution of the clamping bolts is expectedly non-uniform. This may cause local variation in GDL intrusion. This problem is further compounded by the heterogeneity in GDL micro-structure and physical properties which may cause a maldistribution of GDL intrusion. Such an inhomogeneous GDL intrusion was already assumed in the modeling [23], but experimental verification is still missing.

Although many of the problems associated with water management have been investigated, it still imposes a critical technical challenge to the commercialization of PEM fuel cells. In this project, Rochester Institute of Technology (RIT), General Motors (GM) and Michigan Technological University (MTU) have focused on exploratory studies that address water transport, accumulation and mitigation processes in the gas diffusion layer (GDL) and flow field channels of the bipolar plate (BPP). This has been accomplished by a systematic experimental and modeling program that began at the component level, then synthesized this fundamental learning into combinatorial ex-situ experiments with nearly full visual access, and then progressed to increasingly more complex in-situ experiments that utilized advanced diagnostic methods such as current density, high-frequency resistance (HFR) distribution and neutron radiography.

General Motors, a world leader in fuel cell technology for automotive applications, has a long record to use neutron radiography to visualize water in an operating fuel cell [97-100]. Based on their two-dimensional neutron radiography results, the liquid water accumulation in the GDL and bipolar plate channels has been mapped and quantified. Due to its wider and wider application in fuel cell research, the neutron imaging technique has been significantly improved in recent years. Several new technologies have been developed. A relatively high temporal resolution, up to 7.5 Hz compared to the conventional 0.1 Hz acquisition rate, has been developed at NIST and has demonstrated the ability to reconstruct the 3D liquid water distribution in an operating fuel cell [101]. Another new technology is the implementation of an emerging neutron detection technique that produces images of water distribution at a much higher spatial resolution. The spatial resolution has been experimentally verified to be 20 μm [102], compared to the previous resolution of $\sim 125 \mu\text{m}$. These new developments are expected to

dramatically expand the fuel cell water management studies and greatly enhance our understanding of these issues.

Over the past several years, General Motors has developed and refined a method for measurement of fuel cell current density and high-frequency resistance (HFR) distributions. This patented method [103], uses printed circuit board technology to position small shunt resistors in series with a flow field plate that has been segmented. Similar methods have been reported by Cleghorn et al. [104], Hakenjos and Hebling [105], among others. The combined measurements of local current density and HFR provide a very useful quantitative indication of the level of local flooding or dehumidification. Experiments conducted at GM over the past 3 years on a variety of fuel cell platforms clearly show that under certain conditions, dry and wet regions can exist simultaneously within the active area. Furthermore, GM has many years of experience in varying GDL and channel properties to enhance fuel cell water management [106-108].

The two-phase flow stability (flow maldistribution) and water distribution in parallel multi-channels is critical to water management in fuel cells. Parallel channel instability during the boiling process in minichannels has been extensively studied at RIT [109-111]. Balasubramanian and Kandlikar [112] present a detailed experimental study involving high-speed photography to investigate the two-phase flow in microchannels. The water droplet emergence in the fuel cell cathode channel was then studied in a single channel-GDL combination with the high-speed camera technique.

III. RESEARCH PROGRESS

III-1. Task 1: Baseline System Definition

III-1.1. Select Baseline Material Package

The baseline material package and test section design were described in detail in [113]. For all initial experiments, the fuel cell was assembled using the following components:

- Membrane electrode assembly: Manufactured by W.L. Gore & Associates, Inc., with an 18 μm thick proton exchange membrane, and catalyst loadings on anode and cathode of 0.2 and 0.3 mg Pt/cm², respectively (Figure 3.1.1).
- Gas diffusion layers: Grafil U-105, manufactured by Mitsubishi Rayon Corporation, with 7% by mass polytetrafluoroethylene (PTFE), and a microporous layer as described by Ji et al. [114] and O'Hara [115].

The membrane electrode assemblies (MEAs) were selected to provide near benchmark performance, but with thrifed catalyst that approaches the long-term USDOE targets for platinum group metal (PGM) loading: 0.3 mg PGM/cm² electrode area in 2010, and 0.2 mg PGM/cm² electrode area in 2015 [2]. The GDL material was selected based on the requirement of commercial availability, in a quantity sufficient to accommodate the needs of the project throughout its 3-year duration. Also, it was considered essential that the base substrate have well characterized physical properties, with performance at or near benchmark, to ensure that the results and findings of the project advance the state-of-the-art in fuel cell science.

Figure 3.1.1 – Dimensions of MEAs for in-situ fuel cell experiments (mm).

III-1.2. Design and Fabricate Test Sections with Common Design

To satisfy the objectives of our fuel cell water management research program, a 50 cm² test apparatus was designed to represent the aspect ratio and flow field geometry of practical fuel cell hardware, in accordance with performance targets published by the United States Department of Energy (USDOE) [2]. Also, published data were used to select “optimal” geometrical features, such as the flow field channel cross-section. The apparatus was designed specifically for application of the neutron

imaging method for visualization of liquid water accumulation and dynamics at the scale of the flow field channels and gas diffusion layers [27, 28, 116].

A. Channel and Land Widths

In several numerical and experimental studies, the variation of cathode channel and land width was shown to have a marked influence on PEMFC performance. For example, Shimpalee and Van Zee [117] considered the effects of varying the channel and land widths for a fixed depth of 0.55 mm. In this work it was predicted that under automotive operating conditions, a wider channel (1.0 mm vs. 0.7 mm) with a minimal land width (0.7 mm vs. 1.0 mm) will improve performance and flow distribution uniformity. Investigations by Scholta et al. [118] concluded the correlation between land width and cell performance was not as sensitive as that of channel hydraulic diameter variation. In addition, it was determined that small dimensions were preferred for high current densities and larger dimensions were better for low current densities. Ahmed and Sung [119] took the approach of varying the channel-to-land ratio for a fixed channel width of 0.8 mm and height of 1.0 mm. Their conclusion was that at high current density the optimal channel-to-land width ratio is in the range of 1.3 to 1.4. Yoon et al. [120] examined the effect of varying the land width for a fixed 1.0 mm wide channel. Results of this study concluded that cell performance improved as the cathode land width got narrower. It was also noted that a larger channel area was especially beneficial to high-power cell operation.

Based on the studies cited above, cathode channel and lands widths of 0.7 and 0.5 mm, respectively, were selected for the 50 cm² test apparatus design. These dimensions are within the range of the best performance identified in [118], while also satisfying the wider channel constraint found to perform best under automotive operating conditions [117]. The resulting channel-to-land ratio is 1.4, which correlates well to the optimal ratio recommended in [119].

PEMFC channel optimization studies have focused on the cathode side because of the slow reaction kinetics and mass transport effects, the latter due to the much smaller diffusion coefficient of oxygen in nitrogen relative to that of hydrogen. For this reason, the anode land dimension can be larger than the cathode. Because hydrogen diffusing through nitrogen (resulting from cross-over from the cathode through the membrane) has a binary diffusion coefficient that is roughly three times larger than that of oxygen diffusion in air, the land dimensions on the anode side of the plate were scaled to three times that of the cathode. This anode land scaling results in 1.5 mm lands with the channel dimensions kept constant on both sides of the PEMFC.

There are a number of additional reasons for increasing the width of the lands on the anode side, including:

- reducing the number of channels increases the hydrogen volumetric flow per channel;
- reducing ohmic loss through increased land contact area; and
- relaxing the sensitivity to anode-to-cathode compression point alignment.

Increased flow is desirable with a humidified anode gas stream where liquid water can form in the channels from condensation as the hydrogen is consumed. The contact resistance change will be minimal relative to other impacting factors such as membrane conductivity, but is directionally correct. Compression point alignment of anode lands relative to cathode land is imperative to avoid GDL fracture and possible mechanical puncture of the membrane.

B. Channel Depth

The repeat distance of the bipolar plate must be considered in the determination of the appropriate channel depth. To meet the USDOE target volumetric power density target of 2 kW/L, the plate thickness, which dictates the channel depth, must be minimized. However, channel depth has a lower limit due to GDL intrusion which occurs when the GDL deflects into the channel cross-section after the assembly is compressed (Figure 3.1.2). Data from Rapaport et al. [121] demonstrated that the flow redistribution sensitivity is reduced as the channel depth is increased. Specifically, it is shown that the percentage of flow deviation varies linearly with channel depth. This study considered channel depths ranging from 0.25 mm to 1.0 mm and the percentage of flow deviation associated with carbon fiber GDL intrusion under fuel cell assembly compression was found to be 46.0% and 10.5%, respectively. It is also shown that the magnitude of intrusion is minimized by reducing the channel width. Although this work is not directly linked to fuel cell performance, these issues are often speculated to contribute to cell-to-cell flow variations in full PEMFC assemblies [122]. Such variations in gas flow can lead to channel-level accumulation of liquid water.

Aside from considering the interaction of the fuel cell hardware with the GDL, another important factor is the manufacturing dimensional variation for molded carbon composite and stamped steel plates [123]. Considering all these factors, a channel depth of 0.4 mm is determined to be optimal for both the anode and cathode channels.

Figure 3.1.2 – GDL intrusion into fuel cell channel.

C. Channel Length

The channel length was determined by combining the geometrical features outlined above with the USDOE 2010 target volumetric power density of 2 kW/L for an 80 kW system operating on direct hydrogen. Since no further size constraints are defined, appropriate dimensions are derived as described below.

Peak power density is typically obtained near 0.6 V/cell at a current density of 1.3 A/cm² or higher [124]. The peak potential required from a PEMFC assembly is related to an entire automotive system, which can be dependent on factors such as level of battery hybridization, power converter efficiency, and the traction motor used. Recent publications indicate this value varies between 200 and 300 V for 80 kW systems [125-127]. For the current design, a 200 V potential at peak power was assumed for best efficiency of power conversion at minimum and maximum voltages. If each cell contributes 0.6 V in series, an assembly of 334 cells will be required.

The channel dimensions defined previously, in addition to a 0.6 mm high coolant channel (height maximized to reduce coolant flow resistance), results in a minimized repeat distance of 2 mm, including the thickness of the GDL and MEA. Rigid compression plates of 25 mm thickness are required at each end of the assembly, and the combination of all components yields a 718 mm overall height, as shown in Figures 3.1.3 and 3.1.4. Considering the total volume of 40 L, the resulting footprint for gas/coolant supply headers and active area is 557 cm². Given the maximum gas flow rates required for the electrochemical reaction, cooling at peak power, and the total cross-sectional area of the channels for each, a conservative 40% of the footprint area was allocated for the area of the non-active flow regions and manifolds. The remaining 335 cm² is therefore available as active electrochemical area. This active area defines the region where chemical reactions take place to provide the electric current requirement of 400 A, for an 80 kW system operating at 200V. The corresponding current density is 1.2 A/cm².

With the active area size defined, one must lastly determine its aspect ratio. The channel length should be minimized to reduce the gas pressure differential along the length of the channel. Conversely, the number of channels should be minimized to maintain sufficient volumetric flow per channel to remove liquid water, thus avoiding reactant flow maldistribution. Given the lack of published information on the optimal active aspect ratio, the relative importance of the effects of channel length and number of channels are assumed to be comparable, thus resulting in the optimal active area being square (aspect ratio 1:1) with straight channels. This aspect ratio yields a channel length that spans the active area length of 18.3 cm.

For small scale in-situ experiments, a 50 cm² test section that represents full scale parameters is required. As shown in Figure 3.1.5, to maintain the defined linear channel length of 18.3 cm the corresponding width of the active area for the 50 cm² test apparatus will be 2.73 cm. Based on the anode and cathode channel-land geometries outline above, this active area size will result in 22 cathode channels and 11 anode channels.

Figure 3.1.3 – Fuel cell repeat distance.

Figure 3.1.4 – Fuel cell assembly geometry.

D. Flow Channel Pattern

An additional consideration regards the flow field channel pattern. Although a straight channel will have the least pressure differential, patent literature suggests that fine pitch PEMFC flow fields require safeguards to avoid misalignment such that a cathode land is compressed adjacent to an anode channel [128]. This is prevented by configuring anode and cathode channels according to Figure 3.1.6, where anode channels form a sinusoidal pattern that is out of phase to a similar pattern in the cathode flow field. This configuration will increase the channel length by only 2% with an 11° angular channel switchback every 5 cm.

Figure 3.1.5 – 50 cm^2 fuel cell active area geometry.

Figure 3.1.6 – Flow field pattern to avoid mechanical shear associated with straight channels (610: anode lands; 620: cathode lands) [128].

E. Channel-to-Header Transition

When considering water management in a full PEMFC assembly, the interaction between the flow distribution channels and the exhaust header must also be taken into account. The driving force for liquid water removal drastically changes in this region where the channels with hydraulic diameter on the order of 0.1 to 1 mm empty into a common exhaust flow volume with a cross-sectional area increase of several orders of magnitude. This transitional region is further complicated by the requirement for sealing between plates. Although two-phase flow in this region has not been widely addressed in the open literature, it is known to be a critical aspect of bipolar plate design based on fuel cell patents and patent applications [129, 130]. Figure 3.1.7 illustrates one such configuration where the channel gas flow is diverted underneath the plate seal. To accurately represent water handling behavior in a full fuel cell assembly, such features must be considered as they represent regions where flow redistribution and contact line pinning of gas-liquid interfaces can occur.

The final test apparatus design (Figure 3.1.8) took into account all of the practical fuel cell constraints outlined in this section. Unlike the majority of previous fundamental fuel cell studies conducted with square flow fields and rather arbitrary channel geometries, this test section accurately represents a small-scale portion of practical fuel cell hardware for automotive propulsion applications.

The test section (shown in exploded view in Figure 3.1.9) was also designed for compatibility with the experimental techniques to be used in the current research program. The materials have high neutron transmission, allowing for excellent sensitivity to liquid water when performing in-situ neutron radiography. There are provisions for borescope visual access in the outlet manifolds. A current distribution tool can be inserted into the stack assembly, as is planned in Task 6. There are numerous pressure, temperature, and voltage probes throughout the fixture to monitor local variations in operating parameters. The test section also can be run in a single-cell or multi-cell stack configuration.

Figure 3.1.7 – PEMFC assembly plate inlet cross-section describing flow transition required for plate sealing. Similar channel-to-header flow transitions exist at exit of reactant flow paths (106: MEA; 110: bipolar plate) [129].

Figure 3.1.8 – Anode and cathode plate designs, and overlap of channel patterns in the fuel cell active area. Orientation shown was used in neutron imaging experiments.

Figure 3.1.9 – Exploded view of test section for fuel cell experiments with neutron radiography.

III-2. Task 2: Baseline Performance Characterization

III-2.1. Baseline Ex-situ Multi-channel Performance Characterization

The main focus of this subtask is to investigate the two-phase flow in simulated parallel PEMFC channels with the Baseline system (including Baseline GDL and the channel design). For this purpose, the instantaneous channel flow rate (flow maldistribution), pressure drop, and the flow structure are studied by using the entrance region pressure drop method [131], differential pressure transducers, and high-speed visualization, respectively. The ex-situ test setup is carefully calibrated in order to accurately measure the instantaneous flow rates in individual channels. A quantitative description of the channel flooding is established and the pressure drop signatures for each flow pattern are identified. The results obtained from these measurements help to provide a better understanding of the relationships among flooding, pressure drop, and flow structure.

A. Test Section for Ex-Situ Multi-Channel Experiments

In this section, the ex-situ multi-channel experiment setup with full visual access is described. Figure 3.2.1 shows the exploded view of the test section assembly. The core components of the test section are a gas channel plate, GDL sample, a water channel plate, and gaskets to seal the assembly. Figure 3.2.2 shows the detailed designs of the air channel plate and water channel plate, which provide air and deionized water at the preset flow rates, respectively. The gas channels consist of eight parallel channels, each 183 mm long, 0.7 mm wide, and 0.4 mm deep with a land width of 0.5 mm between adjacent channels. The channel shape is weaving with a 5° weaving angle to avoid mechanical shear on the GDL associated with straight channels. The channel geometry and dimensions follow the common channel design in Task 1.2. The inlet and exit headers (see Figure 3.2.1 (a)) are modified to account for the particular requirements of the ex-situ experiments, including the measurements of the total pressure drop between inlet and outlet and the mass flow rate in each channel. In order to accurately measure the mass flow rate in each channel, the pressure drop over a small distance will be measured with differential pressure sensors and then converted to the mass flow rate. To accomplish this, three rows of holes are made in the straight section of the channels to hold the pressure taps. Downstream of the pressure tap holes, another hole is drilled to create a provision for dowel pins, which will be used to block the channels individually or in any combination for the purpose of flow measurement and sensor calibration. The channels exit into a symmetric manifold setup with a pressure tap to measure the outlet pressure.

The channels on the waterside manifold have the same geometry and dimensions as the gas channels except that the waterside channels are sectioned into four segments corresponding to the four water chambers. The use of four chambers allows for uniform water flow through the entire GDL, and is superior to the use of a single chamber along the entire channel length, due to the fact that a single chamber would promote water flow primarily towards the outlet end of the channels (due to highest available pressure difference between the air and water sides). The water flow rate in each chamber was controlled independently by four individual syringe pumps, allowing each chamber to support a different water injection rate if desired. Three holes were drilled from each water channel to each water chamber, resulting in a total of 24 holes per water chamber across the 8 channels, and 12 holes per channel across its entire length, as shown in Figure 3.2.2 (b). Each hole had a diameter of 0.7 mm which is equal to the gas channel width. Both the gas channels and water manifold are machined out of Lexan® plates, which are then vapor polished to provide excellent optical clarity. This test section simulates the water production at the PEMFC cathode electrode as well as the transport through the cathode GDL to the gas channels.

Figure 3.2.1 – The exploded view of the test section assembly. The numbers in the figure represent: 1: stainless steel side plates; 2: aluminum end plate; 3: posts to fit the inner diameter of the springs; 4: aluminum lower plate; 5: springs; 6: PTFE gasket; 7: water chamber plate; 8: GDL; 9: parallel air channel plate; 10: aluminum block plate. The test section is assembled by compressing it to the appropriate force and then screwing into place via mounting holes in side plates.

Figure 3.2.2 – Design of the (a) parallel air channels and (b) water manifold, for the ex-situ multi-channel two-phase flow experiments.

Figure 3.2.3 schematically shows the experimental setup. Dry, clean air generated from a Zero Air Generator (Parker HPZA-30000, Haverhill, MA) flows through a bank of rotameters, which control the total air flow rate, and then into the gas inlet manifold. The input air flow rate is measured by a digital flow meter (Omega FMA-1620A) for the lower flow range of 0-1200 sccm (corresponding to a superficial air velocity range of 0-8.9 m/s) and by rotameters for the higher flow rates. The air flow rate in each individual channel is obtained through the entrance region pressure drop in each channel measured with eight differential pressure sensors (Honeywell FP2000, with accuracy 0.25% in the range of 0-15 kPa). The total pressure drop across the flow field is also measured with a differential pressure sensor (Honeywell Sensotec FDW2AT) which has an accuracy of 0.25% or better in a range of 0-35 kPa. All pressure data are collected with a LabView program through a DAQ system (National Instruments). Deionized water (18.2 MΩ, Millipore) is independently delivered to each of the four water chambers through four syringe pumps (Harvard). Before acquiring data, the water injection and air flow at desired flow rates are run for enough time until the steady state is reached (normally within a few minutes). The data are taken over a period of more than 10 minutes. The water flow patterns inside the gas channels are

captured by a Photron high-speed camera with a long-distance microscopic lens. Videos are recorded with a resolution of 1024x1024 and a frame rate range of 60-2,000 fps. A halogen source dual fiber optic light guide is used for illumination. All optical equipment and the test setup are mounted on a vibration isolation table.

The Baseline GDL fabricated by General Motors with the procedure described in Task 1.1 is used for the ex-situ multi-channel experiments. The GDL has a thickness of approximately 230 μm . The hard-stop PTFE gasket is implemented to ensure the appropriate compression under the compressive load. The test section is assembled under a compression of 2068 kPa (300 psi). A compression ratio of about 20% for GDL is achieved with this clamp pressure. During experiments the GDL is placed in a vertical down flow orientation. The test section is kept at ambient temperature (about 24 °C) throughout the experiments.

Figure 3.2.3 – Ex-situ multi-channel experimental setup.

B. Individual Channel Flow Rate Calibration

A unique feature of the ex-situ multi-channel test section is that it allows the mass flow rate in each channel to be measured simultaneously and separately. The principle of measuring the mass flow rate in each channel is based on the fact that the pressure drop between two points along the channel is monotonically dependent on the mass flow rate in the channel. The validity of measuring the channels mass flow rate using this approach has been verified in the same group [131].

Since the theoretical equations describing the individual channel flow rates as a function of the entrance region pressure drop are not readily available for the specific geometry tested, a calibration curve is experimentally developed for each channel. A plastic sheet instead of a GDL is used for the calibration since it will allow air flow to be completely blocked off with the use of dowel pins. During the

calibration, only the channel of interest is kept open while all other channels are closed using the dowel pins, and air is passed through the channel. The flow rate is measured with a digital flow meter (Omega FMA-1620A), which has an accuracy of ± 10 sccm over a range of 0-1000 sccm. The pressure drops in each channel are measured with differential pressure sensors (Honeywell FP2000) and recorded on a computer through a LabVIEW program. The calibration data show that the output voltage of the pressure sensor in the open channel varies monotonically with mass flow rate, while the voltages of the blocked channels keep a constant value. The pressure sensor voltages are plotted against the flow rate which is fitted by a polynomial equation. This procedure is repeated for each of the eight channels. A set of calibration equations is hence obtained for each channel.

In order to test the validity of the calibration equations, a measurement is made where all eight channels are opened and air of a known mass flow rate is passed through and the pressure sensor voltage on each channel is recorded. The mass flow rate in each channel is calculated from the pressure sensor voltages by using the corresponding calibration equation. Figure 3.2.4 shows the comparison between the calculated total mass flow rate (the sum of all eight channels) and the input mass flow rate. From this graph, it is seen that the results agree to within 5 percent up to a flow rate of 4500 sccm. This flow rate is equivalent to an air stoichiometric number of 15 for the studied channel area as it would be used in a H_2 -air fuel cell at a current density of 1 A/cm^2 . Since PEM fuel cells are usually operated at an air stoichiometric number much lower than this value, the calibration equation set is demonstrated to be good for most of the ex-situ and in-situ testing in this project. At higher flow rates, the calculated mass flow rates deviate from the input mass flow rate.

Once the calibration curves are obtained, they are applied to measure the instantaneous flow distribution in the ex-situ multi-channel test section combined with GDL and under single-phase gas flow and two-phase flow conditions. With this information, it is possible to assess the effects of certain parameters on the distribution of reactants and water products of fuel cell reactions in the channels.

Figure 3.2.4 – Comparison of total calculated and measured mass flow rates for the ex-situ multichannel flow experiment test section.

C. Flow Maldistribution under Single-Phase Gas Flow and GDL Intrusion

After the calibration of the individual channel flow rate, the plastic sheet is then replaced with a GDL sample. Figure 3.2.5 shows the instantaneous individual channel flow rate with the Baseline GDL sample at different input air flow rates under the single-phase gas flow condition. For comparison, the results for the plastic sheet are also shown in this figure.

For the case of the plastic sheet, a similar flow distribution pattern is observed for the three input flow rates: 300, 1000 and 3000 sccm. The flow is rather uniformly distributed among eight channels, except for a slightly higher flow rate in the central channels due to possible manifold effects. In contrast, severe flow maldistribution is observed for the Baseline GDL at the tested input flow rates. A maximum deviation of about 25% is obtained from the mean flow rates at the total flow rates in the range of 300 to 3000 sccm. The possible cause for the maldistribution may be due to different intrusions resulting from the compression effects of the GDL.

Under compression, the GDL usually intrudes into the channels and decreases the channel cross-sectional area, leading to a higher pressure drops in the entrance region (which is recorded and used for the calculation of the individual channel flow rate) and consequently higher calculated flow rates. The GDL intrusion can be further demonstrated by the higher pressure drop across the entire channel for the GDL case than for the plastic sheet, as shown in Figure 3.2.6. This figure shows the comparison of experimental measurements and predicted pressure drops as a function of total air flow rate. The plastic sheet results represent non-intruded channels and thus yield the lowest pressure drop for a given flow rate. The actual GDL measurements yield a higher value of pressure drop over the entire flow rate range. The three lines represent the results from the simulation with three values of intrusion, which was assumed to be uniform. It is seen that the GDL data matches closely (within 10%) with the intrusion simulation results except for the highest flow rate case. This indicates that it may not be appropriate to consider the intrusion to be uniform throughout the channel. Instead, it may act as a series of orifices whose characteristics may not be represented by a simple uniform intrusion model. An uneven distribution of intrusion is again clearly observed in Figure 3.2.7. The intrusion was measured with a confocal microscope in the central section of each channel under a compression of 2.07 MPa. An intrusion in the range of 20-40 μm was obtained, which is comparable to the flow measurement (see Figure 3.2.6)

Figure 3.2.5 – Flow maldistribution for (a) Baseline GDL and (b) plastic sheet under single-phase gas flow condition at different input air flow rates. The input air flow rates for the top figures, the middle ones, and the bottom ones are 510, 1000, and 3000 sccm, respectively.

Figure 3.2.6 – Total pressure drop for the cases of intruded channels (with GDL) and non-intruded channels (with plastic sheet) as a function of air flow rate. The test section is compressed to 2.07 MPa. The lines show the results from fluid flow model without intrusion and with 10% and 20% intrusion.

Figure 3.2.7 – GDL intrusions measured optically in the central region of gas channels under a compression of 2.07 MPa.

Figure 3.2.8 shows the equivalent intrusion of the Baseline sample analytically calculated as a function of compression. The results from the CFD simulation and the microscopic measurements are also shown in this figure. A similar value is obtained for the GDL intrusion by the three methods, for example, an intrusion of about 45 μm is found for the Baseline GDL at 2.07 MPa compression. This value is significant compared to the channel height of 400 μm . This is responsible for the higher calculated channel flow rate (Figure 3.2.5) and the much higher total pressure drop (Figure 3.2.6) for the Baseline GDL compared with the plastic sheet. The intrusion of GDL is likely non-uniformly distributed due to the non-uniformity of the GDL properties. This may be responsible for the severe flow maldistribution with the GDL (Figure 3.2.5).

Figure 3.2.8 – Comparison of intrusion from fluid flow model and ANSYS simulation results.

D. Two-Phase Flow Dynamics

Ex-situ experiments are designed to study the water transport characteristics in a gas channel under a two-phase flow condition mimicking the actual fuel cell channels. For this purpose, liquid water is injected at the back side of the GDL, simulating the water production in the cathode catalyst layer within a PEMFC, while the air at desired flow rates is passed through the gas channels. Two-phase flow is thus obtained in the parallel channels.

The water injection rates and air flow rates are selected to match the water production and gas flow rates at the cathode side of a PEMFC. Table 3.2.1 shows the air flow and water injection rates as well as the corresponding current densities. The current density is not actually produced during ex-situ experimentation, rather it provides an idea of what a real fuel cell with the same flow field would produce

with the given water generation rates. The superficial air velocity, Reynolds number, and water superficial velocity are calculated based on the designed channel cross-section area and are also listed in the table. Table 3.2.1 displays air flow rates associated with a stoichiometric ratio of 1 for each water flow rate; however, the air stoichiometries ranging from 1 to 45 are studied (larger ratios applied only to lower water injection rates). The superficial air velocities are varied accordingly.

Table 3.2.1 - Air and water flow rates used in testing and corresponding operating current density, Reynolds number of air and superficial velocities.

Water Injection Rate (mL/min)	Air Flow Rate at Stoic Ratio = 1 (sccm)	Current Density* (A/cm ²)	Superficial Water Velocity, U_L (m/s)	Superficial Air Velocity, U_G (m/s)	Reynolds Number, Re_a
0.00	0	0.0	0.0	0.0	0.0
0.02	66	0.2	1.5×10^{-4}	0.5	16.2
0.04	132	0.4	3.0×10^{-4}	1.0	32.3
0.10	330	1.0	7.4×10^{-4}	2.5	80.8
0.20	660	2.0	1.5×10^{-3}	4.9	161.7

*Current density values found by back calculating what the associated water and air flow rates would produce in a real fuel cell with same channel number and dimensions (with an active area of 18.4 cm²).

In this work, the two-phase flow dynamics in the gas channels is explored through the measurement of the instantaneous gas flow rates in individual channels by means of the entrance region pressure drop method [131] and the simultaneous high-speed imaging of the flow structures. Three water flow patterns, namely slug flow, film flow and mist flow, have been observed for the two-phase flow in the ex-situ experiment with baseline GDL. In general, slug flow occurs at low air flow rates, mist flow appears at very high air flow rates, and film flow appears at intermediate air flow rates. It is worthy to point out that the entrance region occurs before the introduction of water so that only single-phase gas flows in this region.

Generally, at lower air flow rates, large water (static and dynamic) holdup is observed due to the lower air velocities and severe flow maldistribution is observed. Figure 3.2.9 shows the flow rate in eight channels and their summation as a function of time for a superficial water velocity of 3×10^{-4} m/s (water injection rate of 0.04 mL/min) and a superficial air velocity of 1.7 m/s (corresponding to air flow rate of 198 sccm or air stoichiometry of 2). The most significant result from this figure is seen at 85 s, when the flow rate in channel 4 drops sharply from 35 sccm to about 10 sccm, and the flow rates in other channels (e.g. channel 2, 5 and 6) increase to maintain the constant total flow rate. The simultaneous high-speed video images of the flow structure are shown in Figure 3.2.10. A large slug is clearly observed to form in channel 4 and it moves very slowly. Figures 3.2.9 and 3.2.10 clearly display the blockage of the gas flow by slug formation in the channels and the resultant severe flow maldistribution. In Figure 3.2.10 stationary water holdup (large droplets) is also observed in channels 5 and 6. They may affect the flow distribution in these channels as well, but to a much lesser degree. It is important to note that the flow rate in channel 4 is not reduced to zero upon the slug formation. This may indicate a semi-slug [132] in which the gas phase remains, to some extent, continuous. Through careful investigation of a large number of high-speed videos, water accumulation is seldom observed to contact the hydrophobic GDL surface, even with the combination of the highest water injection rate and the lowest air flow rate.

Figure 3.2.9 – The instantaneous flow rate in eight channels and their summation taken over a period of 250 s for the two-phase flow at superficial water velocity of 3×10^{-4} m/s (water injection rate 0.04 mL/min) and superficial air velocity of 1.7 m/s (198 sccm, corresponding to stoichiometric ratio of 2). The numbers in the figures represent the channel number.

Figure 3.2.10 – The water flow structure, captured as a still picture from a video, for the same experiment as Fig. 3 with superficial water velocity of 3×10^{-4} m/s (water injection rate 0.04 mL/min) and superficial air velocity of 1.7 m/s (198 sccm) for (a) at the beginning of video recording and (b) after 100 sec. The numbers in the figures represent the channel number.

Figure 3.2.11 shows the corresponding total pressure drop for the same experiment as in Figure 3.2.9. This figure clearly indicates that the slug flow increases the total pressure drop, in the range of 0.05 kPa, in spite of the fact that the slug only occurs in one channel (channel 4 for this experiment). The total pressure drop maintains at higher value until the slug is removed by the air flow. The ΔP features shown in this figure are unique for slug flow and can thus be used as an indicator of slug flow. The ΔP features for other flow patterns (film and mist flow) will be explained later. The residence time for each slug can be readily obtained based on the ΔP – time plot. For example, a residence time of over 150 s is observed

for the slug in Figure 3.2.10, which is in agreement with the channel flow rate decrease in Figure 3.2.9. The slug residence time decreases significantly as the air flow rate increases.

Figure 3.2.11 – The variation of total pressure drop as a function of time recorded in the same experiment as in Figure 2.8.

As superficial air velocity increases above about 7.4 m/s, the flow maldistribution decreases significantly and the slug or semi-slug flow is replaced by the water film flow. The typical film flow results are shown in Figure 3.2.12 where the water flow rate is 0.04 mL/min and the air velocity of 7.9 m/s (2700 sccm, corresponding to stoichiometric ratio of 8). The film flow is characterized by the much smaller variation in the channel flow rates (Figure 3.2.10 (a)) and the periodic fluctuations in the total pressure drop (see Figure 3.2.10 (b)). Small variation, as low as 4.3% for the maximum deviation from the mean channel flow rate in Figure 3.2.12, is observed in the air flow rate in each channel, unlike the case of the slug flow where large changes, as high as 75% for the channel 4 in Figure 3.2.9, in air flow rate are detected. The periodic fluctuations in the pressure drop may be attributed to the unsteady-state motion of the water film along the channel wall.

Figure 3.2.12 (c) shows an enlarged water flow structure captured as a still picture from a video. The water film formation along the channel is dictated by the Concus-Finn condition [133]:

$$\theta + \alpha < \frac{\pi}{2} \quad (3.2.1)$$

where θ is the contact angle of water on the channel wall and α is the half-angle formed by the channel corner. The contact angle of the Lexan channel is measured to be around 60° . For the rectangular channel ($\alpha = 45^\circ$) used in this experiment, Eq. 3.2.1 is not satisfied and therefore water cannot be wicked into the channel corner to form a stable, continuous film, and liquid water collects on the channel walls in the form of large droplets. Due to the drag force of the downward air flow as well as gravity, large droplets

deform along the channel wall and form a film-like structure. When the drag force and gravity overcome surface tension forces, the film-like structure starts to move, leading to a thick leading face and a much thinner tail, as shown in Figure 3.2.12 (c).

As superficial air velocity further increases, corresponding to air stoichiometry above 10, little or no water accumulation in the channels is observed. Liquid water (in the form of droplets) is removed from the GDL surface directly by the shear force of the gas flow, followed by mist flow. Figure 3.2.13 shows the individual channel flow rate plot at a superficial water velocity of 3.0×10^{-4} m/s (water injection rate 0.04 mL/min) and a superficial air velocity of 24.6 m/s (corresponding to air stoichiometry of 25), as a typical example of mist flow. No flow rate variation is observed, which agrees with flow structure visualization. In mist flow tiny water droplets are suspended in the gas stream. Evaporation is also expected to contribute significantly to the water removal at such high air flow rates.

Figure 3.2.12 – The film flow observation of the baseline GDL at water flow rate of 0.04 mL/min and air velocity of 7.9 m/s (2700 sccm, corresponding to stoichiometric ratio of 8): (a) the flow distribution, (b) the total pressure drop, and (c) enlarged water flow structure captured as a still picture from a video.

Figure 3.2.13 – Instantaneous flow rate plot (left plot) and pressure drop (right plot) for a superficial water velocity of 3.0×10^{-4} m/s (water flow rate 0.04 mL/min) and a superficial air velocity of 24.63 m/s (3302 sccm, corresponding to stoichiometric ratio of 25).

The total pressure drop data in the ex-situ multichannel flow experiments is recorded and analyzed in terms of the two-phase friction multiplier [134] as defined in Eq. 3.2.2,

$$\Phi_g^2 = \frac{\Delta P_{2\phi}}{\Delta P_g} \quad (3.2.2)$$

where $\Delta P_{2\phi}$ and ΔP_g are the pressure drop with two-phase flow and with only single phase gas flow in the channel, respectively. Φ_g^2 provides a good indication of water holdup in the gas channel. Figure 3.2.14 shows the two-phase friction multiplier for the hydrophilic channel as a function of air velocity and water velocity. The results for the non-treated channel are also shown in Figure 3.2.14 for comparison. The most outstanding result from this figure is that Φ_g^2 for the hydrophilic channel approaches a constant value that is above unity at higher water velocities, while Φ_g^2 for the non-treated channel approaches unity at all water velocities investigated in this work, with $\Phi_g^2=1$ representing mist flow.

Figure 3.2.14 – Two-phase friction multiplier as a function of the superficial air velocity under different superficial water velocity for the Baseline system.

E. Two-Phase Flow Pattern Map

The flow dynamics and the flow pattern for the baseline GDL are summarized by a two-phase flow map, as shown in Figure 3.2.15. Please note that there is a transition between the slug/film and film/mist regions rather than sharp boundaries. From this figure, the flow pattern is apparently a strong function of air flow rate. As air flow rate increases, the flow pattern changes from slug to film and finally becomes mist flow. The flow pattern is dependent on water flow rate as well. As water flow rate increases, the film and slug flows occur more readily at lower air flow rates.

Slug flow is undesired for fuel cell operation due to the severe flow maldistribution, which may lead to the non-uniform distribution of the current density. The non-uniformity in the current density has been found to be detrimental to the fuel cell performance and the durability. On the hand, mist flow provides an efficient removal mechanism for liquid water in a channel. However, it is usually impractical for fuel cell application because it requires very high air flow rates. Film flow is thus considered the most preferred flow pattern for the fuel cell operation because it provides a relatively fast water removal mechanism and a relatively uniformly distributed gas flow, and, at the same time, it does not require high pressure drop. This is in agreement with the flow pattern map in Figure 3.2.14.

Figure 3.2.15 – Parallel channel flow pattern map obtained from the ex-situ experiment at ambient conditions and vertical down flow orientation. The air and water velocities in the figure are the nominal velocities calculated based on the flow rates and the ex-situ test section design.

III-2.2 Baseline Fuel Cell Experiments with Visual Access

A. Test Section

In-situ visual investigation of an operating fuel cell has been used in the past with great success [4]. Such testing is also applied in the current RIT in-situ fuel cell experiments. A transparent fuel cell has been built, based on the design in subtask 1.2, to allow for the direct visualization of the two-phase flow in fuel cell channels. This cell incorporates the common channel size and geometry designed by General Motors. Figure 3.2.16 shows the exploded view of the designed transparent fuel cell. The cell is constructed of a pair of aluminum plates mated with a polycarbonate plate (Lexan). The flow field is formed on a gold-coated copper plate with a thickness of 0.4 mm. Twenty-two weaving channels are made through the copper plate for the cathode flow field, which has an active area of 50 cm². For the anode side, 11 channels are formed. The copper plates double as the current collector, with the gold coating preventing corrosion and increasing the electric contact. The optical visualization is achieved through the Lexan window which is placed outside the anode/cathode flow field plate. The thickness of the Lexan piece is minimized to allow for sufficient heat conduction and thus for minimal temperature gradient. The cell and the flow field plates are shown in Figure 3.2.17.

In addition to the visualization, the measurements of total pressure drop between gas inlet and outlet and the flow distribution in each channel are also considered in this transparent fuel cell. A similar header design as in Figure 3.2.2(a) is implemented to allow for these measurements. Such a test section is also be used in Task 5.0.

A FCATS™ G040 base fuel cell test station was customized and purchased from Hydrogenics Test Systems to meet the demands for accurate in-situ testing. Integral features of the test station include the precise measurement and control of reactant gas flow rates, temperatures and pressures, fuel cell humidification, and the capability for high frequency resistance (HFR) measurements and other fuel cell performance metrics.

Figure 3.2.16 – Exploded view of a transparent fuel cell. 1: end plate; 2: die springs; 3: viewing window; 4: metal case; 5: gas in/out; 6: heating water in/out; 7: Lexan plate; 8: cathode and anode flow fields.

Figure 3.2.17 – A 50 cm² fuel cell with visual access based on the design specified in subtask 1.2. The upper picture shows the overview of the transparent fuel cell and the lower one shows the channels made on a gold-coated copper plate.

B. In-Situ Fuel Cell Experiments

In conjunction with ex-situ multichannel experiments, the in-situ fuel cell experiments with visual access have been carried out on the baseline system at RIT. The test conditions were derived from an inevitable “threshold” operating condition for fuel cells, one that contained high water levels as seen through GM’s neutron radiography testing. The initial in-situ test conditions were designed to be 35 °C, dry inlet gas, and ambient pressure. Three stoichiometric ratios, 1.5:2.5 (anode:cathode), 1.5:5 and 3:8, were tested. Following the completion of this test condition, the results were compared to ex-situ experimental results and a post mortem analysis was conducted. Further experiments were then carried out using humidified gas streams.

In situ characterization of the Baseline GDL material was performed at a cell temperature of 35 °C, with both 100% RH and dry inlet gases, at three stoichiometric ratios (anode:cathode) 1.5:2.5, 1.5:5. 3:8. Cell performance with the Baseline GDL was characterized using polarization curves. The high frequency resistance (HFR) was also measured for baseline characterization. The polarization curves and HFR measurements for each stoichiometric ratio with fully humidified inlet gases are shown in Figure 3.2.18.

As seen in the figure, the cell performance for stoichiometric ratios of 1.5:2.5, and 1.5:5 was very comparable, both promoting higher cell performance than the 3:8 ratio. The HFR measurements show that the highest membrane hydration (lowest HFR) is achieved with a stoichiometric ratio of 1.5:2.5. Therefore, the best overall Baseline GDL performance was obtained with the stoichiometric ratio of 1.5:2.5. During in-situ experiments it was noted that the operational current density was limited at $\sim 0.6 \text{ A/cm}^2$, which was most likely due to the increased ohmic resistance within the fuel cell caused by dehydration of membrane.

Figure 3.2.18 – Baseline GDL performance characterization. Cell temp. 35 °C, 100% RH inlet gases, stoich ratios (an:ca) 1.5:2.5, 1.5:5, 3:8.

An additional characterization metric used for Baseline GDL characterization is a flow pattern map. Two-phase flow observations made using the optical visualization system were used to construct a flow pattern map showing slug, film, and mist flow dominant regions. A comparison of ex-situ and in-situ flow maps at dry inlet flow conditions is shown in Figure 3. 2.19. Ex-situ water flow rates were converted to their corresponding current densities, and superficial velocity of air was converted to volumetric flow rate (sccm) to match in-situ parameters. The comparison shows that the flow pattern maps possessed similar progressions from slug to film to mist flow as the air flow rate increases. The transition lines also have similar trends as their slant indicates that higher air flow rates were needed to bring about transitions when current density and thus water presence was higher.

The effect of inlet gas relative humidity on the two-phase flow pattern map can be seen from Figure 3.2.20, where the Baseline GDL is tested under the condition of 100% RH inlet gases. Typically more than one flow pattern exists simultaneously at each test condition; therefore, ‘dominant’ is used to describe the most prevalent two-phase flow pattern observed. As compared to Figure 3.2.19, increasing

inlet RH increases the regions of slug flow and film flow. This is expected due to the increased water presence in the gas channel, partially from water condensation.

Figure 3.2.19 – Comparison of in-situ (right figure) and ex-situ (left) flow maps. In-situ experiment was carried out at 35 °C and dry anode and cathode gases, and the numbers denote the anode/cathode stoic ratio.

Figure 3.2.20 – Baseline GDL cathode flow pattern map. Cell temperature 35 °C, 100% RH inlet gases.

Total pressure drop measurement across the channels was also used for Baseline GDL characterization. Figure 3.2.21 shows the total anode and cathode pressure drops for each stoichiometric ratio and current density. As expected, the pressure drops for the higher stoichiometric ratios were larger due to the increased gas flow rate. The pressure drop also increases as current density is increased due to the higher flow rates.

Figure 3.2.21 – Baseline GDL anode and cathode total pressure drop. Cell temp. 35 °C, 100% RH inlet gases, stoich ratios (an:ca) 1:5:2.5, 1.5:5, 3:8.

Typical examples of the instantaneous flow rates in individual cathode channels are shown in Figure 3.2.22 for dry and 100% RH operation conditions. Much larger and more frequent fluctuations are observed for the humidified gas case than for the dry gas case. This is attributed to the higher water buildup in cathode channels for the humidified gas.

Figure 3.2.22 – Instantaneous flow rate in individual channels for fuel cell experiment at 35 °C with (a) dry inlet gas and (b) humidified gas with 100% RH.

III-2.3 Baseline Fuel Cell Freeze-Thaw Experiments with Neutron Radiography

A. In-Situ Testing Protocols and Steady-State Water Distributions

All neutron imaging experiments were conducted at the National Institute of Standards and Technology (NIST), in a facility jointly developed by GM and NIST for fuel cell research (Figure 3.2.23). In Task 2.3, GM and NIST collaborated to acquire and analyze in-situ neutron images for an automotive fuel cell operating space representing 30-80 °C at 0.05-1.5 A/cm². The liquid water content for each condition was quantified and compared such that “worst case” shutdown conditions could be established. An example of such analyses is shown in Figure 3.2.24, where the effect of cell operating temperature on water accumulation at constant voltage with fixed reactant stoichiometric ratios, pressure (150 kPa) and inlet relative humidity (50%) is compared. It was shown that water content decreased monotonically with temperature. At low temperatures, the water carrying capacity of the reactant streams is reduced, and therefore less product water can be removed in the vapor phase. The most significant water hold-up, at both the channel level and within the GDL/MEA layers, occurred at moderate voltage (0.7 V). In an automotive fuel cell system such conditions are unavoidable, as in these experiments dry inlet gases and low pressure (which would produce relatively little liquid water) were applied. A fuel cell system warming from ambient temperature would surely transition through such a condition. For short drive cycles, it is conceivable that the system would shut down during a low temperature transient and subsequently freeze. The baseline characterization by GM and NIST has focused on identifying wet shutdown conditions that generically apply to all PEM fuel cell systems.

Figure 3.2.23 – Neutron Imaging Test Station at NIST

Figure 3.2.24 – Effect of cell operating temperature on water accumulation at constant voltage with fixed reactant stoichiometric ratios, pressure (150 kPa) and inlet relative humidity (50%).

Another representation of some of the initial steady-state results, all acquired at a constant voltage of 0.8V, is shown in Figure 3.2.25. The gray-scale images of water content are scaled such that dark black is indicative of thicknesses expected for channel water slugs, while the middle of the gray scale range corresponds to water content that can exist at the scale of the gas diffusion layers (GDLs). As expected, the quantity of liquid water accumulated in the channels and GDLs is a strong function of temperature. Because of the highly non-linear temperature dependence of water vapor saturation pressure, the reactant streams are capable of removing much more water in the vapor phase at 75 °C than at 30 °C. At temperatures of 30, 35 and 45 °C, the inlet humidifiers were bypassed because of the difficulty in precisely controlling dew points. Given the limited vapor carrying capacity at low temperature, using relatively dry gas (dew point ~ -10 °C) has little impact on water accumulation. This is indicated by results at the lower cell operating temperatures have more water present, especially at low current density (i.e., relatively high voltage) where the reactant flow rates are the lowest, and insufficient pressure differential is available to convectively remove water from the channels and GDL. From the initial portion of the experimental program, it was necessary to identify features of the fuel cell water accumulation which, upon shutdown and subsequent freezing, would create large resistance to reactant flow during the next start-up cycle. Such features are clearly evident from a pseudo-color reproduction of the water distribution obtained at 35 °C under a constant 0.4 A/cm² condition (Figure 3.2.26). Here, channel water content has been accentuated by mapping the black end of the gray scale to red, while smaller quantities of water that exist in the GDL are shown as green. From this color representation, it is evident that certain areas of the fuel cell may present freeze start problems related to ice formation:

- anode channels, which are clearly distinguishable from the cathode side due to the known flow field patterns (Figure 3.1.8),
- significant GDL saturation across most of the active area, although from these two-dimensional measurements it is not known how the GDL-level water is proportioned between the anode and cathode
- channel-to-header transitions under the seal glands, which contain appreciable amounts of water on both the anode and cathode, and
- edges of the flow field plates at the exit manifolds.

Once the water distributions under pertinent steady-state conditions were understood and quantified, GM's project activities transitioned to air purge and freeze start experiments which focused on dynamic water removal and accumulation behavior within the fuel cell active area.

B. Cathode Air Purge Evaluation with the Baseline Material Set and Design

With saturation states for a wide range of operating conditions defined, the next objective investigated was freeze shutdown preparation with gas purge. Liquid water response to cathode gas purge was recorded with high temporal resolution neutron imaging (1 second per image). Only cathode gas purge was evaluated as anode purge is not practical in most fuel cell systems. The maximum cathode purge flow is scaled based on a compressor sized to provide flow at an oxygen stoichiometric ratio of 1.3 at 1.5 A/cm². Using the maximum amount of dry cathode flow the hydration state of the membrane was monitored in time by high frequency resistance (HFR) measurements. Referring to Figure 3.2.27, one observes that the membrane dry-time out is significantly longer as the cell operating temperature is decreased. Subsequent in-situ purge dynamics experiments combined the HFR measurement (indicative of the level of membrane hydration) with neutron imaging, which provides the spatial water distribution at the level of the GDL and channels. As expected, as the HFR increases, there is a simultaneous decrease in the water content within the active area. Representative results are provided in Figure 3.2.28, where the shutdown condition ($t = 0$) corresponds to the 35 °C case with constant density of 0.4 A/cm², as shown in Figure 3.2.26. The plot of total fuel cell water volume as a function of time from the start of the purge is given in Figure 3.2.28. It is apparent that there are two distinct regimes of water removal: a relatively rapid elimination of anode channel water which occurs within the first 30 seconds due to system pressure release, followed by a slower drop in water content as GDL and MEA scale water is removed by evaporation. Pseudo-color neutron radiographs of the water distributions at 30, 60, 150 and 240 seconds after the start of the air purge are illustrated in Figure 3.2.29. At the end of the initial channel water elimination, there is remaining nearly uniform water content across the entire active area. Thereafter, the drying front moves across the active area from the cathode inlet side, but significant water remains in about 1/3 of the active area toward the anode inlet even after 240 seconds of air purging. Once the drying front begins to move inward beyond the edge of the active area (60 seconds after start of purge), there is a clear increase in the high-frequency resistance, which indicates that the drying front has moved down to the level of the membrane-electrode assembly (MEA).

Figure 3.2.25 – Gray-scale neutron radiographs of fuel cell water distributions at constant voltage condition (0.8V), with varying cell temperature and inlet humidification (pressure = 150 kPa; anode/cathode stoichiometric ratios = 2)

Figure 3.2.26 – Neutron radiograph showing critical regions of liquid water accumulation

Figure 3.2.27 – Membrane hydration response (as measured by HFR) to the same volumetric purge flow rate at various shutdown temperatures.

Figure 3.2.28 – Temporal variations of water content and high-frequency resistance during cathode air purge. Shutdown condition corresponds to water distribution shown in Figure 3.2.27.

An extensive matrix of purge experiments was conducted over wide ranges of cell temperature, purge flow rates and humidification levels. There is a striking influence of gas temperature on purge time, resulting from the significant difference in saturation vapor pressure. In Figure 3.2.30, it is apparent that a nearly 4X increase in purge time is required for the evaporation phase of the fuel cell purge at 35 °C relative to 80 °C. This temperature effect is also apparent in terms of steady-state performance and water accumulation. As shown in Figure 3.2.31, there is almost no influence of humidification level on cell water volume or voltage at 40 °C, whereas performance is enhanced significantly with increasing humidification at 80 °C.

One of the important issues in developing efficient purge strategies relates to the location of liquid water, i.e., anode vs. cathode. To improve the fundamental understanding in this area, experiments were conducted with the diffusion media artificially saturated under vacuum (Figure 3.2.32). It was observed that, with a fixed cathode air purge flow rate and humidity, the rate of bulk water removal is nearly independent of whether the water resides in the anode or cathode diffusion medium (Figure 3.2.33). This indicates that the purge dynamics are dominated by the relative humidity conditions of the channel-level air stream, and diffusive/convective transport resistances of the membrane, electrodes or GDLs have a small overall effect. Therefore, for a given shutdown condition, purge time can only be effectively modified by changing the water vapor carrying capacity of the air purge stream.

Investigation of bulk water removal was extended by measuring removal over small “differential” regions of the fuel cell active area where the relative humidity conditions within the channel are approximately constant. These experiments reveal a distinctly faster removal rate from the cathode side than from the anode side (Figure 3.2.34). Therefore, when quantified in this manner, there is a significant resistance introduced by the membrane to anode water removal by the cathode air stream when it is not completely saturated. Applying a similar method to analysis of purge of water generated during in-situ experiments indicates that most water being removed by the air purge resides on the anode side of the fuel cell (Figure 3.2.35).

(a) 30 seconds after start of air purge

(b) 60 seconds after start of air purge

(c) 150 seconds after start of air purge

(d) 240 seconds after start of air purge

Figure 3.2.29 – Water distributions during air purge, corresponding to temporal variation in water volume in Figure 3.3.28

Figure 3.2.30 – Effect of purge temperature on rate of evaporative water removal.

Figure 3.2.31 – Effect of relative humidity on cell voltage and water accumulation at 40 and 80 °C

Figure 3.2.32 – Experiments with purging of artificially saturated anode and cathode diffusion media

Figure 3.2.33 – Rates of water removal with artificially saturated anode and cathode diffusion media.

Mass Transfer Evaluation

Requires differential evaluation where change in channel RH is less significant

Figure 3.2.34 – Mass transfer evaluations on differential elements at the inlet edge of the active area.

Relating Diagnostic Purges to In-Situ Results

Using differential analysis to characterize water removal rates of known saturation in anode vs. cathode enables evaluation of in-situ water removal rates

Figure 3.2.35 – Comparison of purge rates from in-situ experiments to those from experiments with artificially saturated diffusion media.

C. Freeze Start Evaluation with the Baseline Material Set and Design

General Motors and NIST collaborated on developing a fuel cell freeze capability within the existing, jointly-developed neutron imaging station in Gaithersburg, MD. As shown in Figures 3.2.36 and 3.2.37, a freeze chamber (with neutron transparent aluminum “windows”) is situated between the neutron beam tube and imaging equipment. The freeze chamber can easily accommodate the freeze test apparatus shown in Figure 3.2.37, and has enough cooling capacity to rapidly reduce the temperature of the air surrounding the fuel cell to as low as -40 °C.

GM also conducted freeze start experiments at NIST with the baseline fuel cell system. It was observed that for freeze start at -20 °C from a shut-down condition with 15 seconds air purge or less, there was complete blockage of reactant flow paths, as evidenced by the extremely high anode and cathode pressure differentials, and the inability to generate power (Figure 3.2.38). However, with longer shutdown air purges, the reactant ΔP measurements were lower, and it was possible to generate power for some period until the voltage fell below 200 mV (presumably due to ice filling the electrodes). It was additionally determined that the complete reactant flow blockage for short purge times is primarily the result of ice formation at the end of the bipolar plate and at the channel-to-manifold transition region (Figure 3.2.39).

Figure 3.2.36 – Fuel cell freeze chamber with the neutron imaging facility at NIST.

Figure 3.2.37 – Fuel cell freeze chamber with the neutron imaging facility at NIST. 1: Test Cell; 2: Automated control hardware; 3: Heated pressure measurement lines; 4: Reduced coolant volume with in-line heater; 5: Gas heat exchangers; 6: Heated inlet and outlet lines; 7: Wet/dry gas 3-way valves.

Figure 3.2.38 – Comparison of freeze start performance for various shutdown air purge times

Correlating Water Removed During Purge to Frozen Failure Mode

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Figure 3.2.39 – Correlation of freeze start performance to water accumulation observed via neutron imaging

III-2.4 Post Mortem Analysis

Following the freeze/thaw cycling, the baseline system was inspected for damage and surface degradation of the (i) diffusion media surface, (ii) bulk structure and surface coatings of the flow fields, and (iii) the GDL-channel interface. In addition, the sectioned components were inspected for delamination at the membrane-electrode interface. Post mortem analysis employed standard sectioning and microscopy techniques utilizing the Microfluidic & Interfacial Transport (M&IT) Laboratory and the Applied Chemical and Morphological Analysis Laboratory (ACMAL) located at MTU.

A protocol for handling GDL was developed in order to unambiguously assess damage to components which have undergone freeze-thaw cycling. The protocol is necessary to insure that (i) the samples are not chemically contaminated which would change the wettability, (ii) the samples are handled consistently between institutions, and (iii) damage due to sample separation methods is known prior to assessment of damage resulting from fuel cell operation and/or freeze-thaw cycling. Summary of handling procedures:

- Wear powder free nitrile gloves.
- Clean all equipment thoroughly with ethanol to remove contaminants.
- Rinse all equipment thoroughly with distilled water to remove residual ethanol.
- Allow all equipment to air dry while covered to prevent dust accumulation.
- Remove gloves and replace with new pair.
- Remove samples from container taking care not to compress or bend them
- Place samples only on or in non-contaminated surfaces and containers when cutting.
- Separate samples using hole punch or razor knife depending upon desired size
- Allow samples separated with hole punch to fall short distance directly into bag or transfer to container holding lightly with tweezers.
- When separating with razor knife damage to unused portion of the sample may occur (due to holding or securing when cutting), be sure to mark this portion so others do not use damaged samples.
- Samples may be held with tweezers and transported (unbent and uncompressed) in aluminum foil inside a plastic Ziploc bag.
- Return unused portions of samples to storage bag. Be sure to mark any contaminated or bent samples and store them separate from the unused samples.

Toray T060 7% PTFE (mass) and SGL 25 BC were imaged in a JOEL 6400 Scanning Electron Microscope after four different sample separation techniques – razor knife, hole punch, scissors and punch and die (as received by GM). Based on analysis the preferred separation techniques include the punch press (GM), hole punch, and razor knife. Unacceptable techniques include scissors and the use of a razor knife in which the sample is compressed or bent. Damage was generally found to be localized within less than 200 microns from the edge using the acceptable separation techniques. No damage was found beyond the damaged edge region. Crack propagation was found when scissors were used in the separation of Toray paper.

Figures 3.2.40 through 3.2.48 show the type of damage resulting from sample separation for the two GDL types. The images were taken using a JOEL 6400 Scanning Electron Microscope. Accelerating voltages of 5 kV, 15 kV, and 20 kV were used (no sample damage was observed). The beam currents ranged between 0.15 and 0.167 nA and specimen currents ranged between 0.064 and 0.097 nA. Magnifications ranged from 10x to 2500x.

Figure 3.2.40 – (a) Toray 100x Image, Hole Punch Edge. (b) Toray 350x Image, Hole Punch Edge

Figure 3.2.41 – (a) Toray 100x Factory Edge. (b) Toray 450x Factory Edge

Figure 3.2.42 – (a) Toray 100x Knife Edge (b) Toray 450x Knife Edge

Figure 3.2.43 – Toray at 1500x magnification showing capillary traps formed by webbing between fibers.

Figure 3.2.44 – Toray Cut with Scissors Showing Stress Crack Propagation (circled in red)

Figure 3.2.45 – SGL Factory Edge showing Coated (left) and Uncoated (right) Sides of SGL at 100x Magnification

Figure 3.2.46 – SGL Knife Separation showing Coated (left) and Uncoated (right) Sides of SGL at 100x Magnification

Figure 3.2.47 – SGL Hole Punch Separation showing Coated (left) and Uncoated (right) Sides of SGL at 100x Magnification

Figure 3.2.48 – Vertical Crack in Microporous Layer of SGL at 1500x Magnification

III-3. Task 3: Parametric Studies at the Component Level

Work Statement for Task 3: The objective of this portion of the project is to determine the most effective GDL morphology and wettability for rejecting liquid water. An optimum combination of GDL material, structure and wettability which minimizes the accumulation of liquid water is sought. To that end we are conducting a parametric investigation of GDL properties which influence in-plane and through-plane water transport. The most important parameters relative to liquid water transport in the GDL are:

- *Structure/geometry - fiber diameter and anisotropic porosity.*
- *Materials and wettability - contact angle and contact angle hysteresis measurements correlated to PTFE content and base material (carbon paper, carbon cloth, etc).*
- *Flow conditions - the pressure, gas flow rate and relative humidity in the gas flow channels into which the water must penetrate in order to exit the GDL.*

This task will include modeling and experiments divided into a number of studies. The first set of studies will characterize the material properties of the GDL's. The second set will characterize the transport properties of water in the GDL's. And the third set of studies within this subtask will be an analytical and numerical modeling effort which will develop a local (non-Darcy) model of capillary imbibition in a three-dimensional, anisotropic porous layer subject to a backpressure. The data compiled from these three subtasks will be used to specify a realistic, mass-producible GDL for inclusion into the combinatorial studies.

To achieve the goals stated above, several novel techniques for characterizing GDL material and transport properties had to be developed. GDL structural and morphological properties were characterized via SEM imaging and specialized sample holders developed at Michigan Tech. The work is divided into GDL component studies (3.1) and channel studies (3.2). The GDL component studies are subdivided into material property characterization of structure, morphology and wettability and transport property characterization that focused on the role of capillarity in GDL water transport. Key findings and contributions from Michigan Tech are:

- development of specialized sample holder for SEM imaging of GDL under compression
- development of GDL morphology measurements from SEM image analysis; distributions of pore size, shape, orientation, nearest neighbor, and depth can be characterized
- identified change in electrical conductivity of GDL fibers when under strain
- development of unique contact angle measurement apparatus based on sessile drop method with temperature control and option of generating drops by deposition or by injection through GDL
- contact angle found to be dependent upon drop size, temperature, deposition method, and history (advancing-receding)
- development of a new characterization method for water transport in GDLs; pseudo-Hele-Shaw cell test with the appropriate scaling of test data (C_e and t^*)
- development of a simple, reliable computational tool for predicting water transport in porous layers
- validation of the computational tool through simulation of pseudo-Hele-Shaw tests
- determination of the role that the microporous layer (MPL) and defects in the MPL have on water transport in fuel cells
- determination of the role that wettability and reactant flow channel geometry have on liquid holdup, flow behavior, and pressure drop on two-phase flow

Much of the detailed descriptions and test methodologies of these findings are documented in journal articles, conference proceedings and previous DOE reports. These documents are included in the appendices for reference.

III-3.1. GDL Characterization

A. Characterization of GDL Material Properties - Structure

GDL wettability was measured using a custom-built apparatus also developed at Michigan Tech. Liquid water transport in the GDL was characterized using a pseudo-Hele-Shaw experiment and numerical simulation. The computational tool has been validated experimentally and used to assess the role of GDL morphology, the role of the microporous layer (MPL) and the role of MPL defects on the movement of liquid water transport in fuel cells. For the reactant flow channels, wettability and geometry are critical factors in liquid holdup, flow behavior, and pressure drop of two-phase flow.

A protocol for handling GDL was developed in order to unambiguously assess damage to components which have undergone freeze-thaw cycling. The protocol is necessary to insure that (i) the samples are not chemically contaminated which would change the wettability, (ii) the samples are handled consistently between institutions, and (iii) damage due to sample separation methods is known prior to assessment of damage resulting from fuel cell operation and/or freeze-thaw cycling.

Toray T060 7% PTFE (mass) and SGL 25 BC were imaged after four different sample separation techniques – razor knife, hole punch, scissors and punch and die (as received by GM). The images were taken using a JOEL 6400 Scanning Electron Microscope. Accelerating voltages of 5 kV, 15 kV, and 20 kV were used (no sample damage was observed). The beam currents ranged between 0.15 and 0.167 nA and specimen currents ranged between 0.064 and 0.097 nA. Magnifications ranged from 10x to 2500x. Based on analysis the preferred separation techniques include the punch press (GM), hole punch, and razor knife. Unacceptable techniques include scissors and the use of a razor knife in which the sample is compressed or bent. Damage was generally found to be localized within less than 200 microns from the edge using the acceptable separation techniques. No damage was found beyond the damaged edge region. Crack propagation was found when scissors were used in the separation of Toray paper as shown in Figure 3.3.1. Detailed descriptions on the sample separation technique for both GDL types are reported in [mtu-01] and [mtu-02] and are included in Appendices mtu_a:01 and mtu_a:02, respectively. (delete?)

Preliminary images of GDL samples under compression have been collected using a specialized SEM compression sample holder (illustrated in Figure 3.3.2) developed at Michigan Tech. An estimated force of 20.4 lbf was applied to the GDL sample. One of the images is shown below, Figure 3.3.3. At this low force the fibers bent and did not snap. In order to improve the accuracy of force and displacement data, a base was designed to hold the sample holder as well as six dial test indicators. The sample will be in the center with the six indicators spaced evenly around the mount. This will allow for three indicators on the top plate and three indicators on the middle plate to provide an accurate measurement of the displacement seen by the plates and therefore the GDL.

The intent of the SEM imaging of GDLs under compression was to determine the type and magnitude of stress that resulted in damage and to obtain stress-strain relations for GDLs. During the compression testing the stress exhibited increasing stiffness with strain indicating the possibility of unwanted contributions from in-plane shear effects; a result common with then samples under compression. The stress-strain relationships for GDL materials in the literature are inconsistent and highly dependent upon the technique used. We found the same trend with this attempt.

This technique does allow for easy determination of subsurface damage due to compression. Figure 3.3.4 shows charge accumulation due to compression damage. This sample was compressed under a channel and the edges of the channel are visible from charge accumulation resulting from decreased

electrical conductivity. Details of the sample holder, stress-strain studies and compressive damage studies can be found in references [135, 136] located in Appendices mtu_a:03 and mtu_a:04.

Figure 3.3.1 – Toray Cut with Scissors Showing Stress Crack Propagation (circled in red).

Figure 3.3.2 – SEM compression sample holder. Side view (left) and top view (right) with GDL samples in test fixture.

Figure 3.3.3 – SEM Imaging of Compressed GDL - Location 1 is compressed against a flat surface;
Location 2 is compressed against a 1 mm square groove.

Figure 3.3.4 – Damage due to compression beneath a channel is visible through charge accumulation on the surface.

The electrical properties of a carbon fiber of a GDL under deformation were studied using four point measurement methods inside a scanning electron microscope (SEM). The four-point probe setup

used consists of four equally spaced tungsten metal tips with finite radius. (Figure 3.3.5) The current-voltage characteristics of a carbon fiber before bending and after bending (Figure 3.3.6) experiments were studied. From the graph, it was observe that source sense voltage in both bent and unbent conditions are almost similar, while there is significant difference in drain sense voltage for unbent and bent carbon fiber (Figure 3.3.7). We found out that through bending deformation the electrical resistivity of carbon fibers will be enhanced (Figure 3.3.8). The details of this work are described in an article published in J. Power Sources [137].

Figure 3.3.5 – (a) SEM image of four nanomanipulators independently driven in a SEM chamber. Outermost probes are Source and Drain current and innermost is source and drain sense voltages. (b) SEM image of nanomanipulator tips during electrical measurements of a carbon fiber with no bending deformation [137].

Figure 3.3.6 – SEM image of a carbon fiber during bending (a) the nanomanipulator setup, and (b) the schematic of current and voltage detection in the bended fiber [137].

Figure 3.3.7 – Source current –sense voltage characteristics for unbent carbon fiber and during the bending for the same carbon fiber [137].

Figure 3.3.8 – Kelvin resistance –source voltage characteristics presenting a nonlinear resistance for unbent carbon fiber and during the bending for the same carbon fiber [137].

B. Characterization of GDL Material Properties - Morphology

A detailed analysis of microstructure that included pore roundness, orientation and nearest neighbor distributions was conducted via statistical processing of SEM images of GDLs.

Pore roundness distribution: Pore roundness or form factor, S , is often used to describe shape of structures. The value of S will be 1.0 for a perfect circle and will decrease in magnitude as the outline becomes more irregular. Figure 3.3.9 shows the distribution of pore roundness values of different GDL samples and the calculated statistical parameters including the average or mean, standard deviations, and skewness related to the pore roundness distribution, are given in Table 3.3.1. The calculated average pore roundness for Freudenberg is highest, while Toray is the lowest among the three GDLs. From Table 3.3.1

one can conclude that the pore roundness of Freudenberg and SGL are in the same vicinity (0.55-0.57) and the pore structures in Toray are highly elongated in comparison to the other samples.

Figure 3.3.9 – Pore roundness distributions: (a) Freudenberg, (b) SGL, and (c) Toray

Table 3.3.1. Pore shape analysis of different GDL samples

	Freudenberg	SGL	Toray
Avg Pore Roundness	0.57	0.55	0.23
Standard Deviation	0.23	0.26	0.21
Skewness	0.12	0.13	1.36

Pore orientation distribution: In addition to pore roundness and diameter values, the orientation distribution of pores in GDL samples was studied. The data was plotted in a polar rose plot, which is an angle histogram showing the distribution of values grouped according to their numeric range (viewed as a "polar plot"). A rose plot is useful for viewing the direction of pores distribution in the GDL samples. A typical rose plot consists of three variables, bin size, angle value, and number of counts. From Figure 3.3.10, pores in SGL are more directionally oriented than Freudenberg and Toray.

(a)

(b)

(c)

Figure 3.3.10 – Pore orientation distributions: (a) Freudenberg, (b) SGL, and (c) Toray.

Nearest neighbor analysis: Nearest neighbor analysis examines the distances between each point and the closest point to it. For this purpose, we extracted the pores from SEM images and spatially distributed centroid of the pores. The centroids were connected to their nearest neighbor points and the nearest neighbor distances were calculated. The nearest neighbor index (NNI) measures the degree of spatial dispersion in the distribution based on the minimum of the inter-feature distances. NNI is based on the distance between adjacent point features such that the distance between point's features in a clustered pattern will be smaller than in a scattered (uniform) distribution with random falling between the two. Figure 3.3.11 shows the nearest-neighbor plots for the GDL samples. As can be seen from NNI values, the pores in Toray (NNI=0.62) are distributed more randomly in comparison to other GDL samples. The non-uniform distribution in SGL sample was also confirmed earlier by orientation analysis (Figure 3.3.10).

Figure 3.3.11 – Nearest neighbor distributions: (a) Freudenberg, (b) SGL, and (c) Toray.

Effect of pore Size distribution: One of the more promising distribution characterizations is that of pore size. Through statistical image processing, the pore size distribution can be determined. The distribution is modeled as a two-parameter Weibull distribution similar to that reported by Gostick et al. [76]. Figure 3.3.12 illustrates the process of binning of pore sizes and determination of the Weibull distribution parameters using a cumulative distribution. The variation in pore size distributions for different GDLs is apparent in Figure 3.3.13.

Currently, studies are underway to assess the affect of image magnification, image size, pixel density, and threshold intensity on the Weibull parameters obtained. These results are being compared to existing pore size distributions as determined by mercury intrusion or standard porosimetry. Unfortunately, when publishing porosimetry results from GDL testing, most authors only report the mean pore size and not the distribution. This makes it difficult for comparison and/or validation of alternative methods.

Figure 3.3.12 – Determination of pore size distribution and Weibull parameters for baseline GDL (Mitsubishi MRC-105, 9% PTFE wt.).

Figure 3.3.13 – Variation in pore size distribution and Weibull parameters as determined from statistical processing of GDL images obtained via SEM.

Determination of the pore size distribution was conducted through thresholding to create a binary image from gray-level ones by turning all pixels below some threshold to zero and all pixels above the threshold to one. We have used the OTSU algorithm to automatically perform histogram shape-based image thresholding or, the reduction of a gray level image to a binary image, where all pore regions are shown as background, i.e., carbon fiber region. The threshold value obtained using the OTSU algorithm was 0.2862.

In order to study the effect of intensity on the pore size data, the threshold value was varied between a minimum and maximum value of 0.2 and 0.37, respectively. The Weibull shape (β) and scale (α) parameters were determined for each threshold. Table 3.3.2 lists threshold values and corresponding Weibull parameters for the baseline GDL (Mitsubishi MRC-105, 9% PTFE wt.). The scale parameter increases while the shape parameter decreases with increasing threshold values. From Figure 3.3.14, a marked difference is observed in the pore size distribution between the maximum, minimum and optimum (as determined from the OTSU algorithm) threshold values.

Table 3.3.2. Effect of threshold on Weibull parameters for baseline GDL

Threshold Level	Scale Parameter $r(\alpha)$	Shape Parameter (β)
0.2	19.49	1.56
0.21	19.91	1.55
0.22	20.48	1.49
0.23	20.8	1.46
0.24	21.24	1.41
0.25	21.9	1.42
0.26	24.06	1.46
0.27	24.73	1.41
0.28	26.02	1.4
0.2862	27.1017	1.368
0.29	27.1	1.39
0.3	28.52	1.36
0.31	31.65	1.35
0.32	33.71	1.36
0.33	34.29	1.25
0.34	35.19	1.19
0.35	36.55	1.03
0.36	40.26	0.96
0.37	36.39	0.83

Figure 3.3.14 – Weibull plot of pore size data for different threshold values for the baseline GDL

GDL Microstructure Generation: For a wide range of typical GDL media, such as carbon papers, the microscopic description is rather simple and can be built up from single fibers with a given diameter and the ensemble follows a stochastic distribution. Thus, a stochastic generation model is the method of choice for the microstructure generation due to the low cost and the high speed of the data generation. Nevertheless, a stochastic model for carbon papers can be very complicated if one includes the crimp of the fibers, for example. In order to develop a manageable model for the microstructure generation, the following assumptions are made about the investigated carbon-paper GDLs:

- the fibers are long compared to the sample size and their crimp is negligible,
- the interaction between the fibers can be neglected, i.e. the fibers are allowed to overlap, and
- the fiber system is macroscopically homogeneous and isotropic in the material plane, defined as xy-plane.

With these assumptions, three dimensional GDL models have been reconstructed in Geodict™ using statistical material parameters such as porosity and mean fiber thickness obtained from 2D SEM images. Figure 3.3.15 shows SEM images of different GDL samples. In order to make systematic comparison between the samples, the images were collected in secondary electron mode at 20KeV with 100x magnification. Using the input parameters given in Table 3.3.3, the microstructure of GDLs are reconstructed for three different GDLs including one nonwoven (Freudenberg). The parameter β is a measure of the anisotropy of the fibers.

The stochastic simulation technique creates three-dimensional realization of the non-woven carbon paper GDL based on structural inputs, namely fiber diameter, fiber orientation and porosity which can be obtained directly from the SEM. In the GDL, the fibers are fixed by resin binder. Due to the material properties the binder is a wetting fluid with respect to the carbon fibers. As a consequence the binder fills the small pores, that is, all regions where the fibers are close packed already. We have ignored the impact of amount of binders in GDL. The fiber orientation of the stochastic microstructure generation is reflected by the anisotropy factor β . In our simulation we have consider $\beta = 100$ for all the GDLs.

Table 3.3.3. Parameters used for the reconstruction of the investigated GDLs.

GDL	Length/width(μm)	Thickness (μm)	Fiber diameter (μm)	Porosity	Anisotropy factor (β)
Freudenberg	1024	250	7	0.75	100
SGL	1024	250	7.2	0.88	100
Toray	1024	250	7	0.78	100

Figure 3.3.16 shows the virtual SEM-like images from the reconstructed carbon paper GDLs, and they demonstrate good correspondence with the actual SEM images (Figure 3.3.15). The three-dimensional stochastic reconstruction technique is a Poisson line process with one-parametric directional distribution where the fibers are modeled as circular cylinders with a given diameter and the directional distribution provided in-plane/through-plane anisotropy in the reconstructed GDL microstructure. The three-dimensional reconstructed microstructures of the GDLS are shown in Figure 3.3.17.

Figure 3.3.15 – SEM images of GDL samples: (a) Freudenberg, (b) SGL, (c) Toray.

Figure 3.3.16 – Reconstructed SEM images of GDL samples: (a) Freudenberg, (b) SGL, (c) Toray.

Figure 3.3.17 – Reconstructed SEM images of GDL samples: (a) Freudenberg, (b) SGL, (c) Toray.

Using the three-dimensional reconstruction, the pore size distribution can be determined using the morphological opening with spheres of increasing radius. Figure 3.3.18 shows the pore size distribution of the three reconstructed GDLs. It has been found the average pore diameter of Freudenberg, SGL and Toray are 17.5 μm , 29 μm and 31.3 μm respectively. The Toray and SGL are in good agreement with the image analysis data.

Compression modeling: In a fuel cell stack, the GDL is compressed due to the clamping pressure. It sustains the basic structural features but reduces the pore space in between the fibers as we can see in Figure 3.3.19. The compression model was applied to the reconstructed GDL microstructures in order to realize compression ratios of 0.7 and 0.5. A similar distribution response is observed in all three GDLs compressed 50% as shown in Figure 3.3.20. The pore size distribution curve has become narrower under compression and the tail of the distribution is dramatically reduced. Due to the compression of the GDL, the pore size distribution is expected to shift towards smaller pores. The pore size distribution of Freudenberg GDL, the maxima of the pore size distribution changes from 17 to around 10 μm under 50% compression and there is a loss of a secondary peak in the distribution in the range of 25 μm when uncompressed.

Figure 3.3.18 – Pore size Distribution: (a) Freudenberg, (b) SGL, (c) Toray.

Figure 3.3.19 – Visualization of the virtually compressed microstructures

Figure 3.3.20 – Pore size distribution under compression

C. Characterization of GDL Material Properties - Wettability

A unique contact angle measurement apparatus has been developed to quickly and accurately measure contact angles using the sessile drop method. The apparatus and measurement method are capable of determining contact angles on rough, porous substrates such as GDLs and measurements may be taken at elevated temperatures up to 120 °C. The method developed fits the full Laplace-Young equation to a drop profile and then determines the contact angle from the theoretical fit and the surface of the substrate. This method requires numerical integration, but has significant advantages standard techniques.

There are several standard methods for measuring contact angles. These include using a goniometer, Axisymmetric Drop Shape Analysis (ADSA) [138], as well as many others. A number of these methods are subject to error introduced by user interpretation. Other methods use an empirical fitting technique, such as polynomial fit, which does not accurately represent the drop interface. These methods have a strong dependence on accurate imaging of the contact line region which is a large source of measurement error. The rough surface of the GDL makes it very difficult to accurately determine the contact line and the slope at the contact line. The program developed at MTU eliminates that dependence by fitting the Laplace-Young equation to a portion of the physical drop data and finding the z-plane separately. The spherical cap approximation does not necessarily rely upon accurate imaging of the contact line region, but it is only valid for very small Bond number systems. The drop volume may be quite small and still have a Bond number greater than one because of an implicit contact angle dependency on the wetted area. [139] The technique developed at Michigan Tech is gravity independent; that is, the method is accurate for all drop sizes.

Backlighting of the drop is a crucial step of the data collection process. Koehler illumination is used for backlighting because the light produced is collimated and equal intensity across the imaging field. If, for instance, a convergent or divergent light source were used for image capturing, the image may not accurately represent the physical dimensions of the drop.

The wettability of water on the surface of a GDL has been found to be dependent on the drop size, temperature, and drop generation method. The contact angle measurement apparatus and thermostat housing are shown in Figure 3.3.21. To measure contact angle at higher temperatures, an enclosure was built with Indium Tin oxide (ITO) coated glass windows. The enclosure is heated by thermoelectric heaters. ITO coated glass was used to heat the glass window and prevent condensation which prohibits image capturing process. The enclosure is humidified to prevent excessive evaporation of the fluid at higher temperatures.

Two methods were employed to generate water drops on the GDL surface. The first is the traditional deposition method in which a drop is deposited on the substrate using a hypodermic needle. The second drop generation method is more indicative of fuel cell operation in which the drop is injected through the GDL. The injection stage is shown in Figure 3.3.22. The latter technique also allows for measuring dynamic contact angles on GDLs.

A program has been developed in MATLAB to measure contact angle using Axisymmetric Drop Shape Analysis (ADSA) technique [138]. A fit between the theoretical profile obtained by the Laplace-Young equation of capillarity and the actual drop profile is made. A fit that results in minimum error yields the contact angle at the solid-liquid-vapor interface. A typical fit of the theoretical profile and an actual drop is shown in Figure 3.3.23 where the red line superimposed on the drop image indicates the theoretical prediction of the drop shape after numerical iteration. The contact angle is determined from the theoretical fit at the intersection with the substrate (shown in yellow).

Figure 3.3.21 – Contact angle measurement apparatus for GDLs. The left image shows the illumination path, enclosed heated stage with GDL sample, and long working distance microscope. The right image shows the second level thermostat used to increase the measurement temperature up to 120 °C.

Figure 3.3.22 – Method for generating water drops by injection through the GDL. A schematic of the injection heated plate. The riser around the injection stage allows for enclosing the GDL with the second level thermostat (Figure 3.3.21 right) for elevated contact angle measurements.

Figure 3.3.23 – Theoretical fit on a drop on GDL

Figure 3.3.24 – Contact angle on Toray T060 at different temperatures and drop sizes.

Figure 3.3.25 – Contact angle on Freudenberg at different temperatures and drop sizes.

Figures 3.3.24 and 3.3.25 show the variation of contact angle with change in temperature and drop size on Toray and Freudenberg, respectively. Contact angles were calculated at 22 °C, 40 °C, 65 °C and 90 °C for Toray and at 22 °C, 40 °C, 60 °C and 80 °C with the air saturated. Temperatures were maintained within a limit of ± 1 °C. There is a decrease in the contact angle as the temperature increases

for both GDLs. A large decrease in contact angle at high temperatures for drop volumes of less than 20 μl is observed, particularly in Figure 3.3.24, because of the drops being pinned on individual carbon fibers. Figure 3.3.26 shows the advancing and receding contact angles for water on the baseline GDL. The water drops were generated by injection through the GDL. A considerable difference between the advancing and receding angles is observed due to contact line pinning; particularly in the case of receding contact lines.

Figure 3.3.26 – Advancing and receding contact angle on baseline GDL (Mitsubishi MRC-105).

D. Characterization of GDL Transport Properties – Capillary Flow and Modeling

The results of the water percolation characterization and capillary flow modeling are well documented in several conference proceedings and journal articles. The results are summarized here and the appropriate manuscripts included in the appendices.

During the first stage of the research, an ex-situ experimental setup was designed with the dual purpose of gaining visual access to the water distribution inside the fuel cell and quantifying the amount of water held in the GDL. The test is referred to as a pseudo-Hele-Shaw experiment that consists of sandwiching the GDL sample, roughly two inches in diameter) between thin layers of silicon (PDMS) and polycarbonate. Water is injected into the center of the sample. The wetted area (area occupied by the injected fluid from a top view) and the percolation pressure (pressure required to inject the water) were measured simultaneously in each experiment.

From the observation of the water distribution, three different flow patterns were observed in the GDL. The three patterns, shown in Figure 3.3.27, are viscous fingering, capillary fingering, and stable displacement [140]. In a PEM fuel cell under normal operating conditions water will percolate through the GDL in a capillary fingering mode.

The water distribution inside the GDL was quantified by calculating the wetted area (area cover by the water from a top view) and the length of the water–air interface for each of the flow patterns. In parallel with the observation of the water distribution, the percolation pressure (pressure required to inject the water in the PTL) was measured. The percolation pressure also presents unique characteristics depending on the flow pattern. This research was published in the Journal of Power Sources titled “Existence of the phase drainage diagram in proton exchange membrane fuel cell fibrous diffusion media” [140].

The two measurements derived from the experiment, wetted area and percolation pressure, were combined into a single variable by defining a new scaling for water percolation in porous media. The scaling is based on the ratio between the energy required to inject the water and the energy dissipated due to the viscous stress. When this energy ratio (C_e) is plotted against the non-dimensional time (t^*) a simple logarithmic dependence was obtained as shown in Figure 3.3.28 for Toray T060. The capillary number, Ca , is a dimensionless velocity and depends on the water injection rate. The Ca for the experiments varies from small (10^{-8}) to moderate (10^{-4}). The transition between capillary fingering and stable displacement occurs at $t^* = 1$. The details of the scaling are included in a conference paper “Scaling the Water Percolation in PEM Fuel Cell Porous Transport Layers” [141].

Preliminary results show a constant shift and slope change between the curves for different GDL samples from different manufacturers. This allows for unique characterization of GDLs water transport. Moreover, this characterization technique can be applied to porous materials other than GDLs. An extended manuscript describing the method in more detail and comparing the results for GDLs from different manufacturers is under preparation.

Figure 3.3.27 – The three flow patterns observed in the PTL, left: stable displacement, center: capillary fingering, and right: viscous fingering. Yellow lines identify the water–air interface. Water is inside and air is outside of region defined by the interface line [140].

Figure 3.3.28 – Plot of the energy ratio, C_e , versus the non-dimensional, t^* , time for the experiments (solid lines). Each solid line represents an experiment where the capillary number, Ca , was varied by adjusting the flow rate. Notice the logarithmic dependence obtained for all the experiments [141].

A series of two dimensional numerical simulations using a network model approach were conducted to study the effect the most significant variables affecting the water percolation within the GDL. The numerical model consist of the cross sectional portion of GDL under a single gas channels. The impacts of the morphological and wetting properties of the GDL on the water transport were studied. The details of the network model and the morphology study are described in a conference paper and a journal article currently in review [142, 143]. These two manuscripts are included in the Appendices mtu_a:07 and mtu_a:08, respectively.

The impact of the morphology was analyzed by varying the pore size distribution. These distributions were generated by defining pore size histograms using the Weibull distribution function. Three different GDL structure were generated having the same pore size histogram but different pore arrangement. Because the pore arrangements were different, the water percolates through the GDL forming different array of fingers. This implies that any study of GDL morphological properties should consider the stochastic arrangement of pores. However, even though the water percolates forming different array of fingers; it was found that the percolation pressure is the same for GDLs having the same pore size histogram. The effect wetting properties were studied by varying the contact angle. In contrast to the morphology properties, varying the contact angle only modifies the percolation pressure while water moves through the same set of pores. Additionally, three different GDL scenarios were investigated corresponding to GDL without MPL, GDL with MPL and GDL with an MPL have defects. Comparing these three cases it was found that the overall water content in the GDL was reduced by the addition of the MPL between the GDL and the catalyst layer. This effect was enhanced when considering the addition of perforation or defect in the MPL. The details of the model and simulation results have been submitted to the 218 ECS Conference to be held in October 2010 [144].

Figure 3.3.29 – Three simulations of water transport in a GDL showing the water distribution, shown in blue, at the time that water reaches the gas flow channel. The upper simulation is for a GDL without an MPL using a pore size distribution corresponding to a Toray GDL. The center simulation shows the same conditions, but an MPL has been added to the network model. The lower simulation allows for two defects, or cracks, in the MPL. [142]

The two dimensional network model was extended to a three dimensional version and a series of numerical simulation were performed imitating the conditions occurring in a pseudo-Hele-Saw

experiment. The wetted area and percolation pressure were extracted from the simulations. The energy ratio was calculated and compared with experiment. The pore size distribution and the contact angle were varied in the simulations to adjust the numerical energy ratio in order to match the energy ratio obtained experimentally [144]. The comparison between the numerical and the experimental pseudo-Hele-Shaw experiments are plotted in Figure 3.3.30. The numerical data was generated using a pore size distribution based on a Toray GDL [76] and varying the effective internal contact angle. An effective internal contact angle of 135 degrees collapsed the numerical simulation onto the experimental data [144]. Thus, the behavior of liquid water in GDLs can be effectively characterized experimentally and that behavior captured in a simple computational tool.

Figure 3.3.30 – Comparison of numerical and experimental pseudo-Hele-Shaw experiments showing excellent agreement for Toray paper using an effective internal contact angle of 135 degrees.

III-3.2 Channel Component Studies

Characterization of water in the flow field of a PEM fuel cell was conducted in two main directions; experimental two-phase flow studies and numerical investigation of static plug morphology. Both activities examined the influence of channel geometry and surface wettability.

One of the barriers in the development of reliable PEM fuel cells is the liquid holdup which causes complete blockage of the bipolar plate channels. The static plug morphology is characterized through the critical plug volume (VCR), which represents the minimum amount of liquid necessary for the liquid to completely obstruct a channel. For the considered section geometry (square or isosceles trapezoidal), it is a function of the contact angle as well as the in-plane channel geometry (bend dihedral). Knowledge of the plug volume as a function of these parameters will enable the designer to choose an optimal configuration. For example, a large VCR would make a channel less likely to plug under the same flow conditions when compared to a smaller critical volume. At the same time larger plugs formed in a given length channel imply a reduced number of moving contact lines and implicitly a lower pressure drop across the channel. The knowledge of critical plug volume as a function of wettability will also enable one to differentiate between transition behaviors in square tubes of mixed wettability.

Solutions for minimum volume liquid plugs (critical volume, VCR) have been computed for a baseline GDL with contact angle θ_{base} of 150° and 110° (Figure 3.3.31t). Each data set was obtained by numerical simulations at a considered bend dihedral (90° , 120° , 170° and 180°) while the channel wall contact angle was varied from 50° to 130° . The dependence of the critical plug volume with wall surface wettability and bend dihedral is summarized in the correlations (3.3.1) and (3.3.2) for a base contact angle of 150° and 110° , respectively. The correlation is shown as a solid red line for a typical bend dihedral of 170° .

Figure 3.3.31 – Dimensionless critical volume as a function of channel contact angle, θ , GDL contact angle, θ_{base} , and channel bend dihedral. The channel has a non-dimensional cross section of 0.5×0.5 . The left plot has a GDL contact angle of $\theta_{base} = 150^\circ$ and the right, $\theta_{base} = 110^\circ$. The correlation for the 170° degree bend dihedral predicts the critical volume in the baseline flow field.

$$VCR_{150} = 9.83727611 - 0.707846814 \cdot \theta + 0.0213688425 \cdot \theta^2 - 0.000341921564 \cdot \theta^3 + 0.00000305405871 \cdot \theta^4 - 1.44342695E-08 \cdot \theta^5 + 2.82237529E-11 \cdot \theta^6 + 0.53/\tan(\alpha) \quad (3.3.1)$$

$$VCR_{110} = 0.138512991 + 0.00693698911 \cdot \theta - 0.000481240457 \cdot \theta^2 + 0.0000115412599 \cdot \theta^3 - 1.37149390E-07 \cdot \theta^4 + 7.91651904E-10 \cdot \theta^5 - 1.73608478E-12 \cdot \theta^6 + 0.53/\tan(\alpha) \quad (3.3.2)$$

The correlations are valid for wall contact angles $50^\circ < \theta < 130^\circ$. The bend half-dihedral α varies from 45° to 90° (when $\alpha = 90^\circ$ the last term of the correlation is simply 0). Correlations (Eq. 3.3.1) and (Eq. 3.3.2) are valid for a channel of 0.5×0.5 and it should be corrected accordingly for a square channel of different size. For example if a 1×1 channel is considered, VCR should be divided by 0.53 to obtain the correct critical volume.

An isosceles trapezoidal channel having the parallel sides of 0.57 and 0.73 distanced by 0.45 was also investigated. The trapezoidal cross section is 0.2925 mm^2 and has the same area with a square section of width 0.5408 mm. The critical volume analysis enables a comparison between square and trapezoidal geometry under varied wetting conditions. In Figure 3.3.32, the critical volume behavior changes with the cross section geometry as the wall contact angle, which is varied from 50° to 130° for a fixed $\theta_b = 110^\circ$. In a straight section of the channel, the critical volume is larger for the trapezoidal section for $50^\circ < \theta < 52^\circ$ or $108^\circ < \theta < 130^\circ$. The critical volume is larger in a square cross section for $52^\circ < \theta < 108^\circ$. The correlations describing the critical volume evolution for the square and trapezoidal sections in straight channel with a GDL having $\theta_b = 110^\circ$ (shown as solid lines in Figure 3.3.32 are:

$$\text{VCR, square} = 0.139 - 1.349 \cdot 10^{-5} \theta + 8.52 \cdot 10^{-6} \theta^2 - 5.931 \cdot 10^{-7} \theta^3 + 4.05 \cdot 10^{-9} \theta^4 \quad (3.3.3)$$

$$\text{VCR, trapez.} = 0.596 - 2.289 \cdot 10^{-2} \theta + 4.33 \cdot 10^{-4} \theta^2 - 4.11 \cdot 10^{-6} \theta^3 + 1.51 \cdot 10^{-8} \theta^4 \quad (3.3.4)$$

As one can see in Figure 3.3.32, the critical volume behavior changes with the cross section geometry as the wall contact angle is varied from 50° to 130° while $\theta_b = 110^\circ$ for the considered GDL. In a straight channel the critical volume VCR is larger for the trapezoidal section when $50^\circ < \theta < 52^\circ$ or $108^\circ < \theta < 130^\circ$, while it is larger for the square section in the $52^\circ < \theta < 108^\circ$ range. The trapezoidal section outperforms the square one by 20% for $\theta_w = 120^\circ$ and by 50% for $\theta_w = 130^\circ$. Details of the energy minimization method and more discussion of the results are published in reference [145].

The experimental study of the effect of surface wettability and channel geometry utilized high speed microscopy to visualize the flow structures while measuring pressures and flow rates. The test section is connected through a T-section to the liquid and gas supplying lines. The two-phase mixture flows through the desired test section connected directly to the mixing “T” section. The two-phase flow regimes can be generated by manipulating the single-phase flow rate and supply pressure. The flow morphology is monitored through the microscope’s objective and the images are acquired with the aid of a high-speed camera at the desired rate. The two-phase pressure drop across the channel and across a laminar flow element is recorded and is correlated with a flow meter is for the gas flow rate and a syringe pump for the liquid flow rate. The high speed imaging capability of the Photron Fastcam Ultima APX-RS camera ($\sim 15000 \text{ fps}$) is used to accurately capture the two-phase interface dynamics, a very important feature when investigating phenomena spanning a tenth of a millisecond.

Flow visualization in $500 \text{ }\mu\text{m}$ round and square channels 10 cm long were performed, with water and air as the two phases. The high speed camera was tested at 10,000 and 15,000 fps and a few of the acquired images are presented below in Figure 3.3.33.

Figure 3.3.32 – Liquid hold-up in an 180° dihedral bend (straight channel). The channel cross section is a square (0.54 x 0.54) and trapezoidal (sides of 0.57 and 0.73 spaced by 0.45). The GDL contact angle is $\theta_B = 110^\circ$ and the wall contact angle θ is varied.

There were performed tests to ensure the mixing section will not cause entrance effects that would noticeably alter the two-phase flow data. A unique mixing section was built, which reduces the entrance effects taking advantage of the naturally forming meniscus at the entrance of the test section. Two patterns are distinguished for the entrance flow, a stable nozzle-like flow which develops into annular flow, or an unstable nozzle-like flow which develops into an unsteady annular (annular flow with occasional formation of plugs) or into separated plug flow.

The various polymer coatings were investigated to determine the feasibility of their use in a combinatorial study for water management optimization which accounts for surface wettability. Results of the visualization experiments are shown in Figure 3.3.33. Two-phase flow of air (1.22e-06 kg/s) and water (10.07e-06 kg/s) in 500 μm diameter 120 mm long round channels and in 500 μm wide 100 mm long square channels. The round channel configuration was tested for 20° and 105° contact angle. The square channel was tested for 20° , 80° and 105° contact angle. The images in Figure 3.3.33 depict the square channel case (flow from right to left). The sequence of images from the top line shows an unstable flow regime (plug with moving contact lines and slug flow) characterizing the 80° contact angle case, with expected high pressure drop. The left sequence from the bottom line shows an annular flow regime which is present in the 20° contact angle case. The 105° contact angle case shown in the bottom-right sequence presents a stratified flow morphology which is very stable suggesting a low pressure drop (the bottom image shows the empty channel for reference). The wettability study concluded that variations in contact angle and geometry of the cross-section yield different two-phase flow regimes for identical flow rates. Both contact angle and geometry are two important parameters which need to be included in the optimization process of water management in low Bond number channels.

A comprehensive literature review revealed there are discrepancies in two-phase transition data. There were identified three main issues that could cause these differences: the choice of mixing section, the method of two-phase flow pressure drop measurement and the variation of contact angle/ geometry. The contact angle varies from wetting to non-wetting values as a variety of test section materials and fluids are used. Our experimental results confirm that as contact angle changes also the flow morphology changes. To investigate the effect of contact angle and geometry on two-phase flow morphology in small channels there were performed high-speed visualization experiments of air-water flow in 500 μm wide 100 mm long square and round glass channels, and in coated (contact angle of 105°) 500 μm wide 120 mm long round channels. The flow rates were 10.07×10^{-6} kg/s for water and 1.22×10^{-6} kg/s for air.

Figure 3.3.33 – The effect of wettability on flow morphology in the square geometry.

For the circular section case, a shift in the flow regime transition is observed when the wettability is changed from wetting (contact angle $\theta < 90^\circ$) to non-wetting ($\theta > 90^\circ$) as shown in Figure 3.3.35.. At high gas flow rates and low to moderate liquid flow rates the flow regimes themselves change with wettability, wavy flow becomes rivulet for non-wetting/ intermediate wetting, and annular flow becomes multiple rivulet for non-wetting channels [146]. For the square section case, shown in Figure 3.3.34, the shift in the transition lines occurs when the contact angle is changed from wetting to non-wetting. We can also distinguish another change in the transition tendency for an intermediate wetting case ($45^\circ < \theta < 90^\circ$), which was anticipated and experimentally proven [147]. It is noticeable that the transition lines between dispersed/ churn and slug-annular/annular, and between intermittent (slug/plug) and slug-annular/annular flow regimes shift considerably.

The existing two-phase flow data reiterates the fact that both the contact angle and geometry are important parameters which need to be included in the optimization process of water management in low Bond number channels. This fact was also proven in our experiments, as previously mentioned. As such, it was recognized that wettability and cross-sectional geometry can be used as optimization parameters of the flow fields of a PEM fuel cell.

Figure 3.3.34 – Flow regime transitions in square/rectangular microchannels.

Figure 3.3.35 – Flow regime transitions in round microchannels.

III-4. Task 4: Combinatorial Assessment on Ex-Situ Apparatus

In Section III-2, the research team focused on ex-situ and in-situ characterization of water distributions during steady-state operation, cathode purge sequences and freeze start operation. All of this work was executed using the “baseline” system comprised of:

- flow field channels of nearly rectangular cross-section, with no change in the intrinsic surface energy of the carbon composite flow field material
- commercially available gas diffusion layer (GDL) substrates from Mitsubishi Rayon (U105)
- in-house developed micro-porous layer (MPL), based on earlier General Motors research.

Starting from this section, variations to the baseline system are made in order to find out the combination of GDL materials and flow channel design which give out the optimal ex-situ performance. The variations include:

- Channel surface treatment (hydrophobic or hydrophilic)
- Channel geometries (sinusoidal, trapezoidal or rectangular)
- GDL PTFE treatment
- Microporous layer effect
- GDL substrate thickness

III-4.1. Effects of Channel Surface Treatment on Two-Phase Flow in Gas Channel

In Section III-2, the ex-situ multichannel flow experiments were carried out with gas channels whose surface was not chemically treated, which had a static contact angle of about 60°, for the purpose of simulating the widely used graphite bipolar plate flow field. In this section, the same rectangular channel design as used for the Baseline system was coated to different static contact angles (Table 3.4.1) and the effects of this surface treatment on the two-phase flow in gas channels was studied. The hydrophilic channel was coated by General Motors and was expected to facilitate the removal of liquid water by capillary effects. The hydrophobic channel was in-house treated with Rain-X® and had a contact angle of 105° on the fresh treated Lexan surface. The water contact angles were measured from the images taken by a microscope with a water volume of 30 µL. Table 3.4.1 lists the contact angle values.

Table 3.4.1 Properties of channel surfaces for different surface treatment.

Channels	Channel treatment	Contact angle
Untreated	Rectangular channel on Lexan	59 ± 3
Hydrophilic	Rectangular Lexan channel coated with a hydrophilic coating	11 ± 2
Hydrophobic	Rectangular Lexan channel coated with Rain-X	105 ± 3

Figure 3.4.1 shows the two-phase flow pattern map for the hydrophilic treated rectangular channels with the Baseline GDL. For the purpose of comparison, the two-phase flow map for the Baseline (non-treated) channels is also shown in this figure. Figure 3.4.1 reveals remarked differences between the flow pattern maps of the hydrophilic channels and the Baseline channels. First, the mist flow pattern which occurs in the Baseline channels at higher superficial air velocities does not exist for the case of hydrophilic channels. Second, the transition line between slug and film flow is significantly shifted

toward lower air velocities for the hydrophilic channel compared to that of the Baseline channel. These two results indicate that the hydrophilic surface treatment enhances the formation of the water film along the channel wall and therefore reduce the tendency of the slug flow. This is beneficial to fuel cell operation because the slug flow should be avoided because it readily leads to flow maldistribution and the non-uniform distribution of current density. On the other hand, the film flow does not cause significant flow maldistribution and would allow for a more uniform current density distribution. Although the hydrophilic surface treatment also reduces the mist flow tendency at high air velocities (see Figure 3.4.1) due to the strong capillary effects, which may indicate the increased difficulty of complete removal of water films by gas purge, these very high air flow rates are seldom used in real fuel cell operation.

Figure 3.4.1 – Comparison of two-phase flow pattern maps for hydrophilic treated rectangular channel ($\theta = 11^\circ$) and Baseline (non-treated) channel ($\theta = 60^\circ$) with Baseline GDL in the ex-situ multi-channel test apparatus.

The total pressure drops for the hydrophilic treated and the Baseline non-treated channels are compared in term of the two-phase friction multiplier, as shown in Eq. 3.2.2. As already demonstrated in Section III-2, Φ_g^2 provides a good indication of water holdup in the gas channel. Figure 3.4.2 shows the comparison of the two-phase friction multiplier for the hydrophilic and Baseline channels. The most outstanding result from this figure is that Φ_g^2 for the hydrophilic channel approaches a value that is above unity, while Φ_g^2 for the non-treated channel approaches unity at all water velocities investigated in this work. $\Phi_g^2=1$ represents mist flow. This is in agreement with the flow pattern map (Figure 3.4.1).

Figure 3.4.2 – Two-phase friction multiplier as a function of the superficial air velocity for (a) the hydrophilic treated channel and (b) Baseline channel.

The rectangular flow channel was also made hydrophobic ($\theta = 105^\circ$) by treatment with Rain-X[®]. A significant character of the water flow structure in the hydrophobic channels is the presence of large number of water droplets or small slugs, due to the interaction of water with the hydrophobic channel wall. Figure 3.4.3 shows these typical flow patterns. The flow pattern in the hydrophobic channel is

dominated by water droplets or small slugs. The flow pattern map shows only two major patterns, droplet + slug and droplet + film, and no mist flow is observed in the studied water and air superficial velocities, as shown in Figure 3.4.4. This is significantly different from that of the Baseline channel. The transition line from slug to film flow is at the similar location as the Baseline channel, indicating no significant benefit is obtained for water transport in channel. This is further supported by the pressure drop data (Figure 3.4.5).

The hydrophobic coating of Rain-X is not stable. It can be washed off by water especially at high air flow rate. Thus, it has to be recoated after a few experiments. This creates large uncertainty on the experimental data. In addition, this coating cannot be used to the real fuel cell channel. It is necessary to fabricate a stable hydrophobic surface to assess its influence.

Figure 3.4.3 – Images of two-phase flow structures in the hydrophobic treated channels at two flow conditions. The left image shows the flow pattern of water droplets + slugs, the right image shows the flow pattern of droplet + water film.

Figure 3.4.4 – Two-phase flow pattern map of (a) hydrophobic treated rectangular channel and (b) Baseline channel.

Figure 3.4.5 – Pressure drop of the ex-situ multichannel experiment with the hydrophobic channel.

III-4.2 Effects of Channel Geometry

In order to incorporate geometric features that are more representative of full-size automotive hardware into the ex-situ multi-channel flow experiments, two new channel geometries, sinusoidal channel representing the stamped metal bipolar plate and trapezoidal channel, representing the molded carbon composite bipolar plate, are designed and fabricated. Figure 3.4.6 shows the detailed geometric feature and dimensions for the channel cross-section of the sinusoidal and trapezoidal channels. These channels were designed to maintain their hydraulic diameters as close as possible to the Baseline channel design. Table 3.4.2 compares these dimensions to the Baseline channel design.

Similar to the Baseline channel, for each geometry eight parallel channels were fabricated into a Lexan™ plate which was then vapor polished to provide excellent view access. The channels are also wavy with 11 ° angular channel switchback every 5 cm in order to avoid misalignment effects and mechanical shearing of the GDL caused by straight channels. The inlet header was specially designed to account for the particular requirements for the ex-situ experiments, including the measurements of the mass flow rate in each channel and the total pressure drop between inlet and outlet. The same design has been used with the Baseline system.

Figure 3.4.6 – Details of channel cross-section for (a) sinusoidal channels and (b) trapezoidal channels.

Table 3.4.2. Geometric features of the new sinusoidal and trapezoidal channels compared to the “baseline” rectangular channels.

	Rectangular	Trapezoidal	Sinusoidal
Channel Opening (mm)	0.7	0.728	0.94
Base Width (mm)	0.7	0.57	-
Maximum Depth (mm)	0.4	0.45	0.45
Land Width (mm) (assume 1.2mm spacing)	0.5	0.471	0.26
Open Perimeter (mm)	1.5	1.484	1.412
Closed Perimeter (mm)	2.2	2.213	2.352
Area (mm ²)	0.28	0.2922	0.274
Hydraulic Diameter (mm)	0.509	0.528	0.467

The two-phase flow patterns that emerged in both the sinusoidal and trapezoidal channels were similar to the rectangular channels. Three basic patterns, namely slug, film, and mist flow, were observed in the sinusoidal and trapezoidal channel, as shown in Figure 3.4.7 and Figure 3.4.8, respectively. However, a major difference was found on the film pattern in the sinusoidal channel. The water film in the sinusoidal channels appeared to collect on the back wall of the channel rather than on the side walls and corners of the rectangular and trapezoidal channels. This may be beneficial in keeping the water away from the GDL surface.

The two-phase flow pattern maps for the sinusoidal and trapezoidal channel as well as rectangular (Baseline) channel are summarized in Figure 3.4.9. The differences for the three channel geometries can be seen in the transition from slug to film flow pattern. In the rectangular channel the transition line between slug flow and film flow occurs at slightly lower air velocity. There is also slightly larger mist flow zone in the rectangular channels at the lower water velocities. In general, however, the flow patterns for these three geometries are relatively similar.

Figure 3.4.7 – Images of two-phase flow patterns in the sinusoidal channel under different flow conditions: (a) Slug flow: $U_G = 4.9$ m/s (660 sccm), $U_L = 1.49 \times 10^{-4}$ m/s (0.02 mL/min); (b) Film flow: $U_G = 19.6$ m/s (2642 sccm), $U_L = 7.44 \times 10^{-4}$ m/s (0.1 mL/min); and (c) Mist flow: $U_G = 14.74$ m/s (1981 sccm), $U_L = 1.5 \times 10^{-4}$ m/s (0.02 mL/min).

Figure 3.4.8 – Images of two-phase flow patterns in the trapezoidal channel: (a) slug flow, (b) film flow and (c) mist flow.

Figure 3.4.9 – Two-phase flow patterns for (a) sinusoidal channel, (b) trapezoidal channel and (c) rectangular baseline channel.

III-4.3 Water Breakthrough Dynamics in GDL

The uniqueness of two-phase transport in fuel cell gas channels lies in the presence of the porous GDL. Commonly used GDL materials for PEMFCs are carbon fiber based paper and cloth. These materials are highly porous (having porosities of about 80%) to allow reactant gas transport to the catalyst layer, as well as liquid water transport from the catalyst layer. In order to facilitate the removal of liquid water, GDLs are typically coated with a non-wetting polymer such as polytetrafluoroethylene (PTFE) to make them hydrophobic. Additionally, a fine microporous layer (MPL), consisting mainly of carbon powder and PTFE particles, is generally applied to the GDL side facing the MEA (membrane-electrode assembly) to further increase cell performance. The extreme structural and chemical heterogeneity of GDLs substantially complicates the studies of liquid water transport. In this work, the liquid water breakthrough dynamics across GDLs with and without a microporous layer (MPL) are studied in an ex-situ setup which closely simulates a real fuel cell configuration and operating conditions.

Water breakthrough dynamics, characterized by the capillary pressure and water saturation, were determined with an ex-situ test section which had the same channel geometry as the Baseline channel design (see Figure 3.4.10). A shorter channel length, about 30 mm long, was used in this test section. The water breakthrough locations were recorded with a Nikon CCD camera (Coolpix P80, Tokyo, Japan) with the help of a hydrophilic wicking medium (Porex X-4588, Porex Technologies Corp., Fairburn, GA), which was placed on top of the GDL. The capillary pressure of water in GDL is directly determined by a differential pressure transducer (Honeywell FDW2AR), which measures the liquid pressure referenced to the atmospheric pressure:

$$P_c = P_{water} - P_{air} \quad (3.4.1)$$

where P_{water} is the liquid pressure at one side of the meniscus and P_{air} is the air pressure at the other side of the meniscus within the GDL.

Liquid water was delivered at a very low rate of 10 $\mu\text{L}/\text{min}$, which corresponded to equivalent water production rate at current density of about 1.2 A/cm^2 and a capillary number ($C_a = \frac{u\mu_{nw}}{\sigma}$, where u , μ_{nw} and σ are the velocity, viscosity and surface tension respectively of non-wetting fluid) on the order of 10^{-6} .

Two types of GDLs, Baseline GDL and SGL 25 (SGL Carbon Group, Wiesbaden, Germany), with and without MPL coating, were studied in this work. All of these GDLs are carbon paper based and treated with PTFE to increase their hydrophobicity. SGL 25BC sample had a 30-50 μm thick MPL on one side and Baseline GDL had a 10 μm thick MPL. These two types of GDLs were chosen because they had similar GDL pore structure, thickness, and in-situ fuel cell performance (see Section III-2).

In the first experiment, the water breakthrough behavior through a GDL without MPL was studied. Figures 3.4.11 and 3.4.12 show typical water breakthrough dynamics through initially dry GDLs without MPL. The breakthrough capillary pressures, read as the first peak pressure, are 1.78 kPa and 5.78 kPa for SGL 25BA and Baseline-A sample. The most outstanding feature from these figures is the dynamic characteristics of water breakthrough in the GDL: dynamic capillary pressure and the dynamic breakthrough locations. This former is apparently seen from the fluctuation of the capillary pressure after the breakthrough, which is commonly observed for all GDL samples. The recurrent water breakthroughs cannot be accounted for by current pore-network models which predict a constant pressure after breakthrough due to the assumption of a continuous water path through GDL [77]. In contrast, the dynamic capillary pressure observed reveals a breakdown of the water pathways caused by the water

drainage on the GDL surface. The second distinct characteristic is the dynamic water breakthrough locations, i.e., the breakthrough location changes with time, as illustrated by the inserted images in Figures 3.4.11 and 3.4.12. Bazylak et al. [66] observed a similar phenomenon and they accounted for the phenomenon in terms of the branching of the network of water pathways. However, we found this phenomenon was closely related to the dynamic capillary pressure.

The critical capillary size corresponding to the breakthrough was calculated from the breakthrough pressure based on the Young-Laplace equation:

$$P_c = \frac{2\sigma\cos\theta}{R_c} \quad (3.4.2)$$

where R_c is the equivalent capillary radius, σ ($= 0.072$ N/m) surface tension for water, θ contact angle of water inside GDL pores, approximately taken as the contact angle of water on PTFE sheet (120°). The GDL water saturation after the breakthrough experiment was measured. The results are listed in Table 3.4.3.

Figure 3.4.10 – Schematic of the water breakthrough experimental setup and a 3D view of the water chamber.

In second experiment, the water breakthrough in GDLs with MPL was investigated. In these tests, the MPL was placed facing the water inlet, simulating the configuration in fuel cell operation. Figure 3.4.13 shows the water breakthrough behavior through an initially dry SGL 25BC sample, as a typical example. Recurrent breakthroughs are observed, similar to the cases of GDLs without MPL, indicating the dynamic feature of the breakthrough process. However, no shifting of water breakthrough locations was observed in either Baseline or SGL 25BC GDLs. This is in sharp contrast to the GDL samples without MPL (see Figures 3.4.11 and 3.4.12) in which the changing of breakthrough locations is always observed. This difference must originate from the MPL, suggesting that the MPL plays a role in stabilizing the preferential water pathways.

Significantly higher breakthrough capillary pressures were obtained for GDLs with MPL, due to the additional water flow resistance caused by the MPL. However, equivalent capillary radius corresponding

to breakthrough (R_c) are much larger than the average MPL pore size (see Table 3.4.3). This finding indicated that water flows through the defects in the MPLs. These defects, including the cracks and discontinuity in MPL, provide the preferential water transport pathways through the MPL and decrease the breakthrough pressure radically. From Table 3.4.3, much lower water saturations were observed for GDLs with MPL than GDLs without MPL. This result indicates that MPL greatly reduces the water saturation in GDL. A similar result has been reported in literature and was explained by the limitation of water access to the GDL by the MPL [57, 58].

Based on these observations, we have proposed a new water transport mechanism to account for the water breakthrough in GDLs. This mechanism is based on Haines jumps, a description of the discontinuous drainage displacement employed in geological disciplines [74,148]. In slow drainage process, the interfaces between fluids remain unmoved until the pressure in the displacing fluid increases to a value exceeding the capillary pressure at the largest restriction. At this point, the invading fluid suddenly moves into the adjacent pores, accompanied by a negative capillary pressure drop as a result of the readjustment of the interfaces between fluids and porous medium. In the case of water breakthrough in GDLs, the bursting droplet grows fast as it carries away water from adjacent GDL pores. However, the supply of water is often not sufficient for the droplet to fill the larger pore (i.e. gas channel). This “choke off” effect leads to empty pores in the GDL, which break down the continuous water paths. These emptied pores are refilled afterwards as water is constantly injected and the bursting process occurs again, leading to the recurrent breakthrough behavior. As the “choke offs” break down the original water paths and water spontaneously readjusts its interfaces inside GDL pores. This water/air interface relaxation process may lead to a new preferential pathway in the GDL and result in a new breakthrough location. Figure 3.4.14 shows the schematic water transport processes in GDLs with and without MPL.

Figure 3.4.11 – Water breakthrough behavior through an initially dry SGL 25BA sample. The inserted images are still pictures taken from videos. The numbers in the figure indicate the peak pressures. BT denotes “breakthrough”.

Figure 3.4.12 – Water breakthrough behavior through an initially dry Baseline-A GDL (without MPL). The numbers in the figure indicate the peak pressures. BT denotes “breakthrough”.

Table 3.4.3. GDL Properties, water breakthrough pressures (P_b), water saturation at breakthrough ($S_{w,b}$), equivalent capillary radius corresponding to breakthrough (R_c), and information about the emergence of new break sites in different GDLs.

GDL	Structure	Thickness ¹ (μm)	PTFE ² (wt%)	Porosity (%)	V_{pore} (μL)	P_b (kPa)	$S_{w,b}$ (%)	New break locations	R_c (μm)
Baseline -A	No MPL	200 ± 3	7.0	87	29	7.4 ± 1.1	4.7 – 12.2	yes	19.5
Baseline -B	w/ MPL	208 ± 3	7.0	80	28	12.7 ± 1.4	2.4 ± 0.2	no	11.3
SGL 25BA	No MPL	183 ± 3	5.0	88	27	1.7 ± 0.5	2.6 – 7.1	yes	80.9
SGL 25BC	w/ MPL	225 ± 3	5.0	80	30	6.7 ± 1.2	0.8 ± 0.2	no	21.5

Note: 1. Thickness was measured with a micrometer;
2. PTFE content was taken as the manufacturer value.

Figure 3.4.13 – Water breakthrough behavior through a SGL 25BC sample. The inserted image is the still picture taken from the video and reveals the water breakthrough location.

Figure 3.4.14 – Schematic of water drainage in GDL (a) without MPL, displaying a large number of water entry points into the GDL; and (b) with MPL, restricting water entry into GDL only at the crack/defect locations in the MPL.

III-4.4 Effects of GDL Materials on Two-Phase Flow Dynamics in Gas Channels

In this study, the effects of GDL structure (i.e. with and without MPL), PTFE content and thickness on the two-phase flow in multi-parallel channels were investigated. The effect of the microporous layer (MPL) was studied with Baseline, SGL and GM MPL coated TGP-H GDLs. For PTFE content effects, commercially available single-layer Toray carbon papers containing 0 wt%, 20 wt% and 40 wt% PTFE were investigated. The effects of the GDL thickness were studied with two types of GDL, Toray TGP-H and SGL. All of the samples were tested with the Baseline rectangular channel design under the identical operating conditions and test parameters, as previously used for the characterization of Baseline GDL. All the GDL samples are listed in Table 3.4.4.

Table 3.4.4. Summary of GDL samples.

GDL	Thickness (μm)	Structure	PTFE (wt%)	GDL PTFE treatment by
Baseline	230	With MPL	7	GM
SGL 25BC	235	With MPL	5	SGL, Inc.
SGL 35BC	325	With MPL	5	SGL, Inc.
SGL 10BC	420	With MPL	5	SGL, Inc.
Toray 030 + MPL	100	With MPL	~ 7	GM
Toray 060 + MPL	200	With MPL	~ 7	GM
Toray 090 + MPL	290	With MPL	~ 7	GM
TGP-H-060 carbon paper	190	No MPL	0	E-Tek, Inc.
TGP-H-060 carbon paper	190	No MPL	10	E-Tek, Inc.
TGP-H-060 carbon paper	190	No MPL	20	E-Tek, Inc.
TGP-H-060 carbon paper	190	No MPL	40	E-Tek, Inc.
TGP-H-120 carbon paper	380	No MPL	10	E-Tek, Inc.
TGP-H-120 carbon paper	380	No MPL	20	E-Tek, Inc.
Baseline without MPL	220	No MPL	7	GM
SGL 25BA	190	No MPL	5	SGL, Inc.

A. Effects of Miroporous Layer

As previous section indicated, MPL has important effect on water transport through GDL, not only limiting the number of water entry locations into the GDL (such reduce water saturation), but also stabilizing the water paths or morphology. As a result, these effects are expected to important influence on two-phase flow dynamics in gas channel.

Figures 3.4.15 - 3.4.17 show the comparisons of the flow pattern maps in the Baseline gas channels for Baseline, SGL and Toray GDLs, with and without MPL. A significant effect of MPL on channel two-phase flow dynamics was observed. The most outstanding result was that the GDL without MPL increased the tendency of film flow. For example, it shifted the slug-to-film flow transition to a greatly

lower superficial air velocity and completely eliminated the mist flow pattern in the high air flow regime compared to the case of GDL with MPL. The visualization of the gas channel and the GDL surface revealed that a lot more water emergence sites were observed in the GDL without MPL compared to the sample with MPL, as demonstrated in Figure 3.4.18 for Baseline GDLs. Some of the breakthrough locations are highlighted with arrows in Figure 3.4.18. Similar observations were also made for SGL GDLs. A direct consequence of this difference is that water transports out of the GDL sample without MPL more uniformly across the entire surface, favoring the formation of water film along the channel wall. In contrast, water emerges from GDLs containing an MPL through just a few locations, which leads to the formation of long slugs. This is closely related to their respective water transport mechanisms in these GDLs. The GDL without MPL features dynamic breakthrough locations, leading to a larger number of breakthrough locations, while the GDL with MPL has only limited breakthrough locations.

Figure 3.4.15 – Flow pattern maps for (a) Baseline GDL (with MPL) and (b) Baseline GDL without MPL. The Baseline channel design is used for these tests.

Figure 3.4.16 – Flow pattern maps for (a) SGL 25BC (with MPL) and (b) SGL 25BA (without MPL). The Baseline channel design is used for these tests.

Figure 3.4.17 – Flow pattern maps for (a) TGP-H-060 7wt% PTFE with GM coated MPL and (b) TGP-H-060 10wt% PTFE (without MPL). The Baseline channel design is used for these tests.

Figure 3.4.18 – Comparison of water flow structure in gas channels combined with Baseline GDL (a) with and (b) without MPL at $U_G = 7.4$ m/s and superficial water velocity of $U_L = 7.4 \times 10^{-4}$ m/s. Several water emergence locations in the channels are indicated by the arrows.

B. Effects of GDL PTFE Content

Figure 3.4.19 shows the comparison of the two-phase flow pattern maps for Toray TGP-H-060 carbon paper treated with different PTFE contents (0 – 40wt %). The most outstanding result from this figure is the remarkable difference between the flow pattern map of the plain Toray carbon paper (0% PTFE) and those of treated to different PTFE contents (10 – 40wt % PTFE). Instead of showing a general film flow pattern, a new flow structure pattern is observed for the plain carbon paper. In this pattern the entire GDL is wetted and covered by a continuous water film. This is in sharp difference from all other

GDLs, where the water film is formed along the channel walls and little water resides on the GDL surface due to the hydrophobicity of the GDL. For PTFE treated Toray carbon papers only two flow patterns, slug and normal film, are displayed and no mist flow is observed. This is in agreement with Baseline and SGL samples without MPL. As PTFE content increases, the transition line from slug to film shifts to higher superficial air velocity, due to the increased hydrophobicity. At PTFE content above 20 wt%, no significant difference in flow pattern is found with further increasing hydrophobicity. Similar results are also obtained for TGP-H-120 GDLs.

B. Effects of GDL Thickness

A series of SGL samples, including SGL 25BC (230 μm), SGL 35BC (325 μm) and SGL 10BC (420 μm), were tested with the ex-situ multi-channel experiment to study the effect of GDL thickness on two-phase flow dynamics in gas channel. In addition, a Toray series (Toray 030, Toray 060 and Toray 090), which were teflonated and coated with a microporous layer by GM, were also investigated.

The two-phase flow pattern maps for the three SGL GDLs are summarized in Figure 3.4.20. The differences for the three GDL samples are insignificant. Similarly, the two-phase pressure drops (Figure 3.4.21) also show little difference between the three GDL samples. These results are in contrast to the water accumulation in GDL observed by neutron radiography, where the thicker cathode GDL displays larger water thickness in GDL. This indicates that the GDL thickness has little influence on the two-phase dynamics in gas channel, but has significant influence on the GDL water accumulation. This is expected because the channel two-phase flow is more dependent on the properties of gas channels, such as channel geometry and size, surface energy, and manifold design. On the other hand, the water accumulation in the GDL is highly related to the water morphology and dead-ends in the GDL. A thicker GDL is expected to have more dead-ends of water and to have more branching of water paths. Higher water accumulation is thus expected for the thicker GDL.

Similarly, little influence is found for Toray GDL thickness on the two-phase flow dynamics in channels (Figure 3.4.22).

Figure 3.4.19 – Comparison of the two-phase flow pattern maps of Toray TGP-H-060 carbon paper of (a) non-treated and (b) treated with different PTFE contents.

Figure 3.4.20 – Effect of SGL GDL thickness on the two-phase flow pattern maps: (a) SGL 25BC (235 μm), (b) SGL 35BC (325 μm) and (c) SGL 10BC (420 μm).

Figure 3.4.21 – Effect of SGL GDL thickness on the two-phase pressure drops at water flow rates of (a) 0.02 mL/min (superficial water velocity $U_L = 1.5 \times 10^{-4}$ m/s) and (b) 0.04 mL/min ($U_L = 3.0 \times 10^{-4}$ m/s). The two-phase pressure drops are normalized by the single-phase air flow pressure drop.

Figure 3.4.22 – Two-phase flow pattern maps for (a) Toray 060 with MPL and (b) Toray 090 with MPL.

III-4.5 Scanning Acoustic Microscopy for GDL Water Distribution Characterization

A key component to water management and control is the gas diffusion layer (GDL), commonly constructed of carbon paper. Its role within the cell is to ensure even distribution of reactant gasses and removal of excess product water while not inhibiting the flow of electrons between cells. Two common problems of poor water management are flooding and membrane dehydration. Excess water can inhibit reactant gas transport while improper membrane hydration reduces proton conductivity. To solve these problems, knowledge of the propagation characteristics of gas and water within the GDL is required. With varying levels of success, neutron and x-ray imaging techniques have been used to study water distribution within the GDL. While both methods can resolve high resolution 2D maps of water in-plane, neither can produce three dimensional distributions. In an effort to overcome this deficiency ultrasonic imaging was proposed.

Ultrasound imaging is a well established technology that has many applications for three dimensional reconstruction. The most common use is for medical applications, where ultrasound has been successfully utilized to image most parts of the human anatomy. Equally successful is the use of ultrasound to scan for internal fractures or anomalies within performance critical parts. However the use of ultrasound to image a GDL, a highly inhomogeneous material with micron size features, presents a new challenge. With the use of high frequency transducers and tuned signal processing, this objective is being pursued. Ultimately, extracting meaningful information and new insights to the water distribution characteristics of various GDLs.

A high frequency ultrasound system is required to study the acoustic response characteristics of the GDL. The system developed for this research is made up of five key components, the transducer, pulser/receiver, high speed digitizer, linear motion stages, and software control logic (Figure 3.4.23). These components along with an independently designed waterbath were used to perform various scans of GDL samples.

The core of the system is the microscope itself, housing a waterbath which allows for acoustic coupling between the transducer and the GDL. Figure one depict a cross-section of the microscope where the placement of the GDL with respect to a vacuum chamber can be seen. A plate with 1mm wide slots

separated by a pitch of 2.5mm supports the sample while precise pressure differentials can be applied across the GDL face. The objective is to capture scans during and after forced saturation.

Figure 3.4.23: Cross-section view of the scanning acoustic microscope.

Two motorized stages control transducer position in a plane parallel to the GDL. Focusing of the beam is left to a single manual stage oriented mutually perpendicular the other two axes. Overall the system has a submicron positional accuracy and a scanning area of approximately 200 mm².

The acoustic source is a focused 20MHz wideband transducer with a 7mm diameter aperture. The resolution of the beam is defined by the full width half maximum (FWHM) of the intensity profile at any given depth. Quantification of the system beam intensity map was performed using a 12.7 μ m diameter tungsten wire acting as a point source target. The corresponding FWHM at the focal plane was measured to be $\sim$ 90 μ m. The temporal resolution of the system is governed by the duration of the transmitted pulse and is inversely related to the bandwidth. Measurements of the transmitted pulse were acquired by reflections off a polished steel plate acting as an acoustic reflector. While the received pulse is the result of two-way propagation and the convolution of two transducer response functions, the dispersion effects are insignificant. The temporal resolution defined by FWHM was found to be 44 ns or $\sim$ 32 ns. With this knowledge of the acoustic beam profile all scans performed were focused and set to a pixel size of 20 μ m for the optimal balance between efficiency and image resolution.

For each pixel location a timed sequence of events must occur for proper operation. When the transducer reaches a new pixel location, control logic triggers the pulser/receiver to transmit a new pulse. In addition to pulse production the pulser/receiver is responsible for receiving and amplifying the echo signals. The conditioned echo signal from the pulser/receiver is then sent to the digitizer. The same trigger signal sent to the pulser/receiver is also routed to the digitizer, initiating a defined recording sequence.

Two time parameters define the recording sequence. The first is the initial delay from trigger reception to the start of signal recording. To conserve memory and resources the time delay between pulse generation and reception of the first echo signal, approximately $8\mu\text{s}$, need not be recorded. The second time parameter will be the recording duration for each pixel. Its value is set based on the two-way propagation time through the GDL. Taking this thickness to be 380 microns and approximating wave propagation speed in the GDL to be equivalent to water, the two-way propagation time in the GDL is around $0.5\mu\text{s}$. To ensure full coverage of reflected acoustic energy the typical capture duration for each pixel is set to $1.024\mu\text{s}$, resulting in 512 data points acquired at 500MHz.

The control software is broken into two main programs, one for data acquisition and logging and the other is for analysis and presentation of results. Both of which are run using LabVIEW, a graphical programming environment uniquely suited for data acquisition and presentation.

The first program developed is responsible for all operations associated with performing and logging scans. It can be sectioned into four main parts, pulser/receiver communication, trigger generation, path generation and positional control, and data acquisition and logging. The system is capable of multiple scanning modes, M, B, and C-scans, with two different trigger operations, iterative and continuous.

The second program is responsible for analyzing the acquired data. It is capable of multiple RF signal corrections including but not limited to non-linear attenuation compensation, frequency domain filtering, and pulser/receiver gain correction. For any given scan time frequency domain analyses can be performed like pulse detection and measurements, spectrum content and reference comparisons, and multiple statistical analyses. In addition, multiple scans can be compared using a range of quantification methods, peak trend, average spectrum, B-line backscatter, image difference, and scan cross-correlation. All of which compare different aspects of the scans relative to each other or to a specified reference.

The purpose of this research can be broken into two sections. The first objective was to observe the basic acoustic response from the GDL as there is no prior work for a basis. After a clear understanding of GDL-acoustic coupling a research objective was defined.

After familiarization of the developed system, initial scans of the GDL revealed echo signals with seemingly random shape. The echo signals also showed large variations in shape and magnitude with scanned position. Continued investigation demonstrated that the saturation level of the GDL had a huge effect on the apparent attenuation of the signal. Initial B-scans showed no back reflection of the GDL support until high levels of saturation. It was determined that the primary acoustic reflector was encapsulated air within the GDL, substantiated with theoretical validation.

From quantification tests that define the system resolution it was found that the microstructure of the GDL falls into diffractive scattering. This is between specular and diffuse scattering where backscatter theories are well defined. The result is an acoustic resolution that cannot resolve individual fibers within the GDL, producing a response which is the phase sensitive summation of all reflections within the resolution cell (Figure 3.4.24).

Figure 3.4.24: Plot illustrating random nature of received echo signals.

The signal, however, is deterministic. For any one location there is a distinct and consistent echo pattern. If enough information is known about theinsonified region of the GDL the received echo signal can be reproduced. The difficulty lies in the reverse problem, trying to extract information about the structure from the semi-random signal. This phenomenon is known as speckle, the result of constructive and destructive interference showing no inherent relation to the physical structure imaged.

The first set of investigations attempted to quantify the change in acoustic attenuation with saturation. Given the nature of the GDL microstructure and its relative size compared to the imaging resolution cell, a large data set was needed to define the average echo amplitude with depth. This was accomplished by identifying all peaks in the received A-line signals and plotting their amplitude versus the time of arrival. For the standard 2 by 2 millimeter scanned area and a pixel size of 20μm approximately thirty thousand echoes were identified for any given scan. With that the recorded time-gate was split into 50 equal sections where the corresponding echo amplitudes in that time frame were averaged. The trend in average echo amplitude was then fit to an exponential decay with scaling constant a , dampening constant b , and an offset c .

$$A(t) = ae^{-bt} + c \quad (3.4.3)$$

Figure 3.4.25: Plot of detected peaks with fit trend line.

Figure 3.4.25 illustrates this method for a sample C-scan of 4 mm^2 . To capture the relation between saturation and acoustic attenuation six scans were considered. The first being a dry reference and the following five exhibited increasing saturations.

A sample of Toray 120 carbon paper with zero PTFE content was inserted into the waterbath. After being filled with two inches of water a square area of 4 mm^2 is scanned. Upon completion a constant vacuum is applied to the chamber under the GDL causing a pressure differential across the GDL thickness. The process was repeated for four increasing levels of pressure. The corresponding amplitude trends are shown in Figure 3.4.26.

Figure 3.4.26: Plot illustrating the decrease in acoustic attenuation with increasing saturation.

Table 3.4.5: Listing of applied differential pressures used for the corresponding scans.

Scan	ΔP Applied kPa (psi)
GDL-C- Scan_136	0.50 (0.07)
GDL-C- Scan_137	1.72 (0.25)
GDL-C- Scan_138	3.45 (0.50)
GDL-C- Scan_139	6.89 (1.00)
GDL-C- Scan_140	13.79 (2.00)
GDL-C- Scan_141	20.68 (3.00)

The trends show a clear decrease in attenuation with an increase in applied pressure. The shape of the trends are also consistent with theory as the effects of acoustic shadowing are clear. GDLs with higher saturation levels show increased acoustic energy deeper in the sample compared to the dryer samples. Logically this makes sense given the reduced reflected energy earlier in the sample, leaving more energy to be transmitted into and reflected from deeper sections.

In order for ultrasonic waves to be reflected an acoustic impedance mismatch boundary is needed. The primary source of acoustic reflection within a GDL is from water/air boundaries. Given the large difference in acoustic impedances, greater than 99% of the incident energy is reflected. As air is being displaced by water during the saturation process the dominance of water/air boundary reflections are reduced, leaving the A-line RF signal closer to full dependence on reflection from the GDL microstructure. The result is reduced confidence in the echo signal having a correlation to the physical condition within the insonified region.

Plots of the acoustic backscatter over a 4mm^2 area reveal coherent regions of high and low ultrasonic reflectivity. Backscatter being defined by the sum of all data points squared at each pixel location, ij , where N is the number of data points recorded at each location. This quantity considers the cumulative effect of all reflected energy within the GDL.

$$B_{ij} = \sum_{k=0}^{N-1} A(k)_{ij}^2 \quad (3.4.4)$$

Intuitively the regions of high acoustic backscatter correspond to pockets of air while lower value areas reveal saturated sections of the GDL. However, there is no secondary validation to the speculation given the uncertainty in the constructive and destructive interference in the received signal.

Figure 3.4.27 below depict sample C-scan images of the backscatter received for a dry reference scan and vacuum saturated scan after 0.5psi.

Figure 3.4.27: Typical C-scan images illustrating change after differential pressure application. (a) C-Scan_263 Dry Reference Image, (b) C-Scan_268 image from 0.5psi Δp .

It can be seen that the regions of high acoustic reflectivity suffer reduced area and backscatter after a pressure differential is applied across the GDL face. Simple image subtraction reveals areas of altered backscatter. The problem with this method is the inconsideration of altered A-line shape with consistent backscatter. For a sample location where interference defines the shape and reflected energy a simple reduction or change in the position of air within the insonified region results in a major change in A-line shape but little change in backscatter energy. The consequence is a missed alteration from the dry condition to a now saturated condition.

This phenomenon can be illustrated with a simple example. Figure 3.4.28 show the results of two different methodologies used to quantify the changes in GDL saturation. Figure 3.4.28a is the result of image subtraction between a dry reference scan and a scan after a 0.25psi pressure differential is applied across the GDL. Figure 3.4.28b shows the variation in saturation by quantifying the change in the A-line signal at each pixel location from the dry reference scan.

Figure 3.4.28: Two method for identifying regions of water intrusion. Sample is of Toray 120 plain after 0.25psi Δp . (a) C-Scan_136-137 image difference, (b) C-Scan_136-137 scan correlation.

Clearly the simple image subtraction method misses areas of altered A-line signal where as the correlation method captures all locations of altered reflectivity. The following defines the values used to quantify the variation in A-line signals at each pixel location, as used in Figure 3.4.28b.

$$S_{ij} = \left\{ \left| \frac{\sqrt{H(CC_{ij\tau})^2 + CC_{ij\tau}^2}}{\sqrt{H(AC_{ij\tau})^2 + AC_{ij\tau}^2}} - 1 \right| + |\beta \phi_{fractional}| \right\} \times 100 \quad (3.4.5)$$

$$CC_{ij\tau} = \sum_{k=0}^{N-1} X(k)_{ij}^* \cdot Y(k + \tau)_{ij} \quad (3.4.6)$$

$$AC_{ij\tau} = \sum_{k=0}^{N-1} X(k)_{ij}^* \cdot X(k + \tau)_{ij} \quad (3.4.7)$$

It is based on the cross-correlation between two scans A-lines. Each scan is compared to the dry reference and a correlation ratio is defined for each pixel location. The advantage of this method is the inconsequence of random echo signals. Assuming that the dry scan is void of water within the GDL any change to the A-line signal must be due to the occupation of water within the insonified region. This is also dependent on the stationary fixture of GDL microstructure as any change in its position between scans would also be a source of altered A-line signals. Using this method of quantifying changes in the A-line signals and the methodology for acquiring scans for varying saturation levels, images of water intrusion upon the GDL can be acquired for different levels of pressure applications.

This method has been applied to a sample of Toray 120 with 20% PTFE loading. In addition to the standard C-scans capturing the before and after pressure saturation images of in-plane water distribution the dynamic change in GDL saturation is also recorded. The time dependent change in acoustic backscatter is quantified by repetitive scanning of a single line across the GDL face during the pressure differential application. Each recorded B-line was approximately one second in duration resulting in a refresh rate of one hertz.

Figure 3.4.29: B-line backscattered energy trace during saturation process.

Table 3.4.6: Listing of applied differential pressures used for the corresponding scans.

Scan	ΔP Applied kPa (psi)
GDL-B- Scan_197	1.72 (0.25)
GDL-B- Scan_198	2.41 (0.35)
GDL-B- Scan_199	3.45 (0.50)
GDL-B- Scan_200	5.17 (0.75)
GDL-B- Scan_201	6.89 (1.00)
GDL-B- Scan_202	13.79 (2.00)
GDL-B- Scan_203	20.68 (3.00)

The scanning was started before the application of pressure across the GDL. This transition can be seen in Figure 3.4.29 as a sharp drop off in acoustic reflectivity. Again, these normalized values represent the average acoustic backscatter over a 2mm scanned line. An average reduction in backscattered acoustic

energy can be attributed to a loss in the primary reflector, air encapsulated within the sample GDL. After the quick change in saturation the acoustic backscatter levels off during the constant pressure application. Once this steady state condition is reached the pressure is relived and the selected area is scanned once again.

It is observed that the state of saturation or acoustic reflectivity is maintained with some level of rebound until the next application of pressure. It is speculated that the cause of this rebound is the result of water being forced into pores only balanced by the pressure gradient within the GDL. Once the pressure is released capillary pressures overcome and force water from previously occupied pores, reducing the effective saturation. This phenomenon has been observed for almost all tests with some showing significant rebound however further investigation was not pursued.

Images depicting the variation from the dry reference scan to those captured after each application of increasing pressure were generated using the cross-correlation method discussed previously. It's clear from the images that preferential regions of the GDL support water intrusion. With greater differential pressure across the GDL these localized regions expand while new locations emerge. This behavior is in contrast to uniform intrusion at a critical pressure. What is observed is the non-uniform spatial distribution of permeability. For any given differential pressure the identified regions of water intrusion do not indicate locations where the applied pressure is the breakthrough pressure, which is commonly used to characterize diffusion media. It does, however indicate the locations where capillary forces and diffusion resistances are overcome, allowing water to displace air within the GDL.

Figure 3.4.30: Two scan correlation images for a sample of Toray 120 20% PTFE loading. (a) C-Scan_229-229-1 0.07psi Δp , (b) C-Scan_229-233 0.5psi Δp .

Currently, the method used does not produce depth information concerning the location of saturation changes. Typically depth information is obtained by time-gating the signal and concerning yourself only with the signal section that corresponds to a certain depth, assuming knowledge of propagation speed is known. Since the method used is based on changes to the signal and not direct relations to the physical media any variation in the signal will cause the remaining echo signal to deviate from the reference. The significance being a single depth value is extractable from any given dry scan correlation. This depth value locates the first alteration within the acoustic beam from the reference scan.

To quantify the progression of saturated coverage an in-house developed algorithm was used to identify isolated areas of significant saturation. Each image was converted to a binary matrix through simple thresholding and analyzed for three quantities, fractional coverage area, number of cells identified, and their average size. This provides a qualitative measure of the saturation progression which can be used for comparisons. The results of the four scans are presented in figures 3.4.31 thru 3.4.33 below. All four were tested under identical conditions differing only in the PTFE loading.

Figure 3.4.31: Fractional saturation coverage versus differential pressure for four different GDL sample with varying PTFE loadings.

Figure 3.4.32: Average identified cell size versus differential pressure for four different GDL sample with varying PTFE loadings.

Figure 3.4.33: Number of identified cells versus differential pressure for four different GDL sample with varying PTFE loadings.

The plot of fractional coverage area reveals a general trend common to all plots. Between zero and one psi differential pressure there is a constant increase in saturated area with pressure. At approximately 0.75 psi there is an inversion in the plots, resulting in a leveling off to a critical saturation level. These plots do show a slight correlation in fractional coverage area with PTFE content. The results for Toray paper with 40% PTFE loading shows the most significant deviation from the other samples. It's clear that for the high PTFE loaded GDL the coverage area surpasses the others at low pressures but settles more quickly, showing a much lower coverage than the other three at higher pressures.

III-5. Task 5: In-Situ Combinatorial Performance

Shutdown purge preparation of proton exchange membrane fuel cells (PEMFCs) is required whenever it may be necessary to restart under sub-freezing conditions. Gas channels must be free of liquid water to avoid cell-to-cell flow maldistributions and the porous electrodes must be sufficiently dry to provide capacity for ice formed from product water during the start-up sequence. A key learning from this project is that the time and energy needed for liquid water removal during cathode purge is predominantly controlled by the volume of liquid water present in flow field channel and within GDLs at shutdown. Thus, the new material and design set selection will focus on changes which are expected to minimize the accumulation of water during steady-state operation, with geometric features that are more representative of full-size automotive hardware. The changes that have been established include:

- flow field channel cross-sections on anode and cathode that more closely represent stamped metal and molded carbon composite bipolar plates;
- significantly increasing or decreasing the flow field material surface energy, to favor formation of either liquid films that can be removed via evaporation, or smaller slugs that can be more easily removed by gas shear;
- thinner GDL substrates, which should proportionally reduce the amount of water that can accumulate before reaching the “critical” saturation level, whereby water starts to be rejected to the flow field channels without further increase in GDL saturation. This behavior has been reported previously in experiments conducted to understand the physical phenomena associated with voltage instability at low power [149].

Some of these changes are applied to the GDL/flow channel system and their performance is evaluated in in-situ fuel cell setup.

III-5.1 Combinatorial In-Situ Multi-Channel Flow Experiments

The baseline characterization studies have identified that water removal during shutdown purge is critical for a robust freeze start. A key parameter identified through in-situ experimentation is the thermal conductivity of the GDL material. This helped steer the RIT in-situ experiments towards investigating GDL's with varying thermal properties. In addition to the baseline GDL, a Freudenberg GDL (slightly lower thermal conductivity than baseline) and Toray TGP-H-060 GDL (higher thermal conductivity than baseline and Freudenberg) were investigated. The thickness of each sample was comparable. The key properties of the samples are summarized in Table 3.5.1.

Table 3.5.1 Summary of GDL samples used in in-situ multi-channel experiments.

GDL	Thickness (μm)	Structure	PTFE (wt%)
Baseline	230	With MPL	7
SGL 25BC	235	With MPL	5
Freudenberg GDL	230	With MPL	In-house PTFE treated by GM
Toray 060 + MPL	200	With MPL	In-house PTFE treated by GM

A comparison of the performance and HFR of each GDL sample is shown in Figure 3.5.1. The performance of each GDL is comparable, with Freudenberg performing slightly better than baseline GDL at higher current densities, and Toray performing slightly better than both GDLs at the highest current

densities. The baseline sample possessed the highest membrane resistance, with the Freudenberg sample slightly lower and the Toray sample having the lowest HFR.

The two-phase flow pattern maps observed in cathode gas channel were compared for each GDL. A combined flow pattern map was created to identify and compare the flow pattern transition regions for each GDL. Figure 3.5.2 shows a comparison of the resulting transition lines. All the three GDLs displayed the similar flow pattern maps, with the flow pattern changing from slug through film to mist flow as air flow rate increases. However, as seen in the figure, for each two-phase flow pattern transition (slug-to-film, and film-to-mist) the Toray and Freudenberg transition lines are shifted to the left of the baseline transitions. The baseline GDL possesses a considerably larger slug region than the other GDL samples. This implies that the Toray GDL has the lowest channel water presence, the Freudenberg is in the middle, and the baseline GDL has the highest channel water holdup. This finding was confirmed by the channel visualization (Figure 3.5.3). In this figure, many large slugs are apparently observed for the case of the baseline GDL, the Freudenberg GDL shows fewer slugs, and Toray GDL barely displays any water slugs. Instead, extensive water condensation is observed in the gas channel tested with Toray GDL.

Figure 3.5.1 – Performance comparison for GDLs with varying microstructure, PTFE content, and thermal properties. Cell temp. 35 °C, 100% RH inlet gases, stoich ratio (an:ca) 1:5:2.5.

Figure 3.5.2 – Comparison of flow pattern transitions for different GDLs tested. Cell temperature 35 °C, 100% RH inlet gases, stoich ratio (an:ca) 1:5:2.5.

Figure 3.5.3 – Two-phase cathode channel visual observation. Current density 100 mA/cm^2 , Cell temp. 35 °C, 100% RH inlet gases, stoich ratio (an:ca) 1:5:2.5. Window 2.

The total anode and cathode pressure drops across the entire flow field for each GDL sample were compared in Figure 3.5.4. All three GDLs showed comparable anode pressure drop. This is in agreement with the anode visualization, where not much water is present in the channels. In contrast, significant difference in pressure drops at the cathode is found between these GDLs.

Figure 3.5.4 – Total anode and cathode pressure drop comparison for different GDLs tested. Cell temp. 35 °C, 100% RH inlet gases, stoich ratio (an:ca) 1:5:2.5.

As seen in the figure, the Baseline and Freudenberg GDLs have a significant presence of slug flow at low current density, while there is virtually no liquid water accumulation (aside from condensation) in the channels with the Toray sample. Figure 3.5.5 shows the same conditions compared at the bottom cell window.

The same observations were found, with considerable liquid water accumulation in the baseline and Freudenberg cathode channels, and very little liquid water activity present in the Toray channels. Figure 3.5.6 shows a comparison of the bottom window at high current density.

Although a greater mist region is seen with the baseline and Freudenberg samples, there was still a greater presence of liquid water activity (primarily film flow) taking place in the channels. The Toray channels consistently had condensation with minimal water activity.

The higher thermal conductivity of the Toray GDL sample contributed to the variations in data when compared to the baseline and Freudenberg samples. More specifically, there is greater water holdup within the GDL due to the higher thermal conductivity of Toray. The visual observations confirmed a greater presence of liquid water in the baseline and Freudenberg channels, while the low HFR for the Toray sample indicated a greater membrane hydration state. Therefore, lower thermal conductivity was found to be a desirable GDL property as it leads to the reduction of water holdup within the GDL prior to cell shutdown and subsequent freeze start up.

Figure 3.5.5 – Two-phase cathode channel visual observation. Current density 100 mA/cm², Cell temp. 35 °C, 100% RH inlet gases, stoich ratio (an:ca) 1:5:2.5. Window 1 (bottom).

Figure 3.5.6 – Two-phase cathode channel visual observation. Current density 500 mA/cm², Cell temp. 35 °C, 100% RH inlet gases, stoich ratio (an:ca) 1:5:2.5. Window 1 (bottom).

III-5.2 Experimental Measurement of GDL Thermal Conductivity

Since GDL thermal conductivity has an important impact on GDL water saturation during fuel cell operation, it is necessary to accurately determine the GDL thermal conductivity and the consequent relationship with water saturation in the GDL. The guarded hot plate method [150] is used to measure the GDL thermal conductivity, in which the heat flow is controlled to be steady and unidirectional. In this method, two identical test samples are placed on either sides of a flat heater comprising of a main heater and an annular guard heater (see Figure 3.5.7). The heater sample stack is then sandwiched between two heat sinks which are liquid cooled to maintain at a fixed temperature. The effect of contact thermal resistance is removed by using two thicknesses of the same GDL material. Figure 3.5.8 shows the test setup used for the thermal conductivity measurement.

Figure 3.5.7 – Schematic for Guarded hot plate method.

Figure 3.5.8 – Test setup used for thermal conductivity measurement.

This method is first validated with PTFE sheets of known thermal conductivity. The two thicknesses used were 127 μm and 254 μm . The tests were performed at room temperature and the uncertainty involved was estimated to be 8.5%. The thermal conductivity for PTFE sheet was measured to be 0.329 W/m.K, which is in very good agreement with the values obtained by Hu et al. [151] and Jen et al. [152].

The effect of compression on GDL thermal conductivity is shown in Figure 3.5.9 for the Toray and SGL GDLs. It was found that the thermal conductivities of both GDLs increased with compression. This increase in GDL thermal conductivity is attributed to the reduction in porosity (or void space) caused by the compression. Figure 3.5.10 shows the variation of thermal conductivity with temperature for Toray and SGL GDLs at the compression of 0.04 MPa. It was observed that the thermal conductivity of Toray

decreased with temperature. Similar phenomenon has also been observed by Khandelwal et al. [153]. The decrease of Toray thermal conductivity with increasing temperature can be attributed to the presence of binder which is carbonized thermo-setting resin. Thermal conductivity of this thermo-setting resin decreases as temperature increases [153]. In contrast, the thermal conductivity of SGL is found to be almost constant with temperature. This is because no binder materials are present in SGL GDLs.

The contact resistance between the GDL surface and bipolar plate provides some critical information regarding the selection of materials for the bipolar plate. The contact resistance is different for different GDL-bipolar material pairs and is dependent on the compression. Figure 3.5.11 shows the plot of contact resistance of GDL-copper pair as a function of compression for Toray and SGL GDLs. The contact resistance for both GDLs was found to decrease with increasing compression. This is expected because of the better contact between the GDL fibers and the surface under compression, thereby leading to lesser resistance to the heat flow. Furthermore, the contact resistance of SGL samples was found to be higher when compared to that of Toray. This may be due to the fact that the SGL samples have a microporous layer (MPL) on one side. MPL has a granular structure, resulting in point contact with the flat surface, which in turn leads to a higher contact resistance. This effect has been found to lead to a higher electrical contact resistance of GDL with MPL than that for GDL without MPL [154]. Hence, by applying the analogy between thermal and electrical properties, it can be concluded that thermal contact resistance of SGL should be higher than that of Toray.

Figure 3.5.9 – Thermal conductivity plot as a function of compression for Toray and SGL GDL samples at 58 °C.

Figure 3.5.10 – Plot of thermal conductivity versus temperature for Toray and SGL GDL samples at 0.04 MPa compression.

Figure 3.5.11 – Plot of contact resistance of GDL-copper pair versus compression for Toray and SGL GDL samples.

III-5.3 Combinatorial Fuel Cell Freeze-Thaw Experiments

A: Effects of Channel Geometry

The baseline channel design consisted of a rectangular geometry (0.7 mm wide x 0.4 mm deep). For the second iteration of the in-situ channel component study, the effects of a more realistic channel geometry that could result from a metal stamping process while maintaining the same hydraulic diameter were investigated (Figure 3.5.12). The neutron imaging experiments with the stamped channel geometry plates combined with the baseline GDL material set were conducted by GM. Figure 3.5.13 shows the comparison of the water accumulation in the fuel cell. No appreciable difference in channel slug formation was found for different channel geometries. Although one observes different amounts of channel level water accumulation between the two experiments, both channel geometries facilitate significant slug formation at a variety of conditions. These results are in good agreement with the micro-scale ex-situ experiments being performed by RIT (Section III-4).

Figure 3.5.12 – Flow field channel cross-sections that simulate stamped metal and molded carbon composite as well as the baseline channel design. The color in the figure represents the simulated stamped metal design.

Figure 3.5.13 – Comparison of slug formation in a stamped metal geometry compared to the baseline rectangular geometry.

B: Effects of GDL Material Properties

Baseline system characterization has identified the most important GDL material properties that affect the water accumulation within GDLs are thermal conductivity and thickness. In the first study, GM evaluated the impact of GDL thermal conductivity on saturation at various operating conditions. Results indicated that water accumulation is sensitive to thermal conductivity, especially at higher temperatures (see Figure 3.5.14). Increased thermal conductivity effectively lowers the MEA temperature and thus, the concentration gradient that drives water vapor from the electrode to the channel. As shown in Figure 3.5.14, reducing the saturation pressure near the MEA with an increased thermal conductivity GDL will effectively bring the condensation front deeper into the GDL, resulting in higher steady state liquid water content. Since saturation pressure varies nonlinearly with temperature it was observed that the difference in saturation occurs at higher temperature operating conditions but is not prevalent at lower temperatures.

Figure 3.5.14 – Impact of thermal conductivity on GDL saturation at 80 °C.

The effects of variations in GDL thermal conductivity, thickness, and durability have been evaluated for optimized water removal at various shutdown conditions. The recent results indicate that the diffusion resistance in the cathode GDL has a dominant impact on the volume of water accumulation in the fuel cell at steady-state. A series of experiments was conducted in which Toray 030 and 090 (nominal thicknesses of 100 and 300 μm , respectively) diffusion media were combined in different combinations on anode and cathode (MPL used in all cases). As shown in Figure 3.5.15, the steady-state water content with fully humidified inlet reactant streams was greatest when a thick cathode GDL was used; this impact is also observed in the significantly higher mass transport loss at high current density (Figure 3.5.16). By contrast, the thickness of the anode GDL had a relatively small effect on both water content and fuel cell performance.

Figure 3.5.15 – Water distributions with different combinations of thin and thick diffusion media.

Figure 3.5.16 – Polarization curves, water volume and HFR with different combinations of thin and thick diffusion media (same conditions as Figure 3.5.15).

C: In-situ GDL Durability Studies

The baseline characterization also revealed that shutdown purge time and energy is mainly constrained by the quantity of liquid water retained in the GDL during operation prior to shutdown. These evaluations were done with new GDL and there is a general concern expressed in open literature that the hydrophobic properties of GDLs degrade over time, thus the saturation properties may change [155]. To evaluate this effect, GM provided GDL from an automotive stack that had ~3000 hours of operation and compared it with neutron radiography to a 200 hour sample. The results shown in Figure 3.5.17 do not demonstrate a significant change in saturation behavior. At the condition shown (80 °C, 200 kPa outlet, 100% RH inlet gas), amongst many others tested, the water distribution and overall quantity of water was not affected by aging the GDL 3000 hours. This result enabled the team to apply saturation results obtained with new GDLs to fuel cell operation, independent of durability considerations.

Figure 3.5.17 – Saturation impact of 3000 hours of operation in an automotive stack.

D. GDL Water Removal and Ionomer Drying

Previous results have identified that water removal during shutdown purge is critical for a robust freeze start. Conversely, the ionomer must not become over dried during purge because poor proton conductivity at sub-freezing start conditions will occur. In order to investigate this relationship between ionomer drying (as indicated by high frequency resistance, HFR) and water removal, GM employed the

distributed current and temperature measurement tool with simultaneous neutron radiography [156]. The results shown in Figure 3.5.18 have allowed our team to refine the theoretical relationship between GDL water removal and ionomer drying.

Figure 3.5.18 – Distributed current, HFR and temperature measurements during shutdown gas purge correlated to liquid water removal from GDL.

The shutdown operating space and corresponding high frequency resistance (HFR) has been mapped for several operating conditions at various current densities. The example shown in Figure 3.5.19 demonstrates the relationship between liquid water distribution and local HFR. The HFR distribution correlates directly with the local water content.

Figure 3.5.19 – Liquid water and HFR distributions for varying current densities.

Of particular interest for freeze shutdown preparation is the relationship between liquid water saturation and membrane water content (indicated by HFR) as liquid water is removed. Ideally the liquid water is removed without over-drying the purge gas inlet. The functionality of this relationship is shown in Figure 3.5.20, where it was observed that HFR increases exponentially once liquid water is removed from the adjacent GDL and channels. However, there is also a time lag in this exponential increase.

Figure 3.5.20 – HFR, liquid water and temperature response to a cathode purge.

Shutdown purge preparation of proton exchange membrane fuel cells (PEMFCs) is required whenever it may be necessary to restart under sub-frozen conditions. Gas channels must be free of liquid water to avoid cell-to-cell flow maldistributions and the porous electrodes must be sufficiently dry to provide capacity for ice formed from product water during the start-up sequence. Through GM's investigation of local gas diffusion layer (GDL) drying behavior and the corresponding high frequency resistance (HFR) response using novel neutron radiography and distributed current density measurement methods, it has been shown that the saturation state and local ohmic resistance for a constant bulk HFR vary based on the purge condition. The results also show that ionomer drying does not occur until water in the GDL substrate has been removed, and thus purge time is constrained by GDL saturation properties. The practical implication of this finding is that when a particularly bulk HFR must be achieved to facilitate freeze start (say, 0.2 to 0.3 Ω cm²), there is a wide variation in the local MEA hydration state over the fuel cell active area. As shown in Figure 3.5.21, when the bulk HFR attains its "optimal" level, the inlet edge of the active area is completely dry while the outlet edge retains more than 50% of its initial water content. This variation obviously has important efficiency and durability implications, and must be comprehended in an intelligent shutdown purge strategy.

Figure 3.5.21 – Local HFR and water content variation during cathode purge sequence

From the data of local HFR and water content shown in Figure 3.5.21, it is apparent that there may be a general relationship between these two parameters, because as the water content decreases there is a systematic increase in HFR that appears to follow a common functional form. To test this hypothesis, all of the 96 local HFR measurements (from the distributed printed circuit board tool described previously) were plotted against the local water content values for a particular purge condition. The results in Figure 3.5.22 demonstrate that there is a very strong correlation between HFR and effective water thickness, and that significant increase in local HFR due to ionomer drying does not occur until the GDL layer above the MEA is substantially free of liquid water. For the purge condition in Figure 3.5.22, this transition occurs at a measured water thickness of about 20 μm .

Diagnostics developed during the baseline characterization revealed that a significant quantity of liquid water is retained in the anode GDL and channels [157]. For a successful freeze start, the majority of this water must be removed at shutdown by a cathode purge. During this purge, anode water must be transferred through the membrane and this process limits the rate at which water is removed [158]. To minimize the quantity of water that can accumulate within the anode GDL GM evaluated both thinner and more thermally conductive GDLs. The effects of variations in GDL thickness and thermal conductivity have been evaluated by GM for optimized water removal at various shutdown conditions.

Figure 3.5.22 – Correlation between liquid water thickness and HFR during cathode purge.

III-6. Task 6: In-Situ Performance with Water Distribution and Current Density Measurement

III-6.1 Water Removal at Shutdown

GM has previously reported water removal rates along the channel during shutdown air purge through the cathode [158]. This work established that water is primarily removed through evaporation during the purge, a key finding regarding shutdown preparation and material optimization for freeze. In this previous work the location of water accumulation in the through-plane dimension was inferred through a series of experiments measuring the mass transfer coefficient of water removal from the cathode GDL versus from the anode GDL (through the MEA) with cathode air purge. These results indicated that water accumulation in the anode GDL is rate limiting and must be controlled for reduced purge time and energy.

GM measured water accumulation in the through-plane dimension directly with high resolution neutron imaging instruments at NIST. These measurements were executed with the baseline material set and same operating conditions that have been previously reported. Figure 3.6.1 demonstrates the fidelity of this measurement as one can clearly observe liquid water in the various components of the cell. In Figure 3.6.1, increased water accumulation due to condensation under the lands verifies similar observations made in the in-plane dimension. However, data in the through-plane dimension shows the interaction that water under that land has with the channel wall, a mechanism that cannot be observed with in-plane imaging. Liquid water is observed to form droplets at the GDL/channel wall interface.

Figure 3.6.1 – High resolution neutron image of through-plane water distribution in the baseline material set at 80 °C.

The through plane measurement was also used to validate water accumulation and removal mechanisms. As previously reported, this is evaluated at a variety of practical fuel cell operating conditions. Lower temperature conditions are particularly useful for analysis as the inlet gas does not require humidification (one knows with certainty that all water accumulation results from the reaction) and evaporation mechanisms occur at a slow rate (reduces temporal resolution requirements). Results from a precondition and purge at 35 °C are shown in Figure 3.6.2. During the precondition in Figure 3.6.2, the majority of water accumulation is occurring within the anode GDL layer. This result directly

confirms the previously inferred water accumulation location in the through-plane dimension [158]. These data clearly demonstrate that the water removal rate during shutdown purge for freeze is constrained by water transfer through the membrane.

Figure 3.6.2 – Through-plane liquid water gradients during 35 °C purge.

III-6.2 Varying Anode GDL Thermal Conductivity along the Channel

The through-plane data previously described demonstrates that reducing water accumulation in the anode GDL is a critical parameter for improving shutdown purge efficiency. During this project our team investigated means of accomplishing this with varied GDL thermal conductivity and thickness. In summary, the results reported in Q3 2009 showed that the mass transport performance was most influenced by changes in the cathode GDL thermal conductivity and thickness. From these experiments it was found that water accumulation was minimized and performance was maximized with a thinner more thermally resistive cathode GDL. These variations in the anode GDL were not found to have a significant impact on performance as diffusion resistance is less critical within the hydrogen gas volume. GM applied these findings to our current material set to prove that water accumulation can be manipulated without impacting performance by varying anode GDL properties along the channel.

In a first experiment, the anode GDL thermal conductivity was increased near the inlet and outlet, an area generally observed to have high ohmic resistance due to inlet gas drying in counter flow. This configuration is shown graphically in Figure 3.6.3, where the baseline GDL was continuous across the entire cathode and placed in the center of the anode while a GDL with higher thermal conductivity was placed at the anode inlet and outlet.

Figure 3.6.3 – Graded anode GDL configuration.

Results for neutron imaging with this configuration are shown in Figure 3.6.4. At 80 °C the water accumulation in regions with increased anode GDL thermal conductivity is clearly observed. In Figure 3.6.4, the regions with higher thermal conductivity and increased water volume are the result of water vapor reaching saturation pressure closer to the MEA and condensing deeper within the GDL. Although overall water content was increased, there was no negative performance impact because only the anode GDL was altered, Figure 3.6.5. In fact, performance was slightly improved by reducing the proton resistance near the counter flow inlets. With regard to purge optimization, this material set is clearly not ideal for reduced water content but it does demonstrate the key parameters in executing such an optimization.

Although thermal conductivity is effective for manipulating water accumulation in the GDL at 80 °C where saturation pressure gradients are significant, it has been shown to have little impact at lower operating temperatures. A comparison of graded anode GDL to the baseline at low operating temperature is shown in Figure 3.6.6. At 35 °C nearly all water produced must exit in the liquid phase, thus another solution for liquid water reduction must be considered.

Figure 3.6.4 – Neutron images of baseline GDL compared with graded anode GDL at 80 °C.

Figure 3.6.5 – Performance and high frequency resistance (HFR) of baseline and graded anode GDLs (polarization curve condition: 80 °C, 95% RH, 1.5/1.8 anode/cathode stoichs, 150 kPa).

Figure 3.6.6 – Comparison of baseline to graded anode GDL at low temperature (35 °C).

For mitigation over the entire operating range the interaction between the water accumulation in the GDL and the channel wall is essential, as previously highlighted in Figure 3.6.1. This interaction can be exploited by increasing the surface energy of the channel wall, thereby enabling water to wick into the channel instead of forming large droplets. GM investigated this mechanism by altering the contact angle of the baseline flow fields from 90 ° to less than 15 °. Water accumulation in the hydrophilic flow field was then compared to the baseline with neutron imaging. The results shown in Figure 3.6.7 are consistent with that from a wide range of operating conditions where a hydrophilic channel is observed to reduce water slug formation in the channels. Moreover, while the overall water retention is reduced and there is no impact observed in performance as shown in Figure 3.6.8.

Figure 3.6.7 – Comparison of channel water slug accumulation for baseline and hydrophilic flow fields.

Figure 3.6.8 – Performance and high frequency resistance (HFR) of baseline and hydrophilic flow fields (polarization curve condition: 80 $^\circ\text{C}$, 95% RH, 1.5/1.8 anode/cathode stoichs, 150 kPa).

III-6.3 Stack Related Water Accumulation

Throughout this project water accumulation and removal has been studied on the single cell level. These experiments have shown that freeze shutdown preparation time is largely influenced by the quantity of liquid water retained in the channels and GDL during operation. However, single cell studies fail to capture the variation in saturation that may occur in a fuel cell stack [149]. GM studied this variation with a planar four cell stack that was designed for compatibility with neutron imaging at NIST. This fixture is shown in Figure 3.6.9, where each cell of the stack is connected in series with external bus bars while the inlets and outlets are connected by common manifolds.

Figure 3.6.9 – Planar stack with common manifolds used for neutron imaging experiments.

The fixture shown in Figure 3.6.9 allowed observation of stack-level liquid water transport in individual cells during polarization, stoichiometric ratio sensitivity, and purge and start-up experiments. This also enabled direct observation of the relationship between liquid water accumulation and performance with confidence due to precise control of flow and temperature. Stack researchers often attribute variations in cell voltage to liquid water accumulations and this fixture combined with tools developed during the course of this project will provide data to further elucidate the link between voltage instability and water accumulation.

The first experimental campaign with the planar stack was focused on stoichiometric sensitivity. During these experiments anode and cathode stoichiometric ratios were varied while liquid water content and cell voltage was monitored. An anode stoichiometric sensitivity experiment is shown in Figure 3.6.10. As the hydrogen flow rate is decreased, cell voltage eventually becomes unstable. The data in Figure 3.6.10 shows that the water content in each cell increases proportionately with changes in anode

flow at a constant current density of 0.4 A/cm^2 . In this experiment, cell 3 has the highest voltage loss but has a lower overall water content when compared with other cells in the stack. To investigate this further, consider the neutron image in Figure 3.6.11 taken at 15000 seconds (relative to timescale in Figure 3.6.10). Here it is observed that cell 3 has a different water profile than the other three cells. Cell 3 has less water accumulation in the anode channels but more in the GDL. This experiment was repeated twice on the anode and cathode, and the cell that was first to lose voltage appears to be random. However, regardless of which cell fails, the general observation that the failing cell has the highest GDL water content holds in all experiments. This result indicates that under flooded conditions, GDL water content is more critical than channel-level water slugs. In a stack configuration it is hypothesized that channel slugs increase convective flow through GDL, thereby reducing transport length and saturation. Conversely, one cell in a stack with less water in the channels will not drive as much flow through the GDL, thus enabling a higher local saturation value.

Figure 3.6.10 – Anode stoichiometric sensitivity experiment with planar stack.

Figure 3.6.11 – Neutron image of planar stack water accumulation at $t = 15000$ sec.

IV. PUBLICATIONS AND PRESENTATIONS

Book Chapters

1. J. S. Allen, S. Y. Son, and S. H. Collicott, "PEMFC Flow-Field Design for Improved Water Management", *Handbook of Fuel Cells - Fundamentals, Technology and Applications*, W. Vielstich, H.A. Gasteiger and H. Yokokawa (Eds.), Volume 5: Advances in Electrocatalysis, Materials, Diagnostics and Durability, John Wiley & Sons Ltd., pp. 687-698, Chapter 46 (2009).
2. Trabold, T.A., Owejan, J.P., Gagliardo, J.G., Jacobson, D.L., Hussey, D.S. and Arif, M., *Handbook of Fuel Cells - Fundamentals, Technology and Applications*, W. Vielstich, H.A. Gasteiger and H. Yokokawa (Eds.), Volume 5: Advances in Electrocatalysis, Materials, Diagnostics and Durability, John Wiley & Sons Ltd., Chinchester UK, pp. 658-672, Chap. 44 (2009).

Journal Publications

1. Owejan, J.P., Owejan, J.E., Gu, W., Trabold, T.A., Mathias, M.F., "Investigation of Water Transport Mechanisms in Diffusion Layers of PEMFCs," *J. Electrochem. Soc.*, submitted for review (2010).
2. E. Medici and J. S. Allen, "Study of Wettability and Morphological Properties Effects on Water Percolation in Gas Diffusion Layers of PEMFC", *J. Electrochem. Soc.*, submitted for review (2010).
3. A. Herescu and J. S. Allen, "Liquid Holdup in the Bipolar Plate Channels of a PEM Fuel Cell", *ECS Transactions - 2009 Fuel Cell Seminar & Exposition*, Volume 26, "PEMFC/DMFC R&D I", scheduled to be published in March 2010.
4. Z. Lu, M. Daino, C. Rath and S.G. Kandlikar, "Water Management Studies in PEM Fuel Cells. Part III, Dynamic Breakthrough and Intermittent Drainage Characteristics from GDLs with and without MPLs," *Int. J. Hydrogen Energy* (2010), doi:10.1016/j.ijhydene.2010.01.012.
5. Owejan, J.P., Gagliardo, J.J., Falta, S.R. and Trabold, T.A., "Accumulation and Removal of Liquid Water in Proton Exchange Membrane Fuels Cells," *J. Electrochem. Soc.*, Vol. 156, B1475-B1483 (2009).
6. Z. Lu, S. G. Kandlikar, C. Rath, M. Grimm, W. Domigan, A.D. White, M. Hardbarger, J. P. Owejan and T.A. Trabold, "Water Management Studies in PEM Fuel Cells. Part II: Ex-situ Investigation of Flow Maldistribution, Pressure Drop and Two-Phase Flow Pattern in Gas Channels," *Int. J. Hydrogen Energy*, 34, 3445-3456 (2009).
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8. S.G. Kandlikar, Z. Lu, W.E. Domigan, A. D. White, M.W. Benedict, "Measurement of Flow Maldistribution in Parallel Channels and its Application to Ex-situ and In-situ Experiments in PEMFC Water Management Studies," *Int. J. Heat Mass Transfer*, 52,1741-1752 (2009).
9. S.G. Kandlikar and Z. Lu, "Fundamental Research Needs in Combined Water and Thermal Management within a Proton Exchange Membrane Fuel Cell Stack under Normal and Cold-Start Conditions," *ASME J. Fuel Cell Sci. Tech.*, 6, 044001 (2009).
10. S.G. Kandlikar, Z. Lu, T.Y. Lin, D. Cook, M. Daino, "Uneven Gas Diffusion Layer Intrusion in Gas Channel Arrays of Proton Exchange Membrane Fuel Cell and Its Effects on Flow Distribution," *J. Power Sources*, 194, 328-337 (2009).
11. S.G. Kandlikar, Z. Lu, "Thermal Management Issues in a PEMFC Stack – A Brief Review of Current Status," *Appl. Therm. Eng.*, 29, 1276-1280 (2009).
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13. E. F. Medici, J. S. Allen, "Existence of the Phase Drainage Diagram in Proton Exchange Membrane Fuel Cell Fibrous Diffusion Media," *J. Power Sources*, 191(2), 417-427 (2009).
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Conference and Presentations (presenter shown in **boldface**)

1. **M. M. Daino**, S. G. Kandlikar, "Evaluation of Imaging Techniques Applied to Water Management Research in PEMFCs" ICNMM2009-82031, *Proceedings of the ASME 2009 7th International Conference on Nanochannels, Microchannels and Minichannels ICNMM2009*, Pohang, South Korea, 2009.
2. **J. M. Sergi**, Z. Lu, S. G. Kandlikar, "In Situ Characterization of Two-Phase Flow in Cathode Channels of an Operating PEM Fuel Cell With Visual Access," ICNMM2009-82140, *Proceedings of the ASME 2009 7th International Conference on Nanochannels, Microchannels and Minichannels ICNMM2009*, Pohang, South Korea (2009).
3. E. F. Medici and **J. S. Allen**, "Drainage in Gas diffusion Layers of PEM Fuel Cells," 62nd Annual Meeting of the APS Division of Fluid Dynamics, Minneapolis, MN, November, 2009.
4. E. F. Medici and **J. S. Allen**, "Drainage in Gas diffusion Layers of PEM Fuel Cells," 62nd Annual Meeting of the APS Division of Fluid Dynamics, Minneapolis, MN, November, 2009.
5. **A. Herescu** and J. S. Allen (2009). Liquid Holdup in the Bipolar Plate Channels of a PEM Fuel Cell, Palm Springs, CA.
6. **E. Mádici** and J. S. Allen, Scaling the Water Percolation in PEM Fuel Cell Porous Transport Layers, Proceedings of the Third International Conference on Porous Media and its Applications in Science, Engineering and Industry, June 2010, Montecatini, Italy.
7. **E. Mádici** and J. S. Allen, Drainage in Gas diffusion Layers of PEM fuel cells, American Physical Society, 62nd Annual Meeting of the APS Division of Fluid Dynamics, November 2009, Minneapolis, MN, USA.
8. **E. Medici** and J. S. Allen, Study of the Effects of Transport Porous Layer Wettability and Morphological Properties on the Water Percolation in PEMFC, Proceedings of the 216th Electrochemical Society Meeting, October 2009, Vienna, Austria.
9. **E. Mádici** and J. S. Allen, Two dimensional network model simulations of water percolation through a GDL, Proceedings of the Twentieth International Symposium on Transport Phenomena, July 2009, Victoria, BC, Canada.
10. **J. S. Allen**, "Fuel Cell Activities at the Michigan Tech Microfluidics & Interfacial Transport (MnIT) Lab", presented at Ballard Power Systems, July 7, 2009, Burnaby, Canada.
11. J.W. Lechnyr, D. L. Fritz and J. S. Allen, "Imaging of Fuel Cell Diffusion Media Under Compression", 20th International Symposium on Transport Phenomena (ISTP-20), Victoria, BC, Canada, July 7-10, 2009.
12. A. Herescu and J. S. Allen, "Effect of Surface Wettability on Viscous Film Deposition", 7th International ASME Conference on Nanochannels, Microchannels and Minichannels, ICNMM2009, Pohang, South Korea, June 22-24, 2009.
13. **J. LaManna**, S. G. Kandlikar, "A Critical Review of Water Transport Models in Gas Diffusion Media of PEM Fuel Cell," ICNMM2008-62201, *Proceedings of the Sixth International ASME Conference on Nanochannels, Microchannels and Minichannels ICNMM2008*, Darmstadt, Germany, 2008.
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15. **J.P.Owejan**, J.G. Gagliardo, J.M. Sergi, and T.A. Trabold, "Two-Phase Flow Considerations in PEMFC Design and Operation," ASME ICNMM2008, *Proceedings of the Sixth International ASME Conference on Nanochannels, Microchannels and Minichannels ICNMM2008*, Darmstadt, Germany (2008).
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26. **J. S. Allen**, "A Discussion of Capillary-Scale Two-Phase Flow and the Implications for Water Management in PEM Fuel Cells", POSTECH Workshop on Water Management of Fuel Cells, Pohang, Korea, August 31, 2007.

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1. R. Stacy, "Contact Angle Measurements on Rough Surfaces", M.Sc. Thesis, Michigan Technological University, July 2009.
2. J. Lechnyr, "Imaging of Fuel Cell Diffusion Media Under Compressive Strain", M.Sc. Thesis, Michigan Technological University, May 2009.
3. A. Radhakrishnan, "Thermal Conductivity Measurement of Gas Diffusion Layer Used in PEMFC", M.Sc. Thesis, Rochester Institute of Technology, December 2009.
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