V.B.3 Visualization of Fuel Cell Water Transport and Performance Characterization under Freezing Conditions

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Objectives

- Improve fundamental understanding of the water transport processes in proton exchange membrane fuel cell (PEMFC) stack components under freezing and non-freezing conditions.
- Optimize materials, design, and surface properties of gas diffusion layer (GDL) and bipolar plate to alleviate flooding and suppress regions of dehumidification.
- Develop experimental and modeling tools to evaluate ex situ and in situ performance of PEMFC stack components.

Technical Barriers

This project addresses the following technical barriers from the Fuel Cells section of the Fuel Cell Technologies (FCT) Program Multi-Year Research, Development and Demonstration (RD&D) Plan:

(A) Durability
(C) Performance
(D) Water Transport within the Stack

Technical Targets

This project is directed at developing a better water management strategy within PEMFC stacks. Insight gained will be applied toward the design and demonstration of a robust fuel cell that meets the following DOE technical targets as outlined in the FCT Multi-Year RD&D Plan:

- Unassisted start from low temperature: -40°C
- Durability with cycling at operating temperature of ≤80°C: 5,000 h
- Energy density: 2 kW/L

Accomplishments

In this project, 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 GDL 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. 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.
- 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 $\theta \sim 10^0$) facilitates the removal of liquid water by capillary effects and by reducing water accumulation at the channel exit. It was also found that a GDL without a microporous layer (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 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.
- Determined the effect of surface wettability and channel cross section and bend dihedral on liquid holdup in fuel cell flow channels.

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Introduction

Water management is critical to the successful implementation of PEMFCs in various industry sectors. Water management is especially challenging under low temperature conditions due to the low water carrying capacity of the reactant stream and the possibility of water freezing within the fuel cell assembly, which results in premature degradation. This project is directed at developing a better water management strategy within PEMFC stacks. To achieve these objectives, the project has been focused on the following technical issues:

1. Two-phase (water and gas) transport in the fuel cell stack, including the GDL, flow channels, and their interfaces.
2. Structural and surface properties of materials and how they change during operational events, such as freeze/thaw.
3. Experimental and modeling tools to evaluate ex situ and in situ performance as well as local variations in current density and water distribution.

Approach

The objectives of this project were accomplished through an iterative approach that starts 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 density, high-frequency resistance distributions and neutron radiography. The success of the project lies in new materials, improved design concepts and operating strategies. Both experimental and modeling tools will be used to evaluate ex situ and in situ performance.

Results

Previous studies under this project have identified the most import GDL material properties that affect the water accumulation within GDLs are thermal conductivity and thickness. Decreased thermal conductivity effectively increases the MEA temperature and thus, the saturation pressure gradient that drives water vapor from the electrode to the channel, resulting in lower steady-state liquid water accumulation within GDLs. Thinner GDLs simply hold less water. To minimize the quantity of water that accumulates within the GDLs, the effects of variations in GDL thickness and thermal conductivity have been evaluated by GM for optimized water removal at various shutdown conditions. A series of experiments were conducted with Toray 030 and 090 (nominal thicknesses of 100 and 300 μm, respectively) diffusion media, which are more thermally conductive than the baseline GDL, that combined different combinations on the anode and cathode (MPL used in all cases). As shown in Figure 1, 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. By contrast, the thickness of the anode GDL had a relatively small effect on both water content and fuel cell performance.

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 the 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 [1]. The results in Figure 2 demonstrate that there is a very strong correlation between HFR and effective water thickness, and that a significant increase in local HFR due to ionomer drying does not occur until water in the GDL substrate has been removed. For the purge condition in Figure 2, this transition occurs at a measured water thickness of about 20 µm. The results indicate that purge time is constrained by GDL saturation properties.

Water accumulation in the through-plane dimension was directly measured with high resolution neutron imaging instruments at the National Institute of Standards and Technology. These measurements were executed with the baseline material set and same operating conditions that have been previously reported. When preconditioned and purged at 35°C, the majority of water accumulation was observed to occur within the anode GDL layer. This result directly confirms the previously inferred water accumulation location in the through-plane dimension. The data clearly demonstrates

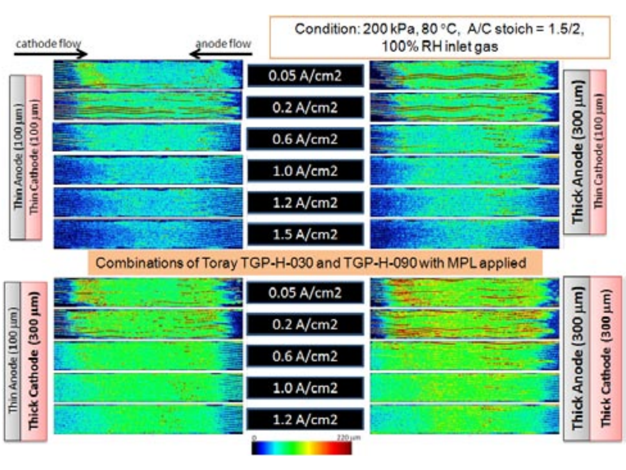

FIGURE 1. Water Distributions with Different Combinations of Thin and Thick Diffusion Media

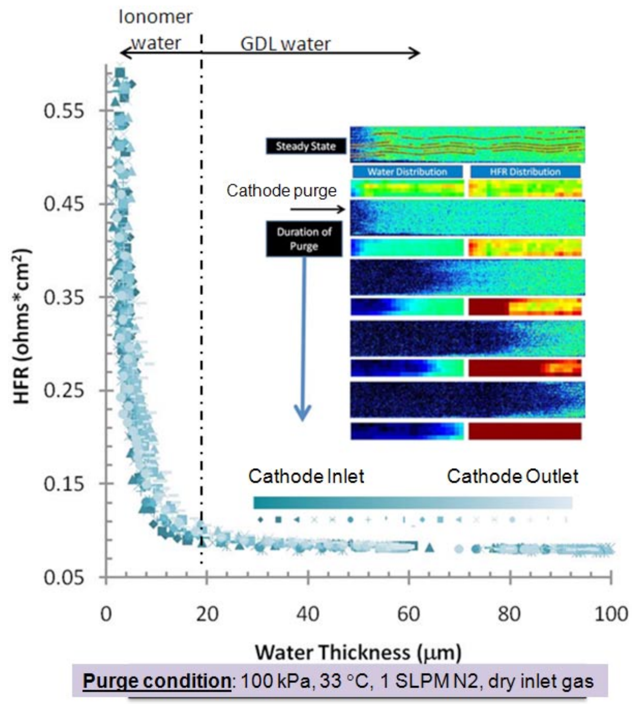

FIGURE 2. Correlation between Liquid Water Thickness and HFR during Cathode Purge

that the water removal rate during shutdown purge for freeze is constrained by water transfer through the membrane.

Various changes to the baseline GDL-channel systems, including channel surface treatment (hydrophobic or hydrophilic), channel geometries (sinusoidal, trapezoidal or rectangular), GDL Teflon® (poly-tetrafluoroethylene, PTFE) content and GDL thickness, were implemented in order to obtain the combination of GDL materials and flow channel design which give out the optimal ex situ performance. The channel surface energy displays significant impact on channel two-phase flow. The hydrophilic channel (contact angle, θ ~10°) was found to facilitate the removal of liquid water and decrease the slug formation tendency compared to the case of non-treated channels (θ ~60°), while the hydrophobic channel (θ ~105°) displays a large number of stationary water droplets or small slugs. The effects of different channel geometries, including sinusoidal geometry representing the stamped metal bipolar plate and trapezoidal geometry representing the molded carbon composite bipolar plate, on the two-phase flow in channels, were compared to the rectangular geometry (maintaining same hydraulic diameter) and no significant impact was found in terms of the two-phase flow pattern map. This confirms the validity of the selection of the baseline rectangular channel design. The effects of GDL PTFE content and thickness on channel two-phase flow were carried out using Toray GDL with different thickness (190 µm for TGP-H-060 and 380 µm for TGP-H-120) and different PTFE contents (0-40 wt%). While GDL thickness shows little influence on the ex situ two-phase flow, the PTFE content shows remarkable impact on the flow pattern map. Plain GDL (non-PTFE treated) was shown to be completely wetted by water and a continuous water film was developed on GDL surface. In contrast, PTFE treatment promotes the formation of water slugs and films along the channel walls and little water resides on the GDL surface due to its hydrophobicity. As PTFE content increases, the transition from slug to film flow shifted to higher superficial air velocity, and no significant difference in flow pattern was found with further increasing hydrophobicty at PTFE content above 20 wt%.

Water breakthrough dynamics, characterized by the capillary pressure and water saturation, were determined ex situ with baseline and single gas layer GDLs with and without MPL. The water breakthrough in GDLs has been found to occur at a few preferential locations in both baseline and single gas layer GDLs, with the dynamic characteristics of this process having been observed. The dynamic behavior was reflected in two aspects: dynamic capillary pressure (or recurrent breakthroughs) and dynamic breakthrough locations (or changing of breakthrough locations with time). Generally small water saturations (less than 10%) were observed for GDLs at breakthrough and MPL was found to further reduce the water saturation in GDL. No changing of water breakthrough locations was observed in GDLs with MPL. This result suggests that MPL play a role in stabilizing the preferential water pathways.

Based on these observations, we have proposed a new water transport mechanism to account for the water breakthrough in GDLs (Figure 3). This mechanism is based on Haines jump dynamics [2,3]. Water drainage through a GDL occurs in a step-wise process. The water in GDLs remains unmoved until the point at which the pressure in water increases above the capillary pressure at the largest restriction and, at this point, the invading water suddenly moves into the adjacent pores. In the case of water breakthrough on the GDL surface, 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 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.

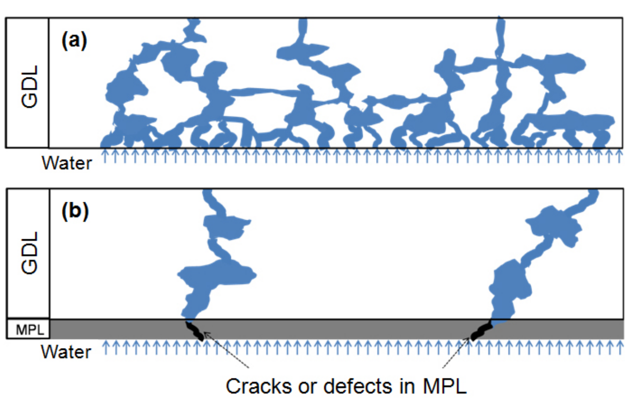

FIGURE 3. Schematic of water drainage in a GDL (a) without MPL, displaying a large number of water entry points into the GDL; and (b) with MPL, restricting water entry into GDL only at the crack/defect locations in the MPL.

The pseudo-Hele-Shaw experiment was conducted to determine the water distribution inside the fuel cell and to quantify the amount of water held in the GDL. 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 (Ce) is plotted against the non-dimensional time (t*) a simple logarithmic dependence was obtained.

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 consists of the cross-sectional portion of GDL under a single gas channel. The impacts of the morphological and wetting properties of the GDL on the water transport were studied. 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. Even though the water percolates, forming a different array of fingers for different pore size distributions, it was found that the percolation pressure is the same for GDLs having the same pore size histogram. The effects of 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. 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 a perforation or defect in the MPL.

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 experimental data. The comparison between the numerical and the experimental pseudo-Hele-Shaw experiments are plotted in Figure 4. An effective internal contact angle of 135 degrees collapsed the numerical simulation onto the experimental data. Thus, the behavior of liquid water in GDLs can be effectively characterized experimentally and can be captured in a simple computational tool.

A new model for predicting the morphology of water in the flow field has been developed using *Surface Evolver*. A parametric study of the critical volume at which a liquid drop will transform spontaneously into a liquid plug in a channel has been completed for variations in the channel bend dihedral, channel contact angle and GDL contact angle. This model can be used to predict the rate of liquid plug formation for a given current density and flow field configuration.

Conclusions and Future Directions

A major driving force for this research project 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:

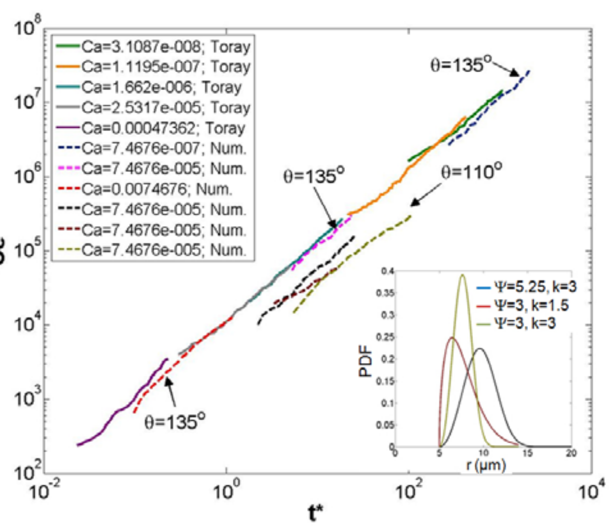

FIGURE 4. Comparison of Numerical and Experimental Psuedo-Hele-Shaw Experiments Showing Excellent Agreement for Toray Paper using an Effective Internal Contact Angle of 135 Degrees

- 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.

FY 2010 Publications/Presentations

Book Chapters

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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

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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).

12. J.J. Gagliardo, J.P. Owejan, T.A. Trabold, T.W. Tighe, "Neutron Radiography Characterization of an Operating Proton Exchange Membrane Fuel Cell with Localized Current Distribution Measurements," *Nuclear Instruments and Methods in Physics Research Section A: Accelerators, Spectrometers, Detectors and Associated Equipment*, 605 (1-2), 115-118 (2009).

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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 7^{th} International Conference on Nanochannels, Microchannels and Minichannels ICNMM2009*, Pohang, South Korea (2009).

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