

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

Satish Kandlikar (Primary Contact),  
Thomas Trabold, Jeffrey S. Allen  
Rochester Institute of Technology  
2001 Gleason Building  
76 Lomb Memorial Drive  
Rochester, NY 14623  
Phone: (585) 475-6728; Fax: (585) 475-7710  
E-mail: sgkeme@rit.edu

DOE Technology Development Manager:  
Donna Ho  
Phone: (202) 586-8000; Fax: (202) 586-9811  
E-mail: Donna.Ho@ee.doe.gov

DOE Project Officer: David Peterson  
Phone: (303) 275-4956; Fax: (303) 275-4788  
E-mail: David.Peterson@go.doe.gov

Technical Advisor: John Kopasz  
Phone: (630) 252-7531; Fax: (630) 972-4405  
E-mail: Kopasz@anl.gov

Contract Number: DE-FG3607GO17018

### Subcontractors:

- General Motors, Honeoye Falls, NY
- Michigan Technological University, Houghton, MI

Project Start Date: March 1, 2007  
Project End Date: February 28, 2010

### Objectives

- Improve fundamental understanding of the water transport processes in the 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 Hydrogen, Fuel Cells and Infrastructure Technologies (HFCIT) 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 HFCIT Multi-Year RD&D Plan:

- Unassisted start from low temperature:  $-40^{\circ}\text{C}$
- Durability with cycling at operating temperature of  $\leq 80^{\circ}\text{C}$ : 5,000 h
- Energy density: 2 kW/L

### Accomplishments

In the last year, the project 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.
- Implemented changes to the baseline channel surface energy and GDL materials and evaluated their performance with the ex situ multi-channel experiments. It was also found that the microporous layer (MPL) promotes the formation of the mist flow pattern at high air flow regimes and the formation of large slugs in the channels in the low air flow regime. Both of these two effects are related to the reduction of the water saturation and

- the number of water breakthrough locations in the GDL caused by the MPL.
- Simultaneously visualized the water transport on cathode and anode channels of an operating fuel cell. It was found that under 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 the 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 the 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 the 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 of the GDL sample can be obtained simultaneously. This imaging technique reveals internal damage to the GDL due to compression.



## 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:

- Two-phase (water and gas) transport in the fuel cell stack, including the GDL, flow channels, and their interfaces.
- Structural and surface properties of materials and how they change during operational events, such as freeze/thaw.

- 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 will be 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

One of the important issues in developing efficient purge strategies relates to the location of liquid water, i.e., anode vs. cathode. 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. This independence indicates that the purge dynamics are dominated by the relative humidity conditions of the channel-level air stream and for a given shutdown condition the 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 rate over small “differential” regions of the fuel cell active area where the relative humidity conditions within the channel are approximately constant. These experiments revealed a distinctly faster removal rate from the cathode side than from the anode side (Figure 1), and implied that a significant resistance was introduced by the membrane to anode water removal by the cathode air steam. Applying a similar method to the analysis of purge of water generated during in situ experiments indicates that most of the water removed by the air purge resides on the anode side of the fuel cell.

The baseline characterization revealed that shutdown purge time and energy are mainly constrained by the quantity of liquid water retained in the GDL during operation prior to shutdown. Increasing GDL thermal conductivity will effectively lower the MEA temperature and, thus, decrease the concentration gradient that drives water vapor from the electrode to the channel. The impact of GDL thermal conductivity on saturation at various operating conditions was tested. Initial results indicate that water accumulation is sensitive to thermal conductivity, especially at higher temperatures, as shown in Figure 2. This is due to the

# Mass Transfer Evaluation

Requires differential evaluation where change in channel RH is less significant

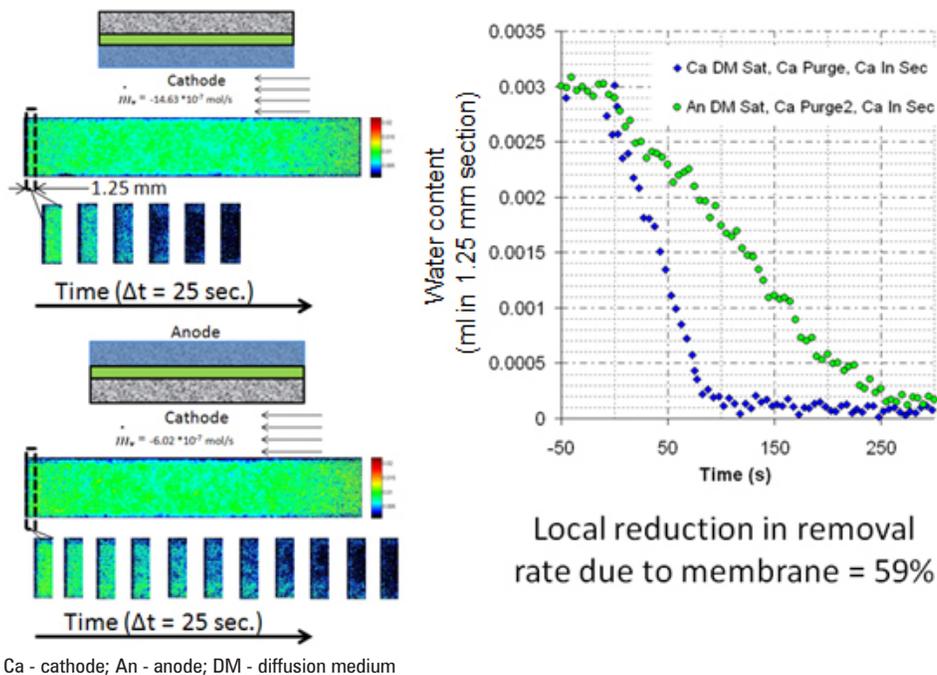


FIGURE 1. Mass Transfer Evaluations on Differential Elements at the Inlet Edge of the Active Area

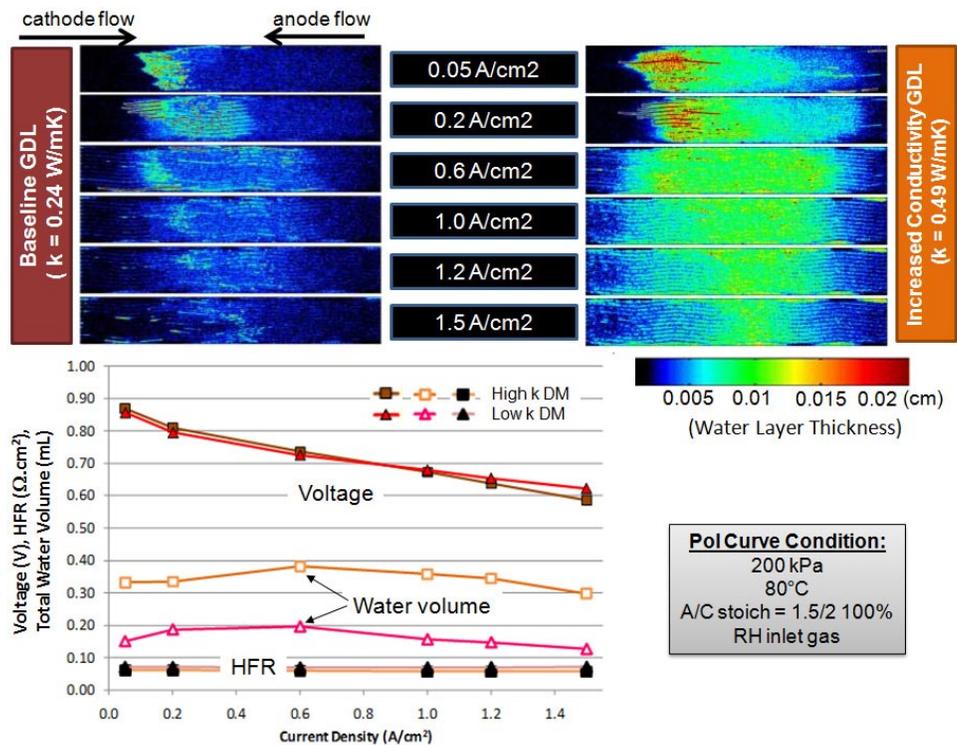


FIGURE 2. Impact of Thermal Conductivity on GDL Saturation at 80°C

fact that reducing saturation pressure near the MEA with an increased thermal conductivity GDL effectively brings the condensation front deeper into the GDL, resulting in higher steady state liquid water content.

Freeze start experiments were conducted with the baseline fuel cell system. It was observed that the freeze start at  $-20^{\circ}\text{C}$  from a shut-down condition with 15 seconds air purge or less fails due to the complete blockage of reactant flow paths caused by the ice formation at the end of the bipolar plate and at the channel-to-manifold transition region. However, with longer shutdown air purges, it was possible to generate power for some period until the voltage fell below 200 mV (presumably due to ice filling the electrodes).

Changes to the baseline channel surface energy were implemented by treating the channel with a hydrophilic coating ( $\theta \sim 11^{\circ}$ ) provided in-house by General Motors and the effects of this change on the two-phase flow in channels were studied. The hydrophilic channel was found to facilitate the removal of liquid water compared to the case of non-treated channels ( $\theta \sim 60^{\circ}$ ) (Figure 3). For the hydrophilic channels, the transition line of slug/film patterns is significantly shifted toward lower air velocities, indicating the reduced slug formation tendency. It was found that the MPL promotes the formation of not only the mist flow pattern but also large slugs in the channels. This is ascribed to the role of the MPL which reduces the water saturation and limits the water breakthrough locations in the GDL which is predicted numerically as shown in Figure 4.

During the in situ fuel cell experiments with visualization on both cathode and anode it was found that, under dry hydrogen/air conditions at lower temperatures ( $35^{\circ}\text{C}$  in this study), the cathode channels display a similar flow pattern map to the ex situ experiment at similar conditions, as expected. On the anode side it was found that: i) anode liquid water formation occurs largely due to condensation of water vapor which is transported through the anode GDL; ii) the greatest liquid water activity was observed downstream, similar to that observed in the cathode channels, indicating a transition point from single- to two-phase flow along the channels; and iii) the water content in the anode channels decreases and the water content in the cathode channels increases as current density increases.

The pseudo-Hele-Shaw experiments on GDLs demonstrate the importance of drainage transport mechanisms which are not properly accounted for in current transport models of PEMFCs. A two-dimensional numerical model (see Figure 4) was developed to study drainage transport in the GDL. Five contact angles and six pore size distributions for a GDL with an MPL were studied. The contact angle affects the percolation pressure, but not the saturation curve. The average pressure at which the water percolates through

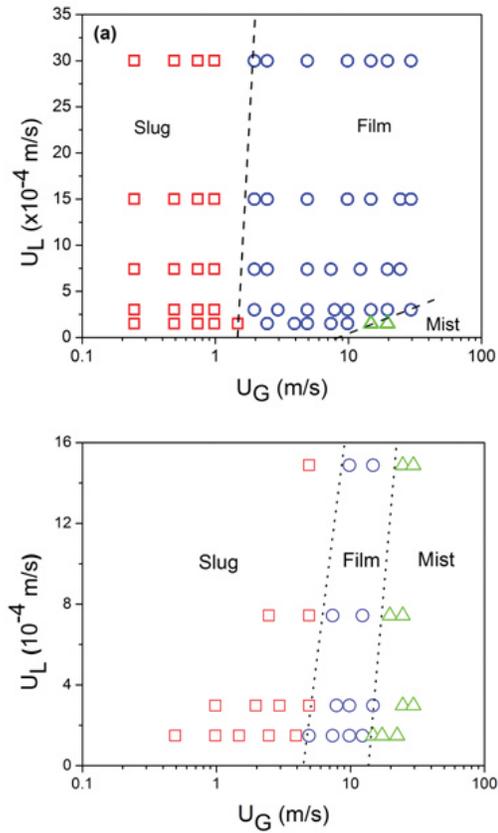


FIGURE 3. The two-phase flow pattern map for (a) hydrophilic channel and (b) non-treated channel tested with baseline GDL in the ex situ multi-channel test apparatus.

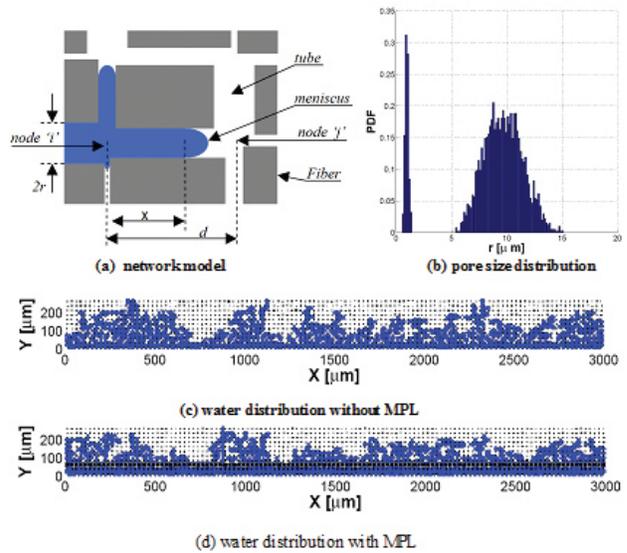


FIGURE 4. Numerical simulation of water transport in the cathode. Water distributions are shown (c) without an MPL and (d) with an MPL when liquid water first enters the flow channel. Blue represents water, white represents air, and black represents the fiber structure of the diffusion media.

the gas diffusion layer decreases as the average pore size increases. The effect of the MPL is to reduce the amount of water in the GDL which enhances capillary fingering and subsequently facilitates reactant transport to the catalyst layer. The presence of the MPL also results in a high pressure in the catalyst layer forcing the anode and cathode catalyst layers and the PEM to be fully saturated with water (see Figure 4).

Static contact angle measurements have shown the contact angle of water on GDLs to be dependent on the material, the temperature and the drop size. As the drop size decreases, so does the static contact angle. The drop size dependence of the contact angle has been previously reported on polymeric, substrates. The effect is exacerbated on the GDLs most likely due to the drop deposition method as well as the rough, porous surface and the poly-tetrafluoroethylene coating.

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.

Statistical analysis of GDL images taken in a SEM has been shown to provide information on distributions of pore size, pore shape, pore orientation, and nearest neighbors. In addition, stereo SEM imaging allows for determining of the distribution of pore depth and volumes. The SEM image analysis has the potential to replace traditional porosimetry techniques for characterizing GDLs.

## Conclusions and Future Directions

In the last year, changes to the baseline GDL and flow channel were implemented and the performance was evaluated with ex situ and in situ experiments. GDLs with lower thermal conductivity and channels with hydrophilic coating have been demonstrated to facilitate the water removal and decrease the water accumulation in fuel cells. Water accumulation locations and water removal dynamics during shutdown purge have been clarified. New developments in advanced techniques, including a new printed circuit board device and SEM image analysis of GDL morphology, have provided new insight into the water distribution and transport inside a fuel cell.

A key contribution from the previous studies is that the time and energy needed for liquid water removal during cathode purge is predominantly controlled by the volume of liquid water present at shutdown. Thus, in the future, the new material and design set selection will focus on changes which are expected to

minimize the accumulation of water during steady-state operation. These directions include i) GDLs having lower thermal conductivity and thinner thicknesses (it is reasonably assumed that thinner GDL will have less water accumulation), ii) the flow field material with significantly increased or decreased surface energy, which are 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, and iii) the channels with geometric features that are more representative of full-size automotive hardware, including stamped metal and molded carbon composite bipolar plates.

The numerical simulation will be expanded to study the effects of cracks on microporous layer as well as to study the effect of mixed wettability (wetting and non-wetting) porous on the gas diffusion media. The ex situ pseudo-Hele-Shaw experiments will be performed on different gas diffusion layers in order to classify them depending on their wettability and morphological properties. The experimental data obtained from this ex situ experiment will be used to validate the numerical simulation through non-dimensional analysis. The sensitivity of pore size distribution data obtained from SEM image analysis, as characterized by the Weibull distribution parameters, to magnification and large pore size cutoff will be studied. The results of this study should allow for a standardization of the technique for characterizing GDL morphology.

## FY 2009 Publications/Presentations

1. 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," submitted for publication in *J. Electrochem. Soc.* (2009).
2. Kandlikar, S.G., Lu, Z., Lin, T.Y., Cook, D., Daino, M., "Uneven Gas Diffusion Layer Intrusion in Gas Channel Arrays of Proton Exchange Membrane Fuel Cell and Its Effects on Flow Distribution," *J. Power Sources*, 2009, doi:10.1016/j.jpowsour.2009.05.019.
3. Kandlikar, S.G., Lu, Z., Domigan, W.E., White, A. D., Benedict, M.W. "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).
4. Kandlikar, S.G. and Lu, Z., "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.*, 2009 (6), in press.
5. Gagliardo, J.J., Owejan, J.P., Trabold, T.A. and Tighe, T.W., "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*, 605, 115-118 (2009).

6. Owejan, J.P., Gagliardo, J.J., Sergi, J.M., Trabold, T.A. and Kandlikar, S.G., "Water Management Studies in PEM Fuel Cells. Part I: Fuel Cell Design and In-Situ Water Distributions," *International Journal of Hydrogen Energy*, 34, 3436-3444 (2009).
7. Zu, L., Rath, C., Grimm, M., Domigan, W., White, A.D., Hardbarger, M., Kandlikar, S.G., Owejan, J.P. and Trabold, T.A., "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," *Intl J. Hydrogen Energy*, 34, 3445-3456 (2009).
8. Parikh, N., Allen, J.S., Yassar, R.S., "Effect of Deformation on Electrical Properties of Carbon Fibers used in Gas Diffusion Layer of PEM Fuel Cells," *J. Power Sources*, in press.
9. Médiçi, E., and Allen, J.S., "Existence of the Phase Drainage Diagram in Proton Exchange Membrane Fuel Cell Fibrous Diffusion Media," *J. Power Sources*, 191, 417-427 (2009).
10. Meng, D.D., and Allen, J.S., "Micro and Nanofluidics for Energy Conversion", *IEEE Nano Magazine*, 2, 19-23 (2008).
11. Trabold, T.A., Owejan, J.P., Gagliardo, J.J., Jacobson, D.L., Hussey, D.S. and Arif, M., "Use of Neutron Imaging for Proton Exchange Membrane Fuel Cell (PEMFC) Performance Analysis and Design," in *Handbook of Fuel Cells: Advances in Electrocatalysis, Materials, Diagnostics and Durability*, Volumes 5 & 6, Vielstich, W., Gasteiger, H.A. and Yokokawa, H. (Eds.), John Wiley & Sons Ltd., Chichester, UK, pp. 658-672 (2009).
12. Allen, J.S., Son, S.Y., Collicott, S.H., "Proton Exchange Membrane Fuel Cell (PEMFC) Flow-Field Design for Improved Water Management," in *Handbook of Fuel Cells: Advances in Electrocatalysis, Materials, Diagnostics and Durability, Volumes 5 & 6*, Vielstich, W., Gasteiger, H.A. and Yokokawa, H. (eds.). John Wiley & Sons Ltd, Chichester, UK, 687-698.
13. Sergi, J.M., Lu, Z., and Kandlikar, S.G., "In Situ Characterization of Two-phase Flow in Cathode Channels of an Operating PEM Fuel Cell With Visual Access," *Proceedings of ASME ICNMM2008, 6<sup>th</sup> International Conference on Nanochannels, Microchannels and Minichannels*, Paper ICNMM2009-82140, Pohang, South Korea, June 22-24, 2009.
14. Gagliardo, J.J., Owejan, J.P., Trabold, T.A. and Tighe, T.W., "Neutron Radiography Characterization of an Operating Proton Exchange Membrane Fuel Cell with Localized Current Distribution Measurements," *Proceedings of the 6<sup>th</sup> International Topical Meeting on Neutron Radiography (ITMNR-6)*, Kobe, Japan, September 14-18, 2008.
15. Owejan, J.P., Gagliardo, J.G., Sergi, J.M. and Trabold, T.A., "Two-Phase Flow Considerations in PEMFC Design and Operation," *Proceedings of ASME ICNMM2008, 6<sup>th</sup> International Conference on Nanochannels, Microchannels and Minichannels*, Paper ICNMM2008-62037, Darmstadt, Germany, June 2008.
16. Lu, Z., White, A.D., Pelaez, J., Hardbarger, M., Domigan, W., Sergi, J., and Kandlikar, S.G., "Investigation of Water Transport in an Ex-Situ Experimental Facility Modeled on an Actual DOE Automotive Target Compliment Fuel Cell," *Proceedings of ASME ICNMM2008, 6<sup>th</sup> International Conference on Nanochannels, Microchannels and Minichannels*, Paper ICNMM2008-62200, Darmstadt, Germany, June 23-25, 2008.
17. Stacy, R.E., "Contact Angle Measurement Technique for Rough Surfaces," M.S. Thesis, Michigan Technological University, June 2009.
18. Lechnyr, J.W., "Imaging of Fuel Cell Diffusion Media Under Compressive Strain," M.S. Thesis, Michigan Technological University, May 2009.
19. Médiçi, E., Allen, J.S., "Two dimensional network model simulations of water percolation through a GDL," *Proceedings of the Twentieth International Symposium on Transport Phenomena*, Victoria, BC, Canada, July 2009.
20. Lechnyr, J.W., Fritz, D.L., Allen, J.S., "Imaging of Fuel Cell Diffusion Media Under Compression," *Proceedings of the Twentieth International Symposium on Transport Phenomena*, Victoria, BC, Canada, July 2009.
21. Herescu, A., Allen, J.S., "The Effect of Surface Wettability on Viscous Film Deposition," *Proceedings of the 7<sup>th</sup> International ASME Conference on Nanochannels, Microchannels and Minichannels*, Pohang, South Korea, June 22-24, 2009.
22. Allen, J.S., "Water Management in Automotive Fuel Cells - Insurmountable problem or opportunity?," invited panel member for *Fuel Cells: The Future of Sustainable Automotive Transportation - Fact or Fiction?*, 2008 ASME International Mechanical Engineering Conference and Exposition, Boston, Massachusetts, November 3, 2008.