V.F.4 Investigation of Micro- and Macro-Scale Transport Processes for Improved Fuel Cell Performance

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Contract Number: DE-EE0000470

Subcontractors:
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- University of Tennessee, Knoxville, TN
- Rochester Institute of Technology, Rochester, NY

Project Start Date: June 1, 2010
Project End Date: May 31, 2013

Fiscal Year (FY) 2011 Objectives

- Characterize saturated relationships in state-of-the-art fuel cell materials.
- Obtain a comprehensive down-the-channel validation data set for a baseline and auto-competitive material set.
- Optimize component models to output bulk and interfacial transport resistances.
- Demonstrate integrated transport resistances with a one plus one-dimension (1+1D) fuel cell model solved along a straight gas flow path.
- Identify critical parameters for low-cost material development.

Technical Barriers

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

(B) Cost

(C) Performance

(D) Water Transport within the Stack

Technical Targets

This project supports fundamental studies of fluid, proton and electron transport with focus on saturated operating conditions. Insights gained from these studies are being used to develop modeling tools that capture fundamental transport physics under single and two-phase conditions. This project addresses the expected outcomes from Topic 4a as follows:

- Validated transport model including all component physical and chemical properties:
  - Down-the-channel pseudo-two-dimension (2D) model will be refined and validated with data generated in the project.
- Public dissemination of the model and instructions for exercise of the model:
  - Project website to include all data, statistics, observations, model code and detailed instructions.
- Compilation of the data generated in the course of model development and validation:
  - Reduced data used to guide model physics to be published and described on project website.
- Identification of rate-limiting steps and recommendations for improvements to the plate-to-plate fuel cell package:
  - Model validation with baseline and auto-competitive material sets will provide key performance limiting parameters.

FY 2011 Accomplishments

- Generated distributed down-the-channel current, ohmic resistance, temperature and liquid water validation data for a baseline material set.
- Developed new characterization methods to measure transport relationships as a function of saturation.
- Generated characterization data for bulk and interfacial transport in bulk membrane, thin ionomer films, dispersed catalyst layers, gas diffusion layers and gas delivery channels.
- Developed wet model framework.

- Published validation and characterization data to a project website at: www.pemfcdata.org.

Introduction

The transport physics associated with fuel cell operation is widely debated amongst researchers because comprehensive micro/nano-scale process validation is very difficult. Furthermore, fuel cell operation has a strong interdependence between components making it difficult to separate the key relationships required for predictive models with ex situ methods. Generally, a validated model that predicts operation based on known design parameters for fuel cell hardware and materials is highly desired by developers. Such a model has been proposed by many research groups for dry (less than 100% relative humidity [RH] exhaust) operation with moderate success, however these modelers unanimously assert that their ability to predict wet operation is limited by two-phase component-level understanding of transport processes. Additionally, as two-phase models continue to be refined; benchmarking progress is difficult due to incomplete validation datasets.

In the current work, our team is developing characterization tools for saturated relationships based on the evolution of a dry 1+1D model for accurate wet prediction [1]. To complement this work we are also developing a comprehensive validation dataset based on a wide proton exchange membrane fuel cell (PEMFC) operating space. As data and modeling reach a final form, these are uploaded to a project website at www.pemfcdata.org. All characterization and validation work is conducted with a common material set.

Approach

This project is organized around baseline and next-generation material sets. These materials define parametric bounds for component and integrated down-the-channel modeling efforts. The baseline material set was chosen based on the commercial state of the art that exists today. The next-generation material set consists of transport impacting parametric changes that are in-line with the DOE 2015 targets for reduced cost while improving durability and performance. For characterization and validation experiments, a standard protocol was also developed to enable the team to conduct experiments with the same boundary conditions.

The first phase of this project was experimentally focused on characterization work that is organized by transport domain, comprising thin film ionmers, bulk membranes, porous electrodes, gas diffusion layers and flow distribution channels. More specifically, the key relationships being investigated are outlined as follows:

- Ionomer Characterization
  - Membrane water uptake, water diffusivity and hydraulic permeability.
  - Oxygen and water transport as a function of ionomer layer thickness.
  - Evidence of nanophase/water morphological changes vs. film thickness.
- Diffusion Layer Characterization
  - Microporous layer thermal conductivity and D/D_{eff} as a function of saturation.
  - Catalyst layer liquid water pressure as a function of saturation, pore size, and hydrophobicity.
  - Substrate thermal conductivity (wet and dry) and D/D_{eff} as a function of saturation.
  - Through-plane saturation and wet region boundary as a function of dT and operating temperature.
- Channel Characterization
  - Carbon fiber paper (CFP) to channel interfacial transport resistance as a function of channel saturation.
  - Channel dP as a function of saturation, temperature, flow, and current density.
  - Manifold dP as a function of saturation, temperature, and flow.

These relationships are required to develop component models that output bulk and interfacial transport resistances to the project 1+1D down-the-channel model. In anticipation of this integrated model, a validation data set is being collected in parallel with small scale hardware specifically designed to include automotive stack constraints [2].

Results

Project Website

The project website was made available to the public at www.pemfcdata.org. This information tool is designed for sharing project data and modeling with the broader fuel cell research community to provide a common validation tool that generates dialog about fundamental transport physics in PEMFCs. A navigational map of the current website is given in Figure 1.

This website contains a 'Home' and 'Project' page that describes the funding, participants, news, approach, deliverables, standard materials and testing protocol. The 'Macro' page contains the down-the-channel validation data for the baseline material set and the next-generation material set will be uploaded in the next phase of the project. The 'Micro' page is continuously being updated with characterization data as it becomes available. The list of model parameters is posted to the 'Parameters' page. This list is currently posted for the dry-based model only, which is available on the 'Modeling' page (the wet model is currently being developed and will be posted in the second phase

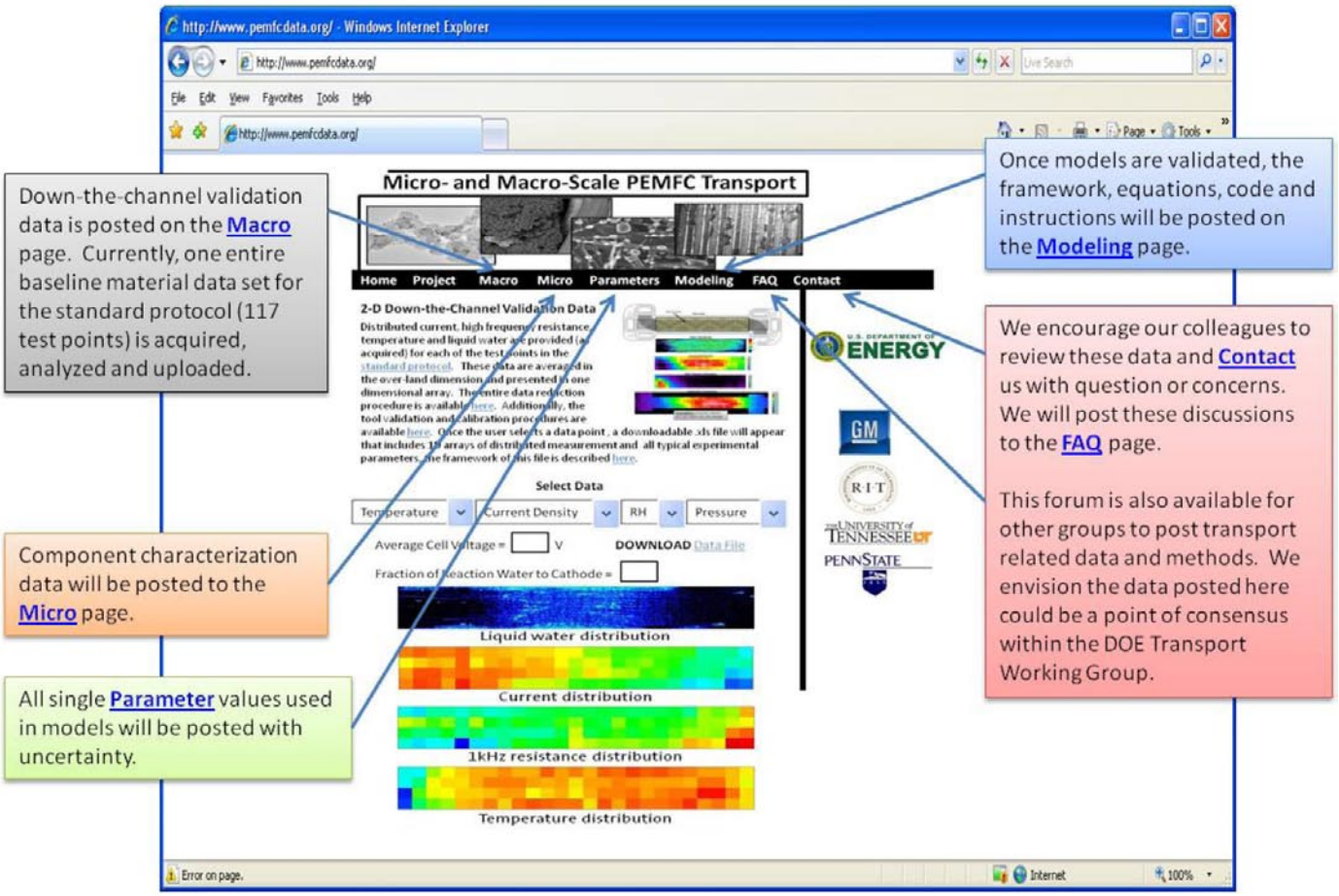

FIGURE 1. Project Website Navigational Map

of the project). Finally, the 'Contact' and 'FAQ' pages are intended to initiate dialog regarding our data and approach.

Baseline Validation Data

Experimental variability was carefully examined prior to collecting the baseline material set data for the 117 point standard protocol. With regard to the controlled test parameters, temperature control with cartridge heaters was found to have the most significant impact on test variation. RH fluctuations within the cell result from temperature variations as heaters cycle, and this impacts all aspects of transport within the cell. Liquid coolant with flow and temperature control was used to mitigate this experimental variability, which was confirmed with our temperature distribution tool by comparing the temperature distributions with and without coolant. This comparison showed a constant temperature profile is achieved with liquid coolant. Moreover, the temperature distribution is more representative of a commercial fuel cell system with coolant, as the temperature gradient should increase toward the coolant outlet side. For this reason, most 50 cm^2 validation experiments will utilize liquid coolant during the course of the project.

The validation data set includes distributed liquid water, current, high frequency resistance and temperature measured across the active area. Additionally, anode vs. cathode water balance based on condensed outlet water was collected for each test point. A tool (shown in Figure 1) was developed to navigate this database such that our team and other interested researchers can select a test point from the standard protocol to download the raw and processed data. Currently the validation dataset is fully populated for the baseline material set.

Transport in Thin Ionomer Films

Ellipsometric, microbalance, and fluorescence measurements on thin Nafion® films have been performed on model surfaces. These characterization techniques on ionomer films with thicknesses between 30 and 600 nm are designed to probe the transport and swelling properties of the thin ionomer films in the catalyst layers. Ellipsometry and microbalance measurements can give us highly accurate measurements of the water content and swelling of these films as a function of RH. The fluorescence measurements shed light on the dynamics of the film, which governs the

water self-diffusion and transport properties. Fluorescence measurements probe the dynamics in the aqueous domains and we have also used grazing incidence small-angle X-ray scattering to probe their structure. Both the water uptake or hydration number (λ) and self-diffusion of water within the film determines its oxygen and proton transport properties as these species move through the aqueous domains of the material. Select microbalance and fluorescence are presented herein to demonstrate the sensitivities being observed in thin films.

Microbalance results shown in Figure 2a indicate that water content for different film thicknesses was similar for Nafion® films on gold thicker than 500 nm [3]. At lower thicknesses, slightly lower water contents were observed, especially at high vapor water activities. The origin of the observed depression in water content is still unclear. Interaction of the ionomer with the Au substrate could constrain the film from swelling, which is essential for water sorption. It is also conceivable that a water impermeable layer (disordering of water channels) at the gas/ionomer interface may contribute to the observation. Fluorescence intensity measurements of 9-([E]-2-carboxy-2-cyanovinyl) julolidine (CCVJ) in thin Nafion® films given in Figure 2b show that the fluorescence response is a function of thickness. Higher I/Io response indicates stiffening of the film upon water uptake which is not observed for the membrane, but has been reported for other thin films [4]. Since the CCVJ fluorescence signal is controlled by the local viscosity or mobility of the sample, it can be used to measure water diffusion in polymers [5]. The I/Io signal will be related to the self-diffusion coefficient of water in the next phase of this work. These measurements indicate different water dynamics in thin and thick films and provide fundamental information on potential differences in proton conductivity and other transport properties as a function of film thickness.

Transport in Diffusion Materials

Several in situ and ex situ measurements are being used to measure transport in the porous components that include the electrode, microporous layer and carbon fiber macroporous substrate. In situ neutron imaging, infrared imaging and acoustic microscopy are being used to map through-plane liquid water distributions within the anode vs. cathode diffusion layers. Ex situ work is focused on thermal conductivity and mass diffusivity as a function of water saturation, and capillary pressure relationships for the baseline diffusion media and catalyst layer are underway. Unique test cells and methodology capable of controlling saturation have been developed to complete this testing.

One characteristic result from the standard protocol has been selected for presentation in this paper and the complete reduced data set has also been made public at the website. Measured with high resolution neutron imaging, Figure 3a shows the effect of anode vs. cathode outlet pressure differentials on water saturation. The operating temperature is 40^{0}C, anode/cathode RH is 95/95% and the current density is 0.8 A/cm^2. It is evident from the plot how the higher pressure on the cathode side shifts the saturation towards the anode and vice versa. These data provide insight into the complex water balance to be modeled. The corresponding voltages have also been recorded in the plot. Polarization curves obtained with fast scans after each operating condition (Figure 3b) demonstrate the effect of the pressure differential on performance. The false color images in Figure 3c show the regions of water accumulation relative to the land/channel geometry for the specific operating conditions. These data also indicate how sensitive anode gas diffusion layer (GDL) saturation is, and this is not typically considered in two-phase models to this point.

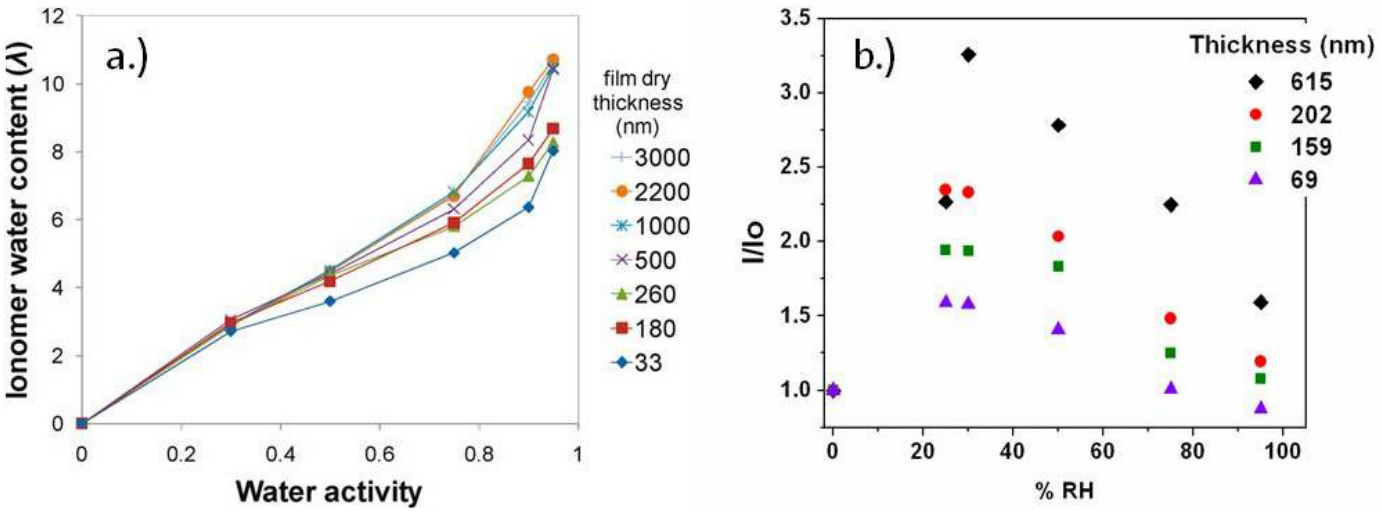

FIGURE 2. Water interaction with varying thicknesses of thin Nafion® films as a function of water activity: a) water uptake at 80°C, b) CCVJ fluorescence response at 25°C.

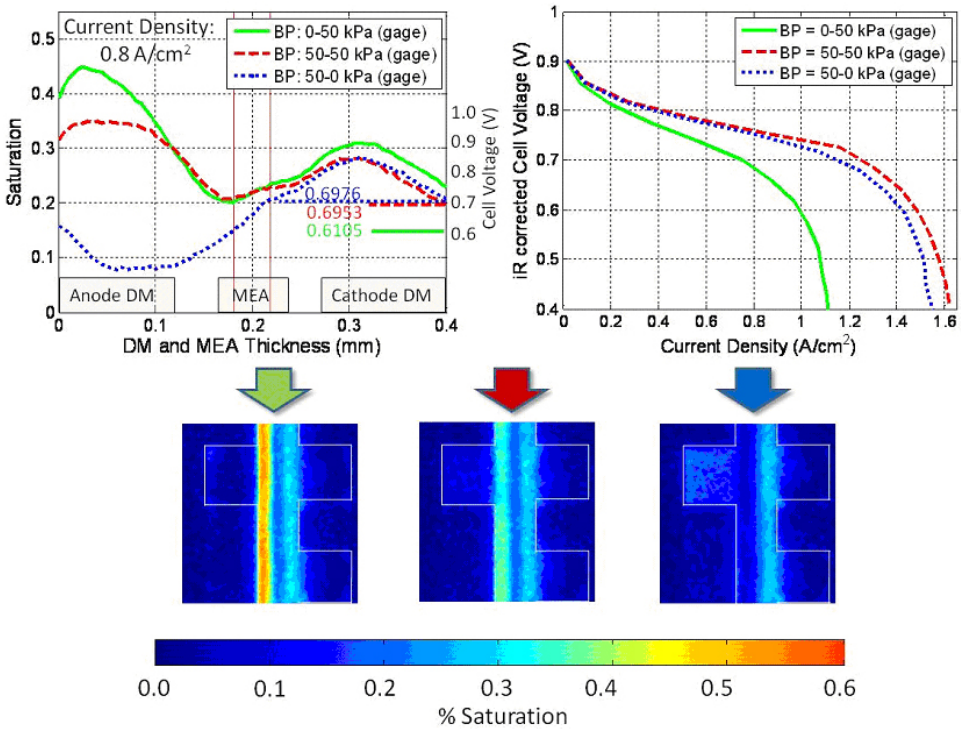

FIGURE 3. Impact of varied outlet pressure: a) GDL water saturation and through-plane, b) polarization curves, c) false color images showing saturation.

Transport in Flow Distributor Channels

Two key components of the down-the-channel model are the relationships between channel water saturation and both CFP to channel interfacial transport resistances, and the channel pressure drop. Therefore, it is critical to establish a well-defined channel water saturation metric. A technique has been developed to quantify the in situ channel water saturation through the combined utilization of high speed videos of the flow field channels during operation and digital image processing [6]. The image processing algorithm automatically detects static and dynamic liquid water, and also characterizes the flow structure of each water object. The water coverage ratio parameter along with channel pressure drop as a function of saturation are providing crucial information pertaining to transport resistance associated with liquid water accumulation in the flow field channels. Sample images showing pre- and post-processed flow field channels and the resulting water detection are shown in Figure 4. In addition to this characterization of water adjacent to the CFP in the active area, experiments are underway to characterize the resistance of liquid water transitioning from the bipolar plate micro-channels in the gas manifolds of a fuel cell stack. Here the combination of low gas shear and contact line pinning has been found to cause water stagnation at the plate edge. This results in additional plate-to-plate flow variations that must be captured in a true two-phase fuel cell model.

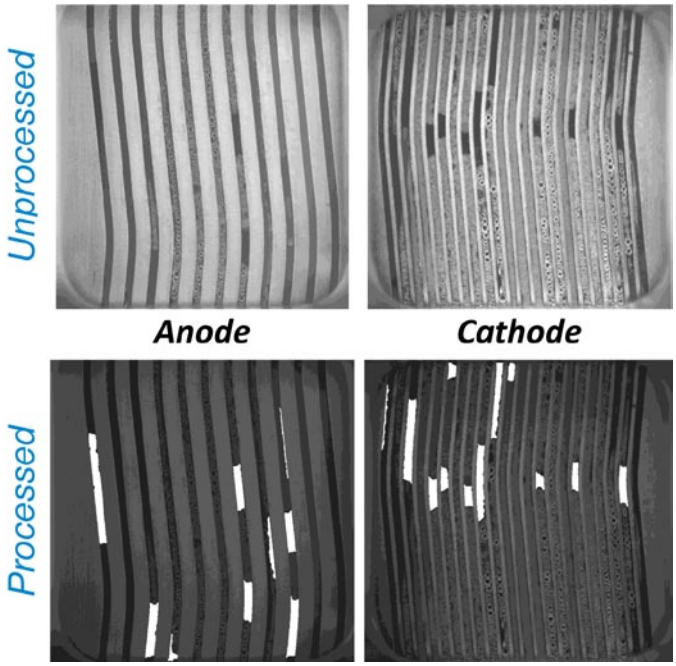

FIGURE 4. Representative unprocessed and processed high speed images of liquid water distribution in both anode and cathode channels. The processed images can provide quantified information of local and overall water coverage ratio.

To optimize the channel design for better water management, the effects of channel surface wettability, cross-sectional geometry and orientation on the two-phase flow in parallel gas channels were investigated. It was found that hydrophilic channels are advantageous over uncoated or slightly hydrophobic channels in terms of uniform water and gas flow distribution and promoting film flow. Stamped metal geometry channels favor film flow when compared to a rectangular geometry. Vertical channel orientation is advantageous over horizontal orientation because it is less prone to slug flow, and facilitates more uniform liquid water distribution and stable operation.

Conclusions and Future Directions

A well organized characterization, modeling and validation framework was developed early in this project. The first phase of execution was largely focused on experimental development with key accomplishments outlined as follows:

- Project is standardized by materials and operating space:
  - Baseline and auto-competitive material sets chosen based on parametric variations that consider degradation and cost vs. performance trade-offs.
- Key relationships required for a wet 1+1D model and characterization methods are defined:
  - Subject matter experts are developing and executing characterization methods to generate physical understanding of fundamental processes.
  - Component models describing processes are being generated and will be used to output bulk and interfacial transport resistances.
  - Modeling framework for 1+1D model is defined.
- Down-the-channel baseline material validation data set complete:
  - Additional repeat experiments being executed to define uncertainty.
- Database on the website for dissemination of data and modeling:
  - Visit www.pemfcdata.org (development will continue throughout the project).

The next phase of this project is focused on refining the component and down-the-channel models in parallel while repeating characterization and validation work for the next-generation material set. This work will support the key deliverable for next year: a validated 1+1D model capable of predicting performance and water balance under saturated conditions with baseline material parameters.

FY 2011 Publications/Presentations

1. J. Gagliardo, J. Fagley, D. Fultz, J. Owejan, "Influence of Through-Plane Thermal Profile on Water Accumulation in Proton Exchange Membrane Fuel Cells" Meeting of the Electochemical Society, Las Vegas, NV. October 2010.

2. Jacob M LaManna, Fengyuan Zhang, Subhadeep Chakraborty, and Matthew M. Mench, Quantification of Through-Plane Liquid Water Gradients and Transport in PEFCs with High Resolution Neutron Imaging. Accepted for Presentation, 2011 ECS Meeting, Montreal Canada.

3. Zijie Lu, Cody Rath, Guangsheng Zhang, Satish G. Kandlikar. Water management studies in PEM fuel cells, part IV: Effects of channel surface wettability, geometry and orientation on the two-phase flow in parallel gas channels, International Journal of Hydrogen Energy (2011).

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5. Sergi, J.M., Kandlikar, S.G., "Quantification and Characterization of Water Coverage in PEMFC Gas Channels Using Simultaneous Anode and Cathode Visualization and Image Processing," International Journal of Hydrogen Energy, Accepted Manuscript, 2011.

6. J. Owejan, DOE Annual Merit Review, Arlington VA, May 12, 2011.

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6. Sergi, J.M., Kandlikar, S.G., "Quantification and Characterization of Water Coverage in PEMFC Gas Channels Using Simultaneous Anode and Cathode Visualization and Image Processing," International Journal of Hydrogen Energy, Accepted Manuscript, 2011.