V.F.3 Investigation of Micro- and Macro-Scale Transport Processes for Improved Fuel Cell Performance

Jon P. Owejan, Wenbin Gu (Primary Contact), Matthew Mench, Michael Hickner, Satish Kandlikar, Thomas Trabold, Jeffrey Gagliardo, Anusorn Kongkanand, Vinod Kumar
General Motors
895 Joslyn Ave
Pontiac, MI 48340
Phone: (585) 953-5552
Email: wenbin.gu@gm.com

DOE Managers
Donna Ho
Phone: (202) 586-8000
Email: Donna.Ho@ee.doe.gov
David Peterson
Phone: (720) 356-1747
Email: David.Peterson@go.doe.gov

Technical Advisor
John Kopasz
Phone: (630) 252-7531
Email: kopasz@anl.gov

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Subcontractors:
- Penn State University, University Park, PA
- University of Tennessee, Knoxville, TN
- Rochester Institute of Technology, Rochester, NY
- University of Rochester, Rochester, NY

Project Start Date: June 1, 2010
Project End Date: November 30, 2013

Overall Objectives

Investigate and synthesize fundamental understanding of transport phenomena at both the macro- and micro-scales for the development of a down-the-channel model that accounts for all transport domains in a broad operating space.

Fiscal Year (FY) 2013 Objectives

- Characterize saturated relationships in state-of-the-art fuel cell materials.
- Obtain a comprehensive down-the-channel validation dataset for an auto-competitive material set.
- Develop multidimensional 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 Office Multi-Year Research, Development, and Demonstration Plan:

(B) Cost

(C) Performance

Technical Targets

This project supports fundamental studies of fluid, proton, and electron transport with a 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. The primary deliverables are:

- Validated cell model including all component physical and chemical properties.
- Public dissemination of the model and instructions for exercise of the model.
- Compilation of the data generated in the course of model development and validation.
- Identification of rate-limiting steps and recommendations for improvements to the plate-to-plate fuel cell package.

FY 2013 Accomplishments

- Auto-competitive validation data set is complete with 95% confidence intervals.
- Several one-dimensional relationships have been established or refined based on parametric and characterization methods developed within the project.
- Demonstrated improved down-the-channel 1+1D model prediction with new relationships integrated.
- Published validation, parametric studies, and characterization data to a project website at: www.pemfcdata.org.

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INTRODUCTION

The transport physics associated with fuel cell operation are 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 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 common material sets that represent current and next generations of PEMFC design.

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 ionomers, bulk membranes, porous electrodes, gas diffusion layers (GDLs), and flow distribution channels. The specifics of these relationships were outlined previously [2]. In anticipation of this integrated model, validation data sets are being collected in parallel with small-scale hardware specifically designed to include automotive stack constraints [3]. Currently, with these experimental methods established, work becomes more modeling focused as the physical mechanisms that govern the observed transport phenomenon are described multi-dimensionally at the component level and evaluated with a 1+1D fully integrated model. This work continuously guides parametric studies with novel material changes.

RESULTS

Validation Data

Compared to the baseline material set, the auto-competitive material set has a thinner membrane, lower cathode catalyst loading and ionomer-to-carbon ratio, advanced flowfield (with shallower channels, narrower lands, and modified exit headers), and notably, a novel anode GDL that is highly tortuous. Using the project protocol that varies outlet temperature, inlet relative humidity, outlet pressures, and current density [4], the auto-competitive validation data set is complete with 95% confidence intervals for the mean established for performance metrics by three separate experimental runs. The lower loaded auto-competitive cell generally shows a lower performance and a higher level of uncertainty, and would require an increased sample size to further reduce the confidence intervals. The auto-competitive cell shows on average 16% more of the reaction water staying on the cathode as a result of the high mass transport resistance anode GDL. Figure 1 compares the measured liquid water distribution, overall water balance, current and high-frequency resistance (HFR) distributions from the auto-competitive materials test to those from the baseline materials test. The water balance value represents the amount of product water moving to the cathode flow-

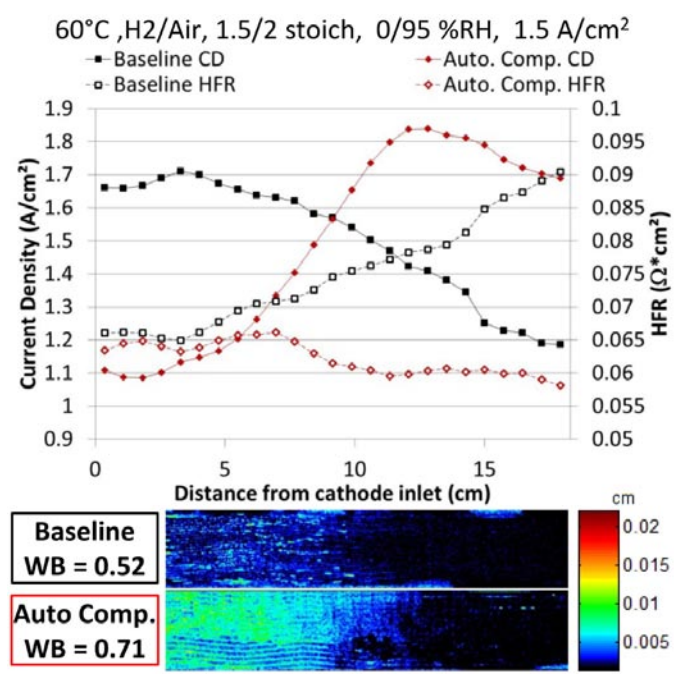

FIGURE 1. Liquid water distribution, overall water balance (WB), current and HFR distribution data: auto-competitive materials vs. baseline materials.

field. The higher diffusion resistance anode GDL drives more product water towards the cathode flow-field, and membrane hydration uniformity down the channel is improved. While similar behavior was observed at 80°C (not shown) for both auto-competitive and baseline materials, an opposite trend in current distribution is clearly seen at 60°C, indicating that the auto-competitive material set yields a higher risk of flooding the catalyst layer at a lower temperature. More liquid water accumulates near the cathode inlet, which overshadows the effect of higher oxygen pressure there on the reaction current.

Transport in Thin Ionomer Films

Platinum loading has to be reduced to meet the DOE cost target of $30/kWe for hydrogen fuel cell power systems for transportation. The local oxygen transport resistance measured by the limiting current method can be used to predict the voltage loss associated with low loaded electrode [5]. Recent experiments from this project have yielded an engineering approach to account for the effect of Pt dispersion on local oxygen transport resistance [6]. To understand the origin of the observed local resistance and develop mitigation methods accordingly, we use a flat model electrode to measure intrinsic transport properties of ionomer without convolution of a porous medium. Successful measurements made for a 100-nm thin ionomer film showed comparable bulk oxygen transport resistance to that of thick (>10 µm) membranes. In collaboration with Lawrence Berkeley National Laboratory and University of Calgary [7], we have measured the ionic domain structure and water uptake of thin films with thickness varying from 50 to 4 nm on Si- and Au-coated wafers. Ionic domain structure is altered in thin films, which will lead to different transport properties. Small domains in thin films decrease the proton conductivity and may change the nature of the catalyst particle/ionomer interface. Figure 2 shows film thickness increase with water uptake at various relative humidity levels with respect to film thickness. Thin films show much higher swelling on Si surfaces, which may be due to less hydrophobic reinforcement because of limited/no ion domain structure. Now that some of the physics of thin films are clarified, we are working on repeating this study on Pt and carbon surfaces, which are relevant to real electrodes, and measuring specific interactions between the ionomer and the Pt/carbon surfaces that may lead to altered thin film properties compared to what we know from bulk membrane measurements.

Transport in Diffusion Materials

GDL gas diffusivity and thermal conductivity are two key transport parameters that determine heat and mass transfer within a cell and thus the cell performance at given operating conditions. The presence of liquid water in porous media enhances heat transfer but impedes mass transport. We have designed and built a Loschmidt diffusion cell to measure the effective diffusion coefficients of partially

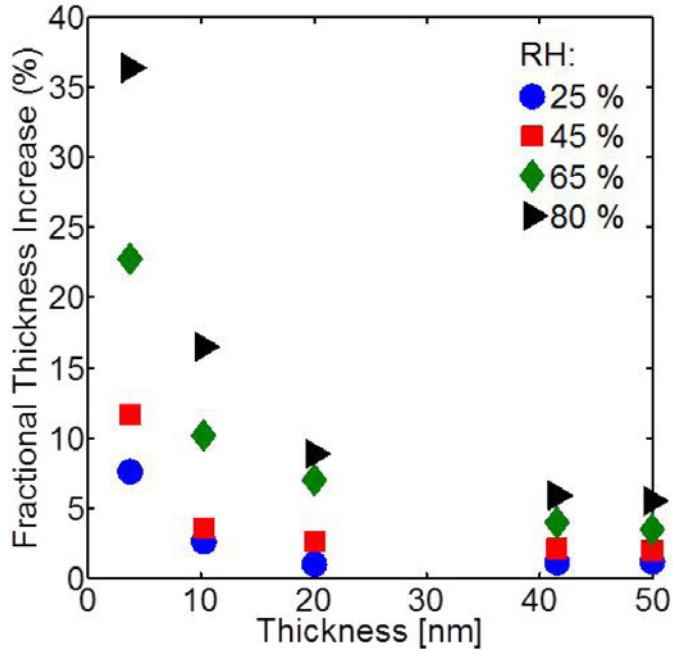

FIGURE 2. Thin-film swelling on Si wafers measured by ellipsometry showing higher water uptake with thinner film.

saturated porous samples. A new analytical solution method has been developed that simplifies diffusion cell design and enables a much more compact design with high precision [8]. We measured GDL thermal conductivity as a function of water saturation as well as compression. It is found that compression has significant impact on auto-competitive material sets but not on baseline materials. Figure 3 shows the measured thermal conductivity for both baseline and auto-competitive material sets in comparison with their theoretical maximum values based on completely connected pores. The departure from this maximum value represents liquid that is non-aligned/connected. At low saturation, the departure from the maximum is greater, indicating that more liquid is present as isolated droplets, as expected from condensation processes.

A two-dimensional component level model was developed for the numerical simulations of the GDL component using the measured transport properties and capillary flow. It considers the effect of compression variation over land and channel on the GDL structure and will allow integration with direct X-ray micro-tomography scans underway, in addition to coupled heat and mass transfer. The simulated liquid water accumulation over land and channel is useful in justifying the one-dimensional simplification of the two-phase 1+1D model and further providing an average value of liquid water saturation for model validation.

Transport in Flow Distributor Channels

Water coverage in the PEMFC gas channel is an important variable within the down-the-channel 1+1D model.

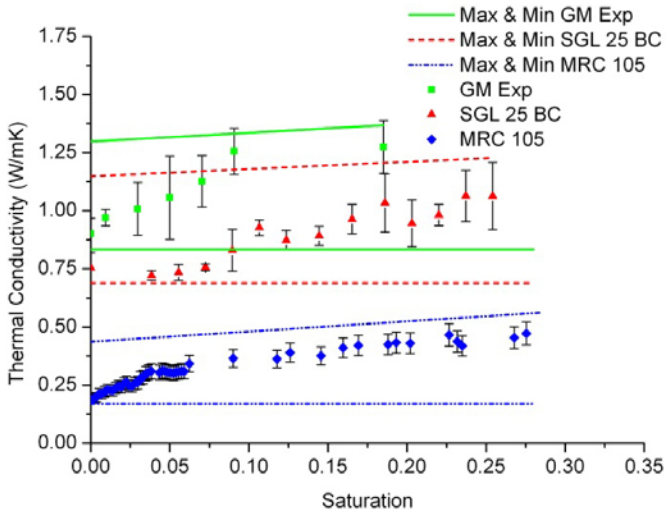

FIGURE 3. Measured GDL thermal conductivity as a function of liquid water saturation in comparison with the theoretical maximum value. The minimum value corresponds to a dry GDL.

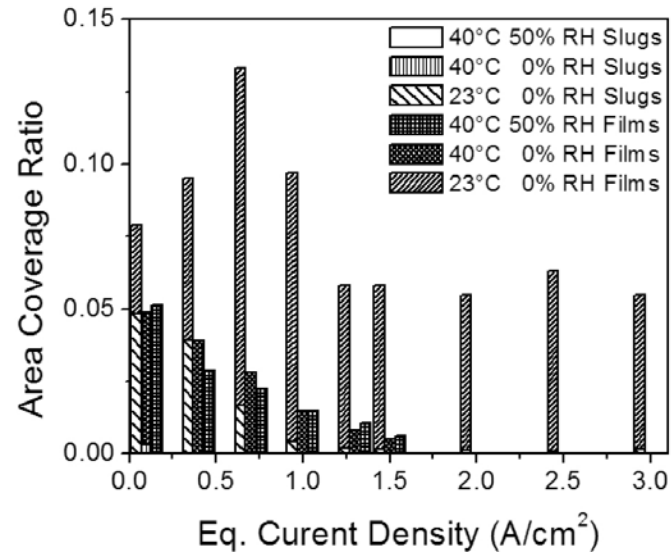

FIGURE 4. The area coverage ratio measured at 40 and 23°C for 0 and 50% inlet humidity conditions.

Multi-channel visualization was performed to quantify the area coverage ratio (ACR), defined as the area of liquid water blocking the reactant channels over the total projected channel area. A flow pattern identification algorithm was developed to distinguish between slug flow and film flow regime within the segmented liquid water. Figure 4 compares the obtained ACR for the different conditions of inlet humidification and temperature under slug and film flow regimes. It can be concluded that the ACR decreases at higher current densities and with increasing temperatures. Higher temperature leads to less liquid water presence in the channels and increased air velocity, which reduces the residence time of the water features within the reactant channels. With increased temperature, no slug flow was observed. Higher current densities and higher temperatures both favored the transition to film flow regime. Slug flow was found to be dominant at the lower current densities at ambient conditions. Oxygen transport resistance at the air flow channel and GDL interface has been further investigated via a numerical approach in the presence of either multiple liquid water droplets [9] or a single film as typical conditions in a PEMFC air flow channel. The interfacial transport resistance, expressed through the non-dimensional Sherwood number (Sh), was found to increase significantly above the fully developed value (Sh = 3.349) in the droplet wake region. The average Sh number in between two neighboring droplets increases with the number of droplets, droplet size, and superficial mean air velocity, with the highest value corresponding to an increase of 122% with respect to the fully developed Sh. A single film was found to decrease the effective Sh at the side region and also affect the downstream region similarly for a comparable length of the film. An elemental modeling scheme has been developed to predict the two-phase pressure drop in the reactant channels. The scheme takes into account the gas consumption down the channel, local water saturation, changing mass quality, and the effect of saturation pressure on water removal from the gas channels in the gas phase. The two-phase pressure drop predictions use the modified English–Kandlikar model within the elemental scheme.

In situ neutron imaging experiments were conducted at low cell temperature (20~35°C) to study active and non-active area water volumes as a function of cell temperature and current density [10]. The newly developed MATLAB®-based image analysis software allows for water thickness quantification for different areas within the cell, so water progression is able to be studied through the flow fields, anode, and cathode independently. The software has the capability to compare changes in water thickness for images taken in succession, so we may get a more accurate understanding of the flow of water through the fuel cell via analyzing multiple images together. Our in situ neutron imaging experiments demonstrated severe flow misdistribution resulting from water accumulation in non-active transitions and water build-up around the edge of the manifold. The extracted pressure drop data suggests that the water mitigation strategy should focus specifically on anode, where most of the reactant is consumed, resulting in an insufficient driving force for water to exit that area.

Modeling

The relationships described above for the various components are summarized with a down-the-channel 1+1D model. More accurately accounting for the transport relationships elucidated in this project has improved predictions of the performance and water balance response to key changes in material and operating parameters. The model

agrees reasonably well with baseline material set validation data. Better agreement in HFR distribution was achieved by considering a parabolic distributed compression load down the channel that results from the printed circuit board used for distributed measurements. For the auto-competitive material set, the model agrees with the data at 80°C and is predictive for overall water balance, but shows large discrepancy in current distribution at a lower temperature. It is hypothesized that the auto-competitive material set yields a more flooded catalyst layer and thus results in an opposite trend in current distribution compared to that shown in Figure 1. The model needs to address the liquid water saturation issue in the electrode.

CONCLUSIONS AND FUTURE DIRECTIONS

A well-organized characterization, modeling, and validation framework was developed early in this project. The first phase (FY 2011) of execution was largely focused on experimental development. The focus gradually shifted to model development while continuing to complete validation data. During the current phase of the project (FY 2013), results from these methods were described with multidimensional component models and summarized in a down-the-channel model that is compared to a comprehensive validation database. Specific highlights from FY 2013:

- Auto-competitive validation data set with 95% confidence intervals established.
- Channel-to-manifold two-phase pressure drop measured as a function of water volume.
- GDL/channel interfacial oxygen transport resistance related to ACR and two-phase channel pressure drop.
- GDL transport resistance transition from dry to wet and thermal conductivity as a function of saturation measured.
- Local oxygen transport resistance correlated to both Pt surface area and the surface area of ionomer film that covers Pt/C catalyst.
- Down-the-channel 1+1D model improved with new relationships integrated, and the need for model refinement identified.

The final phase of this project will be focused on finalizing the two-phase down-the-channel model, wrapping up component characterization and modeling, and reporting. In particular, a better catalyst layer liquid water model will be incorporated to improve current distribution prediction of the auto-competitive material set. Using this model as a guide, the project will be completed with parametric studies focused on rate limiting material constraints for transport within a PEMFC.

FY 2013 PUBLICATIONS/PRESENTATIONS

1. Dishari, S.K., Hickner, M.A., "Confinement and Proton Transfer in NAFION® Thin Films," *Macromolecules*, 46(2), 413-421 (2013).

2. Gopalan, P. and Kandlikar, S.G., "Droplet-Sidewall Dynamic Interactions in PEMFC Gas Channels," *Journal of the Electrochemical Society*, 159(8), F1-F8 (2012).

3. Grimm, M., See, E.J., and Kandlikar, S.G., "Modeling gas flow in PEMFC channels: Part I-Flow pattern transitions and pressure drop in a simulated ex situ channel with uniform water injection through the GDL," *International Journal of Hydrogen Energy*, 37(17), 12489-12503 (2012).

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6. Liu, X., Lin, J., McConnaghy, K.M., Trabold, T.A., Gagliardo, J.J., and Owejan, J.P., "Investigation of channel-to-manifold water transport in proton exchange membrane fuel cells," *Proceedings of the ASME 6th International Conference on Energy Sustainability & 10th International Fuel Cell Science, Engineering and Technology Conference,* Paper ESFuelCell2012-91093, San Diego, CA, July 23–26, 2012.

7. Liu, X., Trabold, T.A., Gagliardo, J.J., Jacobson, D.L., and Hussey, D.S., "Neutron imaging of water accumulation in the active area and channel-to-manifold transitions of a PEMFC," *Proceedings of the ASME 7th International Conference on Energy Sustainability & 11th International Fuel Cell Science, Engineering and Technology Conference,* Paper ESFuelCell2013-18183, Minneapolis, MN, July 14–19, 2013.

8. Modestino, M.A., Allen, F.I., Paul, D.K., Dishari, S.K., Petrina, S.A., Hickner, M.A., Karan, K., Minor, A.M., Segalman, R.A., Weber, A.Z., "Self-assembly and transport limitations in confined Nafion films," *Macromolecules*, 46(3), 867–873 (2013).

9. Koz, M. and Kandlikar, S.G., "Numerical investigation of interfacial transport resistance due to water droplets in proton exchange membrane fuel cell air channels," *Journal of Power Sources*, 243, 946-957 (2013).

10. Cekmer, O., LaManna, J.M., and Mench, M.M., "Alternative analytical analysis for improved Loschmidt diffusion cell," International Journal of Heat and Mass Transfer, 65(10), 883-892 (2013).

11. Owejan, J.P., Owejan, J.E., and Gu, W., "Impact of Platinum Loading and Catalyst Layer Structure on PEMFC Performance," *Journal of The Electrochemical Society*, 160 (8), F824-F833 (2013).

12. Jiang, R. and Gu, W., "Fuel cell membranes with expanded polytetrafluoroethylene (ePTFE) reinforcement: morphology, performance and durability," Paper#L5-3, Electromembrane processes and materials, Satellite Meeting of The 63rd ISE Annual Meeting, Ceský Krumlov, Czech Republic, August 26–29, 2012.

13. Koz, M. and Kandlikar, S.G., "A Preliminary Study for 3D Numerical Simulation of a Through-Plane Temperature Profile in a PEMFC Incorporating Coolant Channels," 10th International Conference on Nanochannels, Microchannels, and Minichannels, Rio Grande, Puerto Rico, July 8–12, 2012.

14. LaManna, J.M., Chakraborty, S., Xu, G., Bothe, J., Zhang, F.Y., Gagliardo, J.J., Owejan, J., and Mench, M.M., "Gas Diffusion Layer Through-Plane Transport Studies," 2012 Electrochemical Energy Storage and Conversion Forum. Knoxville, Tennessee, April 2012. *Jacob LaManna won first place in the 2012 Electrochemical Energy Storage and Conversion Forum Poster Competition.

15. Owejan, J.P., "Neutron metrology methods for in situ diagnostics of transport in electrochemical systems," invited talk at the spring meeting of the Materials Research Society, San Francisco, California, April 2012.

16. Owejan, J.P., "Neutron diagnostics for fuel cells and batteries," invited talk at the Electrochemical Energy Storage and Conversion Forum, Knoxville, Tennessee, April 2012.

17. Owejan, J.P., Owejan, J.E., and Gu, W., "Impact of Platinum Loading and Catalyst Layer Structure on PEMFC Performance," ECS 222nd Meeting, Honolulu, Hawaii, October 7–12, 2012.

18. Gopalan, P. and Kandlikar, S.G., "Effect of Channel Material on the Behavior of Water Droplet Emerging from the GDL into the PEMFC Gas Channels," ECS 222nd Meeting, Honolulu, Hawaii, October 7–12, 2012.

19. Koz, M. and Kandlikar, S.G., "Numerical Simulation of the Interfacial Oxygen Transport Resistance for a PEMFC Cathode Incorporating Water Droplet Coverage," ECS 222nd Meeting, Honolulu, Hawaii, October 7–12, 2012.

20. See, E.J. and Kandlikar, S.G., 2012, "A Two-Phase Pressure Drop Model Incorporating Local Water Balance in PEM Fuel Cell Gas Channels," ECS 222nd Meeting, Honolulu, Hawaii, October 7–12, 2012.

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