

V.F.7 Investigation of Micro- and Macro-Scale Transport Processes for Improved Fuel Cell Performance

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Fiscal Year (FY) 2012 Objectives

- Characterize saturated relationships in state-of-the-art fuel cell materials.
- Obtain a comprehensive down-the-channel validation dataset for a baseline and auto-competitive material set.
- Develop multidimensional component models to output bulk and interfacial transport resistances.
- Demonstrate integrated transport resistances with a one plus one-dimensional (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

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 2012 Accomplishments

- Baseline validation data set is complete with 95% confidence intervals.
- Several 1-D 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.
- Developed novel material solutions to improve key transport limitations.
- Published validation, parametric studies, and characterization data to a project website at: www.pemfcddata.org.



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 [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 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 in the second phase of the project is 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

The project protocol varies outlet temperature, inlet RH, outlet pressures, and current density [4]. With three replicate experiments, the baseline validation campaign resulted in 333 data points for analysis of single parameter (potential, differential pressure, water balance, etc.) and distributed measurements (temperature, current, ohmic resistance, liquid water content). Using three replicates for each test point, 95% confidence intervals were calculated. The majority of these data have upper or lower confidence intervals less than 10 mV centered on the mean and only 5% have upper or lower confidence intervals greater than 30 mV centered on the mean. This level of experimental certainty, resulting from rigorous material preparation and advanced instrumentation, is a significant accomplishment as this enables a higher level of model precision. All baseline data and analyses have been uploaded to the project website and the second phase of validation work with the next generation material set is underway.

Membrane Permeability

By first characterizing the sources of water transport resistance that do not originate in the membrane, experimental methods for measuring water permeability of fuel cell membranes as a function of temperature and RH have been refined. Results show that there is no discernible dependence of the permeability on membrane thickness, suggesting that any localized transport resistance that may exist at the membrane surface is undetectable by this method. It is possible to fit the data to a simple 3-constant empirical expression for the membrane permeability as a function of temperature and RH. Proper accounting of the device resistance turns out to be very important when measuring the membrane water transport properties. At high degrees of membrane saturation, the device resistance can be more than three times larger than that of the membrane itself. Combined with a published expression for the Nafion[®] water uptake as a function of temperature and RH [5], the measurements of membrane permeability can be used to calculate corresponding results for the membrane water diffusion coefficient. The diffusion coefficient increases monotonically with membrane hydration, with little or no change occurring above 50% RH. The current result is compared to literature in Figure 1 [6-10].

Transport in Thin Ionomer Films

Performance loss at high current density gets progressively worse as Pt loading is decreased in dispersed catalysts. This apparent transport loss has been shown to occur at or near the Pt surface. Measurement of coverage

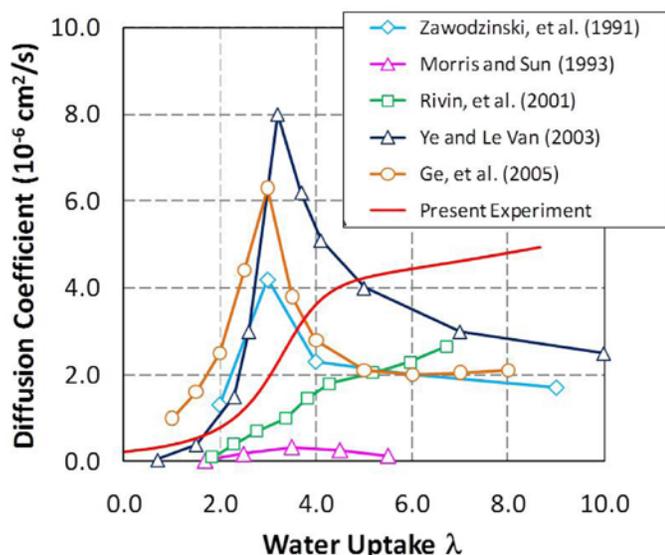


FIGURE 1. Water diffusion coefficient for a Nafion® membrane at 30°C determined in the present experiment compared with corresponding results from five previous experiments [6-10] at temperatures from 25-32°C, all plotted as a function of the water uptake.

dependent kinetics have further isolated the magnitude of this residual loss [11]. Recent fuel cell experiments from this project with varied Pt dispersions at a given loading (Figure 2) along with modeling of limiting current at an individual Pt particle based on oxygen transport through the ionomer demonstrate that the trends observed in pressure independent transport resistance are only resolved if a substantial interfacial resistance is occurring at both the gas and Pt interfaces. This transport theory is being further investigated using a model system with a well-defined flat Pt surface that is coated with thin ionomer films. This project is also investigating the behavior of thin ionomer films with ex situ methods.

Because of the small oxygen transport resistance in thin ionomer films (10-1,000 nm), if any oxygen-transport resistance not associated with transport through the ionomer film (i.e. the device resistance) was comparable to the resistance of the ionomer film, the film transport measurement would be compromised. The device resistance is originated mainly from the oxygen transport in the gas phase; therefore it can be measured by varying the gas pressure. The device resistance was quantified using a 1- μm thick Nafion® film. The resistance was less than 3 s/m when measured at 80°C and the effect of gas RH was also found to be negligible. This resistance is equivalent to ~10-nm thick ionomer film and by assuming the same oxygen transport properties as those of bulk membranes; the ionomer film measurement should be reliable down to ~100-nm with less than 10% uncertainty. The measured oxygen diffusivities (2×10^{-7} and 6×10^{-7} cm^2/s at 40°C and 80°C, respectively) in this 1- μm thick film were consistent with that measured

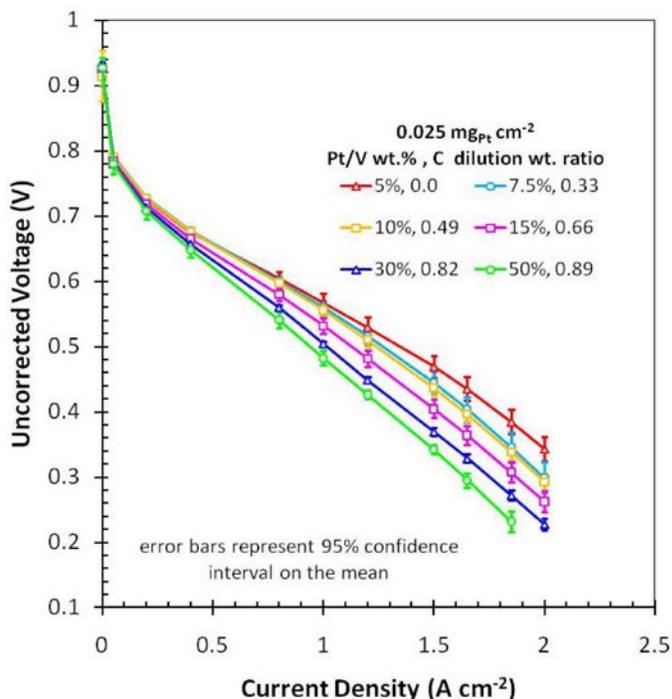


FIGURE 2. Performance of varied Pt dispersions at $0.025 \text{ mg}_{\text{Pt}}/\text{cm}^2$ with electrode thickness kept constant using bare carbon dilution at H_2/air , 65% RH, 80°C, 150 kPa operating conditions.

previously for bulk membranes. This investigation is currently ongoing with thinner film thicknesses.

Using ex situ methods we have measured significant differences in the proton dynamics of membranes and thin Nafion® films using fluorescence. A more proton accepting environment in bulk membranes relative to thin films was observed. The origin of the suppressed deprotonation is likely due to the different morphologies in the membrane and thin film. A less interconnected structure in the thin film would lead to lower deprotonation due to the isolated water-filled ionic domains in the material. We have also measured the thickness swelling as a function of RH by ellipsometry and the hydration number as a function of RH by quartz crystal microbalance (QCM). On SiO_2 , thinner Nafion® films swell more than thicker films. This trend is consistent for both adsorbed films (from Queen's University) and spin-coated films (from Penn State) of Nafion® on SiO_2 . The thickness swelling results were confirmed with QCM hydration number measurements that show more water being absorbed into thin films than thick films.

Transport in Diffusion Materials

Several in situ and ex situ measurements have been developed 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 were used to map through-plane liquid water distributions within the anode vs. cathode diffusion layers. These data were combined with limiting current experiments that measure the increase in transport resistance associated with liquid water accumulation.

Additional ex situ measurements of thermal conductivity and mass diffusivity as a function of water saturation and capillary pressure relationships for the baseline GDL and catalyst layer were also completed. These data are being used to support the model development by isolating specific parameters in component validation data. These key transport relationships are now included in the model.

Based on results from the baseline experiments and modeling it was determined that within practical constraints the only material-based mechanism to adjust the overall water balance was with changes to the macroporous diffusion substrate. An experimental GDL with significantly increased tortuosity has been designed and fabricated using a simplified and lower energy process [12]. The advanced material set for fuel cell testing includes the high tortuosity GDL on the anode side, while the baseline GDL continues to be used on the cathode side. By increasing the anode GDL tortuosity

to greater than 7 while maintaining all other properties approximately constant, comparable average performance is observed along with a reduced sensitivity to RH, as well as 11% to 44% more product water being removed on the cathode side (depending on operating conditions). Fast reaction kinetics and hydrogen gas transport enable the fuel cell to tolerate decreased effective diffusivity on the anode side. Due to the lower cost fabrication process and reduced carbon fiber content, the current anode GDL is more compressible than desired. Thus, a mixture design study is ongoing to determine a formulation that maintains high tortuosity and reduces compressibility.

Transport in Flow Distributor Channels

Interfacial oxygen transport resistance in the presence of liquid water causes a significant concentration drop across the channel-GDL interface. The effect of liquid water was numerically studied and expressed with the Sherwood number (Sh). The numerical model was validated against the theoretically predicted fully developed Sherwood number for a dry channel ($Sh = 3.36$). The Sherwood number was numerically calculated by introducing experimentally obtained droplet and film shaped obstructions. Figure 3 shows the Sherwood number down the channel length for two consecutive droplets 2 mm apart and for a single 5-mm long film. The Sherwood number over the dry regions was also reported to further characterize the local oxygen mass transport near water obstructions. The small increase in Sherwood number in the vicinity of the first droplet was due to increased gas mixing, while the significant increase near the second droplet was due to the impinging developing flow of the wake region behind the first droplet. The effect of water contact area was non-negligible for the film simulation as shown in Figure 3. The Sherwood number in the dry region along the film was greater than the fully developed value but a significant reduction was observed for the effective Sherwood number. These case studies of channel water obstructions show that a simple scaling of the fully developed Sherwood number is insufficient to accurately describe the local Sherwood number. This novel approach will be further used to obtain a statistical description of the effective Sherwood number by utilizing experimentally obtained liquid coverage in the operating space of the standard test protocol.

Transport resistance associated with two-phase flow in the flow distribution system beyond the active area is also being characterized. This project activity focused on understanding the relationship between fuel cell operating conditions and water accumulation at the channel-to-manifold interface, and correlating these in situ data to ex situ two-phase pressure drop measurements. At relatively low temperature conditions for which product water will be present in the liquid phase, it was found that accumulated water within the active area is a strong function of both

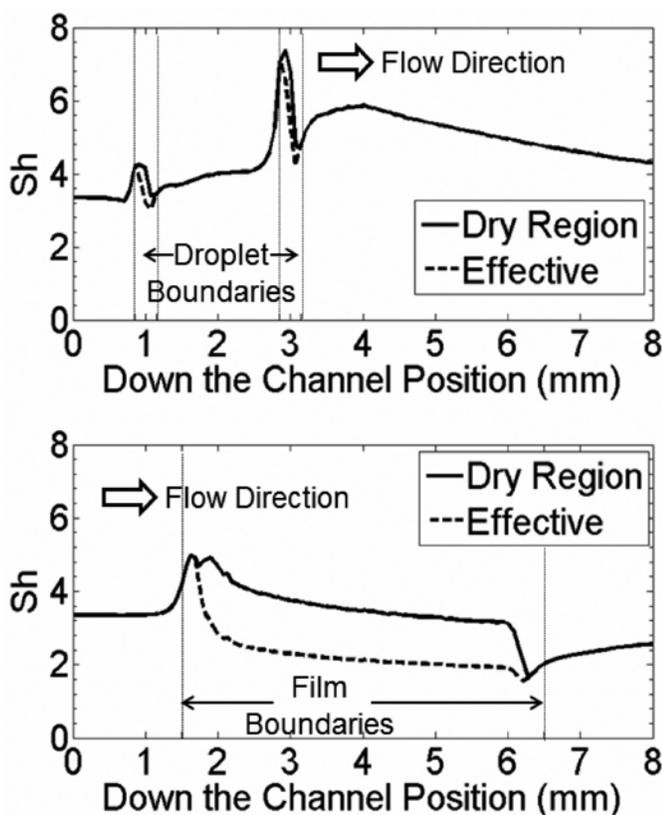


FIGURE 3. The dry region and effective Sherwood number in the presence of two consecutive droplets and a 5-mm long film. The channel-GDL oxygen interfacial transport resistance is highly dependent on local water obstructions and is insufficiently described by a simple scaling of the fully developed Sherwood number.

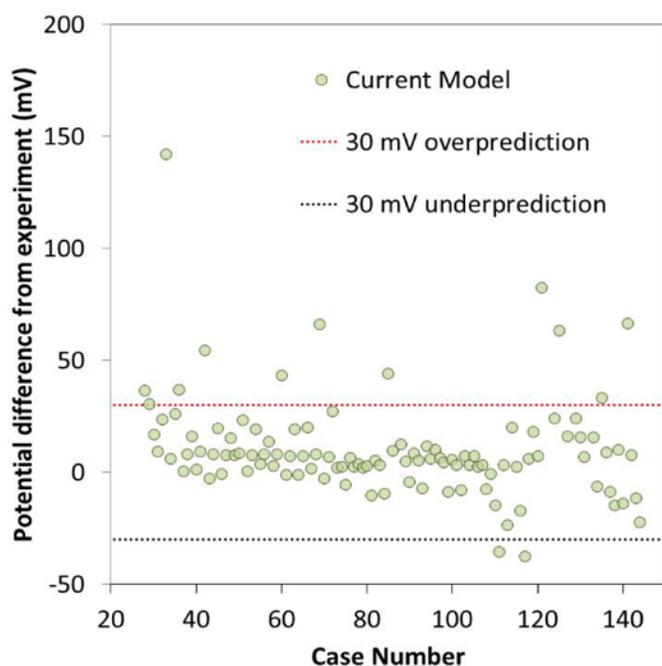


FIGURE 4. Down-the-channel model predictions for all test cases in the project protocol [4] with maximum experimental error indicated.

current density and anode/cathode pressure, whereas water in the anode exit is nearly independent of these operating variables. These in situ two-phase flow dynamics were simulated in an ex situ apparatus in which water and air flow rates can be independently controlled to produce conditions of interest at the channel-to-manifold transition region. It was found that water present downstream of the active area can have a significant impact on the overall system pressure drop. These data were used to formulate a generalized expression for the system pressure drop with channel-level water present only downstream of the active 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. Considering the baseline material set with the current model, Figure 4 shows the prediction for the 111 validation test points. Since the majority of the validation data points have a 30 mV or less 95% confidence intervals, Figure 4 demonstrates that the current performance prediction is accurate within uncertainty across most of the experimental space. As the model is finalized during the next phase of the project with liquid/vapor fronts in the porous components (uniform saturation is currently used) we expect to reduce the number of outlying predictions.

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. During the second phase of the project (FY 2012), 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 2012:

- Comprehensive baseline validation dataset with 95% confidence intervals established.
- New steady membrane permeability relationship results in a higher water flux at high RH.
- For a constant Pt loading, pressure independent transport resistance was shown to increase with the ratio of Pt to C surface area, thus indicating that increased ionomer surface area relative to the Pt particles is preferred.
- Coverage-dependent kinetic relationship improves overpotential prediction at less than 750 mV.
- GDL transport resistance transition from dry to wet is refined with a critical saturation value and thermal conductivity as a function of saturation.
- Sherwood number based on statistical representations of measured two-phase flow in channels improves 1D prediction of transport loss in channels.
- Dry entrance and two-phase exit relationships identify residual loss and isolate active area pressure drop.
- Performance and water balance prediction improved based on a comparison to baseline validation data.

The final phase of this project is focused on refining the component and down-the-channel models while completing characterization and validation work for the next-generation material set. The model will be finalized by adding nonuniform saturation relationships in the porous layers and it will be validated with data from the next generation material set that varies key parameters of interest in new materials. 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.

Patents

1. Nicotera, P., Owejan, J.P., Evans, R., Mench, M.M., “Low Cost Fuel Cell Diffusion Layer Configuration for Optimized Anode Water Management,” US Patent Application, filed 2012.

FY 2012 Publications/Presentations

1. LaManna, J.M., Chakraborty, S., Zhang, F.Y., Gagliardo, J.J., Owejan, J.P., and Mench, M.M., “Isolation of Transport Mechanisms in PEFCs with High Resolution Neutron Imaging,” *ECS Transactions*, 41 (1) 329-336 (2011).

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