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

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

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Project End Date: May 31, 2014

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) 2014 Objectives

- Characterize saturated relationships in state-of-the-art fuel cell materials.
- Obtain a comprehensive down-the-channel validation dataset for a parametric study 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 2014 Accomplishments

- Obtained validation data set for baseline materials with low Pt-loaded cathode
- Established or refined several one-dimensional relationships 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

In the auto-competitive material set tested for model validation, a number of parameters, including membrane thickness, anode GDL, cathode catalyst layer composition, flowfield land/channel geometry and manifold exit headers, are changed from the baseline material set. Hence, the performance difference between the two material sets represents a compounded effect of all changes being made at once. To de-convolute the effects of high diffusion resistance anode GDL and cell design differences used in DOE automotive competitive cell builds from low Pt-loaded cathode catalyst layer effects, a parametric study cell built with low Pt-loaded cathode and other baseline materials was tested using the standardized project protocol that varies outlet temperature, inlet relative humidity, outlet pressures, and current density [4]. Compared to the baseline cell, the parametric study cell yielded lower cell voltage and less product water to the cathode flowfield. The lower voltage results primarily from lower Pt loading and slightly higher high-frequency resistance (HFR). And less product water to the cathode flowfield appears to be consistent with higher temperature gradient caused by the lower cell voltage and thus higher heat generation rate. However, both baseline and parametric study cells demonstrate same trend in down-the-channel current distribution, suggesting that lower Pt-loaded cathode in the auto-competitive material set would not be responsible for the opposite trend in current distribution associated with the auto-competitive cell at low temperatures. Instead, the highly tortuous anode diffusion medium is most likely the cause.

Transport in Thin Ionomer Films

With focus on elucidating the structural features and transport properties of thin ionomer films, we have performed extensive gravimetric and volumetric swelling studies to understand how these thin films based on perfluorinated sulfonic acid (PFSA) ionomers uptake water and have compared the properties of thin ionomer films to what is known about PFSA-based membranes. The focus on water uptake and swelling is because the transport properties of these materials is determined in large part by their hydration. We have found that the water uptake of PFSA-based thin films varies with thickness, substrate type, and processing conditions. To understand the swelling processes in more depth, we have undertaken measurements of polymer chain alignment using Fourier transform infrared (FTIR) and ellipsometry. These techniques were chosen because they can be adapted to electrochemical measurements to study

the behavior of thin films under potential control, which is ongoing work. Shown in Figure 1 is the FTIR spectra of 50-nm and 5-nm Nafion® films. The SO_3/CF_3 side chain peaks are enhanced in the thin film spectra indicating alignment of these moieties towards the surface in the thinnest films [5]. Similar observations have been made by studying the birefringence of Nafion® films using spectroscopic ellipsometry [6]. Our goal is to be able to measure the dynamic behavior of these thin films as a function of potential, which can be detected by changes in their FTIR or ellipsometric spectra. These types of measurements focusing on the features of the ionomer-substrate interface may lead to a better understanding of why the oxygen transport resistance at low platinum loading occurs. This work on the structure of the thin films and how the structure correlates with swelling and ultimately other transport properties complements our collaborative work with Lawrence Berkeley National Laboratory on scattering studies [7] as a function of film processing conditions and substrate type.

Transport in Diffusion Materials

We developed an empirical relationship for effective thermal conductivity of partially saturated diffusion media via ex situ material testing [8]. Additionally, we experimentally determined capillary drainage functions of liquid water from the catalyst layer, micro-porous layer, and the interfacial domains [9]. Utilizing the high resolution neutron imaging facility at the National Institute of Standards and Technology, we completed extensive in situ characterization of the impacts of diffusion media design, flow-field interface architecture, and aging, covering
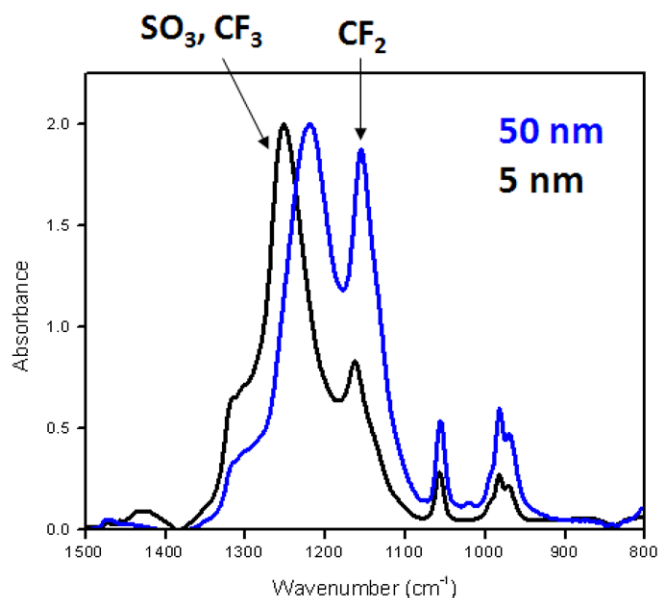
an extremely wide range of operational test conditions. In particular, diffusion media aged in situ for over 2,500 hours has been tested with neutron imaging and show additional water storage during operation. The water balance was found to shift in the aged material from the anode to the cathode, as shown in Figure 2. To understand what has caused the change in water balance, energy dispersive X-ray spectroscopy and X-ray photoelectron spectroscopy were used to determine changes in chemical makeup and surface morphology. The results indicate an increase in carbon-oxygen bonding and increased surface functionalization. These oxygen groups can be responsible for increasing the hydrophilicity of the
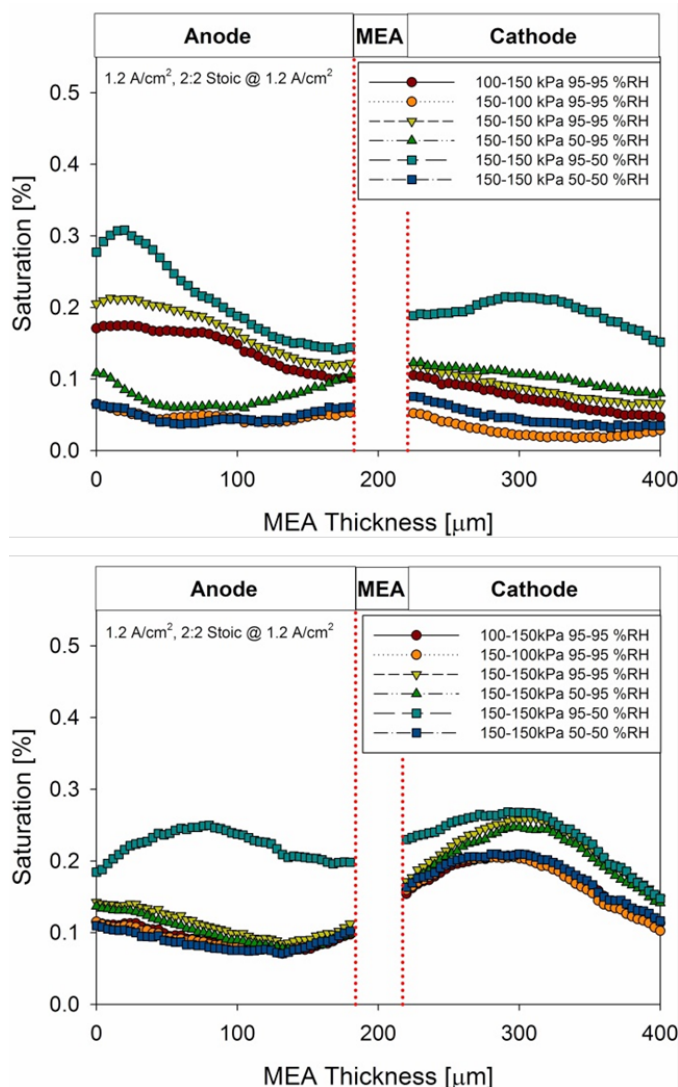

FIGURE 2. Saturation profiles for baseline fresh (upper) and 2,666 hr aged (lower) GDL/MEA packages at 60°C. Test conditions: 1.2 A/cm², 95|95% (An|Ca) constant inlet relative humidity for pressure tests, 150|150 kPa (An|Ca) constant exhaust pressure for concentration gradient tests, constant flow rate at an equivalent stoichiometry ratio of 2:2 at 1.2 A/cm². Profiles are summed along entire imaged area.

FIGURE 1. FTIR-Attenuated total reflectance spectrum of 50-nm thick and 5-nm thick Nafion® thin films showing the change in the CF_3 (backbone) and SO_3/CF_3 (side chain) peak ratios with thickness.

surface, increasing water retention and wicking action. Both anode and cathode GDLs were tested, and the cathode GDL was more affected by ageing. Finally, a GDL component level multi-phase computational model has been developed to address the need for meso-scale modeling within this media. A statistical approach using percolation theory was used to construct appropriate model porous domain structures, and a Lattice-Boltzman approach was used to determine the effective tortuosity and gas-diffusivity of these domains. Additionally, X-ray microscopy was used to determine the three-dimensional morphology of the GDL structure, which can then be directly used as the computational domain in the model. Future publications are being prepared based on the results which demonstrate the prediction of effective diffusivity and tortuosity for the real media morphology as a function of saturation. This result can then be correlated and linked with macroscopic performance models to obtain high-speed predictive performance modeling with greater GDL level transport fidelity.

Transport in Flow Distributor Channels

The emergence of droplets and their interaction with the reactant channel sidewall dictate trends of GDL-channel interface coverage, two-phase flow pressure drop, and transition of flow patterns. These trends are dependent on the corner filling of the channel by liquid water. We conducted ex situ experimentation to establish correlations to predict corner filling behavior as a function of channel design parameters and operating conditions [10]. Liquid water was injected into a single channel that was manufactured to match baseline and auto-competitive designs. The distance from water injection location on the GDL to the channel side wall, materials of GDL and channel walls, corner angle in an auto-competitive channel, and superficial air velocity

in the channel were varied. A channel corner angle of 50° is suggested for improved water removal characteristics. Moreover, correlations were established to predict the corner filling behavior and two-phase flow pressure drop at the instant of droplet removal. A force balanced model has also been developed to provide further insight into the dynamics of the droplet at the time of its interaction with the channel side wall. Consequently, a channel design was suggested to minimize the buildup of liquid water.

Two-phase pressure drop studies from the literature have focused on the fundamental factors that influence the two-phase flow. However, the conditions in the PEMFC reactant channels are unique as there is consumption of gaseous reactants along the length and water is continuously introduced through the GDL. This results in a continuously changing quality of the two-phase mixture. There are temperature gradients both along the length of the channel as well as the cross section of the cell, resulting in evaporation and condensation-driven mass transport in these directions. A step-wise elemental modeling scheme that allows ease of integration into the down-the-channel performance model has been proposed, developed and validated for the prediction of two-phase pressure drop in the reactant channels. The modeling scheme has been tested with several fundamental pressure drop models available in the literature. It is found that the modified English and Kandlikar model [11] works best to predict two-phase pressure drop in PEMFC reactant channels. Figure 3 shows that it has a mean error of 11.6% and 40.2% for cathode and anode, respectively, over the entire range. A mean error of 5.2% was observed for the cathode with a fully humidified inlet.

In investigating channel-scale water transport and accumulation, both within the fuel cell active area and in the non-active areas extending all the way to the anode and
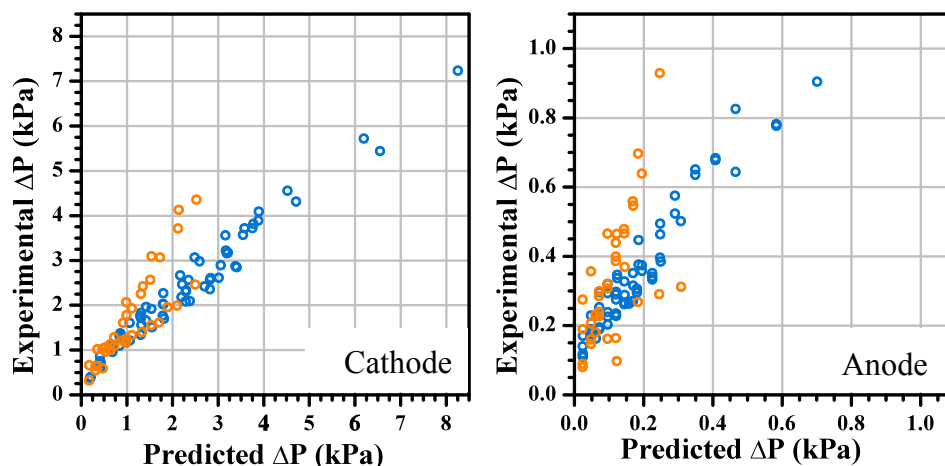

FIGURE 3. Comparison between the modified English and Kandlikar correlation and experimental data. Cell temperature 40°C, Orange – 0% relative humidity Inlet, Blue – 95% relative humidity Inlet, (left) Cathode Side Pressure Drop (right) Anode Side Pressure Drop.

cathode exit manifolds, we carried out ex situ two-phase flow experiments to understand pressure drop performance over a wide range of simulated operating conditions, coupled with in situ experiments applying neutron imaging to directly measure fuel cell water content under low temperature conditions in the range of 20 to 40°C [12]. It was observed that the active area water volume is strongly dependent on cell temperature, and temperature variation of as little as 0.5°C can produce a significant change in water accumulation, which is also reflected in the cell voltage. In general, active area water decreases with increasing current density. However, the water quantity is a function of both cell temperature and anode/cathode pressure. Conversely, the anode non-active water is weakly dependent on current density, presumably because in this region there is little driving force to remove water once it is present. This finding has obvious implications relative to fuel cell operation under freezing conditions, and is indicative of the difficulty of removing anode exit water during shut-down purge. Furthermore, a significant pressure drop was seen over non-active area. On average, the outlet region contributes more to the total (manifold-to-manifold) pressure drop for higher water flow rates, suggesting that water mitigation strategies should focus on outlet non-active area as well as channel-to-manifold interface, especially on anode side.

Modeling

The two-phase, 1+1D down-the-channel model has been improved and tested against the experimental data generated from baseline, baseline with low Pt-loaded cathode, and auto-competitive material sets. Due to lack of experimental data on liquid water saturation within an electrode, the electrodes are allowed to be supersaturated and water saturation therein is evaluated based on local relative humidity by an empirical correlation. Using a single set of parameters, the model agrees fairly well to all three data sets. Figure 4 compares the predicted down-the-channel current and HFR distributions with the measured ones. Significantly, the model captures the opposite trends in current density distribution observed for the automotive competitive and baseline materials plus low-loaded Pt material sets, that is caused by the highly tortuous anode diffusion media in the automotive competitive data set. However, the agreement for the automotive competitive material set comes with a compromise in the agreement for the baseline material set. More work is needed to achieve better quantitative agreement in down-the-channel distributions.

A parametric study was performed for cell component optimization based on the parametric study cell validation data using the two-phase, 1+1D down-the-channel model. The design for six sigma approach was employed to find optimal material properties for better cell performance [13]. Among numerous input parameters, eight were chosen to be the control factors. For the operating condition given in
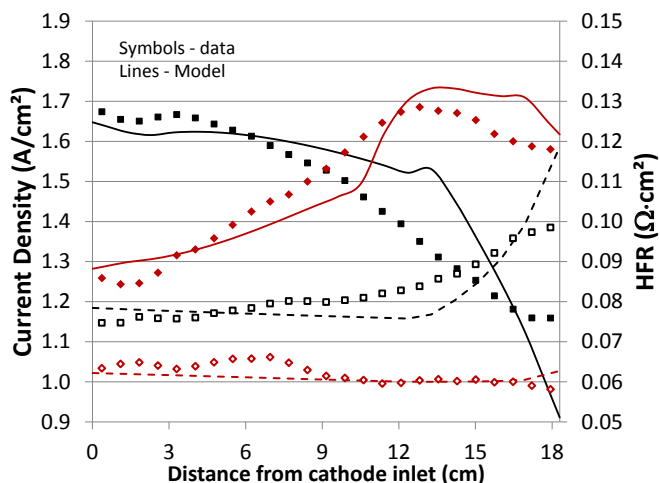

FIGURE 4. Comparisons between model and data for down-the-channel current and HFR distributions. Squares represent baseline materials with low Pt-loaded cathode (0.1 mgPt/cm^2); and diamonds stand for Auto-Competitive material set. The cell operates with H$_2$/Air at stoichimetry 1.5/2.0, 100/150 kPa-abs outlet pressure, 60°C coolant out temperature, 0/95% inlet relative humidity.

Figure 4, the following recommendation can be made for cell component properties in reference to the baseline materials:

- Thinner membrane (12 microns)
- 50% lower membrane water permeability
- 25% less tortuous supporting layer in the ePTFE-reinforced membrane
- 25% less tortuous GDL in the presence of liquid water
- 2X GDL thermal conductivity
- 2X MPL thermal conductivity
- 2X coolant-to-plate thermal resistance
- 50% lower local oxygen transport resistance

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 final phase of the project (FY 2014), 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 2014:

- A new validation data set based on the baseline materials with low Pt-loaded cathode added to the database for model validation.

- Coninued studies on thin ionomer films and ionomer-substrate interactions.

- Neutron imaging data on liquid water saturation within GDL for the effects of GDL type, aging, and flowfield shows the impact of GDL surface properties and heat transfer.

- Validated flowfield pressure drop model includes the effects of water droplet-channel corner interaction, liquid water flow pattern, and local operating condition.

- Significant pressure drop occurs in the non-active, channel-to-manifold region due to liquid water accumulation therein; peak active area water volume exists likely due to gas momentum and hydraulic force balance.

- Down-the-channel 1+1D model improved with new relationships integrated, and the opposite trend in down-the-channel current distribution associated with auto-competitive material set successfully captured.

- A parametric study performed for cell component optimization, and optimal material properties recommended for better cell performance.

The project ended in May 2014. A final report is forthcoming.

FY 2014 PUBLICATIONS/PRESENTATIONS

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15. Xu, G., LaManna, J., and Mench, M.M., "Measurement of Thermal Conductivity of Partially Saturated Diffusion Media under Compression," 2014 ECS Spring meeting, Toronto, Canada, May 12–16, 2014.

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