

V.F.3 Transport in PEMFC Stacks

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- Ballard Material Products, Inc., Lowell, MA
- Virginia Polytechnic (VT) Institute and State University, Blacksburg, VA
- University of South Carolina (USC), Columbia, SC

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Fiscal Year (FY) 2011 Objectives

- Design of fuel cell components targeting specific transport properties:
 - Synthesis of block copolymers.
 - Design of flow fields and gas diffusion layers (GDLs).
- Determination of bulk membrane properties:
 - Water uptake and diffusivity.
 - Gas permeability.
 - Electro-osmotic drag.
- Transient, three-dimensional modeling of fuel cell operation.

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:

- (C) Performance
- (D) Water Transport within the Stack
- (E) System Thermal and Water Management
- (G) Start-up and Shut-down Time and Energy/Transient Operation

Technical Targets

The goals of this project are not to reach specific technical targets put forth by the DOE (i.e., target catalyst loading, target cost per kilowatt). Instead, this project aims to develop fuel cell components (i.e., membranes, GDLs, bipolar plates and flow fields) that possess specific properties (i.e., water transport and conductivity). A computational fluid dynamics model will then be developed to elucidate the effect of certain parameters on these specific properties (i.e., the effect of membrane type and thickness on membrane water transport). Ultimately, the model will be used to determine sensitivity of fuel cell performance to component properties to determine limiting components and guide research.

FY 2011 Accomplishments

- Developed a second system to measure dynamic water uptake and diffusivity of membranes in addition to previously developed static diffusivity apparatus. Water isotherms and diffusivities of various membranes including Nafion® 112, Nafion® 1110 and NRE 212 have been obtained using both systems. We conclusively have shown that membrane interfacial resistance to water transport is negligible.
- Designed segmented cells to quantify fuel cell voltage vs. current at different points along the active area and tested the concept in common 50 cm² hardware with negligible change in performance.
- Characterized customized GDLs in terms of scanning electron microscopy (SEM) microstructure and fuel cell performance and correlated them to various pore structure, tortuosity and hydrophobicity.
- Developed the second iteration of fuel cell flow fields with thin metallic sheets to better correlate with automotive cells. Have also developed segmented cells for these plates.
- Modeled the effect of altering polymer electrolyte membrane (PEM) diffusivity to 6x and 1/6x that of PFSA membranes on fuel cell performance and water distribution.

- Synthesized block polysulfone ether polymers-bi phenyl sulfone (BPSH-BPS) multiblock copolymers with higher block lengths and self-assembled nanostructures, which provide designing guidelines for PEMs and will be used for model tests.



Introduction

Many fuel cell component properties that influence water transport and thermal management are not well-understood [1,2]. A better understanding of how water transport and thermal management can be controlled would represent a significant step forward in meeting the DOE's stated 2015 targets. This project aims for a better understanding of water transport and thermal management by tailoring fuel cell components to exhibit specific transport properties. These transport properties will then be modeled, which will enable the prediction of the effect of changing component parameters on transport properties.

Approach

This project seeks to develop fuel cell components possessing specific transport properties. Membranes will be developed to achieve different ratios of water transport and conductivity. Bulk membrane properties (i.e., diffusivity, water uptake, conductivity) will be evaluated and modeled. GDLs and bipolar plates and flow fields will be developed, and also tailored to achieve specific differences in porosity, tortuosity and hydrophobicity. The fuel cell performance will be evaluated using these components. The model will be used to predict the effect changing component parameters (i.e., changing membrane type and thickness, changing flow field configuration) will have on component transport properties and fuel cell performance.

Results

Membrane Synthesis and Nano-Scale Properties

A dynamic water uptake and diffusivity measurement apparatus was developed. This is a further advancement beyond the static water uptake system made in fiscal year 2010. Dynamic water uptake is of interest for it determines rate of water transport in a changing water activity environment. When the relative humidity (RH) changes in the fuel cell, the water content of the membrane changes, and subsequently the membrane must swell or shrink to accommodate this change. There is debate amongst the fuel cell community if this necessary mechanical work (for expanding a membrane to increase water content) slows water transport compared to a static gradient, where water content is not changing across the membrane thickness. For the dynamic system, a small chamber with a membrane strip (2.2 cm × 0.5 cm) is placed in line with an ante-chamber.

Both chambers are evacuated. The ante-chamber is then filled with water vapor to a selected RH. A valve between the membrane and ante-chamber is then opened. The two chambers equilibrate immediately, then the pressure begins to drop as the membrane absorbs water. By measuring the kinetics of this pressure drop we can determine the diffusivity of the membrane under those conditions. The pressure in the ante-chamber is then increased and the experiment is repeated to determine diffusivity at the next RH level. Similarly the experiment can be performed for desorption. Finally, by knowing the volume of both chambers, the absolute amount of water absorbed can be determined to obtain the water vapor isotherm.

The diffusion coefficients for NRE 212 at 80°C were measured over a range of membrane water contents by absorption and desorption experiments. These dynamically-measured diffusion coefficients are plotted against the diffusion coefficients measured via steady-state analysis in Figure 1, where the lines on the data points represent the 95% confidence intervals. The diffusion coefficients are nearly identical, regardless of the type of experiment performed (i.e., absorption, desorption or steady-state). The inserted figure shows water uptake isotherms for the Nafion[®] 1110 and NRE 212 membrane. The solid curve in the figure is the previously-reported water uptake isotherm described by an empirical equation in the reference [3], which is compared with the dotted line obtained by measuring the weight change of the membrane in contact with water vapor. These two isotherms are very nearly identical, indicating that the dynamic uptake experiments are an alternative valid approach to measuring steady-state water uptake.

To determine the current distribution, a current distribution plate made of a thin copper layer attached to a Kapton film was developed as shown in Figure 2. The plate rests between the flow field and the diffusion media and

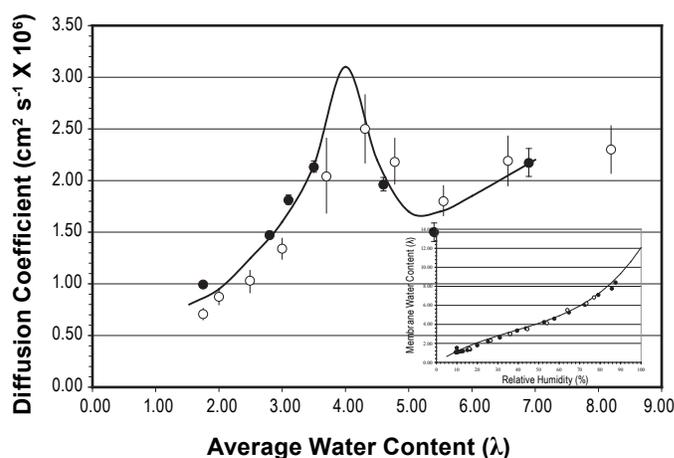


FIGURE 1. Diffusion coefficients measured from (—) steady-state data; (●) dynamic water uptake; (○) dynamic water desorption by Nafion[®] 212 at 80°C. The inserted figure shows water uptake isotherms for the Nafion[®] 1110 and NRE 212 membrane.

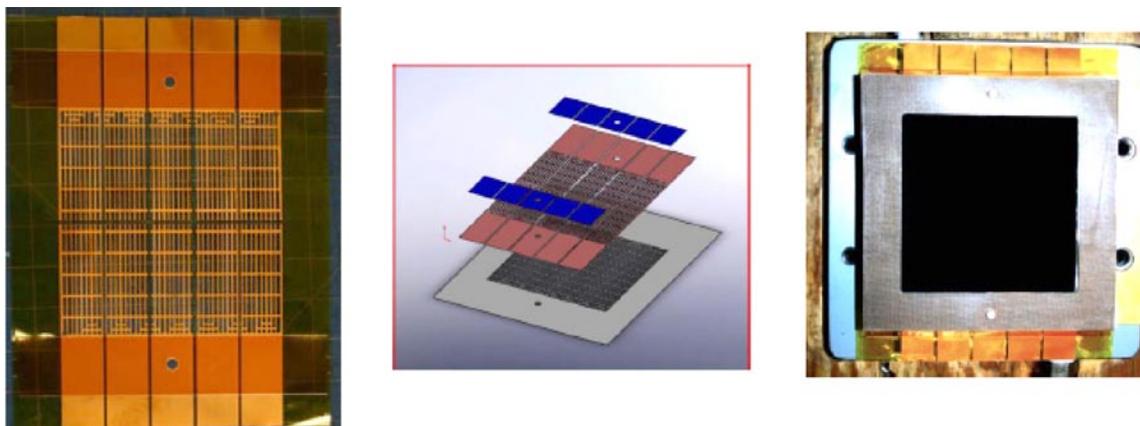


FIGURE 2. A current distribution plate made of Kapton film attached with a thin copper layer. The plate rests between the flow field and the diffusion media and the concept was tested in 50 cm² regular fuel cell hardware.

the concept was tested in 50 cm² regular fuel cell hardware. The current distribution board adds only 7.5 mOhms-cm². The performance discrepancy before and after the current distribution plate addition is negligible. A new flow field with thin metallic sheets was designed and fabricated since heat transport and fluid cooled plates can have a large impact on the current distribution. This thin plate design with central cooling is being used by automotive manufacturers for fuel cell plates and it is essential to mimic the diffusion media/flow field interface as closely as possible.

GDLs with various pore structure, tortuosity and hydrophobicity were custom fabricated by BASF and Ballard Materials. The matrix of GDLs is shown Table 1. They were characterized in terms of microstructure, pore size distribution, and fuel cell performance. The fibers constitute the bare substrate when there is no wet proofing. In contrast, materials fill in between fibers in the GDLs with 10% or 40% wet proofing. For the GDLs with 10% and 40% microporous layer (MPL), SEM images reveal a merge between the substrate and the MPL instead of a well defined and a clear boundary. The effect of wet proofing, MPL and porosity on the MacMullin Number (ratio of transport resistance with the diffusion media compared to without) was investigated. Increasing the wet proofing decreases the porosity of the substrate layer. Consequently, a higher flow resistance is expected as porosity decreases and tortuosity increases. However, the addition of the

TABLE 1. Matrix for Customized GDLs

GD	Layers & % Hydrophobicity	Image #	Avg. Porosity
1	Substrate Only (No wet proofing)	a	0.80
2	Substrate Only (10%)	b, d	0.78
3	Substrate (10%) + MPL (10%)	c	0.75
4	Substrate (10%) + MPL (40%)	f	0.74
5	Substrate Only (40%)	c, g	0.69
6	Substrate (40%) + MPL (10%)	h	0.68
7	Substrate (40%) + MPL (40%)	i	0.69

MPL decreases the MacMullin number. This effect could be related to the different wet proofing treatments of the substrate and the MPL, which can cause an additional driving force in the liquid through the pores during the experiments. Even when the treated surfaces have the same wet proofing percentage the actual contact angle in each surface could be different.

PEM diffusivity in the model was altered to 6x and 1/6x that of PFSA membranes to investigate the effect of diffusivity on performance. Figure 3 shows simulated current density distribution on the MEA surface at three water diffusivities and average current density of 0.6 A/cm² with (a) 75%/25% RH and (b) 25%/25% RH (anode/cathode, co-flow). It is interesting that for both anode humidity conditions, increasing diffusivity gives the most uniformity in current density distribution and 1/6 Dw shows the most non-uniformity in distribution. Also, increasing diffusivity leads to the largest improvement in the dry anode case. This is not surprising as the water needs to diffuse to the anode to counter electro-osmotic drag. The block copolymers being developed are expected to have a very different diffusivity than Nafion[®], and will be used to confirm these predictions.

BPSH-BPS multiblock copolymers with higher block lengths and self assembled nanostructures have been synthesized, which provide designing guidelines for PEMs in term of structure, chemistry and phase separation and will be used for model tests. A cluster of multi-block copolymers comprised of hydrophilic telechelic BPS-100 oligomers and 6FPAEB oligomers, both of which vary in molecular weights (i.e., 7k-7k, 14k-14k, 15k-15k, 10k-18k) have been prepared. They clearly demonstrate different nano-phase separated structures based on transmission electron microscope images. Beyond chemistry and block length, thermal history also influences the PEM properties. Figure 4 shows measured conductivities of 6FPAEB-BPSH100 14k-14k at different annealing temperatures as a comparison to Nafion[®] 212 membrane. It can be seen that annealing at

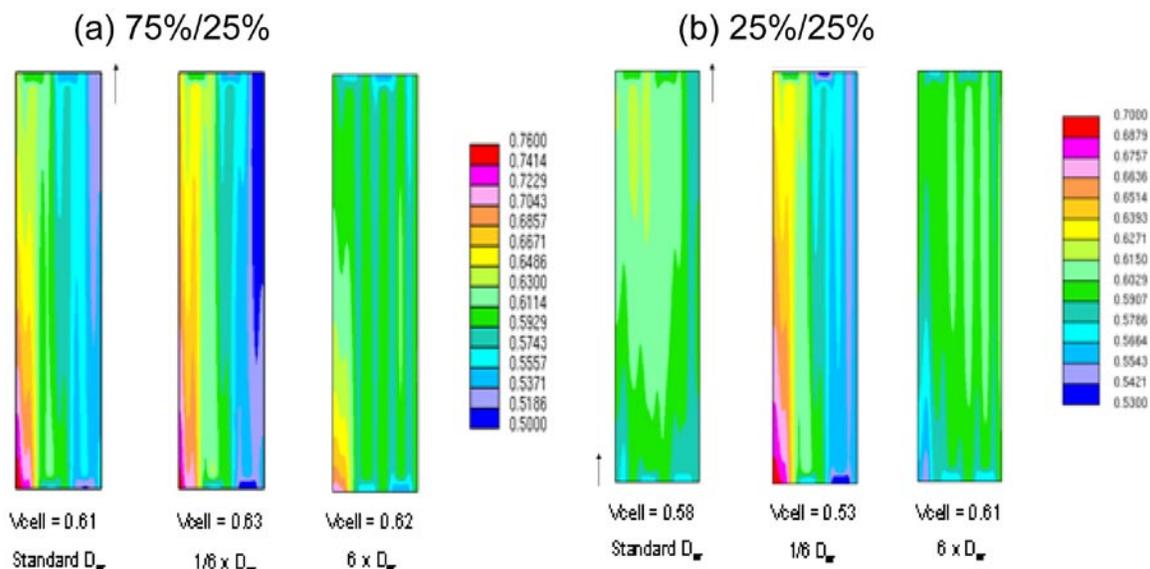


FIGURE 3. Simulated current density distribution on MEA surface at three water diffusivities and average current density of 0.6 A/cm^2 : (a) 75%/25% RH and (b) 25%/25%RH, anode/cathode for a co-flow configuration.

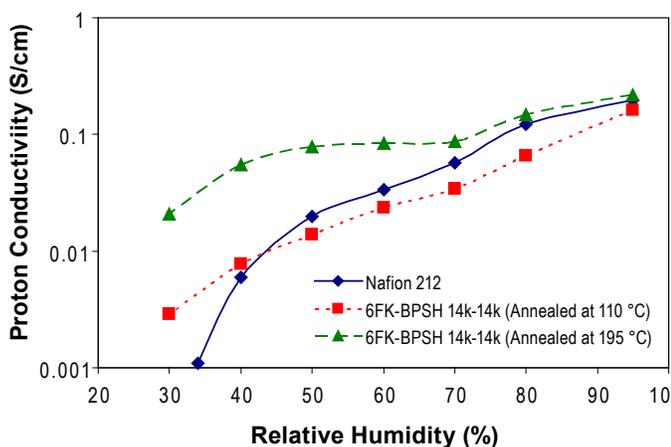


FIGURE 4. Measured conductivities of 6FPAEB-BPSH100 14k-14k at different annealing temperatures as a comparison with Nafion® 212 membrane.

195°C tremendously improves the membrane conductivity in contrast to that at 110°C.

Conclusions and Future Directions

- Many new analytical techniques were developed for characterizing water transport:
 - No interfacial resistance found for Nafion®
 - Static and dynamic diffusivity found to be the same
 - Techniques will be made widely available to the fuel cell research community
- Widely varied PEMs and diffusion media will allow us to model the important parameters of each.

- A base model has been developed and used to describe various performance results with different diffusion media.
- In FY 2012, we plan to: Extend characterizations to alternative materials.
- Extend testing to more realistic automotive platform.
- Down-select alternative polymers and generate larger, consistent materials.
- Confirm model with performance, current distribution and water collection results.
- Use model to determine performance sensitivity to build materials, suggest focus areas.

FY 2011 Publications/Presentations

1. “Transport Studies and Modeling in PEM Fuel Cells,” DOE Annual Merit Review, oral FC054, May 9-12, 2011.
2. “Water Transport in Nafion Membranes Advances”, in Materials for Proton Exchange Membrane Fuel Cell Systems 2011, Asilomar Conference Grounds, Pacific Grove, CA. February 20–23, 2011.
3. “Poly(arylene ether) Random and Block Copolymer Polyelectrolytes for Fuel Cell and Water Purification Membranes”, XII International Symposium on Polymer Electrolytes, Padova, Italy, 29 August – 3 September 2010.
4. “Recent Developments in Linear, Postfluorinated and Terminally Crosslinked Hydrophilic-Hydrophobic Multiblock Copolymer Electrolyte Membranes”, Progress in MEA 2010, La Grande Motte, France, 19–22 September 2010.
5. “Through-Mask Electroetching for Fabrication of Metal Bipolar Plate Gas Flow Field Channels” Vol 33 (1), Polymer Electrolyte Fuel Cells 10, The Electrochemical Society pp. 991-1001 (2010).

6. “Characterization of Microporous Layers in Carbon Paper GDL for PEM Fuel Cell”, in ECS Transactions Vol. 33 (1), Polymer Electrolyte Fuel Cells 10, The Electrochemical Society, pp. 1133-1141 (2010).

References

1. T.A. Zawodzinski, C. Derouin, S. Radzinski, R.J. Sherman, V.T. Smith, T.E. Springer and S. Gottesfeld, *J. Electrochem. Soc.*, **140**, 1041 (1993).
2. T.V. Nguyen and R.E. White, *J. Electrochem. Soc.*, **140**, 2178 (1993).
3. C.K. Mittelsteadt and H. Liu, “Conductivity, permeability, and ohmic shorting of ionomeric membranes,” in *Handbook of Fuel Cells; Fundamentals, Technology and Applications: Vol. 5*, W. Vielstich, H. Yokokawa and H.A. Gasteiger, Eds., John Wiley and Sons, Ltd., Chichester (2009).