V.F.6 Transport in PEMFC Stacks

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Contract Number: DE-EE0000471

Subcontractors:
- Tech-Etch, Plymouth, MA
- Ballard Material Products, Inc., Lowell, MA
- Virginia Polytechnic and State University, Blacksburg, VA
- University of South Carolina (USC), Columbia, SC

Project Start Date: November 9, 2009
Project End Date: August 31, 2013

Fiscal Year (FY) 2012 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

Technical Targets

The goal of this project is to improve the understanding of water transport through a combination of experiment and modelling. The ultimate goal of the project is to create a model that takes the most common variables utilized in fuel cell engineering and predict fuel cell performance. Once established, the model will be used to link improvements in fuel cell components to improvements in fuel cell performance, and thereby focusing future research efforts. This will be accomplished by generating fuel cell components with specific properties, developing new methods to characterize their transport properties, then testing and modelling their performance.

FY 2012 Accomplishments

- Completed the synthesis of a full list of hydroquinone-based hydrophilic-hydrophobic block copolymers (hydroquinone sulfone-hexafluoro bisphenol a benzonitrile [HQSH-6FPAEB]) with lower equivalent weight, structure, chemistry and phase separation.
- Successfully casted copolymer powders to membranes varying in size from 4″x4″ (for standard fuel cell technology plates) to 12″x5″ (for General Motors [GM] plates).
- Automated dynamic water uptake/diffusivity test system and completed diffusivity measurements of VA Tech HQSH-6FPAEB membranes.
- Developed an open-ended hydrogen pump apparatus to characterize electro-osmotic drag coefficient (EODC) and measured EODC for Nafion® membrane and HQSH-6FPAEB hydrocarbon membranes.
- Designed new GDLs and completed pore size distribution measurements with fuel cell performance tests.
- Simulated cell performance and current distribution at various values of the water uptake, membrane diffusivity, and EODC.
- Compared modeling results with segmented-cell data for both serpentine and parallel flow-fields.
- Completed simulation of GM down-the-channel fuel cell and compared with available data and validated modeling result with water balance experiment.

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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 measurable transport properties. These transport properties are then used in a model, which enables the prediction of the effect of changing component parameters on transport properties.

Approach

This project seeks to develop a transport model and test the model by developing 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. Also, GDLs, bipolar plates, and flow fields will be developed and tailored to illustrate specific differences in porosity, tortuosity and hydrophobicity. The fuel cell performance will be evaluated using these components and compared with the model. The model will be used to predict the effect of changing component parameters (i.e., changing membrane type and thickness, changing flow field configuration) on component transport properties and fuel cell performance.

Results

Membrane work on 6FPAEB-HQS100 as well as on previous 6FPAEB-biphenyl sulfone (BPS100) provides design guidelines for polymer electrolyte membranes (PEMs) beyond Nafion® membranes, as the structure, chemistry,

and phase separation of copolymer blocks largely impact the transport properties in PEM fuel cells. Block copolymer HQS100-6FPAEB based on 6FPAEB and HQS100 oligomers have been successfully synthesized. The obtained block copolymers vary in molecular weights (from 6K-6K, 9K-9K, to 11K-11K), ion exchange capacity, and proton conductivity. Giner used polymer powders delivered from VA Tech to cast membranes and subsequently measure water uptake, conductivity, diffusivity, and EODC, as well as fabricate these into MEAs. The properties of these membranes are used in modeling work at USC to investigate the fuel cell performance, water distribution, and current distribution. VA Tech first synthesizes a variety of copolymer powders. These block copolymer powders are then cast into films (from 25 to 50 μm) at Giner. Giner then measures the transport properties which are provided to USC for their modeling work. Also at Giner, catalyst inks are deposited onto the membranes to make MEAs. These MEAs are shipped to USC for fuel cell performance evaluation (See Figure 1).

A dead-end hydrogen pump has been developed for characterizing the EODC of Nafion® membranes and hydrocarbon membranes (see Figure 2). The EODC characterization system consists of two cells: a membrane saturator cell and a hydrogen pump cell. Liquid water is fed with a micro-flow meter to one side of the membrane saturator cell while hydrogen flows into the other side of the saturator cell that was pre-evacuated and shown in Figure 2a. Water vapor pressure is controlled by the saturator oven temperature and total pressure is controlled by the hydrogen mass flow meter/pressure controller. By varying these two pressures we can control the water: hydrogen (H_2O: H) feed ratio. Protons generated by hydrogen oxidation at the anode travel across the membrane and then are reduced to hydrogen at the cathode. The voltage of the hydrogen pump cell can be monitored and its stability depends on how close the feed ratio is to the EODC. The ratio corresponding to the most stable voltage can approximate 2*EODC. The most
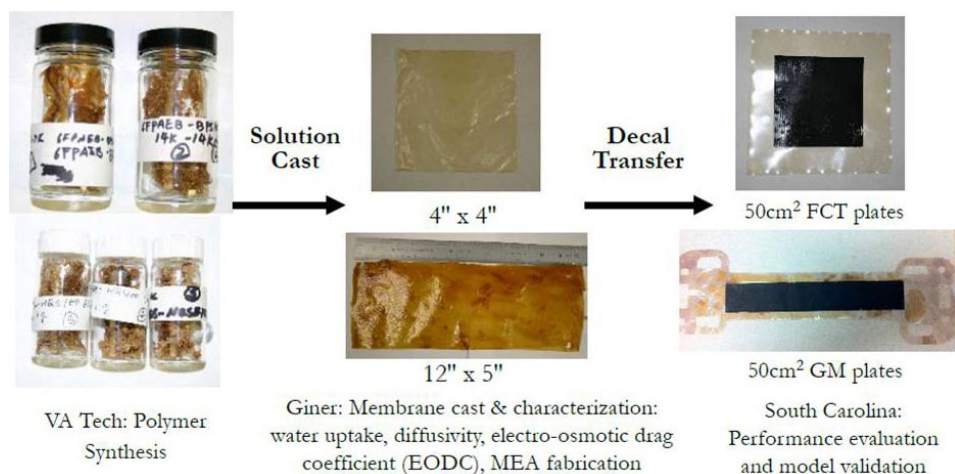

FIGURE 1. Schematic of hydrocarbon membrane development and MEA fabrication
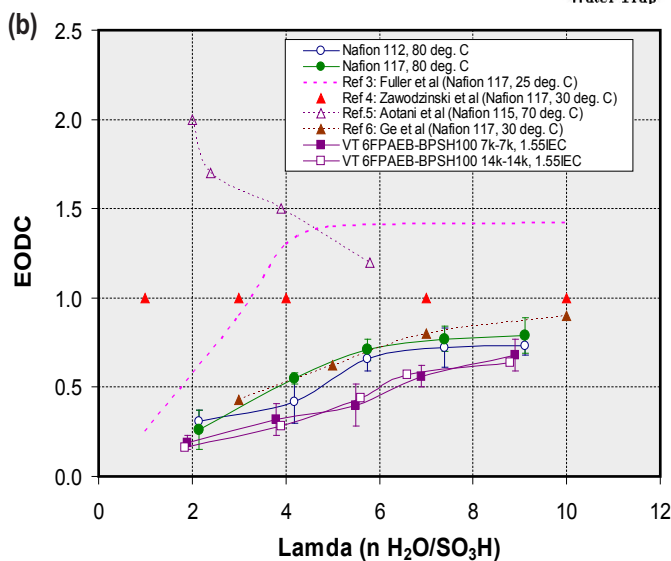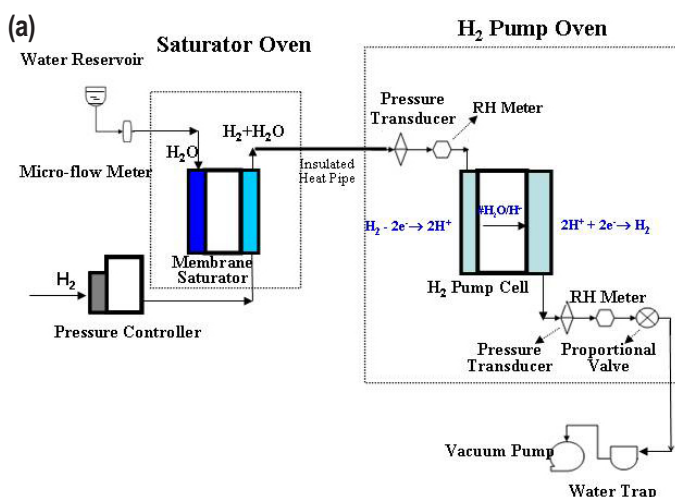
FIGURE 2. Dead-end hydrogen pump for EODC measurements: (a) dead-end hydrogen pump system; (b) EODC measurements for various membranes and from different researchers

distinctive features of the system are that gas/gas diffusion is eliminated prior to the membrane surface, and there is a minimal relative humidity (RH) difference between the inlet and outlet of the hydrogen pump cell (<1%). The other advantages include precisely-controlled water vapor (no condensation) and flexibility in RH and temperature variations. Figure 2b shows the measured EODC of a variety of membranes using this system, as well as a comparison of previous work from several groups. For both the Nafion® membranes (112 and 117) and hydrocarbon membranes (VA Tech 6FPAEB-BPSH100 7k-7k and 14k-14k), the EODC increases as lambda (nH_2O/SO_3H) increases with slightly lower numbers for hydrocarbon membranes. The EODC numbers from this work follow those by Ge et al. However, this figure also reflects significant disagreement between different investigators [3-6].

A total of twelve gas diffusion layers (GDLs) were designed for the purpose of varying transport properties. The newly designed GDLs were modified from three standard Ballard substrates P50, EP40 and P75 by adding two micro-porous layers (MP1 and MP2) with small or large carbon particles either close to or away from the catalysts layer. Each set was treated to provide two different values of diffusivity (See Table 1).

TABLE 1. Principles for designing GDLs

Substrate	Diffusivity Modification	MP1/MP2 (Carbon Particle Size)
P50	Low and High	Small/Large and Large/Small
EP40	Low and HIgh	Small/Large and Large/Small
P75	Low and High	Small/Large and Large/Small

Mercury pore size distributions of newly-designed GDLs were obtained. The baseline of a treated EP40 (i.e., EP40T) has the most pore volume compared to P75T and P50T. All three GDLs have the maximum peak of differential distribution at a pore diameter of 50 μm. Modification of the GDL greatly reduces the volume of large pores. The effect of different GDLs on PEMFC performance was also demonstrated. P75T shows the highest performance at lower humidity whereas EP40T shows the highest performance at higher humidity. Therefore, P75T will be used in the anode and EP40T will be used in the cathode in baseline testing. The MacMullin Number, which is a function of tortuosity and porosity, is often found to follow the equation below [7],

$$N_M = f(\tau, \varepsilon) = \frac{\tau^n}{\varepsilon^m}$$

This relationship has been previously used to characterize the GDLs. The MacMullin Number of these substrates does not appear to follow previous relationships (see Figure 3). The GDLs with micro porous layers have lowered the MacMullin Numbers, a trend which was observed with treatments of Toray TGP-H-060 paper.

Current distributions with a USC-designed parallel flow-field at two conditions were measured using a current distribution board and simulated with the CFD model (see Figure 4): (a) for high RH operation at 1,200 mA/cm^2 and (b) for low RH operation 294 mA/cm^2. First, the CFD model predicts experimental current distribution well. This is reflected in the bar charts where for most segments the two current densities, experimental and CFD-based, are very close. At the wet condition (a), the segment current density decreases from Segment 1 to 5 and from Segment 6 to 10; this is because Segment 1 and 6 are near the inlet, and Segment 5 and 10 are near the outlet. The current decreases for this wet condition because there is sufficient membrane conductivity and because the partial pressure of oxygen decreases as the partial pressure of water increases. The trend at low RH condition (b) is almost opposite from (a) because the dry inlet yields a low membrane conductivity
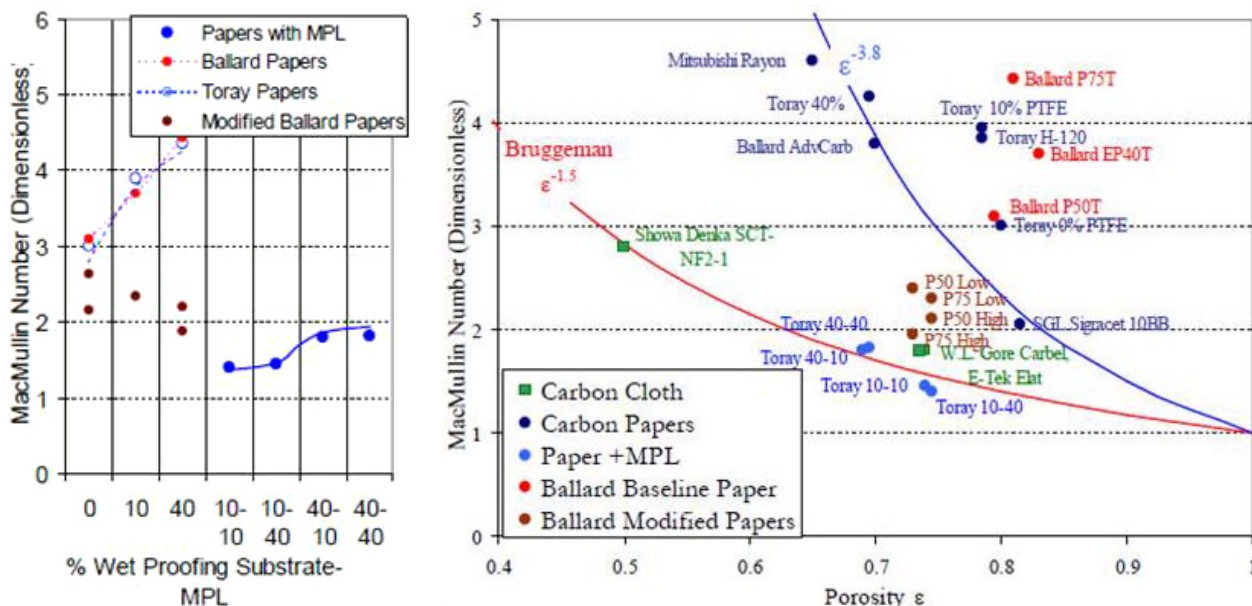
FIGURE 3. MacMullin number for GDL characterization: (left) MacMullin number as function of wet proofing in substrate and MPL (right) MacMullin number as function of porosity.
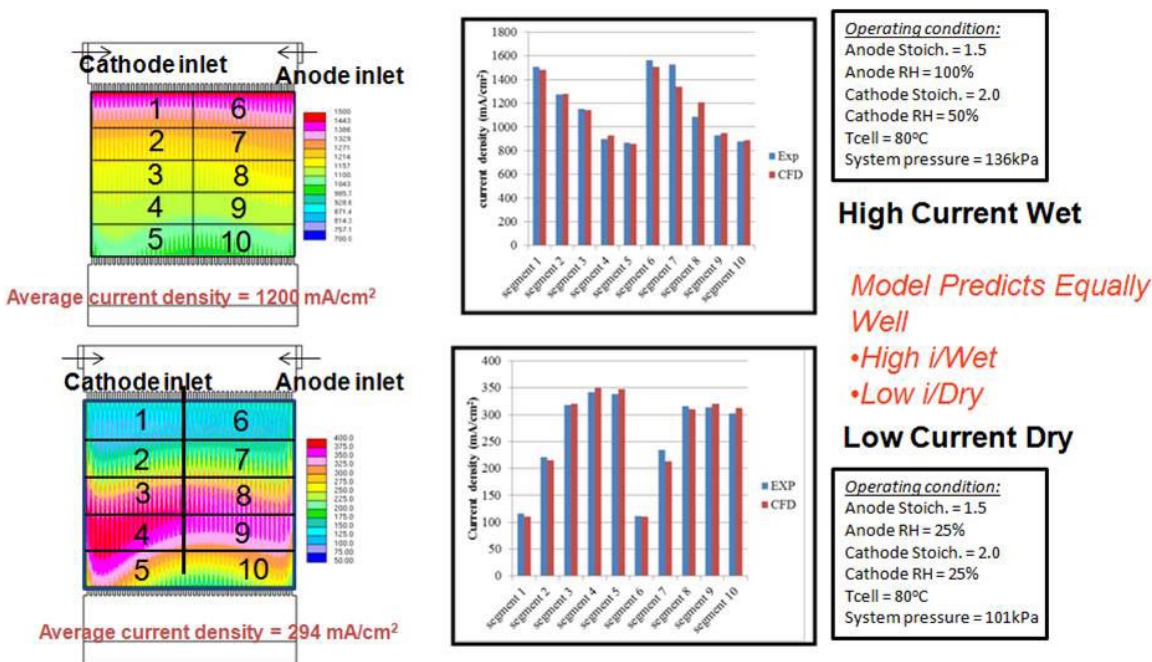

FIGURE 4. Experimental and CFD model-based current distribution on USC parallel metallic plates at two operation conditions: (left) high RH operation at 1,200 mA/cm^2 and (right) low RH operation 294 mA/cm^2.

until sufficient water is produced and accumulated down the channel at sections 3-4 and 8-9 where the current density is a maximum. The current density deceases in sections 5 and 10 because the partial pressure of oxygen decreases. The non-uniformity between sections 4 and 9 is due to the higher velocity in the parallel channel on the cathode side

of the cell; that is because the flow-field was designed for 1.0 A/cm^2 rather than the low flowrates associated with the 0.3 A/cm^2. The modeling results for the GM flow-field were also compared with experimental results from GM (www. pemfcdata.org), including temperature distributions, and they demonstrate excellent consistency (data not shown).

Conclusions and Future Directions

- Widely varied PEMs and diffusion media will allow us to model the important parameters of each.

- Diffusivity measurement systems have been automated for precise control and a variety of hydrocarbon membranes characterized using the advanced system:
  - No interfacial resistance found
  - Techniques widely available to community

- Dead-end hydrogen pump system has been developed for EODC measurements for Nafion® membranes and hydrocarbon membranes:
  - No water condensation found
  - Water diffusion eliminated

- Gas diffusion media with different structure and properties have been designed and characterized and performance compared.

- Experimental and CFD results have been obtained for various flow channels (USC and GM plates) and two results are highly consistent.

- Extend testing and model predictions to additional automotive conditions.

- 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 2012 Publications/Presentations

1. "Transport Studies and Modeling in PEM Fuel Cells," DOE Annual Merit Review, oral FC054, May 13–18, 2012.

2. "Simultaneous Water Uptake, Diffusivity and Permeability Measurement of Perfluorinated Sulfonic Acid Polymer Electrolyte Membranes," ECS Transactions, 41 (1) 101-121 (2011).

3. "Novel Current Distribution Board for PEM Devices," ECS Transactions, 41 (1) 549-559 (2011).

4. "Effect of Microporous Layer on MacMullin Number of Carbon Paper Gas Diffusion Layer," *J. Power Sources,* **207 (1)** 91-100 (2012).

5. "Assessing Porosity of PEM Fuel Cell Gas Diffusion Layers by SEM Image Analysis" , *J. Power Sources*, **197**, 1-11 (2012).

6. "Understanding the Effect of Channel Tolerances on Performance of PEMFCs," *International J. Hydrogen Energy*, **36** (19) 12512-12523 (2011).

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