

V.F.2 Transport in PEMFCs

Cortney Mittelsteadt (Primary Contact), Hui Xu, Shelly Brawn (Giner)
Sirivatch Shimpalee, Visarn Lilavivat (University of South Carolina)
James E. McGrath, Jarrett Rowler (Virginia Polytechnic and State University [VA Tech])
Don Conners, Guy Ebbrell (AvCarb)
Kevin Russell (Tech-Etch)
John W Van Zee (University of Alabama)
Giner, Inc./Giner Electrochemical Systems, LLC
89 Rumford Ave.
Newton, MA 02466
Phone: (781) 529-0529
Email: cmittelsteadt@ginerinc.com

DOE Managers

Donna Ho
Phone: (202) 586-8000
Email: Donna.Ho@ee.doe.gov

Gregory Kleen
Phone: (720) 356-1672
Email: Gregory.Kleen@go.doe.gov

Technical Advisor

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

Contract Number: DE-EE0000471

Subcontractors:

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

Project Start Date: November 1, 2009

Project End Date: April 30, 2014

Overall Objectives

- Design fuel cell components (membranes, gas diffusion layers [GDLs], bipolar plates, and flow fields) that possess specific transport properties
- Establish a computational fluid dynamics (CFD) model to elucidate the effect of component variables on these transport properties
- Determine sensitivity of fuel cell performance to these component properties to identify limiting components for fuel cell transport loss

Fiscal Year (FY) 2013 Objectives

- Design block copolymers with various structure and chemistry
- Determine bulk membrane properties of block copolymers and correlate to their structure and chemistry:
 - Water uptake and diffusivity
 - Electro-osmotic drag
- Evaluate fuel cell performance on block copolymer membranes
- Perform transient, three-dimensional modeling of fuel cell operation on block copolymer membranes

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:

- (A) Durability
- (C) Performance

Technical Targets

The goal of this project is to determine sensitivity of fuel cell performance to component properties to determine limiting components and guide research. This project aims to develop fuel cell components (i.e., membranes, GDLs, bi-polar plates and flow fields), not with the goal of reaching DOE specific technical targets such as catalyst loading and cost targets, but rather that possess specific properties (i.e., water transport and conductivity). A CFD 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 the sensitivity of fuel cell performance to component properties to determine limiting components and guide research.

FY 2013 Accomplishments

- Designed two sets of hydrocarbon block polymers with one varying oligomer and the other varying block length, annealing temperature and ion-exchange capacity (IEC)
- Characterized the water uptake/diffusivity of the above block copolymers and obtained diffusivity at temperatures lower than 80°C

- Characterized electro-osmotic drag coefficients (EODCs) of the above block copolymers and correlated to their chemistry and structure
- Evaluated fuel cell performance of membrane electrode assemblies (MEAs) based on hydrocarbon block copolymer membrane and compared to Nafion[®] membranes
- Simulated cell performance, current distribution, water distribution of MEAs based on hydrocarbon block polymer membranes
- Performed electrode flooding to evaluate the mitigation effects of hydrocarbon membranes compared to Nafion[®] membranes



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 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. 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

Two sets of hydrocarbon block copolymer membranes were designed and synthesized at VA Tech providing 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. Matrix 1 membranes (see Table 1) are based on block copolymer 6FPAEB-BPSH with various block length (7k-7k, 15k-15k, and 10k-18k), IEC (1.55 and 2.01 meq/g), annealing temperature (110 and 220°C). Matrix 2 membranes (see Table 2) contain the same hydrophilic oligomer, BPSH, but a different hydrophobic oligomer, 6FK, 6FPAEB or 6FBPS0. Water uptake, conductivity, diffusivity, and EODC of these block copolymer membranes were characterized at Giner. The properties of these membranes were used by USC to simulate the fuel cell performance, water distribution, and current distribution, which were compared with experimental results of MEAs made from selected block copolymer membranes.

As expected, changing the chain length, IEC and annealing has little effect on the water uptake isotherms (data not shown). Transmission electron microscopy shows clear phase separation for both the 7k-7k and 15k-15k block copolymers. Though there is little difference in water uptake, the smaller block polymers have lower water diffusivity as seen in Figure 1. The figure also shows that

TABLE 1. Hydrocarbon Block Copolymer Matrix 1: Varied Block Length, IEC, Annealing Temperature

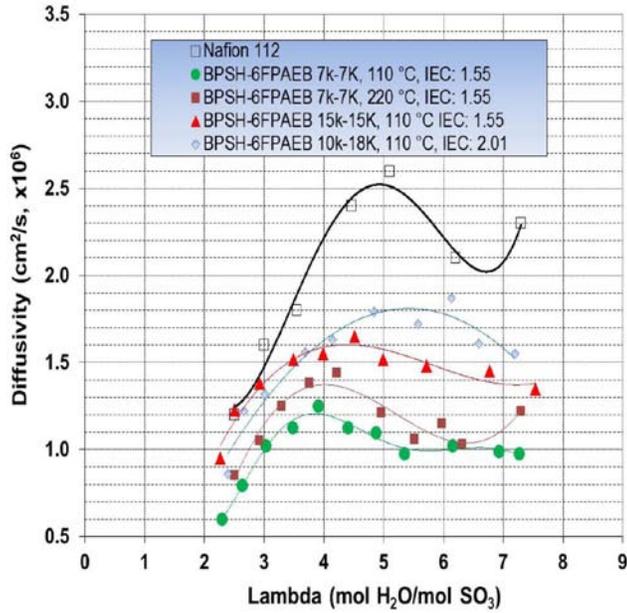
	Polymer	Thermal Treatment Temperature (°C)	IEC (meq/g)
1	6FPAEB-BPSH100 7k-7k	110	1.55
2	6FPAEB-BPSH100 15k-15k	110	1.55
3	6FPAEB-BPSH100 10k-18k	110	2.01
4	6FPAEB-BPSH100 7k-7k	220	1.55
5	6FPAEB-BPSH100 15k-15k	220	1.55
6	6FPAEB-BPSH100 10k-18k	220	2.01

6FPAEB - hexafluoro bisphenol a benzonitrile
BPSH - block polysulfone ether polymer

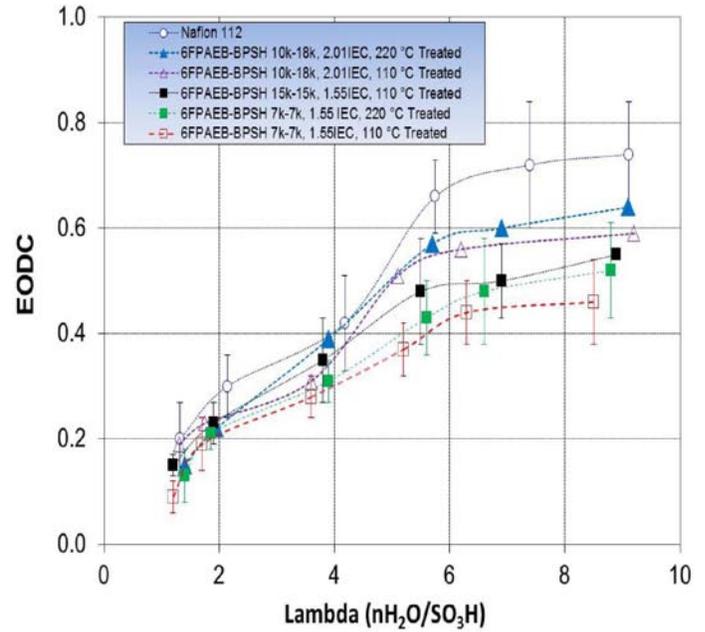
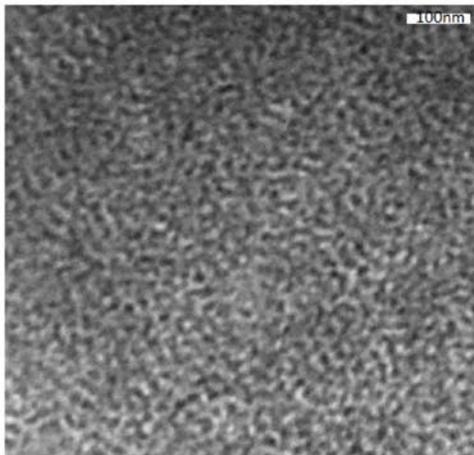
TABLE 2. Hydrocarbon Block Copolymer Matrix 2: Varied Oligomer

Sample	Block Copolymer	Block Length	IEC (meq/g) ^a	Water Uptake (%) ^b	Conductivity (S/cm) ^c
JR-143-2	6FK-BPSH	8K – 8K	1.45	21	0.10
JR-143-3	6FPAEB-BPSH	13K – 13K	1.63	37	0.14
JR-143-4	6FBPS0-BPSH	10K – 10K	1.47	35	0.10

6FK - hexafluoro ketone
 6FBPS0 - hexafluoro biphenol sulfone
 6FPAEB - hexafluoro bisphenol a benzonitrile



7K-7K



15K-15K

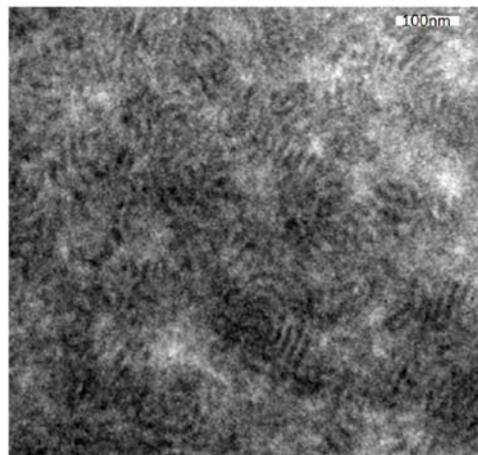


FIGURE 1. Diffusivity and EODC of Matrix 1 Membranes: Varied Block Length, IEC, Annealing Temperature

higher annealing temperature increases the water diffusivity likely due to improved phase separation. The diffusivity of all of the hydrocarbon-based ionomers was significantly lower than that of Nafion®. This is expected as the chain

length increases, the scale of phase separation increases, and the water behaves more like “bulk water”. The EODC of the hydrocarbon membranes with different chain lengths followed the same pattern as diffusivity. EODC also appears

to decrease with chain length as seen in Figure 1, though the results are within measurement error. All the hydrocarbon copolymers were lower than Nafion[®]. This is again attributed to the “tighter” water structure of the short-chain polymers. Under such confinement, it is reasonable that the acid will be more tightly coordinated with the surrounding waters, favoring Grotthus hopping and thereby decreasing the EODC.

Hydrophobicity of the inactive chain may also have a minor effect on EODS as seen in Figure 2. The trend for EODC is in the same order as hydrophobicity of the three inactive blocks (6FPAEB<6FK<6FBPS0). It was not possible to generate polymers with the exact same block length and IEC for this comparison, however, and these polymers also follow the same pattern of block length mentioned above and it is not possible to divorce these effects.

A selected hydrocarbon block copolymer membrane 6FPAEB-BPSH 1000 (13k-13k, IEC=1.7, annealed at 210°C, 30- μ m thick) was made into MEAs, which were tested for fuel cell performance (see Figure 3). It can be seen that at higher humidity, the hydrocarbon membrane gives higher performance than Nafion[®] 112 membrane; however, at lower humidity, Nafion[®] 112 membrane demonstrates better performance. CFD simulations predict similar trends using different properties of these two categories of membranes (hydrocarbon membrane possess lower EODC coefficient

and water diffusivity than Nafion[®] 112 membrane). Using the water transport numbers from the external characterizations of the membranes the CFD model predicts a higher rate of water transport to the cathode, and a subsequently thicker water film at the Nafion[®] MEA cathode, resulting in flooding at lower current densities.

Local distributions of water content in the membrane (Nafion[®] vs. hydrocarbon) and liquid water on the cathode MEA/GDL interface at 95% relative humidity and 0.6 A/cm² were simulated and are shown in Figure 4. Though water contents for both membranes are similar, the higher EODC of Nafion[®] leads to greater flooding at the cathode, predicted in the CFD model and seen in the polarization curves.

CONCLUSIONS AND FUTURE DIRECTIONS

- Two sets of hydrocarbon block polymers have been successfully synthesized with one varying oligomer and the other varying block length, annealing temperature and IEC.
- Diffusivity of the above hydrocarbon membranes have been characterized using Giner’s dynamic water uptake system:
 - All hydrocarbon membranes show lower diffusivity than Nafion[®] membranes.

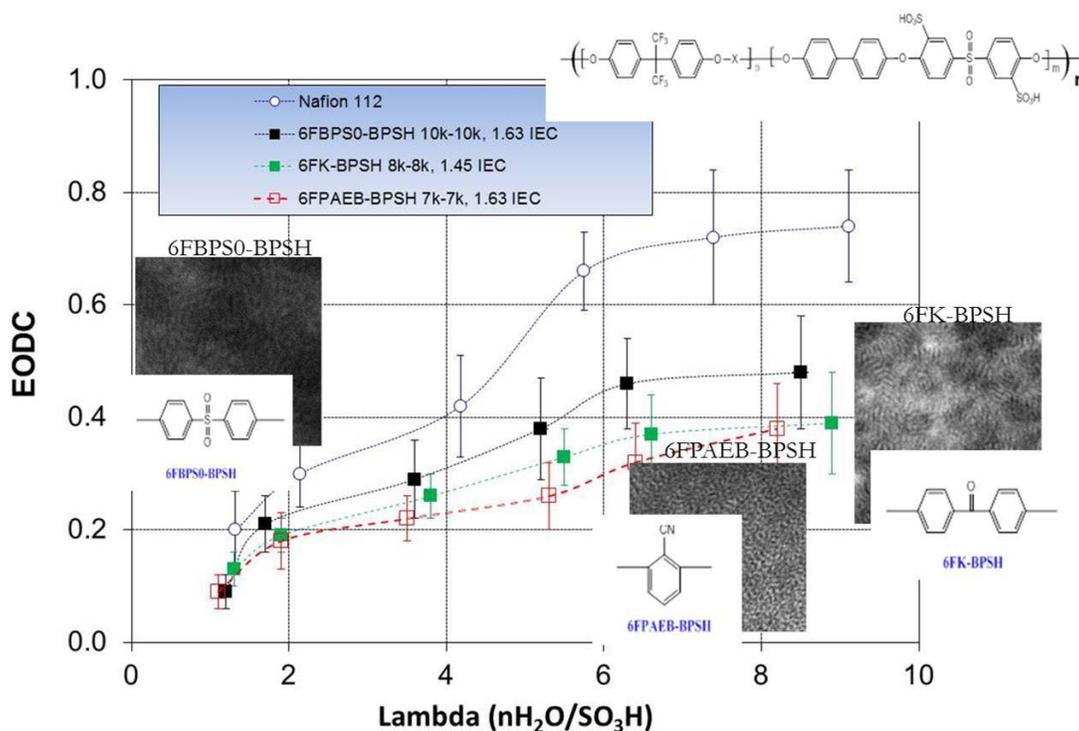


FIGURE 2. EODC of Matrix 2 Membranes: Varied Hydrophobicity of Inactive Oligomer

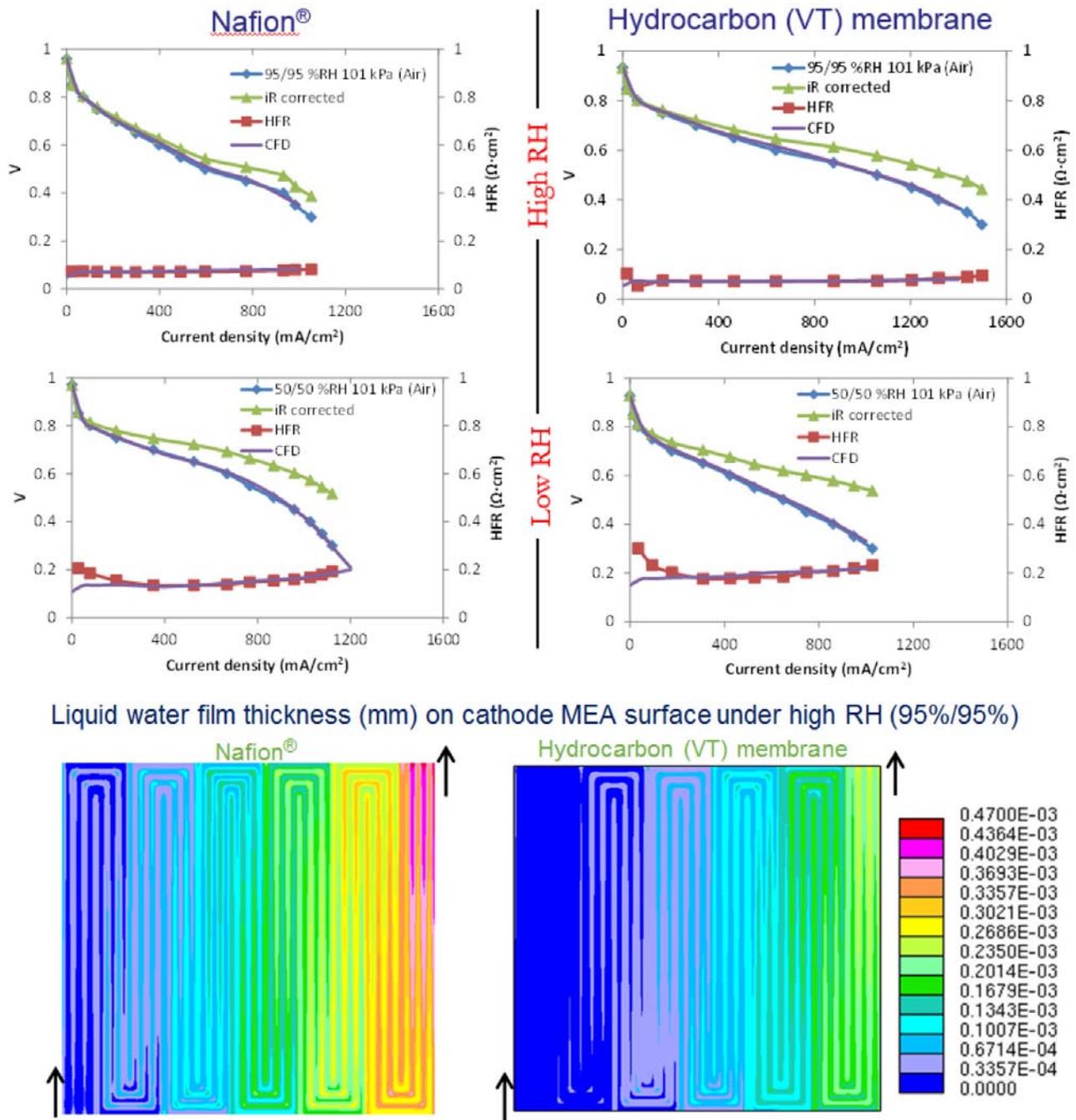


FIGURE 3. Fuel Cell Performance Comparison of Hydrocarbon Membranes with Nafion® Membranes

- Larger block lengths lead to higher water diffusivity. This appears to be due to the longer lengths of order as seen in transmission electron microscope images.
- EODC of the above hydrocarbon membranes have been characterized using Giner’s dead-end hydrogen pump system:
 - All hydrocarbon membranes show lower EODC than Nafion® membranes.
- Differences amongst hydrocarbon materials are less than between those membranes and Nafion®, however they appear to trend towards larger degrees of separation lead to higher EODC.
- Fuel cell performance of MEAs based on hydrocarbon membranes were evaluated and compared to that of Nafion® membranes:

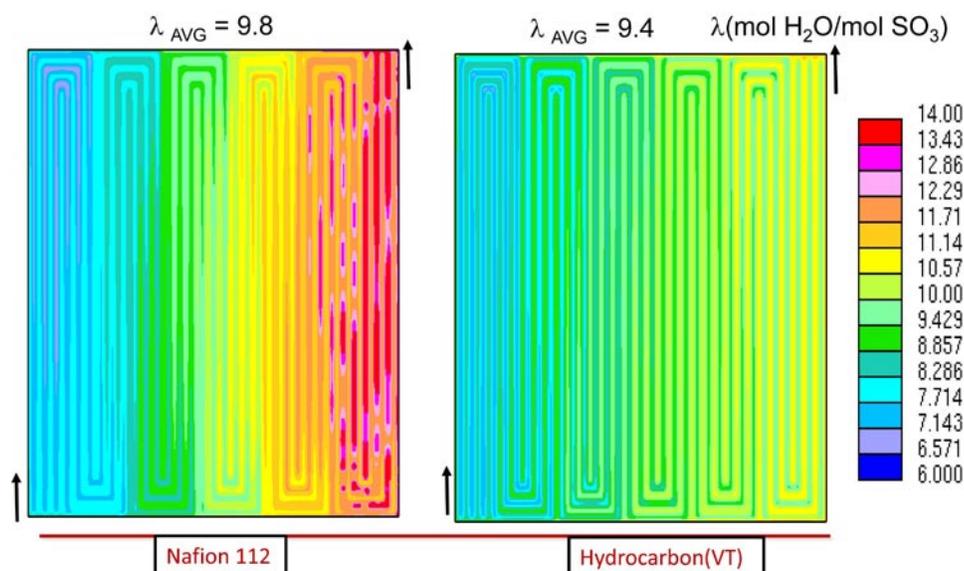


FIGURE 4. Local Distributions of Water Content in Membrane (Nafion® vs. Hydrocarbon) at 95% Relative Humidity

- At higher humidity, hydrocarbon membranes show better performance than Nafion® membranes and vice versa.
- Local distributions of water content in hydrocarbon membranes and liquid have been simulated and compared with Nafion® membranes.
- Develop a new method for measuring diffusion within the diffusion media, while concentrating on the flooded region.

FY 2013 PUBLICATIONS/PRESENTATIONS

1. “Novel System for Characterizing Electro-Osmotic Drag Coefficient of Proton Exchange Membranes,” presented in 220th Meeting of ECS, Abstract #1304, Honolulu, October 2012.
2. M. Martinez, S. Shimpalee, T. Cui, B. Duong, S. Seraphin, J.W. Van Zee, “Effect of microporous layer on MacMullin number of carbon paper gas diffusion layer,” *J. of Power Sources*, **207**(1), 91-100 (2012).
3. “Using a novel current distribution board to understand local transport in PEMFCs”, presented in 220th Meeting of ECS, Abstract #1545, Honolulu, October 2012.
4. Chen, Yu; Lee, Chang Hyun; Rowlett, Jarrett R.; McGrath, James E., “Synthesis and characterization of multiblock semi-crystalline hydrophobic poly(ether ether ketone)-hydrophilic disulfonated poly(arylene ether sulfone) copolymers for proton exchange membranes,” *Polymer*, **53**(15), 3143-3153 (2012).
5. Chen, Yu; Guo, Ruilan; Lee, Chang Hyun; Lee, Myoungbae; McGrath, James E., “Partly fluorinated poly(arylene ether ketone sulfone) hydrophilic-hydrophobic multiblock copolymers for fuel cell membranes,” *International Journal of Hydrogen Energy*, **37**(7), 6132-6139 (2012).

6. “Transport in PEMFC Stacks,” Presented in DOE Hydrogen and Fuel Cell Merit Review Meeting, Arlington, VA, May 2013.

7. V. Lilavivat, S. Shimpalee, H. Xu, J.W. Van Zee, and C.K. Mittelsteadt, “Novel current distribution board for PEMFC,” submitted to *Intl J. of Hydrogen Energy* (2013).

8. V. Lilavivat, S. Shimpalee, H. McCrabb, and J. W. Van Zee, “Fundamental Analyses, Observations, and Predictions of Liquid Droplet Movement on Etched-Metal Surfaces for PEMFC,” submitted to *Electrochimica Acta* (2013).

9. Chen, Yu; Rowlett, Jarrett R.; Lee, Chang Hyun; Lane, Ozma R.; Van Houten, Desmond J.; Zhang, Mingqiang; Moore, Robert B.; McGrath, James E., “Synthesis and characterization of multiblock partially fluorinated hydrophobic poly(arylene ether sulfone)-hydrophilic disulfonated poly(arylene ether sulfone) copolymers for proton exchange membranes,” *Journal of Polymer Science, Part A: Polymer Chemistry* (2013), published online: DOI: 10.1002/pola.26618.

10. The effect of block length upon structure, physical properties, and transport within a series of sulfonated poly(arylene ether sulfone)s, Y. Fan, C.J. Cornelius, H.S. Lee, J.E. McGrath, M. Zhang, R.B. Moore and C.L. Staiger, *Journal of Membrane Science*, **430**, 106-112 (2013).

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).