V.A.5 Neutron Imaging Study of the Water Transport in Operating Fuel Cells

Muhammad Arif (Primary Contact),
David L. Jacobson, Daniel S. Hussey
National Institute of Standards and Technology (NIST)
100 Bureau Drive
Gaithersburg, MD 20899
Phone: (301) 975-6303
E-mail: arif@nist.gov

DOE Technology Development Manager:
Nancy L. Garland
Phone: (202) 586-5673
E-mail: Nancy.Garland@ee.doe.gov

Contract Number: DE-AI-01-01EE50660

Project Start Date: Fiscal Year (FY) 2001
Project End Date: Project continuation and direction determined annually by DOE

Objectives

- Provide neutron imaging-based research and testing infrastructure to enable the fuel cell industry to design, test, and optimize prototype to commercial grade fuel cells.
- Provide a secure facility for proprietary research by industry. Make open research data available for beneficial use by the general fuel cell community.
- Continually improve and develop methods and technology to accommodate rapidly changing industry/academia needs.

Technical Barriers

This project addresses the following technical barriers from the Fuel Cells section (3.4) of the Fuel Cell Technologies Program Multi-Year Research, Development and Demonstration Plan:

(A) Durability

(C) Performance

(D) Water Transport within the Stack

2015 System Targets

- Unassisted start from low temperature: -40°C
- Durability with cycling at operating temperature of ≤80°C: 5,000 h
- System energy density: 650 W/L
- System specific power: 650 Watt/kg
- Energy efficiency: 65% at 25% rated power, 55% at 100% rated power
- Cost: $35/kW$_e$
- Start-up time to 50% power: 30 seconds from -20°C, 5 seconds from 20°C
- Freeze start operation: unassisted start from -40°C
- Durability with cycling: 5,000 hrs

Accomplishments

- Improve spatial resolution of the measurement of the through-plane water content of an operating proton exchange membrane fuel cell (PEMFC). Develop stable, high resolution charge-coupled device (CCD)-scintillator detector system.
  - New high resolution neutron imaging system deployed and in use.
  - Measured spatial resolution is 13 µm.
  - High resolution system using scintillator coupled to CCD achieves sub 20 µm spatial resolution
- Measure fundamental through-plane transport properties of diffusion media (DM) and membranes that incorporates improved measurement uncertainty analysis. Transfer new data analysis suite to fuel cell industry and national labs. Prepare for publication in a peer reviewed journal article demonstrated use of new analysis tools with established models and data.
  - Measured gas diffusion in DM as a function of saturation and electroosmotic drag in hydrogen pumping experiments.
  - In collaboration with Los Alamos National Laboratory (LANL), have studied a range of membrane histories and compositions; results and analysis are being prepared for publication.
  - The measured water content in the DM has been compared to models of the saturation using NIST-developed analysis tools.
- Search for systematic errors in neutron radiography:
  - Determined systematic underestimation of water content due to unaccounted residual water in dry membrane images and beam hardening.
  - Developed experimental method to overcome this systematic undercounting of water.
- Improvements to the Neutron Imaging Facility and fuel cell support infrastructure:
  - Improved the facility fuel cell test stand humidification system allowing for more

accurate humidification of fuel cells designed for high resolution testing.

– Improved the high resolution freeze testing capabilities of the facility.

Introduction

At NIST, we maintain the premier fuel cell neutron imaging facility in the world and continually seek to improve its capabilities. This facility provides researchers a powerful and effective tool to visualize and quantify water transport inside operating fuel cells. Imaging the water dynamics of a PEMFC is carried out in real time with the required spatial resolution needed for fuel cells that are being developed today. From these images, with freely available NIST-developed image analysis routines, PEMFC industry personnel and researchers can obtain in situ, non-destructive, quantitative measurements of the water content of an operating PEMFC. Neutron imaging is the only in situ method for visualizing the water distribution in a "real-world" PEMFC. Unlike X-rays, whose interaction with materials increases with the number density of electrons, neutrons interact via the nuclear force, which varies somewhat randomly across the periodic table, and is isotopically sensitive. For instance, a neutron's interaction with hydrogen is approximately 100 times greater than that with aluminum, and 10 times greater than that with deuterium. It is this sensitivity to hydrogen (and insensitivity to many other materials) that is exploited in neutron imaging studies of water transport in operating fuel cells.

Approach

The typical length scales of interest in a PEMFC are: channels approximately 1 mm wide and 1 mm deep, the DM is 0.1 mm to 0.3 mm thick, the membrane is 0.01 mm to 0.05 mm thick, and the active area is 2 cm^2 to 500 cm^2. Thus, to nondestructively study in situ the water and hydrogen transport in PEMFCs while in operation we will develop new facilities and improve existing capability for obtaining high spatial and temporal resolution neutron images. Employing the mathematical models of neutron scattering, we will develop a software suite that enables users to obtain quantitative measurements of the water content in an operating PEMFC. Due to the complexity of PEMFCs and the large number of open questions regarding water transport in PEMFCs, we will develop partnerships with industry, academia, and national laboratories to train them in the use of the facility, collaborate with them on research projects, and seek their feedback to pursue future technical breakthroughs.

Results

We have worked in close collaboration with LANL to develop a fundamental understanding of the water uptake by the membrane, a critical materials characterization for modeling the through-plane water transport in PEMFCs. This collaborative effort explored multiple sources of measurement uncertainty, both in the neutron imaging system and in the fuel cell operation and assembly; a full journal article is in preparation that will detail the effort summarized here. The most important advancement impacting these measurements has been the recent introduction of the new high resolution microchannel plate detector, with a measured spatial resolution of about 13 µm. The impact of this detector on the measurement of PEMFC through-plane water content can be seen in Figure 1, where images of a test section viewed edge on are imaged at three different spatial resolutions. The right-most image shows the current detector spatial resolution, which is a factor of 20 improvement over the spatial resolution at the start of this project.

Another important refinement that was recently made to the neutron image analysis is the proper accounting of the residual water content of the membrane (both in the active area and under the gaskets) in the dry reference image. For the new detector, the measured neutron attenuation is not linear in water thickness, a known effect called beam hardening. Beam hardening can be modeled by a quadratic function allowing the water content to be accurately estimated from the radiographs. Accounting for the beam hardening effect and the residual water in the membrane modifies the calibration of neutron intensity versus water thickness. Shown in Figure 2a is a comparison of the membrane hydration with and without incorporating the residual water. This

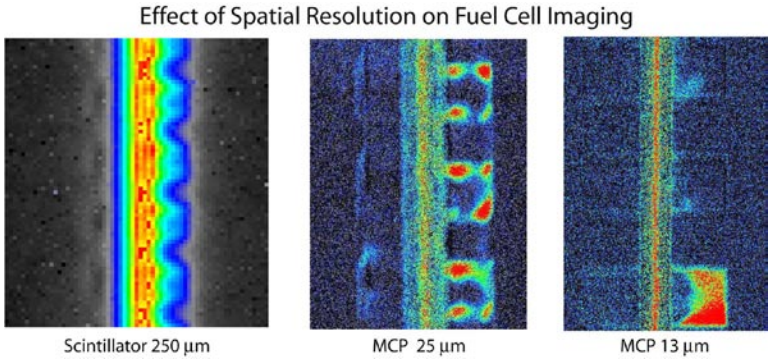

FIGURE 1. Demonstration of the impact that the factor of 20 improvement in the spatial resolution achieved by this project during the last four years has had on the measurement of the through-plane water content.

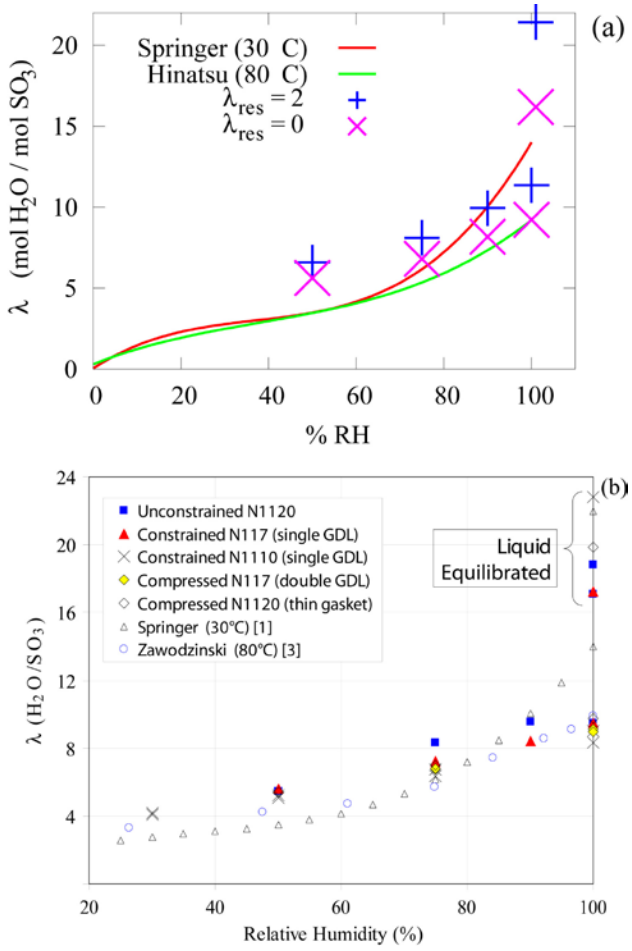

FIGURE 2. a) Comparison of membrane hydration with and without including the effect of beam hardening due to the residual water in the dry image. b) Results of membrane hydration for different membrane compressions after applying the correction for residual water and beam hardening.

systematic effect can now be corrected for by a direct measurement of the membrane water content with neutrons during the experiment. These improvements in the neutron radiography analysis have been combined with improved humidity control and monitoring, improved flow field design, and ex situ thermo-gravimetric analysis (TGA) of the water content of a dry membrane to study the water uptake of membranes under different states of compression, and varying levels of protonation. An initial analysis of these data for the membrane compression study is shown in Figure 2, with a comparison to previous TGA measurements.

The neutron imaging facility staff facilitates and collaborates with a broad group of neutron imaging users with experiments that support the DOE Hydrogen Program. In the past year, neutron imaging data from this unique facility has been used by researchers from six companies, eight universities, three national laboratories, and has been a part of the thesis research of 12 graduate students. Among these projects researchers from General Motors, Rochester Institute of Technology, and the Michigan Technological University used the imaging facility to study a wide range of purge conditions and the impacts of varying thermal properties of the DM on water management. These studies are critical to develop a fuel cell robust enough to withstand the stresses of freeze and achieve the DOE cold start targets. A cell was designed for this work that closely parallels publicly known details of automotive fuel cell designs. This allows the cell to be more representative of commercial automotive designs yet the details of cell operation can be publicly shared. Coupled with neutron imaging measurement of the water content, the design incorporates in situ current, temperature, and high frequency impedance distribution measurements, enabling precise, local correlations between water mass, current density, temperature and high frequency resistance (HFR) (Figure 3a). While HFR measurements probe the state of hydration of the fuel cell membrane, they are not capable of determining the actual amount of water in the fuel cell membrane. Using neutron imaging, which allows quantification of the water content, a correlation between the local HFR and local water content in the fuel cell during a purge can be made (Figure 3b). Here the sensitivity of neutron imaging to water is clearly shown to be as low as 4 micrometers corresponding to a water mass of about 6.5×10^{-8} g per pixel. The correlation clearly shows a marked change in HFR when the amount of water in the cell is roughly equal to the membrane thickness. With this information, accurate models of the dry purge can be derived that aim to reduce the amount of input energy needed to purge the fuel cell stack at shutdown and still start under freeze conditions.

In addition to studying the effects of purge on cold-start, this cell was used to study the effects of varying the properties of the DM on water management, in particular the thermal conductivity. During operation of the cell, the waste heat from the cathode reaction results in a temperature gradient between the membrane and the flow fields, with the membrane at a higher temperature; thus the water saturation pressure at the membrane is higher than at the flow fields. Changing the temperature profile can therefore reduce or increase the amount of water that condenses in the DM. As shown in Figure 4, by raising the thermal conductivity of the DM the temperature gradient decreases, resulting in more condensed water in the DM. Conversely by lowering the thermal conductivity of the DM the temperature gradient increases, resulting in less condensed water in the DM. Overall more condensed water was observed in diffusion media with higher thermal conductivity than ones with lower thermal conductivity. From this data, one can create structured DM, shown in Figure 4d, to optimize the water transport along the length of the active area seen in Figure 4e.

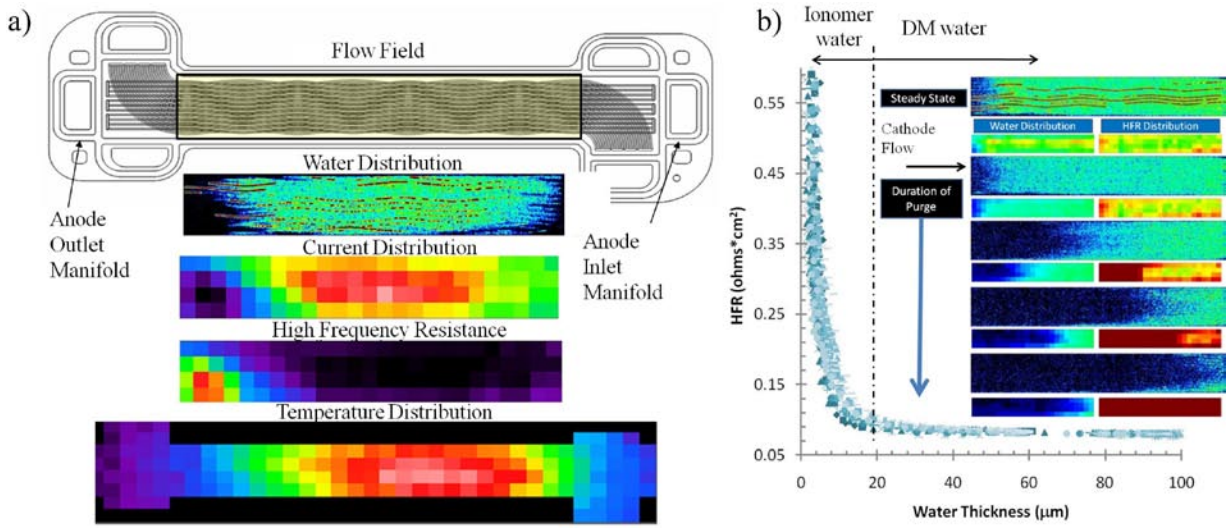

FIGURE 3. Shown here in a) is the fuel cell with representative images of the separate in situ characterizations that were performed at once. The second image from the top shows the neutron image and how it correlates to all the other in situ measurements. Here the water distribution is peaked where the current peaks along with the minimized HFR and a maximum in temperature due to waste heat from the chemical reaction. In b) the local HFR is shown as a function of water mass measured using neutron imaging. The neutron method is capable of measuring the local water content with 4 micrometer uncertainty.

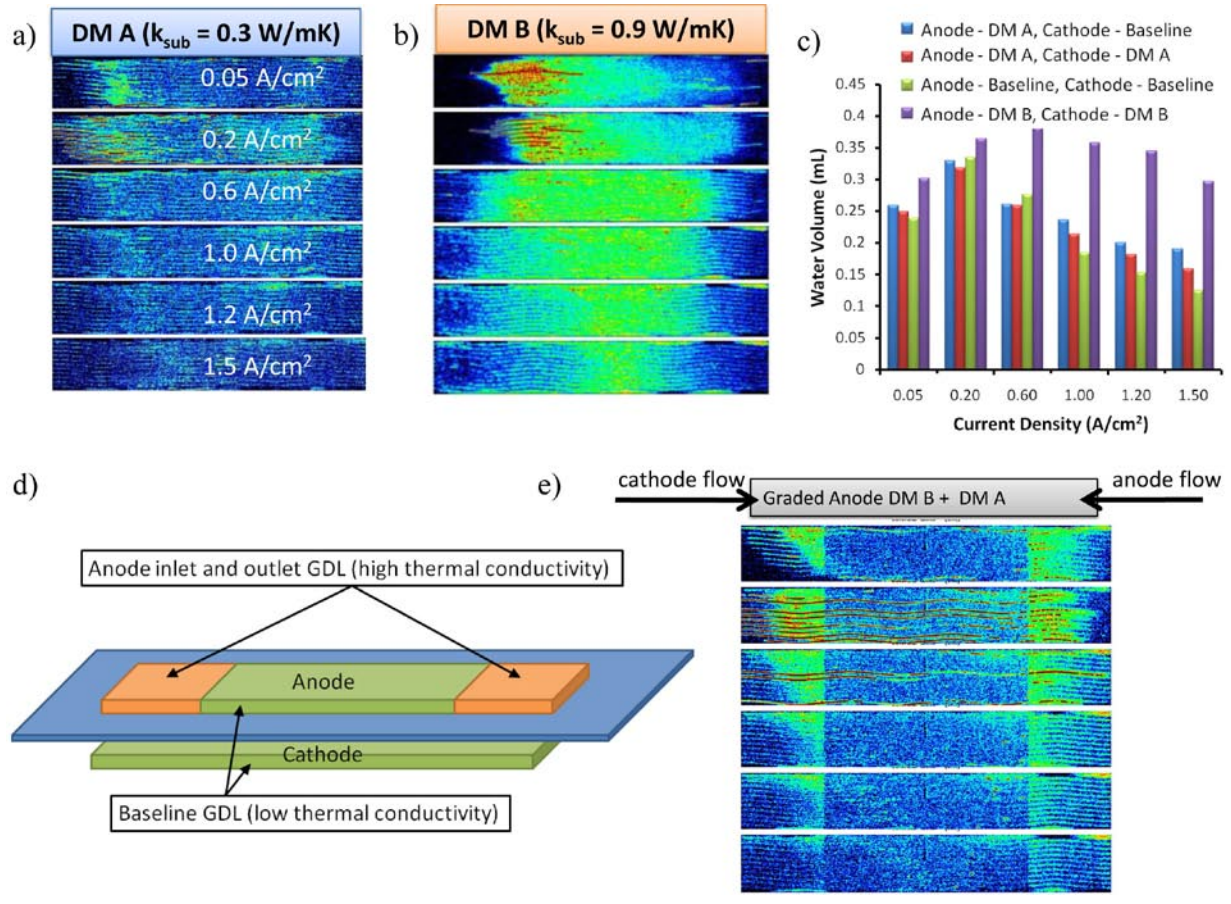

FIGURE 4. Shown in a) are the neutron images of the water distribution of a DM with low thermal conductivity for various current densities and b) a DM with high thermal conductivity. The amount of retained water is plotted in c) for the various current densities for the DMs of varying thermal conductivity. A graded DM is shown in d) where high thermal conductivity DMs are used near the dry inlets to improve membrane hydration seen in e), while low thermally conductive DMs are used in the middle wetter region to reduce flooding in the DM.

Researchers from Pennsylvania State University used the NIST high-resolution detector to image a cell from the edge and varied the hydrophobicity of the flow fields to determine where the retained water was between the anode and cathode [1]. A previous study of the in-plane water distribution showed the surprising result that the cell retains more water with hydrophoboic flow fields at lower current densities [2]. The present study observed that the hydrophobic lands result in small unconnected droplets, preventing the capillary wicking that occurs with the laminar sheets formed on hydrophilic surfaces. Therefore less water was pulled out of the DM into the channel, and more water was present on the anode due to increased back diffusion. This excess water in the DM formed large, connected regions under the flow channels, increasing the likelihood of flooding in the channels, and could have adverse affects on the cell operation during shutdown and startup under sub-zero conditions.

Conclusions

- High-resolution imaging is playing a key role in understanding the through-plane water transport in fuel cells:
  - Current resolution of 13 µm represents a factor of 20 improvement in spatial resolution over a four year period.
  - Fundamental water transport measurements in the DM provide:
    - Understanding of transport in fuel cells with hydrophobic channels.
    - Understanding of the role of phase change induced flow.
  - In situ membrane hydration measurements are critical for accurate models of water transport:
    - Worked with LANL in understanding the hydration of membranes as a function of water activity, membrane compression, and protonation.
    - Determined an experimental method to account for undercounting of water and eliminate this systematic from neutron imaging.
    - Combined results from thermo gravimetric analysis and neutron imaging to correctly analyze data.
- Neutron user program successfully provides users with unique access to neutrons:
  - In the past year, neutron imaging data from this unique facility has been used by researchers from six companies, eight universities, three national laboratories, and has been a part of the thesis research of 12 graduate students.
  - The experiments performed at the NIST neutron imaging facility over the last year have resulted in over 30 publications/presentations.
  - Continued facility improvements to maintain state-of-the-art fuel cell test and control infrastructure.

Future Directions

- Study transport and dynamics in four cell stacks designed for neutron radiography.
- Study water transport in the microporous layer and compare with realistic models of the microporous layer.
- Work with modelers to correlate models and experimental data in an operating fuel cell.
- Develop large area detectors (10 cm by 10 cm) with spatial resolution of less than 15 µm.
- Investigate neutron optical techniques to improve the spatial resolution to less than 10 µm.

FY 2010 Publications/Presentations

1. D.S. Hussey, D.L. Jacobson, M. Arif, K.J. Coakley and D.F. Vecchia, "In Situ Fuel Cell Water Metrology at the NIST Neutron Imaging Facility", J. Fuel Cell Sci. Technol., 7, 021024 (2010).

2. M.A. Hickner, N.P. Siegel, K.S. Chen, D.S. Hussey, and D.L. Jacobson, "Observations of Transient Flooding in a Proton Exchange Membrane Fuel Cell Using Time-Resolved Neutron Radiography", J. Electrochem. Soc., 157, B32-B38 (2010).

3. A. Turhan, S. Kim, M. Hatzell, M.M. Mench, Impact of channel wall hydrophobicity on through-plane water distribution and flooding behavior in a polymer electrolyte fuel cell, Electrochim. Acta, 55, 2734-2745, (2010).

4. M.A. Hickner, D.S. Hussey, "Neutron Radioscopy: Industrial and Scientific Applications", Wiley Encyclopedia of Analytical Chemistry, R.A. Meyers (Ed.), Chapter a9069 (2010).

5. Spernjak D., Prasad A.K., Advani S.G., "In situ comparison of water content and dynamics in parallel, single-serpentine, and interdigitated flow fields of polymer electrolyte membrane fuel cells", J. Power Sources, 195, 3553-3568 (2010).

6. S. Kim, M.M. Mench, "Investigation of Temperature-Driven Water Transport in Polymer Electrolyte Fuel Cell: Phase-Change-Induced Flow", J. Electrochem. Soc., 156, Issue 3, pp. B353-B362 (2009).

7. D. Spernjak, S.G. Advani, and A.K. Prasad, "Simultaneous Neutron and Optical Imaging in PEM Fuel Cells", J. Electrochem Soc., 156 (1), B109-B117, (2009).

8. T.A. Trabold, J.P. Owejan, J.J. Gagliardo, D.L. Jacobson, D.S. Hussey and M. Arif, "Use of neutron imaging for proton exchange membrane fuel cell (PEMFC) performance

analysis and design", Handbook of Fuel Cells, Vol. 5, chpt. 44, (2009).

9. J.P. Owejan, J.J. Gagliardo, S.R. Falta and T.A. Trabold, "Accumulation and Removal of Liquid Water in Proton Exchange Membrane Fuel Cells", J. Electrochem Soc., 156, B1475-B1483 (2009).

10. J.J. Gagliardo, J.P. Owejan , T.A. Trabold, and T.W. Tighe, "Neutron radiography characterization of an operating proton exchange membrane fuel cell with localized current distribution measurements", NIM-A 605, 115-118 (2009).

11. Turhan, A., Kim, S., Hatzell, M., and Mench, M.M., "Impact of Channel Wall Hydrophobicity on Through-plane Water Distribution and Flooding Behavior in a Polymer Electrolyte Fuel Cell", Electrochimica Acta, 55, 2734–2745 (2010).

12. Khandelwal M., Lee S., and Mench M.M., "Model to Predict Temperature and Capillary Pressure Driven Water Transport in PEFCs After Shutdown", Journal of Electrochemical Society, 156, B703-B715 (2009).

13. R. Mukundan and R. Borup, "Visualising Liquid Water in PEM Fuel Cells Using Neutron Imaging", Fuel Cells, 9, 499-505 (2009).

14. Yun Wang, Partha P. Mukherjee, Jeff Mishler, Rangachary Mukundan, and Rodney L. Borup, "Cold start of polymer electrolyte fuel cells: Three-stage startup characterization", Electrochimica Acta, 55, 2636–2644 (2010).

15. R.L. Borup, R. Mukundan, J. Davey, J. Spendelow, D.S. Hussey, D.L. Jacobson, and M. Arif, "In Situ PEM Fuel Cell Water Measurements", ECS Trans. 17, 263 (2009).

16. J.R. Davey, R. Mukundan, J.S. Spendelow, P.P. Mukherjee, D.S. Hussey, D.L. Jacobson, M.Arif, and R. Borup, "Wetting and Drying Responses of Gas Diffusion Layers and Proton Exchange Membrane to Current Transients", ECS Trans. 25, 971 (2009).

17. R.S. Fu, J.S. Preston, U. Pasaogullari, Y. Tabuchi, T. Shiomi, D.S. Hussey, and D.L. Jacobson, "An Investigation of Thermally-Induced Water Transport in Polymer Electrolyte Fuel Cells with Neutron Radiography Imaging Technique", ECS Trans. 25 (1), 543 (2009).

18. P.P. Mukherjee, R. Mukundan, J.S. Spendelow, J.R. Davey, R. Borup, D.S. Hussey, D.L. Jacobson, and M. Arif, "High Resolution Neutron Imaging of Water in the PEMFC Membrane", ECS Trans. 25, 505 (2009).

19. R. Mukundan, R. Lujan, J.R. Davey, J.S. Spendelow, D.S. Hussey, D.L. Jacobson, M. Arif, and R. Borup, "Ice Formation in PEM Fuel Cells Operated Isothermally at Sub-Freezing Temperatures", ECS Trans. 25, 345 (2009).

20. J.S. Preston, R.S. Fu, U. Pasaogullari, D.S. Hussey, and D.L. Jacobson , "An Updated Look at the Role of Micro-Porous Layer on Liquid Water Distribution in Polymer Electrolyte Fuel Cells", ECS Trans. 25, 311 (2009).

21. R.S. Fu, U. Pasaogullari, Y. Tabuchi, T. Shiomi, D.S. Hussey, and D.L. Jacobson, "Neutron Radiography Imaging of Thermally-Induced Water Transport in Polymer Electrolyte Fuel Cells", Meet. Abstr. - Electrochem. Soc. 902 852 (2009).

22. J. Spendelow, R.Mukundan, J.R. Davey, P.P. Mukherjee, D.S. Hussey, D.Jacobson, M. Arif, and R. Borup, "Quantitative PEMFC Water Measurement by Neutron Radiography", Meet. Abstr. - ECS 902 851 (2009).

23. B. McCain, A. Stefanopoulou, and I. Kolmanovsky, "A Dynamic Semi-Analytic Channel-to-Channel Model of Two-Phase Water Distribution for a Unit Fuel Cell," Control Systems Technology, IEEE Transactions, 17, 2009.

24. J. Siegel, A.G. Stefanopoulou, and S. Yesilyurt, "Extracting Model Parameters and Paradigms from Neutron Imaging of Dead-ended Anode Operation," ASME 7th International Fuel Cell Science, Engineering & Technology Conference, Newport Beach, California: 2009.

25. S. Yesilyurt, J. Siegel, and A. Stefanopoulou, "Effects of Nitrogen and Water Accumulation in the Dead-Ended-Anode Operation of PEM Fuel Cells," ECS Meeting Abstracts, San Francisco, California: 2009, p. 359.

26. G. Ripaccioli, J.B. Siegel, A.G. Stefanopoulou, and S. Di Cairano, "Derivation and Simulation Results of a Hybrid Model Predictive Control for Water Purge Scheduling in a Fuel Cell," Proceedings of the 2nd Annual Dynamic Systems and Control Conference, Hollywood, CA,USA: 2009.

27. J. Siegel and A. Stefanopoulou, "Through the membrane & along the channel flooding in PEMFCs," American Control Conference, 2009. ACC '09., 2009, pp. 2666-2671.

28. D.S. Hussey, D.L. Jacobson, M. Arif , "Quantification of Water with High Resolution Neutron Radiography Detection Systems", International Topical Meeting on Neutron Radiography, Kobe, Japan, September 2009.

29. The 7th International Conference on Fuel Cell Science, Engineering and Technology, Visualization of Temperature-driven Water Transport in Polymer Electrolyte Fuel Cells. June 08–10, 2009, Newport Beach, California.

30. A. Turhan, S. Kim, M. Hatzell, and M.M. Mench, 2009. Impact of Surface Energy on Liquid Storage and Through-Plane Liquid Distribution in a PEFC. Presented at the 2nd International Forum on Multidisciplinary Education and Research for Energy Science, Okinawa, Japan Dec. 12–16, 2009.

31. Preston, Joshua, Fu, Richard, Zhang, Xiaoyu, and Pasaogullari, Ugur, "Effect of the Micro-Porous Layer-Gas Diffusion Layer Interface on Water Transport in Polymer Electrolyte Fuel Cells", Proceedings Of The 7th International Conference On Fuel Cell Science, Engineering, And Technology, p. 113-119 (2009).

References

1. A. Turhan, S. Kim, M. Hatzell, M.M. Mench, Impact of channel wall hydrophobicity on through-plane water distribution and flooding behavior in a polymer electrolyte fuel cell, Electrochim. Acta, 55, 2734-2745, (2010).

2. J.P. Owejan, T.A. Trabold, D.L. Jacobson, M. Arif, S.G. Kandlikar, Effects of flowfield and diffusion layer properties on water accumulation in a PEM fuel cell, International Journal of Hydrogen Energy 32 (2007) 4489 – 4502.