V.A.6 Neutron Imaging Study of the Water Transport in Operating Fuel Cells

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Fiscal Year (FY) 2012 Objectives

- Provide state-of-the-art research and testing infrastructure to enable the fuel cell industry to design, test, and optimize prototype-to-commercial grade fuel cells using in situ neutron imaging techniques.
- Provide a secure facility for proprietary research by industry. Provide beam time at no cost to non-proprietary research through a competitive proposal process. 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 of the Fuel Cell Technologies Program Multi-Year Research, Development and Demonstration Plan:

(A) Durability
(B) Cost
(C) Performance

This project is conducting fundamental studies of water transport in the fuel cell. Insights gained from these studies will be applied toward the design of components and operation strategies of polymer electrolyte membrane fuel cells that meet the following DOE fuel cell 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 W/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.
- Durability with cycling: 5,000 hrs.

FY 2012 Accomplishments

- Revealed that a microporous layer (MPL) on the anode and cathode drives product water into the anode gas diffusion layer (GDL), whereas without a MPL, product water exits only through the cathode GDL.
- Showed that on increasing hydration, the conductivity of Nafion® increases faster than expected based on steady-state correlations.
- Submitted for publication a study of systematic effects and required corrections in measuring the membrane water content with neutron imaging.

Introduction

At NIST, we maintain the premier fuel cell neutron imaging facility in the world and continually seek to improve its capabilities to meet the changing needs of the fuel cell community. This facility provides researchers with a powerful and effective tool to visualize and quantify water transport inside operating fuel cells. Imaging the water dynamics of a polymer electrolyte membrane fuel cell (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

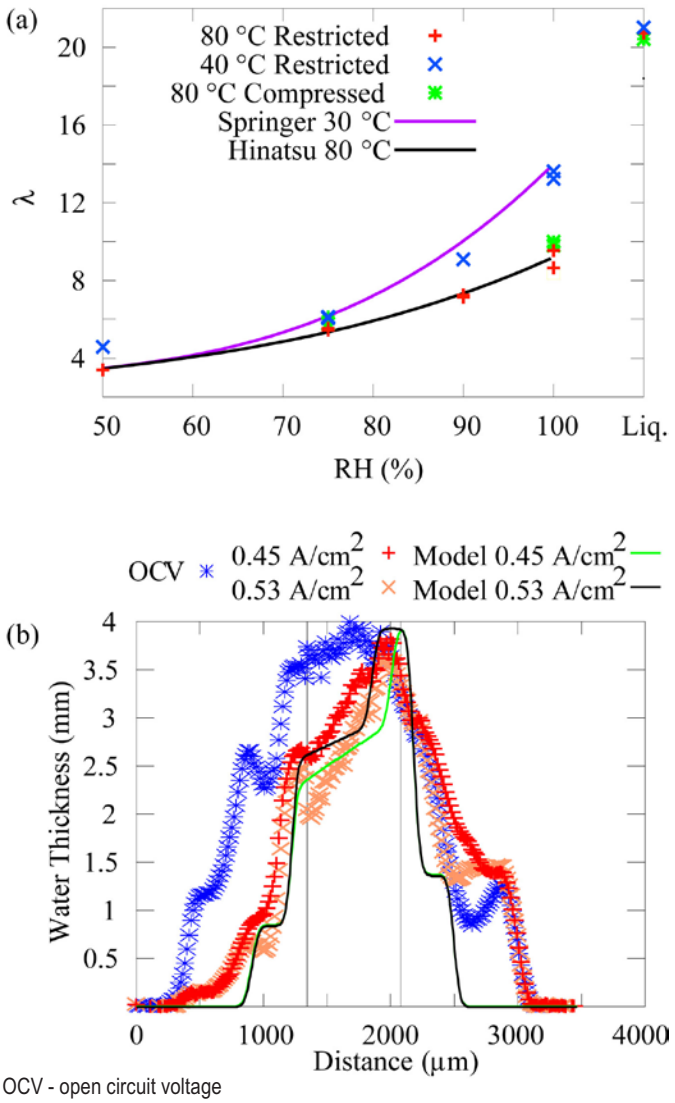
The typical length scales of interest in a PEMFC are: channels approximately 1 mm wide and 1 mm deep, the diffusion media are 0.1 mm to 0.3 mm thick, the membrane is 0.01 mm to 0.02 mm thick, and the active area of test sections can range from 2 cm^2 to 500 cm^2. Though the study of water transport within these length scales is technically very challenging, the unique capabilities of neutron imaging have already successfully addressed many of the questions. However, as fuel cell research matures, the water transport questions become increasingly more demanding, requiring for instance resolving the water content in catalyst layers. To meet these demands, based on fuel cell community feedback and need, we continue to develop new facilities and improve existing capabilities for obtaining higher spatial and temporal resolution neutron images. These improvements will enable users to perform even more detailed, nondestructive, and in situ studies of the water and hydrogen transport in PEM fuel cells to meet DOE goals. In addition, employing mathematical models of neutron scattering, we will develop a software suite that enables users to obtain reliable, accurate, quantitative measurements of the water content in an operating PEMFC. Due to the complexity of PEMFCs and the large number of remaining 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, seek their feedback, and collaborate with them on research projects, to seek measurement breakthroughs that will facilitate the rapid, efficient, and robust development of fuel cells.

Results

The NIST Center for Neutron Research has been completing work under a five year expansion project, which required that the neutron source be shut down from April 2011 until April 2012. After this successful neutron source upgrade the imaging facility is back online and providing fuel cell researchers access to beam time. During the shutdown period, the project focus was on completing analysis of prior data and conducting facility improvements that might have interrupted the fuel cell user program. Numerous updates of the small-scale fuel cell test stand have been carried out, including adding dual liquid coolant temperature control and absolute pressure control. In addition, a large-scale test stand was acquired for running small stacks or automotive scale single cell test sections. In collaboration with one of our testing partners, General Motors, a standard fuel cell and test fixture for high resolution imaging was designed and built and will be available for all facility users. This new fixture allows fuel cell researchers that are new to neutron imaging to quickly start an experiment as the fixture requires only a membrane electrode assembly and diffusion media for testing. The fixture can also accommodate custom flow field designs. To further improve the quantification of water in the fuel cell a neutron energy selector was designed, installed and tested. This device will allow examination of the energy dependent neutron scattering of water, sometimes referred to as beam hardening, and is critical to obtain accurate values of the water content in the membrane in through-plane water measurements of fuel cells.

A full length journal article has been submitted that provides a thorough analysis of systematic effects and required corrections in using neutron imaging to measure the water content in membranes. This work will be the basis for all future analysis of water content in membranes [1] and was a collaborative work involving NIST, Los Alamos National Laboratory and Lawrence Berkeley National Laboratory. To obtain an accurate measurement of the membrane water content from neutron imaging, two critical effects must be accounted for in the image analysis: under typical test section compression the membrane is essentially in a free swelling state [2] and the membrane retains water even after long dry gas purges. If one ignores these effects, neutron radiography measurements will report systematically lower water content in the membrane by 40% to 50%. Shown in Figure 1a is the excellent agreement in the membrane water sorption vs. water activity between historic gravimetric data and the corrected neutron radiography data, including the existence of Schroeder's paradox for Nafion® 117. In addition to steady water sorption measurements, the through-plane water content in a test section with a 1-mm thick membrane, during hydrogen pump mode was measured and compared with a literature-based model [3]. A thick membrane was used to overcome any limitations due to the spatial resolution. Hydrogen pump mode reduced the model complexity as one can neglect product water. In Figure 1b, the maximum measured water content is in good agreement with that predicted from modeling. However, there is disagreement on the effect of Schroeder's paradox on the through-plane membrane water content during operation. The model contains a sharp transition in the water content due to a switching function used to account for Schroeder's paradox, which is not supported by the neutron radiography data. Future studies are planned to investigate the effects of relative humidity (RH) and saturation gradients across the membrane to provide this water transport data to models. The corrections of the systematic effects will also be necessary in the measurement of the water content across commercially competitive membranes as the neutron spatial resolution improves.

Researchers at the University of Tennessee explored the role of the microporous layer in distributing product water throughout the fuel cell [4]. To do this a cell running



OCV - open circuit voltage

FIGURE 1. (a) Comparison of different methods of measuring water sorption measurements as a function of hydration. (b) Comparison of data and model of hydrogen pump data of a thick membrane.

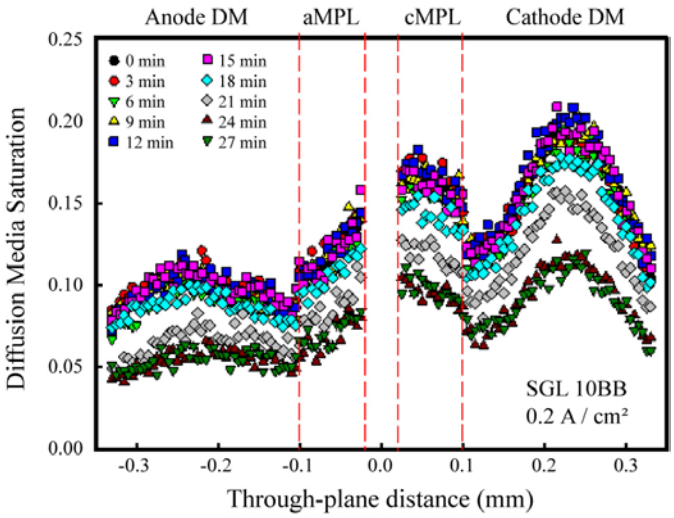


FIGURE 2. Influence of the MPL on the product water revealed by switching the anode gas stream to deuterium.

on hydrogen was switched to deuterium, which allowed the redistribution of product water to be followed throughout the fuel cell. Since deuterium has a factor of 10 smaller neutron scattering cross-section than hydrogen the resulting water signal was reduced when hydrogen was replaced by deuterium. Two test sections were studied, one with a MPL on both the anode and cathode and one with no MPL. The test section was operated for 15 minutes with air, hydrogen and light water for humidification. After steady operation was established, the anode fuel stream was changed from hydrogen to deuterium, while maintaining all other operating conditions. As a result, the product water will be heavy water and will manifest as regions of higher neutron transmission or lower observed light water content. As Figure 2 shows, with a MPL on both the anode and cathode, the product heavy water is distributed both in the cathode and anode GDL substrates, while with no MPL, the product heavy water is primarily in the cathode. From these images it can be seen that the MPL is affecting at least two facets of water transport. First, it is promoting back diffusion through the membrane and into the anode GDL, which could be beneficial for low humidity operation. Second, the overall water content in the GDL substrate is less with a MPL, which will reduce the energy required to purge the cell on shutdown.

In a collaborative study with the University of South Carolina, the membrane conductivity was measured while the RH of the inlet gas was cycled between humidified and dry [5]. The primary finding is that the conductivity increased more rapidly during hydration than one would predict from steady-state correlations. In the test, a Nafion® 117 membrane was placed in a Bekktech 4-point conductivity cell flowing 200 sccm of nitrogen that was either dry or humidified at 50% RH. Thinner membranes were also investigated, as well as different flow rates and humidity levels. All cases followed the general trend shown in Figure 3, where the membrane conductivity is shown in the initially hydrated state (50% RH inlet gases). A switch is made to dry inlet gas at 120 s and the conductivity and water content decrease proportionally as expected from steady-state correlations [6]. After drying for about 120 s, the inlet gas is humidified and one can see that the conductivity rapidly increases compared to the water content, which is an indication that the startup of a cell will result in more efficient operation before the membrane has reached a given hydration state.

There is a continued effort to measure water transport phenomena in automotive-competitive membranes and standard carbon-supported Pt catalysts, for instance to investigate the role of water in carbon corrosion of the catalyst support with neutron imaging. To do this it is necessary to improve the spatial resolution to 1 μm, which

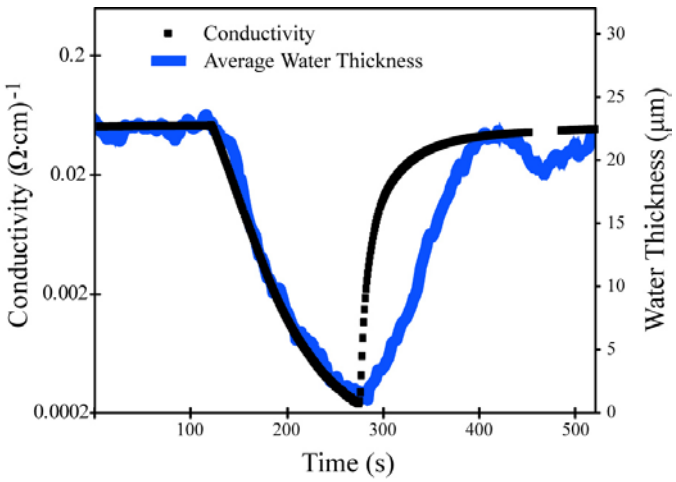


FIGURE 3. Nafion® 117 conductivity during a drying/hydration transient showing that on rehydration the conductivity increases more rapidly than expected based on correlations measured at steady state.

represents a factor of 10 improvement over the state of the art in neutron imaging detector technology. Two paths toward achieving this goal have been identified: the first is using structured illumination to limit the exposed area of the test section to about 1 μm; the second is using a neutron focusing optic that enables magnification of up to 10X. The structured illumination approach requires fabricating an absorbing neutron grating that has neutron transparent sections that are 1 μm wide and are sufficiently separated to be resolved by a detector, or about 50 μm. Full field of view images are obtained by stepping the grating through one period and acquiring images at each step and then stitching the images together. This process will require integration times of several hours and thus the test section must be operated under steady state conditions. The grating fabrication is being carried out at the NIST nanofabrication facility. The primary challenge in the grating manufacture is obtaining a sufficiently thick, stable coating of Gd, the neutron absorber. A neutron focusing optic represents a major shift in neutron imaging facility design in that collimating the neutron beam is not required enabling a much higher (factor of about 100) neutron flux to be used. This will reduce the time to obtain an image of the through-plane water content from the current 20 minutes to about 10 s, allowing a much broader range of fuel cell operating conditions to be investigated. In addition to the increased flux, image magnification is also possible so that the image resolution can be improved over the intrinsic detector resolution; a magnification of 10 is possible which will enable direct measurements of the water content in commercially competitive membranes and standard catalyst layers. A feasibility experiment using an optic with a magnification of 4 is schedule for the first two weeks in July 2012.

Conclusions and Future Directions

- Neutron imaging is a powerful probe to reveal the liquid water transport phenomena in PEMFCs.
  - The effect of the MPL on distributing product water in the fuel cell was investigated using the neutron scattering contrast between hydrogen and deuterium.
  - Combining in situ water sorption and conductivity measurements revealed that the membrane conductivity increases much more rapidly on hydration than expected from correlation derived at steady state conditions.
- Collaborate with the fuel cell research community to provided needed measurements of the water content in operating fuel cells.
  - Accurate measurements of the membrane water content are obtained after applying corrections for all systematic measurement effects.
  - Provide training to fuel cell researchers on how to employ NIST image analysis code that provides water content and uncertainty analysis.
  - The fuel cell test stands have been upgraded and a new fixture for through-plane water content measurements will be available to all facility users.
- Develop methods capable of resolving the liquid water content in commercial membranes and catalyst layers for durability studies by improving the neutron spatial resolution and sensitivity to hydrogen.
  - Image the water in a commercial cathode catalyst layer in a small-scale fuel cell with resolution approaching 1-2 micrometers in order to study degradation mechanisms that are induced by liquid water.
    - Utilize gratings at the thermal neutron imaging facility to improve the spatial resolution by a factor of 10 over the intrinsic resolution of 10 micrometers.
    - Conduct feasibility tests to magnify images of fuel cells by a factor of 10 to thereby improve the spatial resolution using a novel neutron imaging optic to obtain magnified images of an operating fuel cell.
  - Enable higher spatial and temporal resolution images of water transport phenomena during accelerated stress tests of PEMFCs.
    - A factor of 2 or more can be achieved in sensitivity to liquid water by utilizing cold neutrons instead of thermal neutrons.
    - Begin studies of degradation during accelerated stress tests of PEMFCs by completing the design and installation of a cold neutron imaging facility at NIST.

FY 2012 Publications/Presentations

1. D.S. Hussey, D. Spernjak, J. Fairweather, J. Spendelow, R. Mukundan, A.Z. Weber, D.L. Jacobson, and R. Borup (2012) Measuring the through-plane water content of membranes in PEMFCs with neutron radiography. Journal of Applied Physics, submitted.

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13. Selamet, O.F., Pasaogullari, U., Spernjak, D., Hussey, D.S., Jacobson, D.L., and Mat, M., 2011, In Situ Two-Phase Flow Investigation of Proton Exchange Membrane (PEM) Electrolyzer by Simultaneous Optical and Neutron Imaging: ECS Transactions, v. 41, p. 349-362.

14. Spernjak, D., Hussey, D.S., Weber, A.Z., Mukundan, R., Fairweather, J., Brosha, E.L., Davey, J., Spendelow, J., Jacobson, D.L., and Borup, R., 2012, Environmental effects on PEM water content.: Journal of the Electrochemical Society, v. Submitted.

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17. "Isolation of Transport Mechanisms in PEFCs with High Resolution Neutron Imaging", J. LaManna, S. Chakraborty, F. Zhang, M. Mench, J. Gagliardo, and J.P. Owejan, 220th ECS Meeting, Boston, MA, October, 2011.

18. "Interaction of Heat Generation, MPL and Water Retention in Corroded PEMFCs", J.D. Fairweather, D. Spernjak, R. Mukundan, J. Spendelow, K. Artyushkova, P. Atanassov, D.S. Hussey, D.L. Jacobson, and R. Borup, 220th ECS Meeting, Boston, MA, October, 2011.

19. "In Situ Two-Phase Flow Investigation of Proton Exchange Membrane (PEM) Electrolyzer by Simultaneous Optical and Neutron Imaging", O.F. Selamet, U. Pasaogullari, D. Spernjak, D.S. Hussey, D.L. Jacobson, and M. Mat, 220th ECS Meeting, Boston, MA, October, 2011.

20. "High Resolution Neutron Imaging of PEMFCs with Scintillator-Based Detectors", D.S. Hussey and D.L. Jacobson, 220th ECS Meeting, Boston, MA, October, 2011.

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25. "Neutron Imaging for Electrochemistry", D.S. Hussey, D.L. Jacobson, E. Baltic, and M. Arif, ESS, Seminar, Lund, Sweden,12 DEC 2011.

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