V.A.8 Neutron Imaging Study of the Water Transport in Operating Fuel Cells

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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 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 (3.4.4.2) of the Hydrogen, Fuel Cells and Infrastructure Technologies Program Multi-Year Research, Development and Demonstration Plan:

(A) Durability

(D) Air, Thermal and Water Management

Accomplishments

- Quantification of measurement uncertainties in the water volume of fuel cells using neutron radiography due to systematic effects:
  - The contributions to measurement error from possible systematic effects have been measured or estimated and none explain the discrepancies between the modeling and the measured through-plane water content.
  - Measurement of Nafion® water uptake as a function of water activity with high resolution neutron radiography is consistent with existing, published, gravimetric measurements, giving further support that the neutron radiography systematic uncertainties are sufficiently understood.
- High resolution neutron imaging of fuel cells:
  - Visualization of water transport due to thermal gradients reveals the importance of boundary conditions in phase change induced flow.
  - Factor of five improvement in geometrical spatial resolution with new slit apertures without sacrificing overall intensity (optimized for fuel cell imaging).
  - New high spatial resolution system with higher event rate has been tested for operation and is undergoing deployment.
  - Additional backup high resolution detector systems coming online to ensure reliable operation of the imaging facility for fuel cell users of the facility.
- Improvements to the facility impacting fuel cell radiography:
  - New apertures discussed previously allows dramatic improvement of resolution of anode vs. cathode.
  - New EIS-Zahner IM6eX electrochemical workstation for fuel cell impedance spectroscopy measurements.
  - New imaging acquisition software developed by NIST and tailored to the fuel cell facility users.

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 scales of interest in a PEMFC are: channels approximately 1 mm wide and 1 mm deep, the gas diffusion media 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 50 cm^2 to 500 cm^2. Thus, to study in situ, nondestructive water/hydrogen transport in PEMFCs while in operation and hydrogen transport/distribution in hydrogen storage media we will develop new facilities and improve existing capability for obtaining high spatial and temporal resolution neutron imaging. 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 and academia 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

This year the staff of the NIST Neutron Imaging Facility have focused on developing a detailed understanding of systematic errors that can affect the quantification of water in neutron radiography experiments on fuel cells. We have assessed a large set of potential measurement uncertainties in the membrane water content including, non-Lambert-Beer law behavior due to beam hardening, changes in the background, spatial resolution, and differences in the scattering properties of water absorbed in Nafion®. This work was required to address a large discrepancy observed in the published literature between current estimates of the membrane water content during fuel cell operation and that measured by neutron radiography. We have worked in collaboration with the Los Alamos National Laboratory fuel cell team and the modeling effort at Lawrence Berkeley National Laboratory on this project. We performed calibration measurements with a stepped wedge of water with thicknesses the same as those encountered in measurements of liquid saturated membranes. The uncertainty in the results was dominated by the expected uncertainty due to the beam intensity (Poisson counting noise). This showed that there was no systematic deviation from the exponential law of attenuation (Lambert-Beer law). One source of deviation is expected due to beam hardening, but the thickness of water that is typically encountered in PEMFCs used in high resolution imaging experiments is insufficient to cause a deviation from the exponential law calibration technique. Another source of deviation is expected due to incorrect accounting of the scattered neutron background, due to the fuel cell or water, an effect that changes with water thickness. This scattering contribution is small, and does not cause a statistically measurable deviation from the exponential law behavior. A third source of deviation can come from incorrectly subtracting the gamma-ray background. However, the systematic uncertainty introduced by incorrectly accounting for the gamma-ray background as well as the scattered neutron background is at least an order of magnitude smaller than the counting statistics uncertainty typical of high resolution PEMFC images. We have identified a large systematic error due to the finite spatial resolution of the imaging detector. This resolution effect can result in the measured water content being systematically suppressed in small regions. An example where this is most important is the high resolution measurement of water in the through-plane direction. Here the membrane is a thin water saturated region. The rapid change in water content between anode, membrane and cathode can be suppressed due to the finite spatial resolution of the neutron imaging detector. There are mathematical models (deconvolution) that allow one to sharpen an image in order to reduce this effect. However this typically introduces additional noise to the measurement (there may be algorithms that are more appropriate for the high variability of the high resolution neutron image data). A more robust approach is to simulate neutron images from a model prediction of the through-plane water content. The effect of the resolution of the imaging system can be modeled as a convolution of a Gaussian with the predicted water content. This enables direct comparison of model prediction with the neutron data in order to test the sensitivity of the measurement system towards discriminating between different water profile predictions. Another way to avoid this resolution issue is to make the membrane thicker. With a thicker membrane the uncertainty is reduced and/or nearly eliminated. Doing this is critical to decouple any uncertainties arising from a change in the neutron scattering cross section for water absorbed in Nafion®. To do this, special 1 mm thick Nafion® membranes were prepared (Ion Power, Inc.) to measure the water sorption in Nafion® with neutrons. A deviation from published gravimetric measurements could indicate that water in Nafion® has different scattering properties than free water. In this case, the water distribution was observed to be uniform over a large region in the center of the membrane, indicating that the finite resolution is not affecting the measurement. We measured the membrane water content as a function of water activity (relative humidity = 50%, 75%, 90%, liquid saturated,

etc.) and as shown in Figure 1 have found that the neutron radiography results agree within the estimated uncertainties with the values reported from gravimetric methods. Therefore, the neutron cross-section of water in Nafion® is the same as free water. Since the finite resolution effect can result in a severe reduction of the observed membrane electrode assembly water content we have modified the neutron imaging facility to minimize this effect and optimize it for fuel cell use. To improve the spatial resolution due to the geometric blur of the neutron beam, we have introduced a vertical and horizontal slit that reduces the geometric blurring by a factor of 5 along the through-plane direction. By using a slit instead of an aperture the intensity (and therefore the required exposure time) can be maintained avoiding a decrease in the dynamic resolution of the beam. Improvements in the detector spatial resolution are also expected to minimize this effect. These results have been submitted to a peer-reviewed journal, and publication is expected within a year.

Researchers from the Pennsylvania State University used the NIST BT2 high resolution neutron imaging facility to visualize the liquid water flow in the through-plane direction under different thermal gradients (Figure 2). In these tests, two sets of GDLs were studied, one with only a substrate loading of polytetraflouroethylene (PTFE) of 5% by weight and a microporous layer, and with no PTFE content. Initially, one side of the fuel cell assembly was filled with liquid water, while the other side had only vapor, and the two sides were maintained at different temperatures. The GDL with no PTFE showed a slight water flow with no thermal gradient due to a small piezometric head.

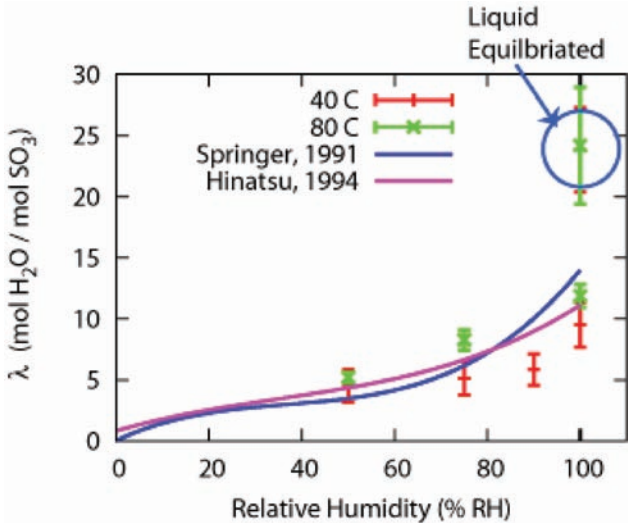

FIGURE 1. Measured membrane water content with high resolution neutron radiography as a function of water activity compared with correlations derived from gravimetric studies. The neutron radiography measurement agrees within uncertainty with the established ex situ data.

Applying a thermal gradient, so that the liquid side was cooler, prevented this slow leakage water flow. Reversing the thermal gradient resulted in significantly higher fluid flow than in the case of that driven by the piezometric head. Images of the GDL containing PTFE showed that with no thermal gradient or when the liquid side was maintained at a colder temperature, the piezometric head was insufficient to induce flow through the hydrophobic diffusion media. However, when the gas-phase side of the test section was colder, the channels were observed to fill rapidly (few minutes) due to phase change induced flow. This visualization work elucidated the critical importance of the vapor boundary layer to phase change induced flow, and was in support of an extensive set of ex situ measurements of thermo-osmosis and phase change induced flow rates in typical fuel cell porous media (Kim, 2009).

As part of the NCNR expansion initiative, we are building a cold neutron imaging facility. This is motivated by the fact that the cross section of water increases as the neutron velocity decreases. As a result cold neutrons have a larger scattering cross-section from water and the detection efficiency in the neutron imaging detector is about a factor of 2 higher. For equal intensity neutron beams, this means that a cold imaging facility will have about a factor of 4 improvement in the water measurement uncertainty. This was confirmed by measuring the attenuation coefficient at a temporary location imaging at the NCNR, and Figure 3 demonstrates that the attenuation coefficient is a factor of two larger for cold neutrons than for thermal neutrons. A set of PEMFC experiments were conducted in collaboration with General Motors, and this data is still under analysis.

In addition, we continue to develop our fuel cell and hydrogen infrastructure. We have added a Zahner electrochemical workstation for in situ electrical impedance spectroscopy and neutron imaging experiments and future segmented or multi-cell experiments. We are in the process of developing a

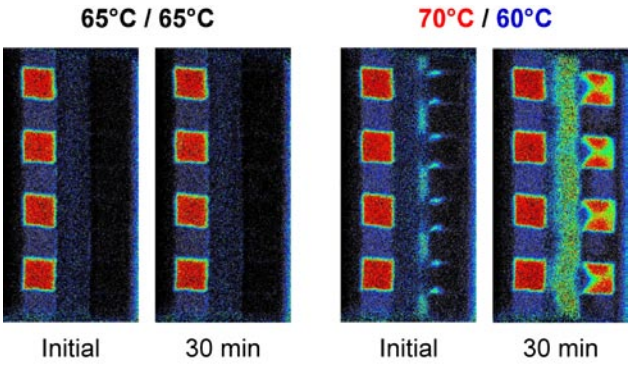

FIGURE 2. Visualization of phase change induced flow with hydrophobic gas diffusion media performed with high resolution neutron radiography.

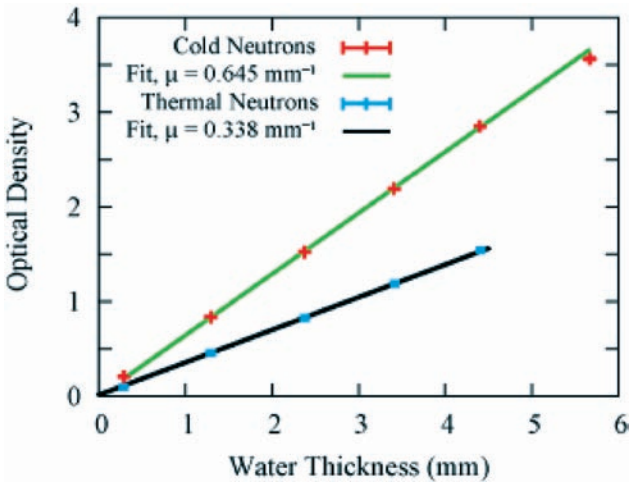

FIGURE 3. Comparison of the Attenuation Coefficient of Water for Thermal and Cold Neutrons

hydrogen distribution manifold for studying hydrogen storage materials. We also plan to add independent anode and cathode temperature control to the fuel cell test stand to enable the measurement water transport phenomena due to thermal gradients.

Conclusions

We have investigated potential sources of systematic measurement uncertainty to ensure data integrity and found that the sources of error cannot fully explain discrepancies between observed and predicted water thicknesses. We have written new analysis code for users to simulate high resolution neutron images to better compare measurement with model predictions. We are collaborating with Los Alamos National Laboratory and Lawrence Berkeley Laboratory to design experiments and improved image analysis to understand the observed discrepancy. We continue to improve and develop our facility for improved image and measurement quality and test and control capabilities.

Future Directions

- Measurement of electroosmotic drag in membranes and gas diffusion coefficients in gas diffusion layers which incorporates improved uncertainty analysis. This work will be aided by development of image simulation from input models. The uncertainty analysis will transferred to facility users as part of the standard image analysis suite.
- Continue advancement of imaging technology and capabilities at the facility, including deployment of a high resolution (better than 15 μm) imaging detector for general user base, design of a cold neutron imaging facility, and implementation of independent anode/cathode temperature control into test stand for routine use.

FY 2009 Publications/Presentations

Refereed Journal Articles

1. J.B. Siegel, D.A. McKay, A.G. Stefanopoulou, D.S. Hussey, and D.L. Jacobson, "Measurement of Liquid Water Accumulation in a PEMFC with Dead-Ended Anode", J. Electrochem. Soc. 155, B1168 (2008).

2. J. Park, Xianguo Li, D. Tran, T. Abdel-Baset, D.S. Hussey, D.L. Jacobson, and M. Arif, "Neutron imaging investigation of liquid water distribution in and the performance of a PEM fuel cell", International Journal of Hydrogen Energy, 33, 3373-3384 (2008).

3. A.Z. Weber and M.A. Hickner, "Modeling and high-resolution-imaging studies of water-content profiles in a polymer-electrolyte-fuel-cell membrane-electrode assembly", Electrochimica Acta, 53, 7668-7674 (2008).

4. 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).

5. D. Spernjak, S. G. Advani, and A. K. Prasad, Journal of The Electrochemical Society, 156 (1), B109-B117, (2009).

6. 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).

Presentations and Conference Proceedings

1. D.S. Hussey and D.L. Jacobson, "Systematic Uncertainties in Neutron Imaging of Proton Exchange Membrane Fuel Cells", Meet. Abstr. - Electrochem. Soc. 802 939 (2008).

2. D.S. Hussey, "Neutron Imaging: Fuel Cells and Phase Gratings", Tulane University Physics Department Colloquium, December 1, 2008.

3. D. Jacobson, D. Hussey, E. Baltic, M. Arif, "Freeze Testing Fuel Cells at NIST Using Neutron Radiography", PEMFC Freeze Workshop, Nuvera February 20, 2009.

4. D.L. Jacobson, D.S. Hussey, E. Baltic, M. Arif, J. Owejan, J. Gagliardo, T. Trabold, "Using Neutron Imaging to Study Hydrogen Fuel Cells and Hydrogen Storage Devices", Hydrogen Symposium 2009, Purdue University, April 22, 2009.

5. D.L. Jacobson, D.S. Hussey, E. Baltic, M. Arif, J. Owejan, J. Gagliardo, T. Trabold, "Understanding Water Transport in Hydrogen Fuel Cells Using Neutron Radiography", International Conference on Neutron Scattering, Knoxville, Tennessee, May 5, 2009.

6. D.S. Hussey, "Principles of Neutron Imaging", International Conference on Neutron Scattering, May 2009.

7. D.S. Hussey, D.L. Jacobson, "Two phase flow visualization with real-time neutron radiography", ASME Heat Transfer, San Francisco, CA, July 22, 2009.

8. S. Kim, M.M. Mench, "Phase Change Driven Water Transport in Polymer Electrolyte Fuel Cells", ECS Trans. 16 (2), 575 (2008).

9. 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 (1), 263 (2009).

10. J. Davey, R. Mukundan, J. Spendelow, D.S. Hussey, D. Jacobson, M. Arif, and R.L. Borup, "Water Dynamics in a PEM Fuel Cell: Effect of Current and Humidity Transients", ECS Trans. 16 (2), 329 (2008).

11. R. Mukundan, J. Davey, R. Lujan, J. Spendelow, Yu Seung Kim, D.S. Hussey, D. Jacobson, M. Arif, and R.L. Borup, "Performance and Durability of PEM Fuel Cells Operated at Sub-Freezing Temperatures", ECS Trans. 16 (2), 1939 (2008).

12. J. Spendelow, R. Mukundan, J. Davey, T. Rockward, D.S. Hussey, D. Jacobson, M. Arif, and R.L. Borup, "High Resolution Neutron Radiography Imaging of Operating PEM Fuel Cells: Effect of Flow Configuration and Gravity on Water Distribution", ECS Trans. 16 (2), 1345 (2008).

13. P.P. Mukherjee, T. Springer, R. Mukundan, D.S. Hussey, D. Jacobson, M. Arif, and R.L. Borup, "Probing Liquid Water Profile in the Polymer Electrolyte Fuel Cell Membrane", ECS Trans. 16 (2), 1027 (2008).

14. D.S. Aaron, A.P. Borole, C.Y. Hamilton, C. Tsouris, D.S. Hussey, D.L. Jacobson, E. Baltic, "Electrochemical Impedance Spectroscopy and Neutron Imaging of Enzyme Fuel Cells", 2009 IACIS International Conference, June 14–19, 2009.

15. A.P. Borole, S. LaBarge, B. Spott, D.S. Aaron, C. Tsouris, D. Hussey, D. Jacobson, "Enhancing Performance of Enzyme Fuel Cells via Use of Gas-Phase Reagents", 2009 ACS Meeting.