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

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FY 2011 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

Technical 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.
- Freeze start operation: unassisted start from -40°C.
- Durability with cycling: 5,000 hrs.

FY 2011 Accomplishments

- Developed methods to achieve better than 10 µm spatial resolution:
  - Further improvements to the spatial resolution require new approaches; one method has shown a factor of 25 improvement in spatial resolution.
  - Improvements to the design of this method will be pursued to achieve ~1 µm resolution to enable measurement of water distribution within commercial membrane electrode assemblies (MEAs).
- Carried out studies of water transport in full-scale hardware and 4-cell stacks:
  - Hydrophilic coatings on bipolar plates reduce water retention and time to purge the cell during shutdown.
  - Diffusion media saturation is linked to individual cell failure in stacks.
- High resolution imaging of water transport in thick catalyst layers and impact of water on fuel cell durability:
  - Strategies to overcome flooding will help improve the performance of polyaniline-derived non-precious metal catalysts.
  - Corrosion results in an increased overpotential, which dries out the cell under operation at constant current due to a larger thermal gradient.

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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 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 (DM) are 0.1 mm to 0.3 mm thick, the membrane is 0.01 mm to 0.02 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

Visualizing water transport in a fuel cell is a process that occurs on several different length scales. In-plane studies require spatial resolution on the order of 100 µm and this capability has existed from the outset of this project. However, to image water transport in the through-plane of a fuel cell in the DM, membrane, and catalyst layers it has been necessary to improve the image resolution, which currently stands at 10 µm. This resolution is well suited to studies of the DM, but to image the membrane and catalyst layer it is necessary to go well below 10 µm. To do this, new methods must be developed due to fundamental limitations that arise from the physics of neutron capture and detection in the detector that limit the overall resolution to 10 µm. Three different methods have been considered for achieving image spatial resolution better than 10 µm. The first utilizes a technique derived from neutron depth profiling (NDP), the second uses optical magnifying lenses, and the third a scanning set of slits. The NDP technique can possibly achieve a spatial resolution of 100 nm, but the field of view in one dimension is severely restricted to about 10 µm due to the need for charged particles from the neutron capture reaction to escape and be detected. Due to challenges in the fabrication of the detection volume, a proof-of-principle detector has not yet been demonstrated. The second method employing a magnifying lens was used with a charge-coupled device and scintillator, and it also results in unacceptably small fields of view, on the order of 2 mm, and initial results demonstrated spatial resolution of order 15 µm, limited by the scintillator thickness. Finally the slit method requires scanning a slit over the region of interest, which provides high spatial resolution in one direction only, but still makes use of a large field of view. Initial tests demonstrated that a detector with an intrinsic 250 µm resolution, when coupled with a 10 µm slit yielded images with 10 µm spatial resolution, as shown in Figure 1. It is expected that this method can be further developed to achieve near a resolution near 1 µm.

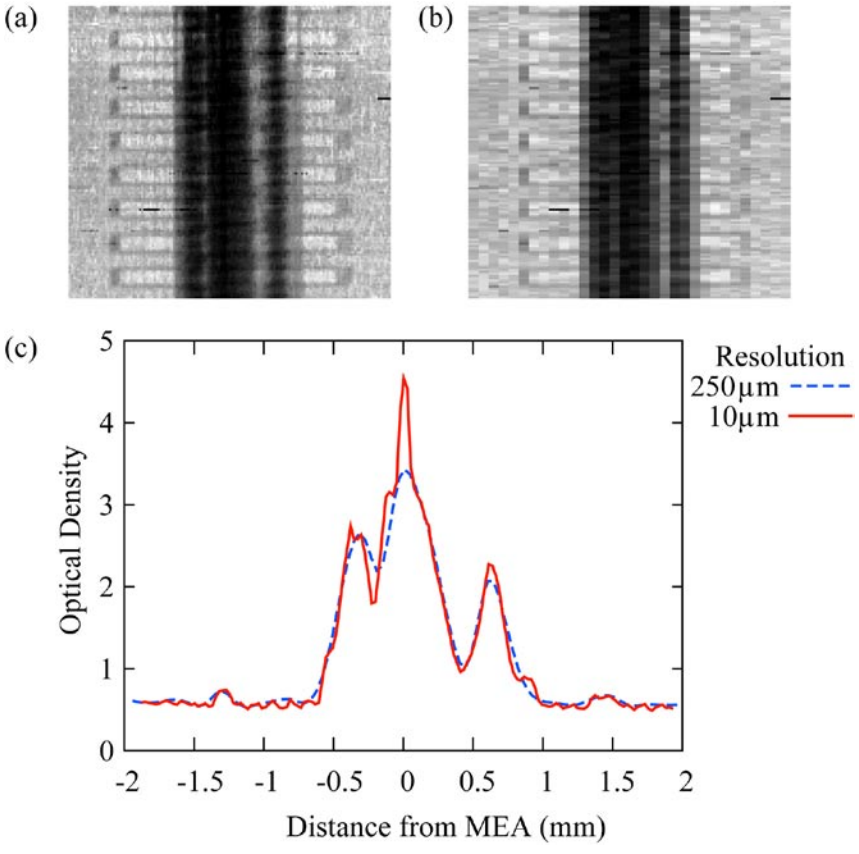

FIGURE 1. Demonstration of improved spatial resolution with a scanning slit. Image of a PEMFC test section is shown with an image spatial resolution of (a) 10 μm (b) 250 μm. (c) Comparison of the through-plane neutron attenuation demonstrating the improvement in resolution.

In collaboration with General Motors, a suite of performance and degradation studies have been carried out on full-scale, commercial hardware. The NIST beam is 26 cm in diameter, which allows nearly the entire full-scale fuel cell to be viewed at once. These full scale images were also captured with a high frame rate (up to 30 Hz) utilizing the amorphous silicon flat panel detector with spatial resolution of 0.25 mm. One output of this work shows the impact of channel surface treatment on water retention (Figure 2). Bipolar plates treated with a hydrophilic coating reduce both the overall water retention during operation and the energy required to purge the active area for in preparation for cold/freeze start. In contrast, hydrophobic treatments increase the amount of water retained by the diffusion media and result in longer times to purge the active area for cold/freeze start. An innovative planar stack was designed to allow radiography studies of stack failure modes. Figure 3 shows the results of using this planar 4-cell stack to study the stability of the stack as a function of anode stoichiometry. This study observed that the cell with the highest DM saturation (Cell 3) is seen to be the first to fail. The other cells (Cells 1, 2 and 4) are seen to have more water in the channels and this channel water diverts gas flow into the DM thus reducing the DM saturation and reducing the electrode flooding. Repeated measurements showed that the cell that failed first varied, but that this cell was always the one that had the highest DM saturation.

Employing the 10 µm spatial resolution micro-channel plate detector, we have collaborated with the Los Alamos fuel cell team in studying flooding in

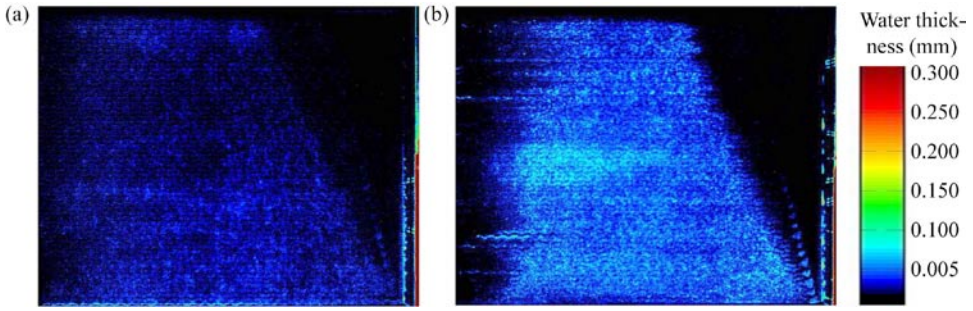

FIGURE 2. Water content of a test section with a (a) hydrophilic bipolar plate (θ_s = 100°) and a (b) hydrophobic bipolar plate (θ_s = 10°). The test section was operated at 0.1 A cm^2, 75°C, and anode (cathode) outlet relative humidity of 121% (108%).

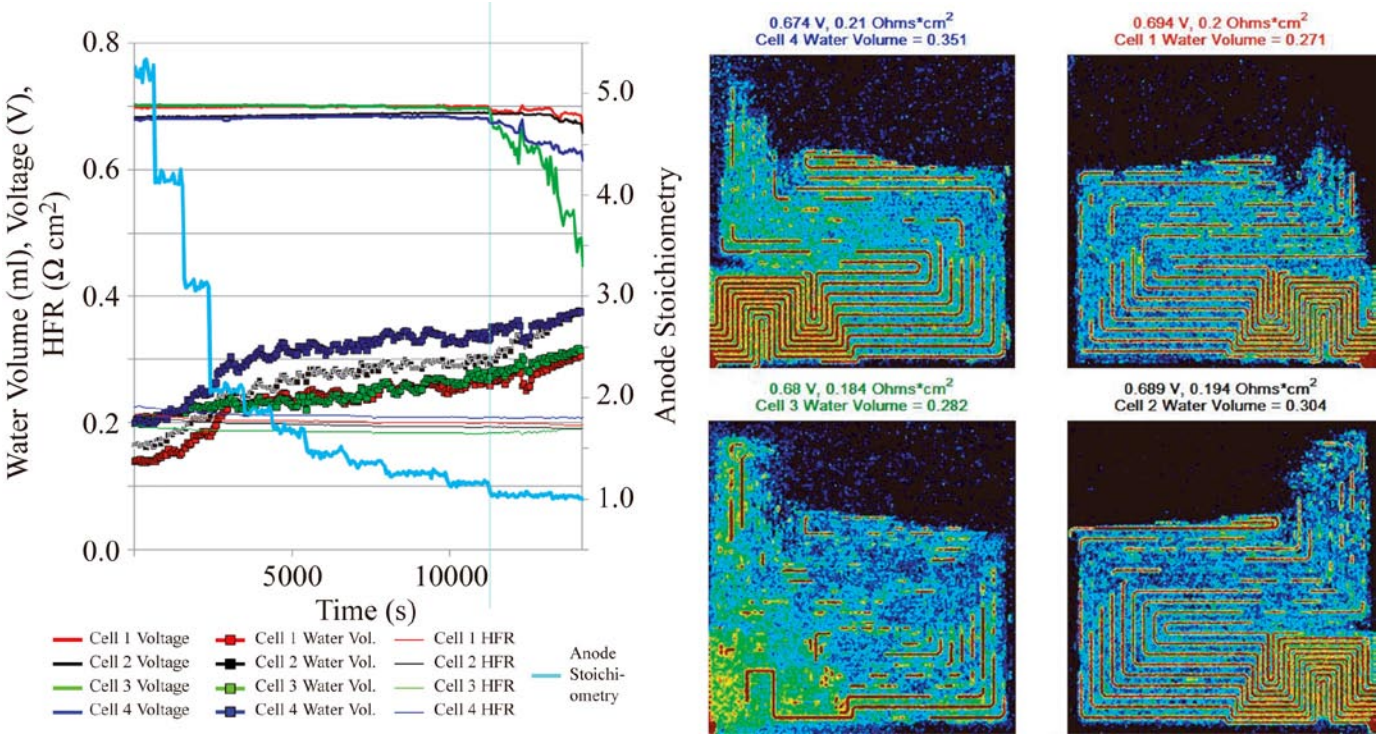

FIGURE 3. Correlation of water content with cell instability in a four-cell stack as a function of anode stoichiometry. The line plot is the voltage, water volume and high frequency resistance at 1 kHz for each cell as a function of the anode stoichiometry. The neutron images are from the point at which the anode stoichiometry drops to about 1, and show that Cell 3, which has the highest gas diffusion layer (GDL) saturation rather than the greatest overall water volume, fails first. The additional water content in Cells 1, 2 and 4 is due to larger channel water content, which diverts flow into the GDL and reduces GDL saturation.

a non-precious group metal (NPGM) oxygen reduction catalyst as well as studying the effects of test two accelerated stress tests (ASTs) on the through-plane water content. In the NPGM study, a polyaniline-derived catalyst was compared to a Pt-based catalyst with a similar thickness. It was seen that the NPGM catalyst retained significantly more water; thus one path to improving this catalysts performance maybe to reduce its hydrophilicity.

The first AST was performed at a constant voltage hold of 1.3 V for 80 min, followed by operation and imaging at a constant current of 0.8 A/cm^2 for 60 min, followed finally by a polarization curve measurement. The goal of this study was to investigate the role of a microporous layer (MPL) on the water transport during degradation. Previous studies have shown that during corrosion the catalyst layer/GDL becomes more hydrophilic, therefore it was expected that water retention due to the increase in hydrophilicity would be a primary contribution to loss of performance during corrosion. Since the corrosion results in a higher overpotential, operation at constant current generates more heat at the membrane. This temperature gradient efficiently transports the water from the catalyst layer to the channel drying out the test section and is a greater effect than the increased hydrophilicity of the corroded catalyst. However, the presence of the MPL improved the test section durability with less water overall in the test section at all points in the AST. The reduced water content due to the catalyst MPL is believed to be the primary factor that leads to less corrosion and better performance.

In the second AST, a test section representing a standard cell from Ballard was cycled under the following conditions: 30 s at 0.6 V, 60 s at 1.4 V, 100% relative humidity, 80°C, 34.5 kPa backpressure, and constant gas flow rates of 1.5 lpm H_2 and 2.5 lpm air. Neutron images, electrochemical impedance spectroscopy (EIS), cyclic voltammatry (CV), and polarization curve measurements were acquired at intermediate cycles to assess the effects of the degradation. The neutron images were taken while operating the cell at a constant voltage of 0.6 V (not constant current as was done in the first AST). The CV data show a loss in electrochemical surface area up to 100 cycles followed by a more gradual loss beyond 100 cycles. The EIS and polarization curve data show only marked performance degradation after 500 cycles. As shown in Figure 4, the neutron images reveal that the water content initially increases during the first 50 AST cycles, but begins to reduce after 100 AST cycles. Additional experiments are planned using the second AST to better elucidate the corrosion mechanism that was observed by the early onset of the reduced water content.

Conclusions and Future Directions

- A range of water transport topics in commercial-sized stacks and small-scale hardware have been studied utilizing neutron imaging:
  - Hydrophilic coating on bipolar plates aids in efficient water removal.
  - Planar stack designs allow for testing and analyzing failure mechanisms in stacks.
  - Catalyst corrosion produces a larger thermal gradient enhancing water removal from the MEA.

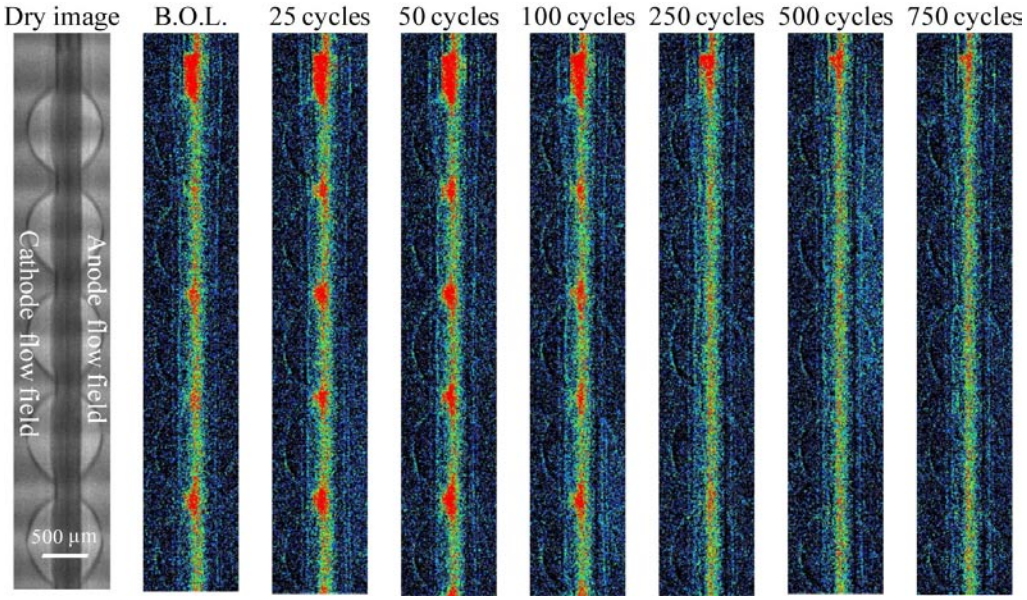

FIGURE 4. Neutron images at intermediary points in the AST cycle from beginning of life (BOL) through 700 cycles. The water content peaks between 25 and 50 cycles. Although the performance after 250 cycles is similar to the BOL, the water content in the cell has already been reduced.

- Future experiments will have enhanced resolution to resolve finer details of membrane and catalyst water profile:
  - Develop new high-resolution techniques to improve the spatial resolution to sub-10 µm with a final goal of 1 µm.
  - Perform experiments to measure and compare with models of water transport through the GDL/MPL/ catalyst and membrane with sub-10 µm resolution.
- Expand avenues of fuel cell research allowing larger cells to be imaged with high spatial resolution and even higher temporal resolution:
  - Improve field of view while maintaining spatial resolution to look at larger fuel cells.
  - Provide higher frame rate capabilities up to 100 frames per second in response to user needs.
- Potentially enhance sensitivity of high resolution fuel cell imaging by adding a new cold neutron imaging capability using a new facility to be built for expansion of the NIST Center for Neutron Research.

FY 2011 Publications/Presentations

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15. T. Matsuura, J.B. Siegel, J. Chen, and A.G. Stefanopoulou, "Multiple degradation phenomena in polymer electrolyte fuel cell operation with dead-ended anode", Proceedings of ASME 2011 5th International Conference on Energy Sustainability & 9th Fuel Cell Science, Engineering and Technology Conference, ESFuelCell2011-54344.

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