V.H.4 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
Email: arif@nist.gov

DOE Manager
Nancy Garland
Phone: (202) 586-5673
Email: Nancy.Garland@ee.doe.gov

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Project End Date: Project continuation and direction determined annually by DOE

Overall 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.

FY 2013 Objectives

- Collaborate and support groups from the DOE Hydrogen and Fuel Cells Program performing water transport measurements with neutron imaging at NIST.
- Deploy new large-area detectors with high spatial resolution for fuel cell water transport measurements.
- Explore and develop high-resolution neutron imaging methods to enable water transport studies of catalyst and membrane electrode assemblies (MEAs).
- Employ a high resolution imaging method to achieve resolution approaching 1 micrometer to resolve water concentration in fuel cell electrodes.
- Determine and correct systematic effects due to spatial resolution effects.
- Build fuel cell infrastructure to enable testing of automotive-scale test sections.

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

(B) Cost

(C) Performance

Technical Targets

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 proton exchange membrane fuel cells (PEMFCs) that meet the following DOE fuel cell targets:

- Durability with cycling at operating temperature of ≤80°C: 5,000 h
- System energy density: 650 W/L
- System specific power: 850 Watt/kg
- Energy efficiency: 60% at 25% rated power
- Cost: $30/kW$_e$
- Start-up time to 50% power: 30 seconds from -20°C, 5 seconds from 20°C
- Assisted start from low temperatures: -40°C
- Durability with cycling: 5,000 hrs

FY 2013 Accomplishments

- Published detailed analysis of making accurate measurements of the through-plane water content of proton exchange membranes using neutron radiography.
- Supported all target areas by imaging larger cell areas with high spatial resolution by acquiring and deploying large area high resolution neutron detectors for imaging MEA and gas diffusion layer (GDL) water content under a wide range of conditions for in situ testing of fuel cells.
- Designed, built and tested a high spatial resolution freeze chamber for testing unassisted starts from -40°C.
- Tested and developed new approaches to measure water related corrosion issues in catalyst membranes which can improve understanding of durability with cycling. To do this methods to achieve spatial resolution near 1 micrometer have been developed and tested.

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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 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 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 are 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 PEMFCs 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 Neutron Imaging Facility provides year-to-year support for the DOE Hydrogen and Fuel Cells Program projects by providing beam time and by collaboration with users on a variety of related neutron imaging projects that support the DOE mission. For FY 2013, proposals from Los Alamos National Laboratory, Lawrence Berkeley National Laboratory, Rochester Institute of Technology, General Motors, Ford Motor Company, Ballard, University of Tennessee, Knoxville, University of Connecticut and University of Michigan have received project support for experiments at the facility accounting for more than 50 days of beam time. Published results from these and previous years experiments are reflected in the publication list attached to this report.

Meeting the requirements for imaging fuel cells has required constant innovation in neutron imaging technology and techniques. Usually one must trade high resolution for field of view of a fuel cell. For example, validation of down the channel models require a large field of view to visualize the channel's length. This means that longer flow channels (>4 cm) must be imaged with lower resolution because the number of pixels in the imaging detector is fixed. To improve the situation detectors with more pixels or larger fields of view are necessary. Until recently detectors that can image a 10 cm field of view with 10 micrometer pixels have not existed. However, recently both larger area microchannel plate detectors and charge-coupled device cameras have become available. Two new systems have been acquired for the user program. The first system is a large area 100 mega pixel charge-coupled device type detector with a pixel pitch of 9 µm by 9 µm shown in Figure 1. Using Gd_2O_2S:Tb scintillators, resolution near 20 micrometers is obtained. The second is a 256 megapixel microchannel plate detector with a 9 cm x 9 cm field of view. This detector is similar in design and capability of the existing NIST 40 mm microchannel plate detectors, with an expected spatial resolution of about 15 micrometers.

Understanding of flooding and degradation issues due to liquid water in catalysts is critical for improving durability and cycling of fuel cells. This requires even better spatial resolution than what has been achieved to date. Currently we can achieve near 13 µm, but to effectively study catalysts it will be necessary to achieve near 1 µm spatial resolution in one dimension of the image. This has pushed the need for innovation in neutron imaging that must go beyond the current limiting spatial resolution. This current resolution

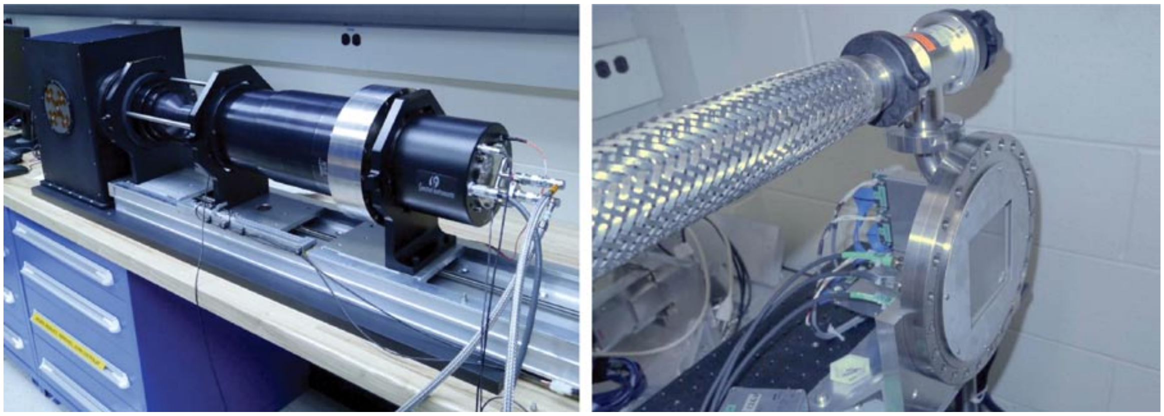

FIGURE 1. New large-area high-resolution detectors for validation of down the channel models of fuel cell operation.

limit is due to the range of charged particles that are used to detect neutrons (3.5 µm–150 µm) and fundamentally limits the spatial resolution. To overcome this limit we have been exploring two methods. The first called structured illumination uses neutron absorbing slits nanofabricated into gratings that are ~2 µm or less in width to define the neutron path illuminating the fuel cell with high spatial resolution in one dimension. The grating can then be translated across the object to obtain a high resolution image along the grating direction, overcoming the resolution limit of the detector. The resulting images can be combined to produce an image with spatial resolution defined by the slit width of the grating. Proof of principle measurements have shown this technique should work, but at a cost of increased integration time. This will require steady-state operation of the fuel cell for many hours.

A second avenue towards achieving 1 µm resolution has also been identified utilizing innovative X-ray lens technology developed by the National Aeronautics and Space Administration based on Wolter mirror optics. This innovation will eventually enable acquiring images with spatial resolution of ~1 µm, without reducing the signal rate to impractically low levels. As recently demonstrated by Liu et al. [1], these focusing neutron optics can be used to form images and show that high intensity will be possible.

Wolter focusing mirrors make the optical design of a neutron-imaging instrument similar to that of optical microscopes, where the resolution does not depend on the beam collimation, but rather on the optics itself. Consequently, the source size, and thus the number of neutrons illuminating the sample increase substantially, leading to higher signal rates. In addition, optical magnification would result in a better spatial resolution at the same pixel size of the detector. Therefore, the use of Wolter optics opens the possibility for significant progress in high resolution thermal neutron radiography, similar to the use of lenses in optical devices.

The use of large-magnification high-resolution optics would help neutron fuel cell imaging to reach 1 µm length scales with reasonable image acquisition times. An estimate of the increased signal rate for a 1:1 optic illustrates the potential gains. At the NIST neutron imaging facility, slit apertures of 2 mm x 20 mm are used to obtain images of fuel cells with about 10 µm spatial resolution. The short dimension of the slit provides high resolution along the through-plane of the fuel cell, while the long dimension provides a higher neutron fluence rate, which reaches about 2×10^{6} cm^{-2} s^{-1}. This low fluence rate requires an image acquisition time of about 10 minutes for an accurate measurement of the water content in a fuel cell. Liu et al. [1] estimate the throughput of the Wolter optic would increase the effective neutron fluence rate to 2×10^{8} cm^{-2} s^{-1} for a gain of 100 over the pinhole optics geometry. Further, the resolution of the image is the same in all directions, as opposed to being more blurred in one dimension, as is the case in the slit image. With such intensity gains it will possible to obtain high temporal (~5 s) and spatial resolution (~10 µm) images of transient processes in fuel cells. As well, tomography data sets with 10 µm voxel resolution could be obtained in a period of less than an hour as opposed to the current ~1 day. The possibility of 10x magnification, coupled with a detector spatial resolution of ~10 µm means that the system resolution could reach ~1 µm. Since the neutron density will be decreased by a factor of 100 from magnification, image acquisition times will be comparable to the current image acquisition time for ~10 µm resolution images (10 min). With this gain in resolution, one would be able to image the water content in standard Pt/C electrodes in fuel cells. Another advantage of an optic for imaging is that the sample no longer needs to be in direct contact with the detector, which allows for ample space both upstream and downstream of the sample, simplifying the experimental setup process. One could also perform simultaneous X-ray and neutron micro-tomography of porous media and in one unique instrument obtain the complementary information from both probes; X-rays to measure the matrix and neutrons to measure the fluid.

The lens tested was not optimized for neutrons, but did demonstrate the potential for the lens to form neutron images with 4x magnification shown in Figure 2. Due to lower tolerances in the manufacture of the lens the resolution was limited to 70 µm; however the test showed that a practical neutron lens was feasible. The 4x magnified neutron image of a fuel cell is shown in Figure 3. Water content is plotted to demonstrate the feasibility of the lens to measure fuel cell water distributions.

High resolution imaging of the water transport during low temperature start-up impacts the DOE targets of unassisted startup from -40°C. Although the NIST freeze chamber has been able to achieve environmental conditions of -40°C to image flow fields, high spatial resolution at temperatures below -20°C has been challenging due to the design of the NIST freeze chamber. In order to extend high resolution freeze testing down to -40°C it was necessary to redesign the NIST freeze chamber to be compatible with high resolution detectors that could not run in a -40°C environment. A new environmental chamber was designed, built and tested to allow high resolution detectors to run at stable ambient room temperature while cooling a fuel cell in close proximity to -40°C with both air and liquid coolants. The fuel cell is located within 4 cm of the high resolution detector to avoid geometric blurring due to the neutron beam. Preliminary measurements were made with a fuel cell and a paper is in preparation describing the experimental setup and results.

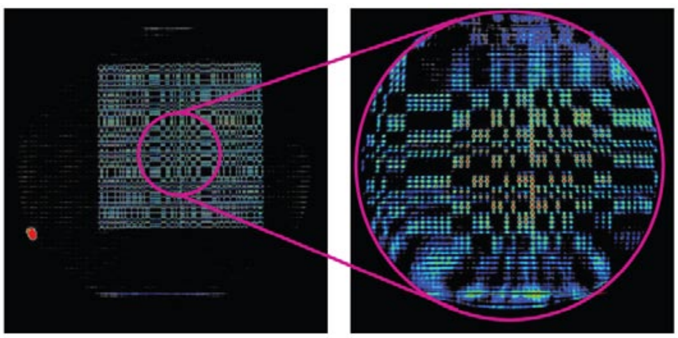

FIGURE 2. Contact radiograph of test pattern on left. Magnified 4x neutron image of test pattern on right.

Through the NIST partnership with General Motors a large-scale test stand was recently acquired and included into the testing infrastructure for the facility. The new large fuel cell test stand is capable operating fuel cells and small stacks at 800 W, 6-1,000 A @ 0.2 V, 0 V–50 V, hydrogen: 0.065 slpm–11.31 slpm, air: 0.239 slpm–26.92 slpm. The test stand is incorporated into the facility testing infrastructure and the facility technical staff are receiving training on calibration, operation and validation testing with the test stand in August 2013 with our testing partners from General Motors. Further reports of this capability and tests made with this stand will be presented at future Annual Merit Reviews.

CONCLUSIONS AND FUTURE DIRECTIONS

- Validation testing of down the channel models of fuel cell operation is now possible with large area, high resolution detectors for fuel cells:
  - Large field of view 10 cm x 10 cm

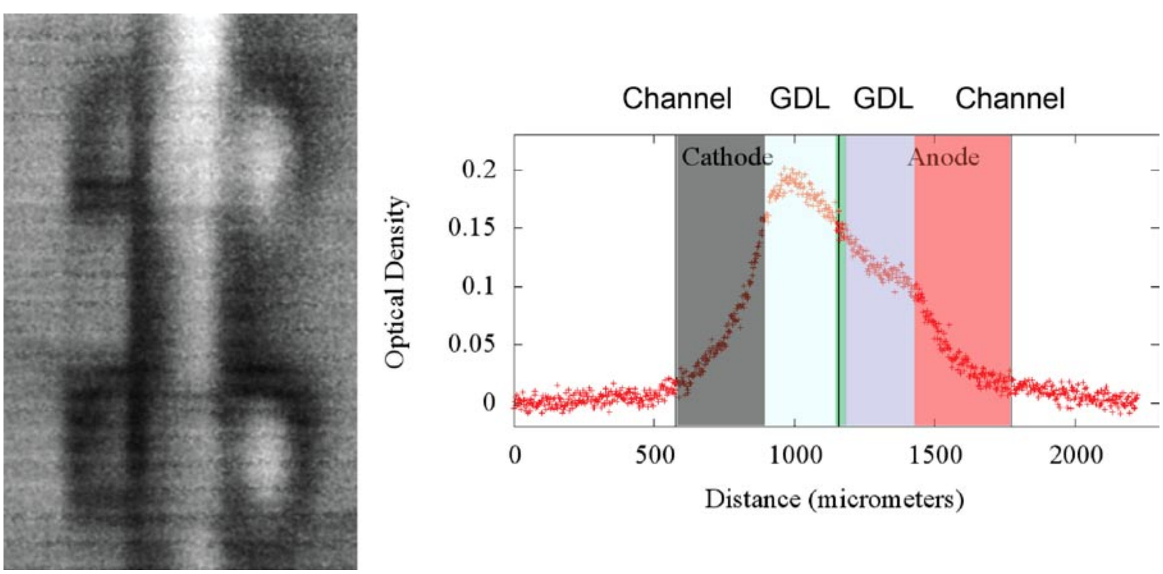

FIGURE 3. Left lens 4x magnified image of a dry fuel cell, right optical density is plotted, which is proportional to the water thickness. An additional calibration measurement is required to accurately convert to water thickness, but was not performed to limited beam time.

  - Spatial resolution 20 µm
  - Image flow fields and manifolds with high spatial resolution
  - Future—support imaging larger cells using large area detectors that maintain high spatial resolution.
- With the goal to study catalysts, we will continue to improve the image spatial resolution with a goal of 1 µm. We have identified new avenues toward high resolution MEA water content:
  - Steady progress made towards grating method
  - Demonstrated prototype neutron microscope to image catalyst/membrane layers
  - Future—deploy grating based structured illumination method to user program
  - Future—develop neutron lens to achieve higher spatial and time resolution
  - Future—develop measurement technique to image catalyst degradation mechanisms due to carbon corrosion and freeze thaw with neutrons
- We have published a detailed exploration of the accuracy and uncertainties associated with water distribution measurements using neutron imaging.
  - Future—incorporate systematic corrections to MEA water content measurements into the NIST analysis software in a user friendly way
- Through-plane freeze measurement
  - New environmental enclosure fabricated and ready for fuel cell testing
- Future general improvements
  - Provide a NIST set of high resolution testing hardware to ensure user testing compatibility with beam line setup
  - Provide support for automotive-sized fuel cell hardware testing
  - Future—incorporate systematic corrections to MEA water content measurements into the NIST analysis software in a user friendly way

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