V.E.1 Neutron Imaging Study of the Water Transport in Operating Fuel Cells

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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 and academia needs.

FY 2017 Objectives

- Collaborate and support groups from the DOE Hydrogen and Fuel Cells Program performing water transport measurements with neutron imaging at NIST.
- Install fuel cell and support infrastructure at the new cold imaging facility.
- 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 µm to resolve water concentration in fuel cell electrodes.
- Develop in situ X-ray imaging for fuel cells at the neutron imaging facility.

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

Technical Targets

NIST 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 2020 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 W/kg
- Energy efficiency: 60% at 25% rated power
- Cost: $\$40/kW_e$
- Start-up time to 50% power: 30 s from -20°C, 5 s from 20°C
- Assisted start from low temperatures: -40°C

FY 2017 Accomplishments

- First 4 µm resolution fuel cell images using slits.
- Installation of a new, second neutron imaging instrument.
- Installation of micro-focus X-ray source for simultaneous neutron/X-ray imaging.
- Components for new high resolution imaging detector systems acquired.

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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 fuel cell 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, fuel cell industry personnel and researchers can obtain in situ, non-destructive, quantitative measurements of the water content of an operating fuel cell. Neutron imaging is the only *non-destructive, in operando* method for visualizing the water distribution in a "real-world" fuel cell. 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.

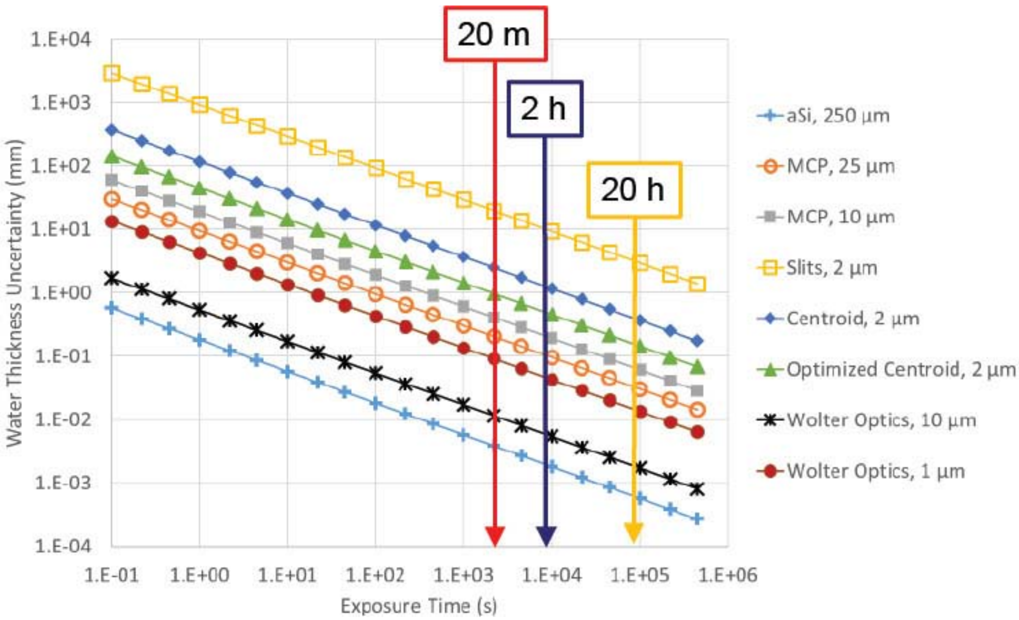
APPROACH

The typical length scales of interest in a fuel cell 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 questions. Thus, 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 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 fuel cell. Due to the complexity of fuel cells and the large number of remaining open questions regarding water transport within the membrane electrode assembly, we will develop partnerships with industry, academia, national laboratories, and the DOE Fuel Cell Technologies Office consortia 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 DOE Hydrogen and Fuel Cell Program projects through beam time and by collaboration with users on a variety of related neutron imaging projects that support the DOE mission. For FY 2017, General Motors, Rochester Institute of Technology, Los Alamos National Laboratory, University of Toronto, University of Connecticut, Colorado School of Mines, and the University of Hawaii have received project support for experiments at the facility. The results published during FY 2017 from these experiments are reflected in the publication list attached to this report.

In consultation with the fuel cell community, one of the leading issues this project has been asked to address is fuel cell flooding and degradation due to liquid water in the catalyst layers. To study commercial grade platinum-based catalysts requires at least a factor of 10 improvement in spatial resolution over the current state of the art, about 15 µm. The limiting factor in spatial resolution for current detector systems stems from the range of charged particles (3.5 µm to 70 µm) that are used to detect neutrons. To overcome this limit, we have been exploring several methods. The first method (slit method) uses nanofabricated neutron absorbing gratings with an opening of ~1 µm or less in width to define the neutron illuminated area of the fuel cell with high spatial resolution in one dimension. By translating the grating across the through-plane direction of the fuel cell, one obtains a high resolution image of the water content from anode to cathode, overcoming the resolution limit of the detector. This method was described as well in FY 2016 annual report and has since been improved to achieve 2 µm spatial resolution. The second method (centroiding method) previously described in the FY 2016 annual report has been significantly improved as of this FY 2017 report. The centroiding method works by capturing images quickly (0.005 s exposures), making it possible to capture individual neutron scintillation events and find the center of mass of each event [1]. During FY 2017 we have realized 1.5 µm spatial resolution through improvements to the center of mass calculation. The centroiding method currently suffers an 83% dead time due to delays in the file saving speed of the computer system and a field of view of about 3 mm × 4 mm. However, there is strong interest in the fuel cell community to use this method, evidence by a rise in users proposals (five new) aimed at using the new method. In the future, the centroiding method can be enhanced using hardware-based designs to run optimally with near zero deadtime and a field of view of about 1 cm diameter. For this reason, the centroiding method has been selected over the slit scanning method described earlier. A comparison of the uncertainty versus exposure time of the various methods is shown in Figure 1.



MCP – microchannel plate

FIGURE 1. Liquid water uncertainty for various methods/detectors. Comparison exposure times are noted for 20 m (ideal), 2 h (centroiding time) and 20 h (slit scan time).

The centroiding method has been used by Los Alamos to look at MEAs with two different ionomer to carbon ratios of 1.1 and 0.9. The results shown in Figure 2 show a clear difference in the shape of the water distribution for the two MEAs. For a ratio of 1.1 we see a more symmetric water distribution for the different operating voltages. For the ratio of 0.9 the distribution is no longer symmetric and is peaked near the cathode [2].

Ultimately resolution of 1 µm is expected to be efficiently and practically achieved using a neutron magnifying lens. By using a neutron lens, it could be possible to increase the neutron intensity by 50–100 times than that currently available. Previously, practical lenses for neutrons have not been available due to the low neutron refractive power of all materials. However, a new X-ray telescope lens technology using thin nickel foil mirrors developed by NASA has shown great promise to provide a practical lens for neutron imaging. By nesting several mirrors, the flux can be increased up to a factor of 100 over that achievable at Beam Tube 2 at the NIST Center for Neutron Research.

An engineering optic (Figure 3) was tested during FY 2016 and showed good figure. To achieve 1 µm spatial resolution, a lens that has an angular resolution of 1 arcsec is necessary. The current fabrication method provides an overall lens figure that achieves this resolution. The tested optic did not achieve this resolution due to surface roughness. However, the surface roughness can be corrected using differential deposition. With 10 mirrors, an increase of 70x can be achieved over previous measurements made at Beam Tube 2 at the NIST Center for Neutron Research (1 s vs. 120 s). Now that the mandrel fabrication method has been established, NIST and NASA will proceed to create nine remaining mandrels starting in September of 2017. NIST will create the basic mandrels and provide these to our partners at NASA for final polishing. Progress has been unavoidably delayed due to an upcoming launch. Future program achievements are expected to have a 1:1 lens by 2020 and a 1 µm magnifying optic by 2021.

In addition to improvements to spatial resolution we have also improved the in situ X-ray method as well. Here we use an X-ray source oriented at 90° to the neutron beam to acquire simultaneous in situ X-ray images during tomography of a fuel cell [3]. Using X-rays to image the cell in situ could allow for better characterization of the interfaces in the MEA that are nearly transparent to neutrons. This would allow for better determination of the MEA boundaries to improve the quantification of the water distribution in the MEA, including the new effort with ~1 µm spatial resolution. The results of 3-dimensional (3D) images taken with 10 µm resolution are shown in Figure 4. We have written a new software tool written using Matlab which incorporates all of the necessary image processing steps to create these 3D images from both neutrons and X-rays into one analysis package available to all facility users.

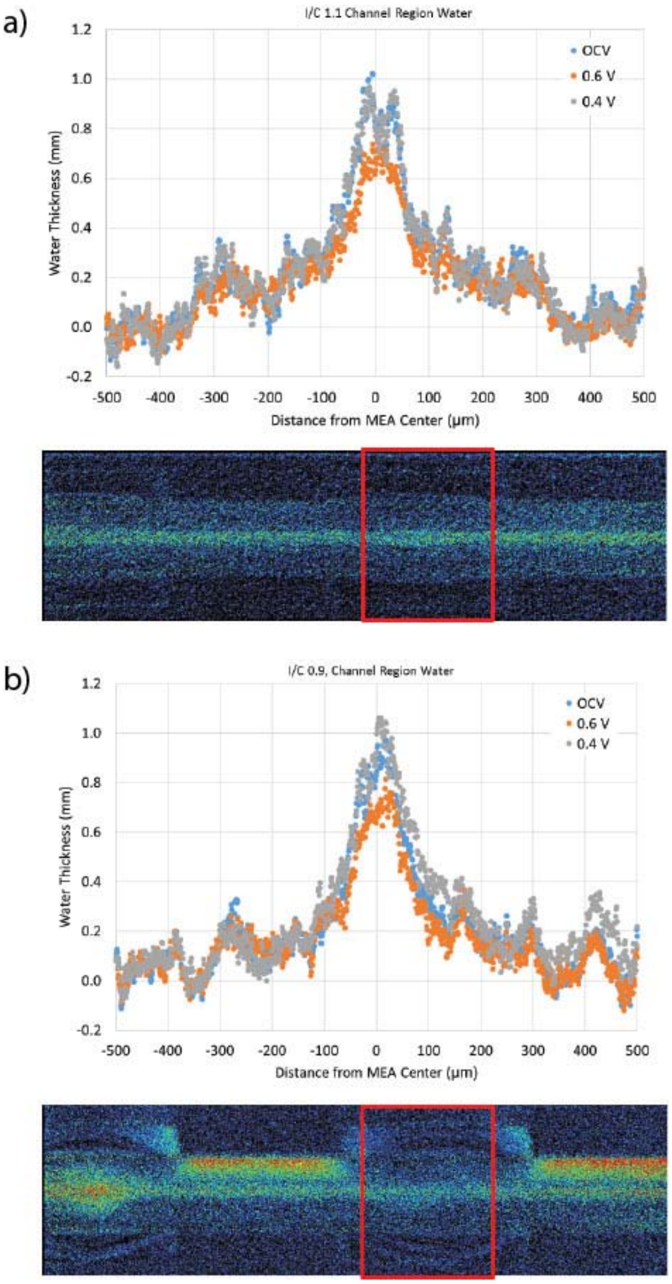


FIGURE 2. Water content comparison for two different ionomer/carbon (I/C) ratio catalysts: (a) 1.1 I/C and (b) 0.9 I/C. Cell conditions: temperature 80°C with constant voltage operation, open circuit voltage (OCV), 0.4 V 100 % relative humidity, 0.6 V, 75% relative humidity. Images are at 0.4 V with cathode on top; plots cathode positive distance from MEA center.

CONCLUSIONS AND UPCOMING ACTIVITIES

- The NIST Neutron Imaging Facility continues to maintain a robust fuel cell user program.

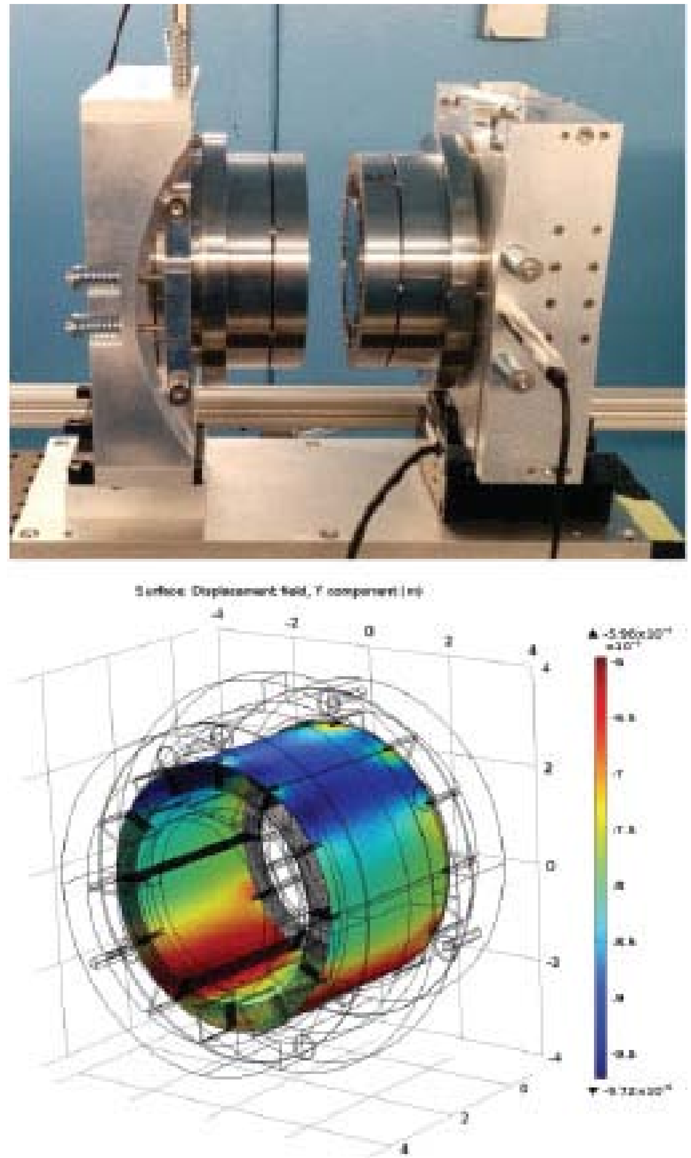
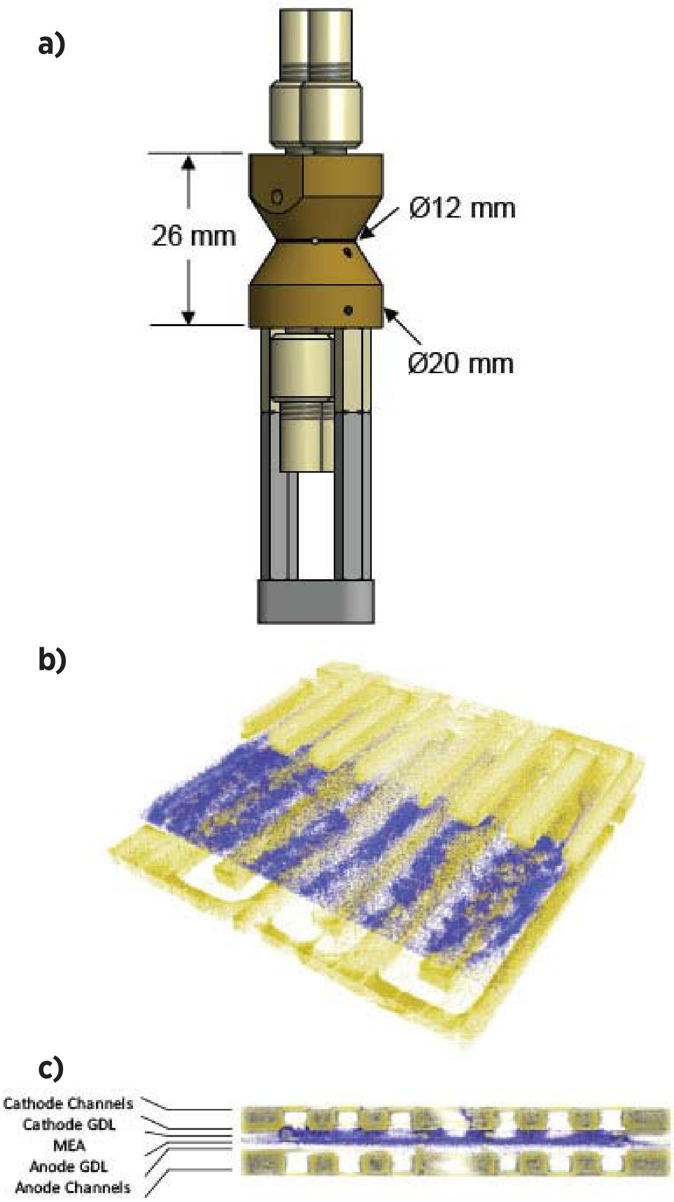


FIGURE 3. Test engineering optic in (a) verifying good figure, surface roughness to be improved with differential deposition. Finite element modeling in (b) shows gravity causes ~80 nm sag of mirrors, which contributes 0.1 arcsec error to resolution or 10% of targeted resolution of 1.0 arcsec needed to achieve 1 µm spatial resolution.

- Good progress has been made towards developing the method to measure liquid saturation values in the catalyst and membrane.
  - Slit scanning:
    - 2 µm spatial resolution was demonstrated.
    - Acquisition time is 17 h, but could be improved to less than 8 h with a smaller grating period.



GDL – gas diffusion layer

FIGURE 4. Fuel cell (a) designed for both X-ray and neutron tomography. The 3D water distribution is shown in (b) and (c) measured with neutrons overlayed with the X-ray image of the hardware and electrode interfaces. Cell active area 0.36 cm^2 active area, ambient temperature, flow both sides 200 sccm, exhaust pressure 150 kPa_a, dew point 25°C, scan time 18 h, 200 mV shown (1.9 A cm^{-2}).

- Centroiding has shown that 1.5 µm resolution has been achieved.
  - Future: Pursue detector package optimization that reduces light losses and incorporates hardware-based centroiding to:
    - Reduce deadtime to near zero.
    - Provide images in real time.
    - Increases field of view to 1 cm diameter.
  - Future: Fabricate planar test section.
- Wolter optics:
  - Flagship method to achieve spatial resolution of 1 µm.
  - Future 2020: high speed 20 µm optics, 2021: 1 µm optics.

- Progress has been made to develop an in situ X-ray method.
  - Developments are scalable to higher spatial resolution.
  - Allows clear distinction of interfaces that are not visible to neutrons.
  - Neutron imaging provides complementary picture of the water distribution.
  - Future: Using X-rays inline will allow for radiographic distinction of interfaces with high spatial resolution.
- User program:
  - New user proposals due to availability of 1.5 µm spatial resolution through the centroiding method.
  - Future: Cold imaging facility is currently being upgraded to include full support.
  - Future: Including electrochemical impedance spectroscopy into the scripting of the test stand would be a great benefit to the users.

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