V.I.4 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/academia needs.

Fiscal Year (FY) 2014 Objectives

- Collaborate and support groups from the DOE Hydrogen and Fuel Cells Program performing water transport measurements with neutron imaging at NIST.
- Improve fuel cell measurement infrastructure based on needs of the fuel cell community.
- Provide support to fuel cell infrastructure to enable testing of automotive-scale test sections.
- 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.

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 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/kWe
- 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 2014 Accomplishments

- Employed a high-resolution imaging method to achieve resolution approaching 1 µm
- Enhanced the fuel cell imaging analysis software to correct for systematic effects due to image blurring
- Developed the technical support infrastructure for testing of automotive-scale test sections
- Improved fuel cell high-resolution image time to improve the experimental throughput of the facility
- Standardized design of the high-resolution fuel cell test cell

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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 in situ 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 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 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, 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 2014 General Motors (GM), Nissan, Los Alamos National Laboratory, University of Connecticut, University of California, Davis, Commissariat à l'énergie atomique et aux énergies alternatives, and University of Tennessee, Knoxville have received project support for experiments at the facility accounting for more than 70 days of beam time. Published results from these and previous years experiments are reflected in the publication list attached to this report.

NIST now provides full support to full-sized commercial and automotive grade fuel cell testing at the facility with a large-scale fuel cell test stand. This stand was developed through the NIST partnership with GM. The facility technical staff has received extensive onsite training on calibration, operation and validation testing from our testing partners at GM. This test stand is capable of 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. Further reports of this capability and tests made with this stand will be presented at future Annual Merit Reviews.

The fuel cell testing community has requested that NIST devise a standardized design for fuel cells used for high-resolution neutron imaging. These types of fuel cells can be difficult to design and field without experience. Through a collaborative effort with our testing partners at Los Alamos National Laboratory, we have identified a robust design that yields good fuel cell performance and image quality. MEAs for this cell design can be taken from existing MEAs, for instance enabling water transport studies during durability tests in 50 cm^2 (see Figure 1). The design uses poly-tetrafluoroethylene (PTFE) gaskets that have high neutron transmission and maintain geometry of the fuel cell very well. Maintaining the fuel cell geometry is critical in high-resolution fuel cell testing as small changes due to swelling of the membrane or lack of parallelism of the end-plates is very apparent. To ensure end-plate parallelism, the design includes cutouts for gauge blocks. Finally the use of porous metal foam flow fields is being investigated to avoid the wavy non-uniformities introduced as the MEA/diffusion media protruded into standard flow field designs.

Understanding flooding and degradation issues due to liquid water in catalysts is a critical step towards 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 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. This year a new apparatus (photo in Figure 2) was designed and tested that will enable fuel cell users to achieve sub 10-µm resolution. This new experimental system was deployed and tested at the facility and the results from a preliminary test are shown in Figure 3. In Figure 3 is plotted the liquid water distribution in an operating fuel cell with the grating and without the grating. The results show that the grating adjusted for 5-µm resolution allows one to differentiate far more detail of the liquid water distribution.

The data from the high-resolution fuel cell images show that improvements to the signal to noise ratio are necessary to improve the quality of the data. This can be achieved with longer integration times or more efficient detectors. Longer integration times will limit the number of fuel cell operating conditions that can be measured. Therefore emphasis has been placed on improving the detector efficiency in order to improve the signal quality. Gadox scintillators have similar spatial resolution and 4 times the stopping power of the microchannel plates currently used for high resolution imaging. However, Gadox produces little light for each stopped neutron and has not been used due to small signal to noise ratios. Modern image intensifiers have been developed that enable high image resolution with stable long-term performance and initial tests showed that an intensifier improved the signal to noise ratio by over a factor of 30. A new detector system based on an intensifier has been designed, and an image intensifier is being procured for fuel cell users. This new system is expected to be available at the

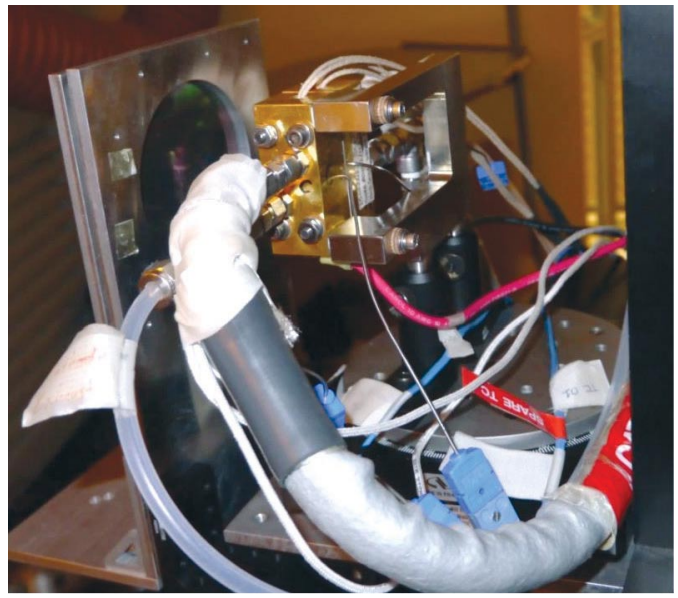

FIGURE 2. Grating set-up now available for users for high-resolution fuel cell testing.

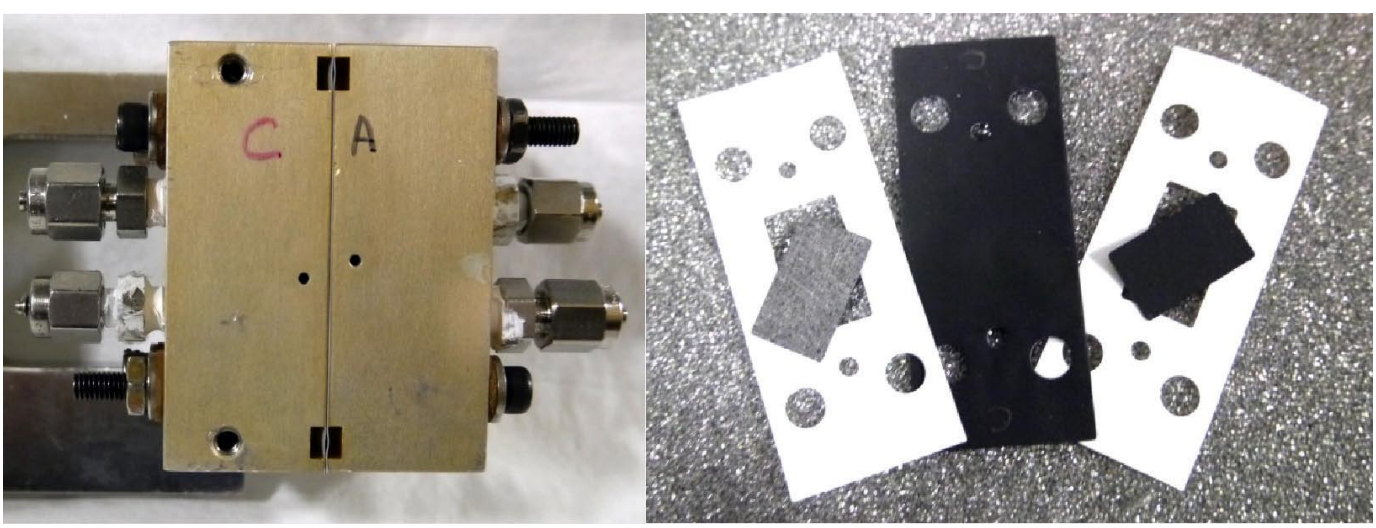

FIGURE 1. Left shows the standardized high-resolution test cell adopted from Los Alamos National Laboratory design. Right shows the MEA cut from existing 50-cm^2 MEA tested for durability shown with the hard PTFE seals.

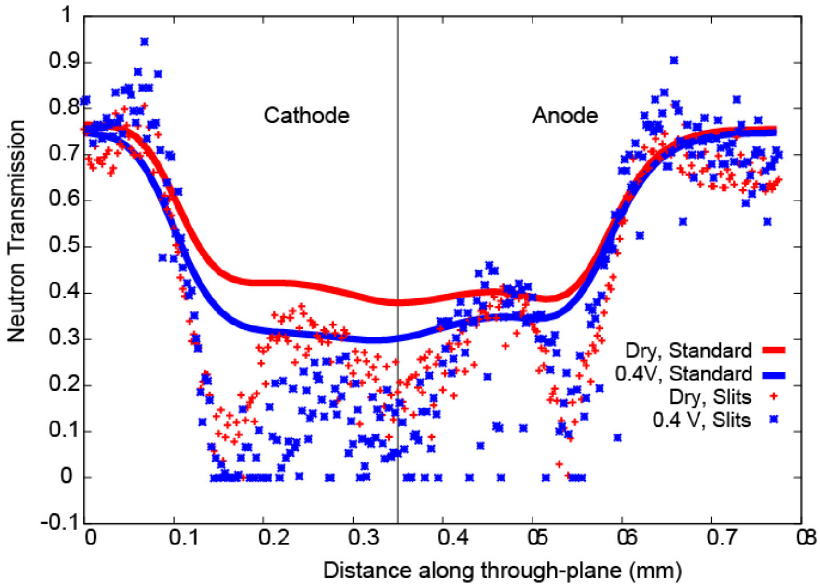

FIGURE 3. Data from initial tests of the gratings for high-resolution fuel cell testing. Solid line shows the standard water distribution measured without gratings. Data points are the spatially resolved liquid water distribution.

facility by January 2015 and is expected to increase the time resolution for high-resolution neutron imaging by a factor of 4 due to the increased neutron detection efficiency.

It could be possible to increase the neutron intensity by 50 to 100 times than currently available using a neutron lens. Previously, practical lenses for neutrons have not been available due to the low neutron refractive power of all materials. However, a new X-ray lens technology developed by the National Aeronautics and Space Administration has shown great promise to provide a practical lens for neutron imaging. This year NIST committed to developing a neutron microscope with a milestone to provide a 1:1 lens with greater than 50 times increase in signal by 2016 and a subsequent lens that will magnify neutron images by 10 times to achieve 1-µm resolution by 2018. If successful this will enable fuel cell researchers to measure water distributions with 1 µm resolution in 20 min as opposed to current 24 hours per image with the grating method.

Ensuring the accuracy of the data analysis techniques used to quantify the water content has been a continuing focus of the NIST fuel cell project. Previously the results of an extensive analysis of systematic effects present when measuring high resolution water distributions in fuel cell membranes identified multiple corrections that are required to do accurate measurements. One of the more significant contributions can be corrected in software using mathematical deconvolution of the data. This capability was added as a new feature in the data analysis software that is available to facility users. In addition an evaluation was made of the importance of this systematic correction to previous fuel cell data sets. It was determined that this would only amount to a 1% correction to the in-plane water distribution, which is a systematic error below the overall uncertainty in previous measurements.

CONCLUSIONS AND FUTURE DIRECTIONS

- NIST Neutron Imaging Facility continues to maintain a robust fuel cell user project with:
  - 11 publications and 8 presentations in 2013
  - Over 70 days of dedicated fuel cell beam time
- Fuel cell infrastructure now fully supports automotive-scale testing:
  - Developed in collaboration with GM
  - Test stand to control automotive-scale cells is available to users
  - NIST staff trained at GM to support calibration and use of the test stand
- Design of standard high resolution fuel cell is available to users:
  - Can use existing membranes from 50-cm^2 test sections
  - Seals well and maintains precise geometry for testing approaching 1-µm resolution
- With the goal to study catalysts, NIST continues to improve the image spatial resolution. New avenues toward resolving the MEA water content include:

  - Employing a grating method to achieve resolution approaching 1 µm with 12 hour acquisition time (end of 2014)
  - Developing a magnifying neutron lens to reach 1 µm with 20 min acquisition time (2018)
- Improve fuel cell high resolution image time:
  - Time resolution for through-plane water content measurements improved by a factor of 4 with 20 µm scintillator detector
  - Future neutron lens will increase time resolution by 50x to achieve image times of 10 s with 10 µm resolution
- Neutron image analysis and corrections:
  - Deblurring algorithms for images of the in-plane water content of fuel cells are demonstrated and published
- Future general improvements:
  - Second new cold neutron imaging facility will begin operation by 2015
  - Continue improvements to achieve 1-µm imaging:
    - Develop neutron lens
    - Improve grating method

FY 2014 PUBLICATIONS/PRESENTATIONS

1. O.F. Selamet, U. Pasaogullari, D. Spernjak, D.S. Hussey, D.L. Jacobson, and M.D. Mat, "Two-phase flow in a proton exchange membrane electrolyzer visualized *in situ* by simultaneous neutron radiography and optical imaging International", Journal of Hydrogen Energy **38** (14) 5823-5835 (2013).

2. J.D. Fairweather, D. Spernjak, A.Z. Weber, D. Harvey, S. Wessel, D.S. Hussey, D.L. Jacobson, K. Artyushkova, R. Mukundan, R.L. Borup, "Effects of Cathode Corrosion on Through-Plane Water Transport in Proton Exchange Membrane Fuel Cells", Journal of The Electrochemical Society **160** (9) F980-F993 (2013).

3. D. Liu, D. Hussey, M.V. Gubarev, B. D. Ramsey, D. Jacobson, M. Arif, D.E. Moncton, and B. Khaykovich, "Demonstration of achromatic cold-neutron microscope utilizing axisymmetric focusing mirrors", Applied Physics Letters **102** (18) 183508 (2013).

4. Hussey, D.S., E. Baltic, K.J. Coakley and D.L. Jacobson, "Improving quantitative neutron radiography through image restoration", NIMA **729** 316-321 (2013).

5. K.J. Coakley, D.F. Vecchia, D.S. Hussey, and D.L. Jacobson, "Neutron Tomography of a Fuel Cell: Statistical Learning Implementation of a Penalized Likelihood Method", IEEE Transactions On Nuclear Science, **60** (5) 3945-3954 (2013).

6. B.M. Wood, K. Ham, D.S. Hussey, D.L. Jacobson, A. Faridani, A. Kaestner, J.J. Vajo, P. Liu, T.A. Dobbins, L.G. Butler, "Real-time observation of hydrogen absorption by LaNi5 with quasi-dynamic neutron tomography", Nuclear Instruments and Methods in Physics Research Section B, 324 95-101 (2014).

7. Spernjak, D., G. Wu, J. Fairweather, D. Hussey, R. Mukundan, R. Borup & P. Zelenay, In situ measurement of flooding in thick Pt and PANI-derived catalyst layers in PEM fuel cells. Journal of the Electrochemical Society, In preparation (2014).

8. D.S. Hussey, D. Spernjak, G. Wu, D.L. Jacobson, D. Liu, B. Khaykovich, M.V. Gubarev, J.D. Fairweather, R. Mukundan, R. Lujan, R.L. Borup, "Neutron Imaging of Water Transport in Polymer-Electrolyte Membranes and Membrane-Electrode Assemblies", ECS Transactions **58** (1) 293-299 (2013).

9. Z. Lu, J. Waldecker, X. Xie, M.-C. Lai, D.S. Hussey, D.L. Jacobson, "Investigation of Water Transport in Perforated Gas Diffusion Layer By Neutron Radiography", ECS Transactions **58** (1) 315-324 (2013).

10. J.D. Fairweather, D. Spernjak, J. Spendelow, R. Mukundan, D.S. Hussey, D.L. Jacobson, R.L. Borup, "Evaluation of transient water content during PEMFC operational cycles by stroboscopic neutron imaging", ECS Transactions **58** (1) 301-307 (2013).

11. X. Liu, T.A. Trabold, J.J. Gagliardo, D.L. Jacobson, D.S. Hussey, "Neutron Imaging of Water Accumulation in the Active Area and Channel-to-Manifold Transitions of a PEMFC" ASME 2013 11th International Conference on Fuel Cell Science V001T01A010-V001T01A010 (2013).

12. Zijie Lu, James Waldecker, Xingbin Xie, Ming-Chia Lai, Daniel S Hussey, and David L Jacobson, "Investigation of Water Transport in Perforated Gas Diffusion Layer By Neutron Radiography", Abstract 1293, 224th ECS Meeting, San Francisco, CA, 2013.

13. Rangachary Mukundan, Dusan Spernjak, Roger Lujan, Joseph D. Fairweather, Daniel S Hussey, David L Jacobson, Andrew J. Steinbach, Adam Z. Weber, and Rod L Borup, "Neutron Imaging and Performance of PEM Fuel Cells With Nanostructured Thin Film Electrodes At Low Temperatures", Abstract 1292, 224th ECS Meeting, San Francisco, CA, 2013.

14. Joseph D. Fairweather, Dusan Spernjak, Jacob Spendelow, Rangachary Mukundan, Daniel S Hussey, David L Jacobson, and Rod L Borup, "Evaluation of Transient Water Content During PEMFC Operational Cycles By Stroboscopic Neutron Imaging", Abstract 1290, 224th ECS Meeting, San Francisco, CA, 2013.

15. Daniel S Hussey, David L Jacobson, Dazhi Liu, Boris Khaykovich, Mikhail V Gubarev, Dusan Spernjak, Gang Wu, Joseph D. Fairweather, Rangachary Mukundan, Roger Lujan, Piotr Zelenay, and Rod L Borup, "Neutron Imaging of Water Transport in Polymer-Electrolyte Membranes and Membrane-Electrode Assemblies", Abstract 1289, 224th ECS Meeting, San Francisco, CA, 2013.

16. Xinyu Huang, Hongying Zhao, and William A. Rigdon, "In Situ Observation of Membrane Degradation in PEM Fuel Cell Via Raman Spectroscopy", Abstract 1431, 224th ECS Meeting, San Francisco, CA, 2013.

17. Yasser Ashraf Gandomi and Matthew M. Mench, "Assessing the Limits of Water Management With Asymmetric Micro-Porous Layer Configurations", Abstract 1542, 224th ECS Meeting, San Francisco, CA, 2013.

18. Toshikazu Kotaka, Yuichiro Tabuchi, Ugur Pasaogullari, and Chao-Yang Wang, "The Influence of the Liquid Water Interaction Between Channel, GDL and CL On Cell Performance", Abstract 1456, 224th ECS Meeting, San Francisco, CA, 2013.

19. X. Liu, T.A. Trabold, J.J. Gagliardo, D.L. Jacobson, D.S. Hussey, "Neutron Imaging of Water Accumulation in the Active Area and Channel-to-Manifold Transitions of a PEMFC" ASME 2013 11th International Conference on Fuel Cell Science.