VI.1 Fuel Cell Membrane Electrode Assembly Manufacturing R&D

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Partners:

- Lawrence Berkeley National Laboratory (LBNL), Berkeley, CA
- Colorado School of Mines, Golden, CO
- Georgia Institute of Technology, Atlanta, GA
- General Motors, Pontiac, MI
- 3M Company, St. Paul, MN
- Mainstream Engineering, Rockledge, FL

Project Start Date: July 16, 2007
Project End Date: Project continuation and direction determined annually by DOE

Overall Objectives

- Evaluate and develop in-line diagnostics for cell and component quality control and validate diagnostics in-line.
- Investigate the effects of membrane electrode assembly (MEA) component manufacturing variations on MEA performance and lifetime to understand the required performance of diagnostic systems and contribute to the basis of knowledge available to functionally determine manufacturing tolerances for these materials.
- Use established models to predict the effects of local variations in MEA component properties, and integrate modeling of the operational and design characteristics of diagnostic techniques into the design and configuration of in-line measurement systems.
- These objectives have strong support from the industry. Specifically, the outcomes of the 2011 NREL/DOE Hydrogen and Fuel Cell Manufacturing R&D Workshop, the Office of Naval Research-funded Manufacturing Fuel Cell Manhattan Project, and the 2013 DOE Energy Efficiency and Renewable Energy Office Quality Control Workshop confirmed the importance of continued development of in-line quality control techniques for cell manufacturing. Our specific development activities have been and will continue to be fully informed by direct input from industry. As new technologies emerge and as the needs of the industry change, the directions of this project will be adjusted.

Fiscal Year (FY) 2016 Objectives

- Complete evaluation of new prototype segmented cell hardware to improve our capabilities to study the effects of defects.
- Complete experiments for single-point membrane thickness measurement by optical reflectance.
- Use our segmented cell test system to perform total cell and spatially resolved performance (polarization) measurements of MEAs with anode and cathode defects at least as small as 0.5 cm^2.
- Based on LBNL predictive modeling, demonstrate an improvement to the infrared/reactive impinging flow (RIF) technique that will decrease noise and/or increase sensitivity, e.g., using a gas knife with an improved jet array design or using a backing configuration to reduce reactive gas loss.

Technical Barriers

This project addresses the following technical barriers from the Manufacturing R&D section (3.5) of the Fuel Cell Technologies Office Multi-Year Research, Development, and Demonstration Plan.

(E) Lack of Improved Methods of Final Inspection of MEAs

(H) Low Levels of Quality Control

Contribution to Achievement of DOE Manufacturing R&D Milestones

This project contributes to the achievement of the following DOE milestones from the Manufacturing R&D section (3.5) of the Fuel Cell Technologies Office Multi-Year Research, Development, and Demonstration Plan.

- Milestone 5.1: Establish models to predict the effect of manufacturing variations on MEA performance. (1Q, 2016)
- Milestone 5.2: Demonstrate improved sensitivity, resolution, and/or detection rate for MEA inspection methods. (4Q, 2016)
- Milestone 5.4: Design and commercialize an in-line QC device for PEMFC MEA materials based on NREL's optical reflectance technology. (4Q, 2017)

Accomplishments

NREL accomplished the following in FY 2016:

- Performed in situ studies of performance effects in cells with as-manufactured and/or created electrode defects.
- Initiated new collaboration with Georgia Tech, leveraging their membrane casting expertise, to fabricate and study the effects of as-manufactured membrane defects.
- Completed an evaluation of a new segmented cell hardware prototype.
- Established methods and initiated in situ failure onset studies of defected MEAs.
- Demonstrated the detection of membrane pinholes at least as small as 25-µm diameter in MEAs and membrane-containing subassemblies using the through-plane reactive excitation (TPRE) technique.
- Developed multi-physics modeling to predict detection limits and potential pathways for in-line implementation of TPRE.
- Demonstrated single-point membrane thickness measurement by reflectance spectroscopy.
- Assisted Mainstream Engineering in demonstrating their optical quality control (QC) prototype.
- Studied the applicability of the RIF technique to non-Pt-only catalysts.
- Expanded multi-physics modeling of RIF technique to further explore potential process improvements.
- Continued collaboration with our industry partners in accordance with our project charter.

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INTRODUCTION

Defects in MEA components differ in type and extent depending on the fabrication process used. The effects of these defects also differ, depending on size, location in the cell relative to the reactant flow-field, cell operating conditions, and the type of component that contains the defect. Understanding the effects of these different kinds of defects is necessary to specify and/or develop diagnostic systems with the accuracy and data acquisition/processing rates required for the speed and size scales of high-volume continuous manufacturing methods. Furthermore, predictive capabilities for manufacturers are critical to assist in the development of tolerances and to enable assessment of the effects of material and process changes.

APPROACH

NREL and its partners are addressing the DOE manufacturing milestones listed above by evaluating, developing, and validating (in-line) diagnostics that will support the use of high-volume manufacturing processes for the production of MEAs and MEA component materials. Prioritization of this work is based on inputs from our industry partners on their critical manufacturing quality control needs. We are focusing on diagnostic capabilities not addressed by commercially available in-line systems; in particular we are evaluating methods to make areal rather than point measurements such that discrete defects can be identified. We are also developing test methodologies to study the effects of the size and/or extent of each important type of variability or defect. These results will assist our industry partners in validating manufacturing tolerances for these materials, ultimately reducing scrap rates and cost, and improving supply chain efficiency. Finally, predictive models are being used at LBNL to understand the operational and design characteristics of diagnostic techniques by simulating the behavior of MEA components in different excitation modes. These results are being fed back to our design effort in configuring the diagnostics for in-line implementation. MEA models are also being utilized to understand the in situ behavior of defected MEAs to guide and further elucidate experiments.

RESULTS

Our major milestone for the past year was addressing a go/no-go decision on further development of the TPRE technique. The criteria for the decision were detection of a pinhole of less than 150 µm at an exposure time to the reactive gas of less than 5 s. These criteria were met, as shown in Figure 1, where a membrane with a 90-µm diameter pinhole was detected in a half-cell configuration. Using a 0.5 slpm flow of hydrogen and a 5 s pulse duration, a temperature rise of 1°C was observed after only 2 s of exposure. In additional studies, pinholes as small as 25 µm were detected. LBNL utilized a hybrid version of their RIF and TPRE multi-physics models to provide an initial analysis of possible pathways to in-line implementation of TPRE. The new model in fact predicted that an impinging-flow version of TPRE could potentially detect small pinholes at small exposure times using hydrogen concentrations in the reactive gas of less than the lower flammability limit in air (4%).

We continued to have a major focus on in situ testing to understand the effects of manufacturing variations in electrodes. A broad range of electrode variations were studied using our segmented cell system, including cathode centered bare spots, defects on the anode vs. the cathode, defects at the inlet vs. center vs. outlet of the cell, defect shape and total catalyst layer volume reduction, thick spots vs. thin spots, comparison of defects as a function

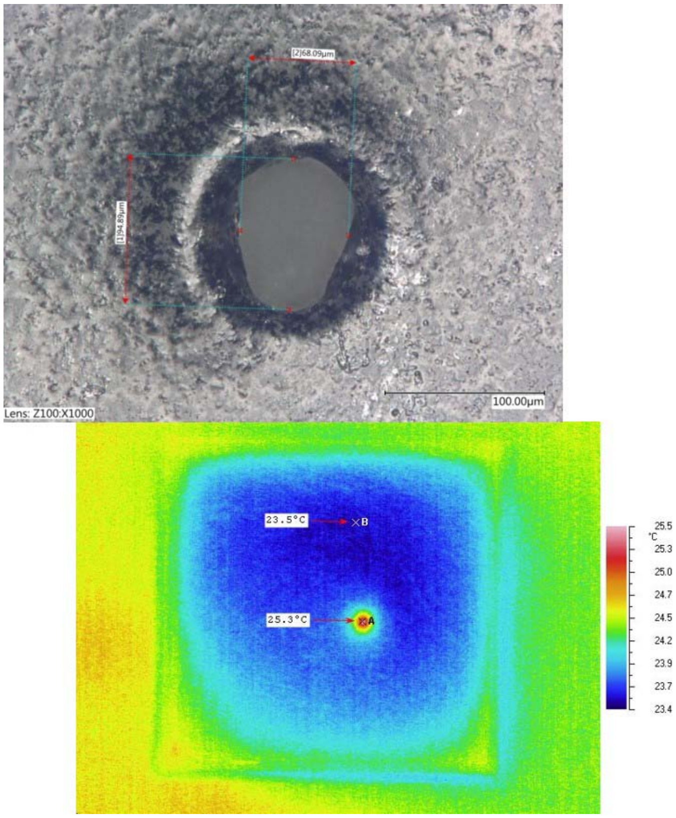

FIGURE 1. TPRE demonstration data, showing optical microscopy of an 18-µm thick membrane sample with a 90-µm diameter pinhole, and the thermal response of a half-cell including this membrane and a gas diffusion electrode with a catalyst loading of 0.2 mg Pt/cm^2. The excitation conditions were a 5 s pulse of hydrogen at 0.5 slpm. A detectable temperature rise of 1°C was observed after 2 s of exposure.

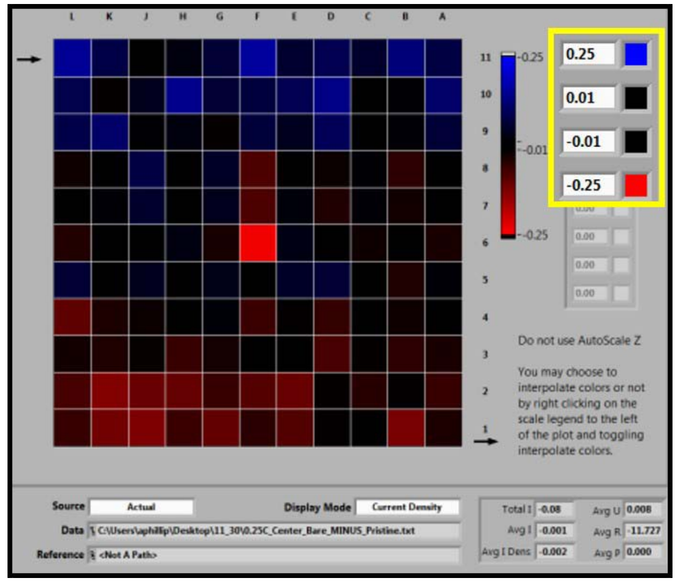

FIGURE 2. Segmented cell data showing the spatially resolved performance effect of a 0.25 cm^2 bare spot in the cathode at a total cell current density of 1.2 A/cm^2. The color scale shows the difference in local current density between the defected cell and a pristine cell. The cell uses a NRE 212 (50 µm Nafion®) membrane and has a nominal loading of 0.2 mg Pt/cm^2 on both anode and cathode, and is operated at anode/cathode conditions of 32/32 % relative humidity (RH), 150/150 kPa, 1.5/2.0 stoich, H_2/air, and a cell temperature of 80°C.

of membrane thickness and nominal catalyst loading, and comparison of defects in catalyst-coated membrane-based MEAs vs. gas diffusion electrode-based MEAs. As an example of these studies, Figure 2 shows the local performance effect of a 0.25 cm^2 bare spot in the center of the cathode. The difference in current density between the defected cell and an associated pristine cell in each of the 121 segments is shown. Red contours indicate poorer performance in the defected cell, while blue contours indicate increased performance. The local effect of the defect in the center segment is clearly seen; however, it is also seen that normal along-the-flowfield variations in cell performance are close to the same magnitude as the effect of the defect. In addition, we performed further development of an accelerated stress test, in coordination with Los Alamos National Laboratory, which would enable us to detect and spatially resolve the onset of failure in a cell. In Figure 3, we show example data from failure testing of a pristine MEA using this testing protocol. Decrease of open circuit voltage and increase in hydrogen crossover current density are used as in situ indicators of failure. Upon indication of failure, we use our novel cell hardware and an infrared camera with a hydrogen crossover test to image the location and extent of the failure.

In a key study that sets the path toward real-time imaging of membrane thickness, we confirmed that optical reflectance spectroscopy could be used with the well-known film interference fringe method to measure single-point thickness of membranes. This was an expected result. However, we also demonstrated that the technique could be used to measure membrane thickness (a) while the membrane was still laminated to one or two casting or protective films, and (b) of membranes with reinforcing layers. These were critical findings given the widespread use of reinforced membranes and the understanding that, until final assembly into an MEA, polymer electrolyte membranes are rarely handled in a stand-alone fashion. We tested different PEMFCs, including several with reinforcing layers, over a range of thickness from 6 to 50 µm. Figure 4 provides visible and infrared spectroscopy of an 18-µm thick membrane, both of which show measurable interference fringes. The inset shows the peak resulting from a Fourier transform of the infrared spectrum, which indicates thickness.

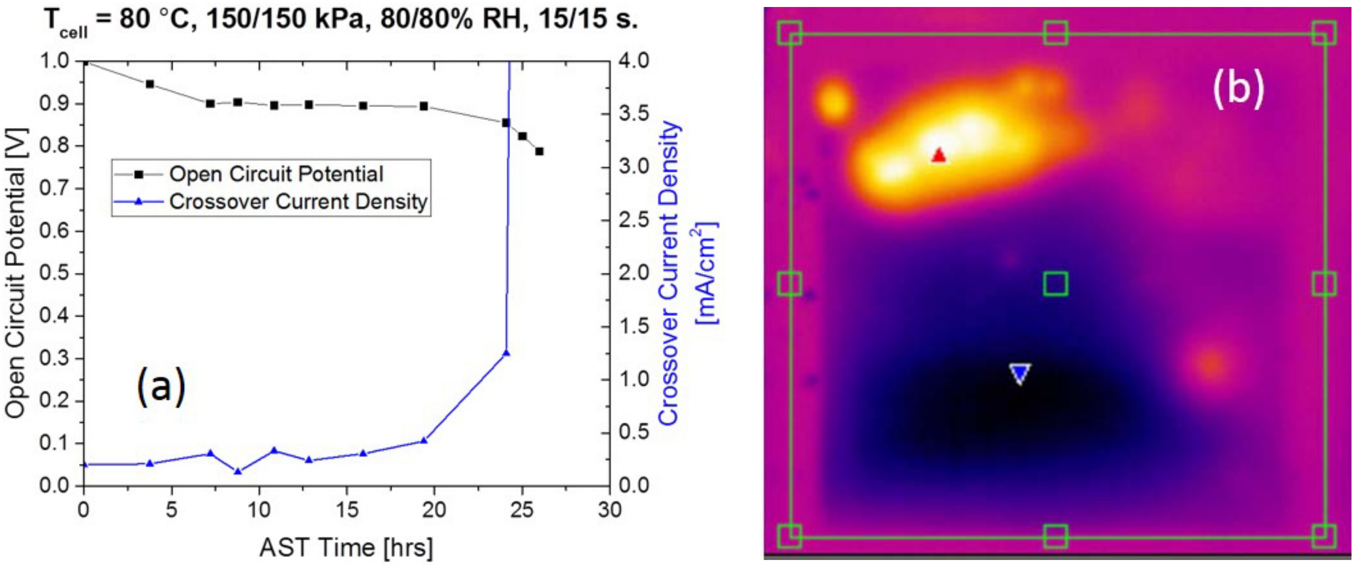

FIGURE 3. Failure study data for a pristine cell having a NRE 212 (50 µm Nafion) membrane and a nominal loading of 0.2 mg Pt/cm[2] on both anode and cathode, operated at accelerated stress test (AST) conditions of 150 kPa, H_2/air, and cell temperature of 80°C, cycling from 0 to 80% RH in 15 s intervals; (a) open circuit voltage and hydrogen crossover current density data showing the onset of the failure, and (b) infrared thermography during hydrogen crossover test showing the location and extent of failure.

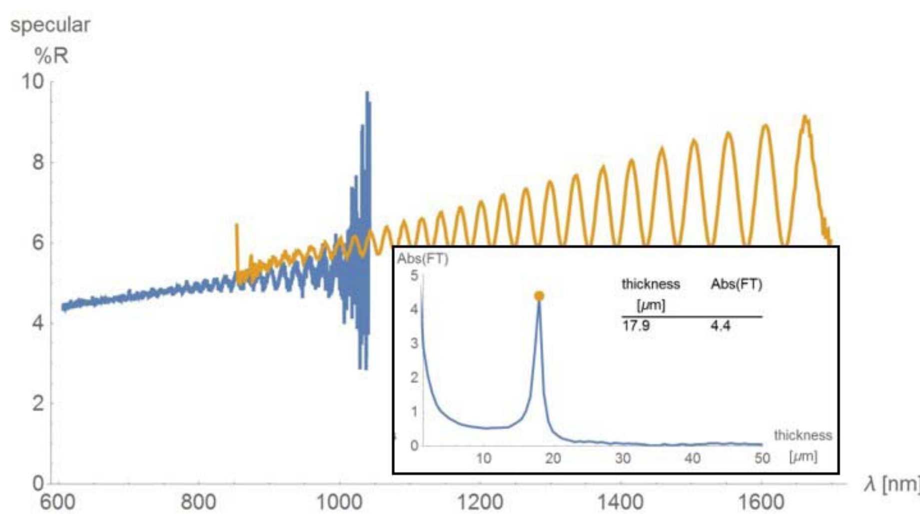

FIGURE 4. Visible wavelength (blue) and infrared wavelength (orange) optical reflectance spectroscopy data for an 18-µm thick membrane showing measurable interference fringes. The inset shows the thickness peak resulting from a Fourier transform of the infrared spectrum.

FUTURE DIRECTIONS

- Demonstrate improvement in RIF detectability based on LBNL modeling.
- Develop a concept, using modeling and experimentation, for in-line TPRE.
- Demonstrate a prototype system for in-line membrane thickness imaging.
- Continue to use predictive modeling and single and segmented cell test methods to study the effects of as-manufactured defects on MEA performance and lifetime using standard or accelerated stress tests.
  - Continue to work toward the implementation of more of our techniques on industry production lines.

SPECIAL RECOGNITIONS & AWARDS/ PATENTS ISSUED

1. Issued US Patent #9,234,843, "On-line continuous monitoring in solar cell and fuel cell manufacturing using spectral reflectance imaging."

FY 2016 PUBLICATIONS/PRESENTATIONS

1. P. Rupnowski, M. Ulsh, B. Sopori, "High Throughput and High Resolution In-line Monitoring of PEMFC Materials by Means of Visible Light Diffuse Reflectance Imaging and Computer Vision," PowerEnergy2015-49212, and presented at the ASME 2015 Power and Energy Conversion Conference, San Diego, CA; July 1, 2015.

2. M. Ulsh, J.M. Porter, D.C. Bittinat, G. Bender, "Defect Detection in Fuel Cell Gas Diffusion Electrodes Using Infrared Thermography," Fuel Cells Journal, DOI: 10.1002/fuce.201500137, 2016.

3. M. Ulsh, P. Rupnowski, B. Sopori, I. Zenyuk, A. Weber, G. Bender, "In-line Quality Control for Fuel Cell and Electrolysis Materials," MRS Spring Meeting, Symposium EE9 invited lecture, Phoenix, AZ; March 29, 2016.