Membrane Electrode Assembly Manufacturing R&D

Michael Ulsh (Primary Contact), Guido Bender, Peter Rupnowski
National Renewable Energy Laboratory (NREL)
15013 Denver West Parkway
Golden, CO 80401
Phone: 303-275-3842
Email: michael.ulsh@nrel.gov

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

Subcontractor:
Colorado School of Mines, Golden, CO

Collaborators:
- Lawrence Berkeley National Laboratory (LBNL), Berkeley, CA
- General Motors, Pontiac, MI
- W.L. Gore & Associates, Elkton, MD
- Mainstream Engineering, Rockledge, FL
- Proton OnSite, Wallingford, CT

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

Overall Objectives

- Perform research and development (R&D) of real-time inspection techniques relevant to membrane electrode assembly (MEA) component critical material properties and validate these techniques under relevant fabrication conditions.
- Study the effects of MEA component fabrication variations on MEA performance and lifetime to understand the required characteristics of real-time inspection systems.
- Develop models to predict the effects of local variations in MEA properties and to improve our understanding of excitation modes during real-time inspection.

Our development activities will continue to be fully informed by input from industry. As new technologies emerge and needs change, the directions of this project will be adjusted.

Fiscal Year (FY) 2019 Objectives

- Obtain low-temperature electrolysis (LTE) membrane samples of typical thickness and with typical manufacturing defects (if available from LTE original equipment manufacturers or suppliers). Perform initial defect detection tests using existing techniques and testbeds.
- Perform studies to understand the impact of electrode coating irregularities, with particular focus on thick spots and how their effects are modulated by aspects of membrane architecture (e.g., thickness and presence of reinforcing material).
- Perform hyperspectral imaging of membrane thickness for LTE and polymer electrolyte membrane fuel cell (PEMFC) membranes, exploring x-y resolution, z resolution, and % coverage; and evaluate the effect of line speed, in accordance with the following measurement criteria: (1) physical resolution of 100 µm or smaller, (2) thickness range for LTE membranes of 50–200 µm, and (3) thickness range for PEMFC membranes of 12–50 µm, and line speed of 2 feet per minute (fpm) or faster.

Technical Barriers

This project addresses the following technical barriers from the Manufacturing R&D section of the Fuel Cell Technologies Office Multi-Year Research and Development Plan[1]:

- (E) Lack of Improved Methods of Final Inspection of MEAs
- (H) Low Levels of Quality Control.

Contribution to Achievement of DOE Milestones

This project contributes to the achievement of the following DOE milestones from the Manufacturing R&D section of the Fuel Cell Technologies Office Multi-Year Research and Development Plan:

[1] https://www.energy.gov/eere/fuelcells/downloads/fuel-cell-technologies-office-multi-year-research-development-and-22

- Milestone 5.5: Develop correlations between manufacturing parameters and manufacturing variability, and performance and durability of MEAs. (4Q, 2018)
- Milestone 5.8: Implement demonstrated in-line quality control (QC) techniques on pilot or production lines at PEMFC MEA material manufacturers. (4Q, 2020)
- Milestone 5.9: Develop imaging-based methods for 100% inspection of platinum-group metal (PGM) loading in electrodes. (4Q, 2020)

FY 2019 Accomplishments

- Completed our co-funded project with Gore, providing full-length full-width in-line mapping of 14 production and experimental rolls of Gore Select Membrane, using NREL-developed automated feature detection and classification algorithms, for a total scanned length of over 1.6 kilometers.
- Developed a new methodology for processing half-cell thermal scanning video data to create a real-time temperature map that is proportional to membrane thickness, in collaboration with GM.
- Assisted Mainstream Engineering in validating their prototype optical inspection techniques.
- Demonstrated that infrared (IR) direct current and reactive excitation methods can detect through-plane membrane fissures and holes in LTE catalyst-coated membranes (CCMs), in collaboration with Nel/Proton.
- Performed optical scanning of titanium porous transport layers (PTLs) and verified detection of both discrete and areal defects, in collaboration with Nel/Proton.
- Demonstrated in-line membrane thickness mapping on a 100+ meter roll of various PEM membranes, in single- and multi-layer constructions, achieving x (cross-web), y (down-web), and z (thickness) resolutions of 0.1 mm, 0.3 mm, and 0.2 µm, respectively, at line speeds of up to 5 fpm.
- Performed single-point ultraviolet-to-visible (UV-Vis) and near-infrared (NIR) spectroscopy on a wide range of membranes to understand the sensitivity of the thickness imaging measurement to wavelength range and resolution.
- Fabricated PEMFC electrodes with thick spots using two fabrication methods, characterized the electrodes using X-ray fluorescence (XRF) and microscopy to understand the local morphology, and initiated total cell and spatial initial performance and drive cycle in situ measurements.
- Obtained membrane pinhole samples of different diameter and membrane type and completed (LBNL) initial steady-state and transient performance modeling of a 10 µm diameter membrane pinhole to predict the impact on performance and water uptake as a function of pinhole location and cell relative humidity.
- Completed Generation 2 modifications to our segmented cell test system, enabling true single-cell operation (i.e., natural current and voltage distribution), interchangeable flowfields, 4-wire resistance measurements on all segments, and improved cell sealing.
- Continued collaboration with our industry partners in accordance with our project charter.

INTRODUCTION

In FY 2005–2007, NREL provided technical support to DOE in developing a new key program activity: manufacturing R&D for hydrogen and fuel cell technologies. This work included a workshop on manufacturing R&D, which gathered inputs on technical challenges and barriers from the fuel cell industry, and subsequent development of a roadmap for manufacturing R&D. In late FY 2007, NREL initiated a project to assist the fuel cell industry in addressing these barriers, initially focusing on in-line quality control of MEA components.

APPROACH

NREL and its partners are addressing the DOE manufacturing milestones listed above by utilizing industry relationships and public forums to understand MEA material, structure, and processing directions and challenges. We then develop real-time inspection techniques, using computational modeling to (a) assist in the development and optimization of unique measurement techniques, and (b) predict the effects of material irregularities on performance. These techniques are validated under simulated processing conditions. In parallel we use specialized in situ testing techniques to perform detailed parametric studies of the effects of material irregularities originating during fabrication and handling on performance and lifetime.

RESULTS

We continued our effort to further understand and implement multi-spectral imaging techniques for in-line real-time mapping of membrane thickness. Initial work focused on fast single-point spectroscopy as a scoping study to understand the applicability of membranes of different composition, structure (including multilayer assemblies) and thickness. Perfluorinated sulfonic acid (PFSA) and non-PFSA membranes, with and without reinforcement, with and without backer and cover sheets, and of thickness 20–175 µm were studied. We found that, for PFSA membranes, we were able to measure thickness regardless of structure for thicknesses up to approximately 50 µm, within the visible spectrum. We were also able to measure the thickness of thicker PFSA membranes, but only in the IR spectrum, for the wavelength resolution of the spectrometers used. This distinction is important in terms of the spatial resolution, frame rate, accuracy, and cost of required detectors for the technique. The spectral signal also depended on the membrane material (for non-PFSA) and method of fabrication. We implemented and validated the learnings of this study on our research web-line in a series of experiments where a roll of membrane materials totaling over 100 meters in length was imaged in real time, using a hyperspectral camera and our dedicated optical inspection platform on the web-line. We also studied the impact of line speed on machine-direction resolution. Generally similar results were seen to the spectroscopy study. Figure 1 shows results from the web-line run for sections of PFSA membranes of three different thicknesses. The false color indicates thickness, and the transverse-direction uniformity at locations indicated by the red lines is shown at the right. A periodic machine-direction variation of thickness can be observed in the 10 and 20 µm samples, while overall the thickness is seen to be quite uniform. The same periodic variation is not seen in the 15 µm sample, though an overall transverse-direction variation along the sample is observed.

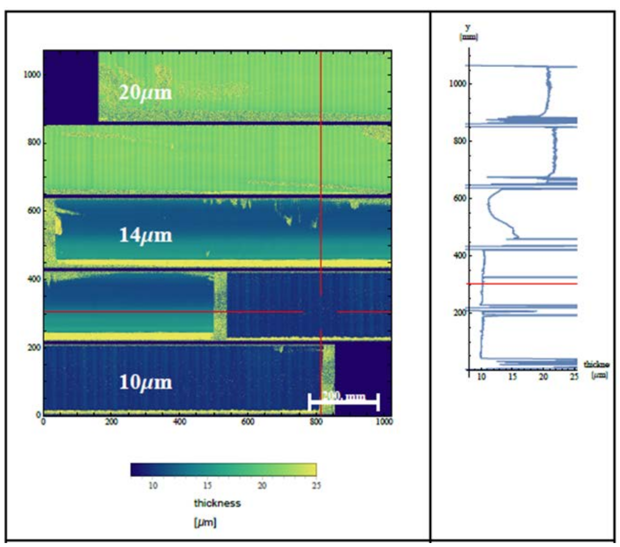

Figure 1. Membrane thickness imaging data from web-line run

Additional highlights of quality inspection tool development during the year included the completion of our co-funded project with Gore. The objective of the project was to develop inspection and data processing methods to provide full-length and full-width membrane roll characterization. Using the dedicated optical inspection testbed and NREL-developed object detection and characterization algorithms (calibrated by Gore defect libraries), full-roll data was provided to Gore for 14 production and experimental rolls of membrane totaling over 1.6 kilometers of web scanned. Several of these membranes were also used in the thickness imaging studies described above.

In work in our ongoing cooperative research and development agreement with GM, we continued to develop a measurement technique for membrane thickness in a half-cell configuration (i.e., while laminated to a gas-diffusion electrode [GDE]). A methodology was developed to process data from each frame of IR data taken during the measurement, stitch that data into a map of temperature for the sample, and then transform the temperature data to thickness data using an empirical correlation developed from GM's samples. A study of error as a function of spatial resolution using this methodology is ongoing.

We also performed first-time assessments of the usefulness of our through-plane IR techniques for LTE materials. In this work, Nel/Proton provided LTE CCMs that had been operated in a stack. We explored both direct-current and reactive-excitation methods to identify discrete failure points based on qualitative testing of each CCM at Proton. Figure 2 shows examples from both measurements, in this case the identification of the same two discrete failure points by the two methods. Overall, the through-plane reactive excitation method detected discrete failures in every CCM identified by the qualitative Proton method. It is expected that these results should be indicative of usefulness of these techniques in identifying as-manufactured defects in these LTE materials.

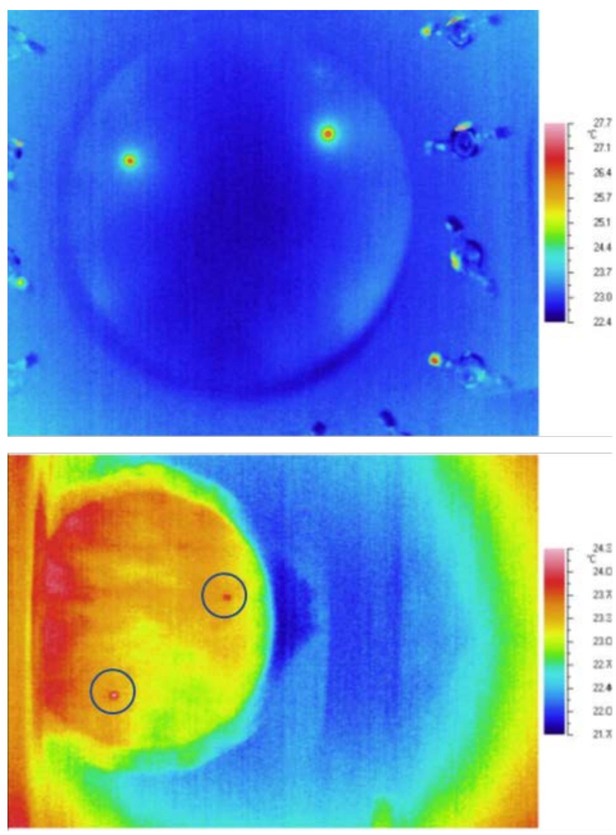

Figure 2. Through-plane reactive excitation (top) and direct current (bottom) detection of CCM failures

Finally, we initiated a study with collaborators at the Colorado School of Mines for early-stage exploration of spectroscopic methods that could lead to new in-line or in-process measurements of composition or properties of electrode inks and layers.

Relative to our in situ studies to understand the impact of as-manufactured irregularities in MEA component materials on performance and lifetime, the majority of our focus during the year was continuing our study of electrode thick spots. In an effort to understand the impact of the morphology of the irregularity on performance, we fabricated thick spots by two different spatially defined methods: drop casting of additional electrode ink and ultrasonic spraying of additional ink using masks with openings of various size. Though covering nominally the same area and resulting in nominally the same amounts of electrode ink, these two fabrication methods were seen to result in very different morphologies and performance impact, with the drop-cast irregularities generally causing the greater effect. We performed both beginning-of-life and drive cycle (using the New European Drive Cycle) testing to assess initial performance and loss of performance over time compared to pristine MEAs. As an example of the findings, Figure 3 shows initial performance results of six different MEAs with thick spots as well as open-circuit voltage and potential at 1.0 A/cm^2 for one of the thick-spot MEAs compared to a pristine one as a function of cycling. The impact of these kinds of irregularities is apparent in both modes of test.

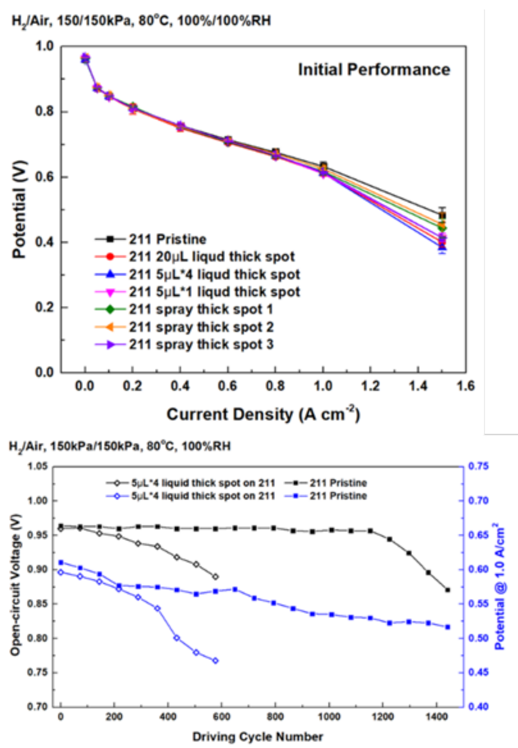

Figure 3. Initial performance (top) and drive cycle (bottom) impacts of electrode thick spots

We also initiated new testing of the impact of pinholes in membranes. Several studies have explored these effects, but no guidelines have been established to understand a threshold of pinhole size or location. We obtained membrane materials of two different thicknesses, and with and without reinforcement, having precision laser-drilled holes of 10, 20, 50, and 100 µm diameter. A key aspect of this study is to understand how the impact of a pinhole might change as a result of the MEA fabrication scheme (i.e., using CCMs vs. GDEs). For example, MEAs have been fabricated with the above-described pinhole membranes by either spraying electrodes on the membrane to form a CCM or hot pressing the membrane with GDEs. Very different in situ and ex situ characterizations of these MEAs are obtained in terms of gas crossover and performance. These studies are ongoing. To assist our understanding of these effects, our partners at LBNL have performed both steady-state and transient modeling to predict the performance impact of an MEA with a 10 µm pinhole. We studied the impact of relative humidity and location in the cell relative to flowfield channels on membrane water uptake and MEA performance. Figure 4 shows representative results from the steady-state model, where the pinhole was predicted to (1) cause increased water uptake in the membrane and (2) cause a slight improvement in performance at 50% relative humidity (RH) but a large decrease in performance at 100% RH.

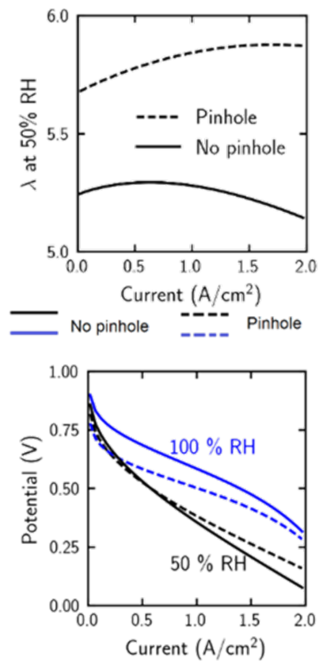

Figure 4. Predicted water uptake (top) and performance (bottom) impact of the modeled pinhole

CONCLUSIONS AND UPCOMING ACTIVITIES

- Complete evaluation of LTE in situ defect study needs in terms of critical defects and needed testing capabilities.
- Evaluate the impact of membrane pinholes (100 to 10 µm) in 25 µm reinforced and non-reinforced membranes both experimentally (NREL) and computationally (LBNL) in terms of possible closure and impact on polarization performance.
- Perform experimental work to understand the impact of line speed on y resolution of membrane thickness imaging; criteria: (1) line speed of 4–30 fpm, (2) minimum web length of 20 m.
- Perform experimental work toward the implementation of hyperspectral imaging for thick membranes (i.e., for LTE applications).

FY 2019 PUBLICATIONS/PRESENTATIONS

1. M. Ulsh, P. Rupnowski, G. Bender, B. Green, A. Phillips, and S. Mauger, "Understanding the Impact of As-Manufactured Defects in PEM Fuel Cell MEA Materials, and Developing Real-Time Characterization Tools for Quality Inspection," poster presentation at the 7th De Nora R&D Symposium, Cleveland, OH, October 2018.
2. M. Ulsh, A. DeBari, J.M. Berliner, I.V. Zenyuk, P. Rupnowski, L. Matvichuk, A.Z. Weber, and G. Bender, "The Development of a Through-Plane Reactive Excitation Technique for Detection of Pinholes in Membrane-Containing MEA Sub-Assemblies," *Intl. J. Hydrogen Energy* 44 (2019): 8533–8547.
3. M. Ulsh, "MEA Manufacturing R&D," oral presentation at the Hydrogen and Fuel Cell Program Annual Merit Review and Peer Evaluation Meeting, Washington DC, May 1, 2019.
4. M. Ulsh, "Fuel Cell Manufacturing R&D," invited talk at Ballard, Vancouver, Canada, May 22, 2019.
5. M. Ulsh, "Update on NREL Fuel Cell MEA QC Development Activities," invited talk at the 2nd Canada-Germany QC Workshop, Vancouver, Canada, May 24, 2019.
6. M. Wang, G. Rome, A. Phillips, M. Ulsh, and G. Bender, "Effective Electrode Edge Protection for Proton Exchange Membrane Fuel Cell Drive Cycle Operation," *ECS Transactions* 92, no. 8 (2019): 351–359.