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

Michael Ulsh (Primary Contact), Guido Bender, Peter Rupnowski, Scott Mauger
National Renewable Energy Laboratory (NREL)
15013 Denver West Parkway
Golden, CO 80401
Phone: (303) 275-3842; Fax: (303) 275-3840
Email: michael.ulsh@nrel.gov

DOE Managers:
Nancy L. Garland
Phone: (202) 586-5673
Email: Nancy.Garland@ee.doe.gov
Jesse Adams
Phone: (720) 356-1421
Email: Jesse.Adams@ee.doe.gov

Partners:
- Lawrence Berkeley National Laboratory (LBNL), Berkeley, CA
- Colorado School of Mines, Golden, CO
- Georgia Institute of Technology (Georgia Tech) Atlanta, GA
- Tufts University, Medford, MA
- General Motors, Pontiac, MI
- W.L. Gore & Associates, Elkton, MD
- Mainstream Engineering, Rockledge, FL
- Altergy, Folsom, CA

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

Overall Objectives

- Perform early-stage development of real-time characterization 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 characterization systems.
- Develop and utilize models to predict the effects of local variations in MEA component properties and to improve our understanding of material-excitation interactions during real-time characterization.
- Study material-process-performance relationships for MEA materials in scalable processes, providing guidance for new process development to lab and academic partners via the Energy Materials Network consortia, including exploration of particle-polymer interactions between ionomers, catalysts, supports, and solvents to better understand their influence on ink structure and stability.
- 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 2017 Objectives

- Evaluate thermal scanning as a technique for thickness and/or property measurement.
- Generate spatially resolved initial performance data for cells with membranes having as-cast irregularities fabricated at Georgia Tech.
- Fabricate and characterize baseline slot-die and micro-gravure roll coated electrodes, at least one of which is to meet the following criteria: (1) achieving a target catalyst loading in the range of 0.05 to 0.2 mg Pt/cm^2, (2) achieving the target loading at a line speed of at least 1 m/min, and (3) achieving at least 70% of the average mass activity (900 mV_IR-free) of MEAs containing spray-coated gas diffusion electrodes (GDEs).
- Generate in situ MEA failure data for cells with electrode irregularities.
- Demonstrate a moving-substrate configuration for the through-plane reactive excitation technique.

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 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 5.3: Validate and extend models to predict the effect of manufacturing variations on MEA performance. (1Q, 2017)

- Milestone 5.4: Design and commercialize an in-line quality control (QC) device for polymer electrolyte membrane fuel cell (PEMFC) MEA materials based on NREL's optical reflectance technology. (4Q, 2017)
- Milestone 1.3: Develop continuous MEA manufacturing processes that increase throughput and efficiency and decrease complexity and waste. (4Q, 2017)
- Milestone 5.5: Develop correlations between manufacturing parameters and manufacturing variability, and performance and durability of MEAs. (4Q, 2018)
- Milestone 5.6: Demonstrate methods to inspect full MEAs and cells for defects prior to assembly into stacks in a production environment. (4Q, 2018)

FY 2017 Accomplishments

- Demonstrated the feasibility of thermal scanning for measuring the thickness of membranes already attached/laminated to GDEs.
- Demonstrated the feasibility of imaging to fully map reinforced and non-reinforced membrane thickness in real time, while the membrane is still attached to one or two liners.
- Evaluated process improvements for the reactive impinging flow technique.
- Performed in situ studies of the impacts of electrode and membrane irregularities on the initial performance, performance over time, and failure of MEAs.
- Demonstrated gravure-coated GDEs with performance comparable to lab-standard fabrication methods.
- Performed extensive studies of the rheology and formulation of electrode inks.
- Increased the throughput of ultrasonically sprayed electrodes by two orders of magnitude while maintaining acceptable MEA performance.
- Expanded multi-physics modeling of the through-plane reactive excitation technique to further assist in the development of an in-line configuration for the technique.
- 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 performing early-stage R&D in the areas of real-time characterization, understanding the impacts of irregularities in MEA materials originating during fabrication and handling, and elucidating how material and fabrication parameters impact MEA performance. We utilize industry relationships to understand MEA material, structure, and processing directions and challenges. We then develop real-time characterization techniques, using computational modeling to (a) assist in the development and optimization of unique measurement techniques and to (b) predict the effects of material irregularities on performance. These techniques are validated under simulated processing conditions. In parallel, we use in situ testing to perform detailed parametric studies of the effects of material irregularities on performance and lifetime. As a new element to the project, we explore material-process-performance relationships in the scalable fabrication of MEA materials. Finally, we publish results in the public domain.

RESULTS

We continued to have a major focus on in situ testing to understand the effects of variations in electrode and membrane materials that originate during the fabrication process. In coordination with Georgia Tech, we performed spatial initial performance studies of MEAs with membranes cast on Georgia Tech's processing line. These membranes had a variety of irregularities that resulted from purposefully casting under conditions on the edge of the process window. Local performance effects were observed using the segmented cell, and increased hydrogen crossover was detected in the cells at the locations of the membrane irregularities using our novel infrared imaging in situ hardware. In an effort coordinated with the segmented cell work, LBNL performed modeling to validate and help explain our findings of locally increased performance at the bends of the serpentine flow-field. This behavior was shown to occur as a result of increased local gas convection in the flow-field channel bend. In electrode studies, we continued to utilize accelerated stress testing (AST) and our infrared hardware to explore the impact of electrode irregularities on failure. Figure 1 shows an example, in this case of a pristine MEA, where cross-over current density was continuously monitored throughout the accelerated aging. Stable values were obtained until approximately 114.7 hours of the test, where an exponential increase in crossover began. By 123.8 hours of the test, the

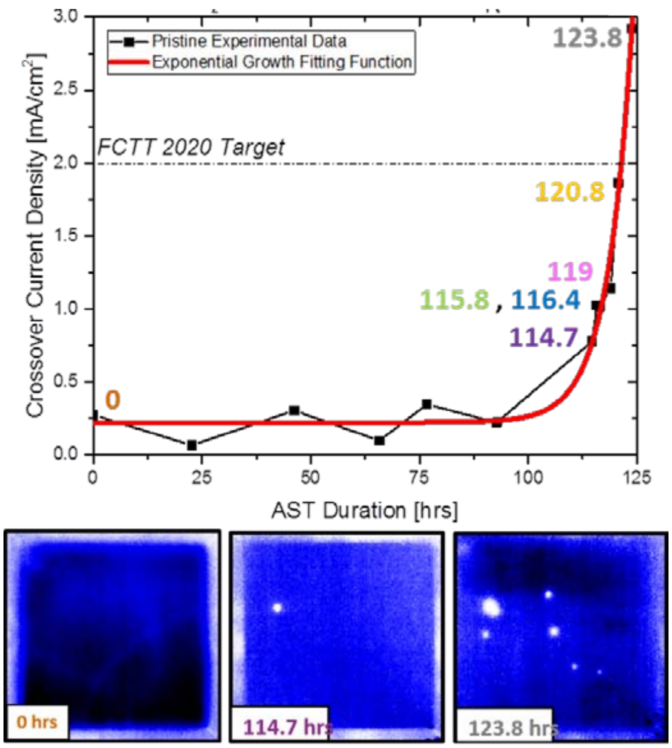

FIGURE 1. Crossover current density data for a pristine MEA aged using a combined chemical-mechanical AST (top); infrared spatial crossover images of the MEA (cathode side) at different times during the AST testing showing the development of multiple failure points (bottom)

MEA had exceeded our failure criteria, the 2020 Fuel Cell Tech Team (FCTT) crossover target for membranes. The infrared spatial crossover images at the bottom of Figure 1 show: on the left at time zero, full membrane integrity; in the center at time 114.7 hours, the development of a single failure point; and on the right at 123.8 hours, the growth of the initial failure point and the development of several other failure points. In coordination with the failure studies, our partners at LBNL and Tufts University performed X-ray computed tomography imaging of MEAs observed to have failed during AST testing. With the spatial crossover imaging as a guide to the location of the failures, X-ray computed tomography was performed and captured in three dimensions the nature and extent of the failure. Figure 2 shows X-ray computed tomography imaging of a location at which two tears in the membrane formed during the AST.

As we mentioned in our report last year, a key area of study recently has been demonstrating real-time membrane thickness imaging. In that report, we showed successful single-point thickness measurements as an initial feasibility step. We have now demonstrated actual real-time imaging of membrane thickness. The method uses a unique areal detector, where the well-known thin-film interference fringe effect is used with fast Fourier transform. The image in Figure 3 shows the thickness map of a nominally 25 µm

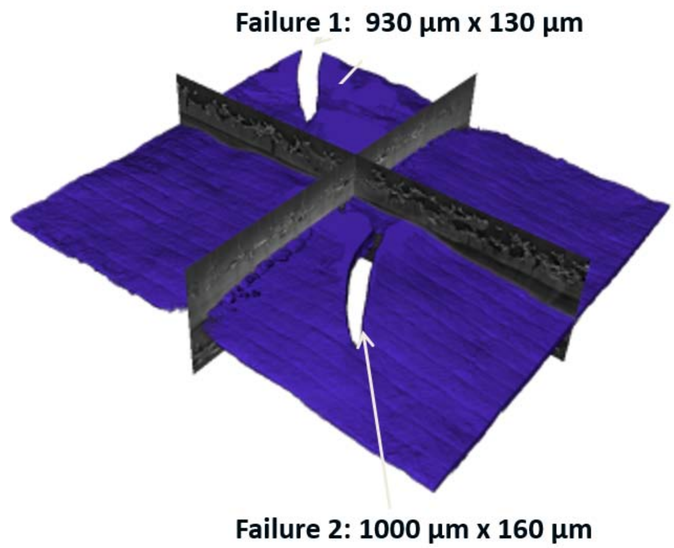

FIGURE 2. X-ray computed tomography data of a failed MEA showing two breaches in the integrity of the membrane

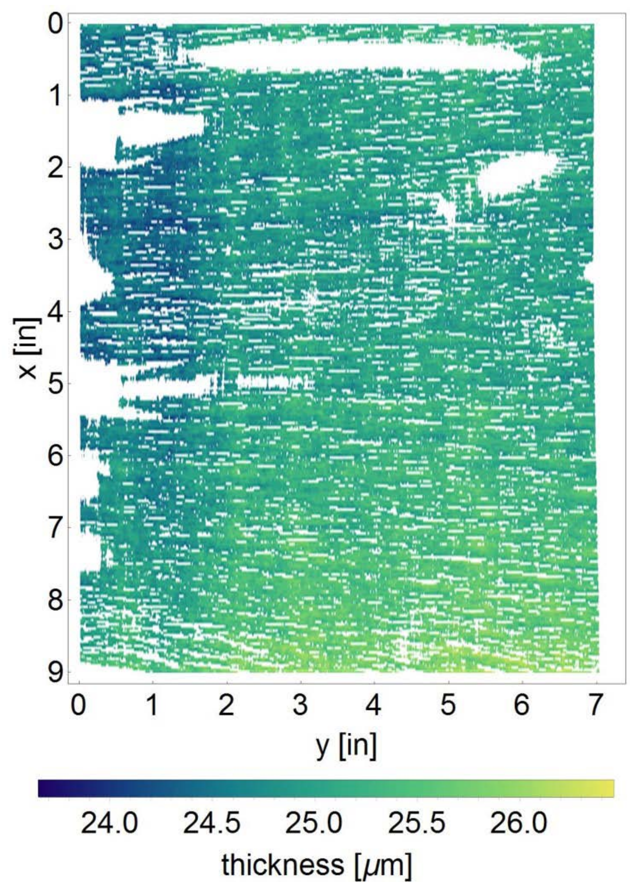

FIGURE 3. Real-time thickness imaging of a nominally 25 µm membrane taken at 5 foot per minute sample speed

membrane taken at a scanning speed of 5 feet per minute. The sensitivity in the z (thickness) direction is significantly less than a micrometer. Critically, we have shown that this technique works for membranes both with and without a reinforcing layer, as well as for membranes still attached to one or two casting/protective liners. In additional exploratory work, we have demonstrated the feasibility of a thermal imaging technique to measure the thickness of membranes that are already attached to a GDE. Generically, we provide a focused thermal excitation to the membrane and measure the peak and/or decay of that excitation, real-time. This measurement is then correlated to a thermal model of the material to back out a physical property, such as porosity or thickness. In an example study of three half-cell samples of membrane thickness zero (bare GDE), 1/3A, and A, we observe a monotonic response of the measurement to the membrane thickness.

In a new element of the project, we have initiated material-process-performance studies of electrode fabrication. In this first year, the focus was on understanding the material, ink, and process modifications needed to transition from a baseline lab-scale process, ultrasonic spray, to scalable processes such as gravure and slot-die coating. Extensive exploration of electrode ink rheology was performed to understand the properties of individual ink constituent (carbon, platinum, and ionomer) solutions as well as combined solutions. Process parameters were also explored. Figure 4 shows the macro-scale uniformity of gravure-coated electrodes fabricated under different roll speeds and different roll patterns. Ultimately, the milestone noted above was achieved, having fabricated gravure-coated electrodes with comparable performance to baseline ultrasonically sprayed electrodes. Slot-die coating studies were also initiated.

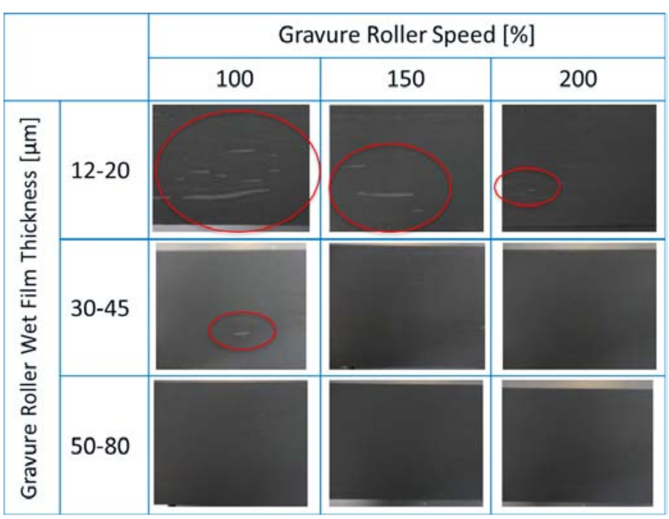

FIGURE 4. Optical imaging of gravure-coated GDE material showing macro-scale uniformity at different roll speeds and with different roll patterns

UPCOMING ACTIVITIES

- Continue to use predictive modeling and single and segmented cell test methods to study the effects of as-fabricated irregularities on MEA performance and lifetime.
- Advance our understanding of the intrinsic detection and excitation physics for novel inspection techniques including membrane thickness imaging, platinum loading imaging, and thermal scanning.
- Advance our understanding of electrode ink rheology and particle-polymer interactions.
- Advance our understanding of scalable fabrication methods for electrodes and membranes, including novel structure and morphology.
- Demonstrate in-line detection of membrane pinholes using through-plane reactive excitation.

FY 2017 PUBLICATIONS/PRESENTATIONS

1. I.V. Zenyuk, N. Englund, G. Bender, A.Z. Weber, M. Ulsh, "Reactive impinging-flow technique for polymer-electrolyte-fuel-cell electrode-defect detection," *J. Power Sources* (332), 2016; p. 372–382.

2. G. Bender, A. Phillips, J. Mackay, J. Porter, M. Ulsh, "The Effect of Catalyst Layer Coating Irregularities on Initial Fuel Cell Performance," presented at the ECS Fall meeting, Honolulu, HI; October, 2016.

3. A. Phillips, G. Bender, J. Mackay, J. Porter, M. Ulsh, "Failure Point Analysis of Defected PEMFC MEAs," presented at the ECS Fall meeting, Honolulu, HI; October, 2016.

4. A. Phillips, M. Ulsh, J. Porter, G. Bender, "Utilizing a Segmented Fuel Cell to Study the Effects of Electrode Coating Irregularities in PEM Fuel Cell Initial Performance," *Fuel Cells*, DOI: 10.1002/fuce.201600214, 2017.

5. M. Ulsh, "Fuel Cell MEA Manufacturing R&D," presented at the Hydrogen and Fuel Cells Program Annual Merit Review; June 2017.

6. M. Ulsh, S. Mauger, K.C. Neyerlin, "Material-Process-Performance Relationships for Roll-to-Roll Coated PEM Electrodes," presented at the Hydrogen and Fuel Cells Program Annual Merit Review; June 2017.

7. U.S. Provisional Patent Application, "Thickness mapping using multispectral imaging."