Fuel Cell Membrane Electrode Assembly Manufacturing R&D

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Subcontractors:
- Lawrence Berkeley National Laboratory, Berkeley, CA
- Colorado School of Mines, Golden, CO
- Tufts University, Medford, MA
- 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 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 models to predict the effects of local variations in MEA properties and to improve our understanding of excitation modes during real-time characterization.
- Study material-process-performance relationships for MEA materials in scalable processes, providing guidance for new process development to partners.

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) 2018 Objectives

- Complete in situ drive cycle testing on MEAs with membrane defects.
- Demonstrate coating of electrodes using processes with different shear behaviors to understand the impact of process shear on catalyst layer morphology and performance.
- Complete the design, construction, and operation of a test bed to facilitate studies of illumination, detection, and material interactions for membrane thickness imaging.
- Perform initial ink development and coating of unsupported catalyst systems.
- Characterize the influence of catalyst ink composition on ink rheology and stability.
- Determine the feasibility of using an optical-reflectance-based technique for imaging the loading of Pt in standard Pt/C electrodes, in accordance with the following criteria: (1) electrodes having loading within the range of 0.05–0.4 mg Pt/cm^2, (2) sensitivity to differences in loading of 0.1 mg Pt/cm^2, and (3) imaging at a speed of at least 1 inch/sec.

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]:

(A) Lack of High Volume MEA Processes

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

(H) Low Levels of Quality Control.

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

Contribution to Achievement of DOE Manufacturing 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:

- Milestone 1.6: Develop fabrication and assembly processes for polymer electrolyte membrane fuel cell (PEMFC) MEA components leading to an automotive fuel cell stack that costs $20/kW. (4Q, 2020)
- 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)
- Milestone 5.7: Develop areal techniques to measure platinum (and other catalyst metals) quantitatively in an MEA. (4Q, 2018)

FY 2018 Accomplishments

NREL accomplished the following in FY 2018:

- Demonstrated high sensitivity of thermal scanning to the thickness of membranes already attached/laminated to gas diffusion electrodes (GDEs) using half-cell materials fabricated by General Motors (GM).
- Completed the design, construction, and operational testing of an in-line test bed for real-time membrane thickness imaging and demonstrated the technique in-line using a state-of-the-art reinforced membrane.
- Performed full-width, full-length high-resolution optical imaging of Gore membrane production rolls, and developed automated defect detection and classification algorithms.
- Designed and built an optical inspection apparatus on the web-line, creating a highly flexible test bed for reflectance or transmission measurements.
- Performed in situ studies of the impacts of electrode and membrane irregularities on the performance and failure of MEAs, supported by X-ray computed tomography (XCT) measurements made by Lawrence Berkeley National Laboratory (LBNL).
- Coated electrodes under different shear conditions to understand the impact of process physics on morphology and performance.
- Performed rheology, zeta potential, and stability studies of unsupported (low-temperature electrolysis [LTE] and platinum-group metal [PGM]-free) and supported catalysts.
- Completed feasibility study of optical methods to image loading in Pt/C electrodes.
- Demonstrated roll-to-roll casting of ionomer membranes.
- Assisted Mainstream Engineering in validating their prototype optical inspection system in-line on our coating line using as-cast membrane materials.
- Demonstrated the through-plane reactive excitation (TPRE) technique on the research web-line; LBNL modeled improved methodologies.
- Continued collaboration with our industry partners in accordance with our project charter.

INTRODUCTION

In FY 2005–FY 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 performance and lifetime 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 (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 to perform detailed parametric studies of the effects of material irregularities on performance and lifetime. We also explore material-process-performance relationships in the scalable fabrication of MEA materials.

RESULTS

We continued our effort to study the in situ effects of pinholes, using membrane samples mechanically punched using a 120 µm micro-needle. We completed an initial set of spatial initial performance (with the segmented cell), prolonged performance, and accelerated stress test (AST)/failure studies. Figure 1 shows results from the catalyst-coated membrane (CCM)-type samples. Figure 1 (left) is an XCT image of a fabricated MEA, showing the as-tested morphology of the pinhole. Figure 1 (center) shows the spatial initial performance effect of the pinhole (located in the center of the MEA) from the segmented cell testing, where red color indicates a decrease in performance in that segment in the defected cell as compared to a pristine cell. Figure 1 (right) shows the results of a combined chemical-mechanical AST, where we see earlier failure of the pinhole MEA as compared to the pristine MEA. And in drive cycle testing (not shown), we see increased performance degradation of the pinhole MEA compared to the pristine MEA. We also studied the impact of electrode defects, namely thin and thick spots. For thin spots, we observed similar performance degradation to that of bare spots, including failure in the drive cycle test when using a 25 µm membrane (as opposed to a 50 µm membrane, which did not fail). Interestingly, this brings up the possibility that the effects of these defects may be due to behaviors at the edges or interfaces of the defects, rather than absolute reduction in catalyst material. For thick spots, we observed high levels of performance degradation, almost always leading to failure during the cycling test (where the pristine did not fail).

We studied the feasibility of using an optical-based technique for imaging the loading of Pt in standard Pt/C electrodes ranging in Pt loading from 0.05 to 0.4 mg/cm^2. We explored both reflectance and transmission modes and obtained different results for different cases of measurement mode, configuration, and sample type. Ultimately, methods with the criteria sensitivity (to variations of 0.1 mg/cm^2) at the criteria measurement speed (at least 1 m/min) were successfully developed. As an example, Figure 2 shows optical reflectance signal as a function of Pt loading for a series of ultrasonically sprayed CCMs. Over a range of loading from 0.5 to 0.35 mg/cm^2, the differences in the data at 0.1 mg/cm^2 intervals were statistically significant.

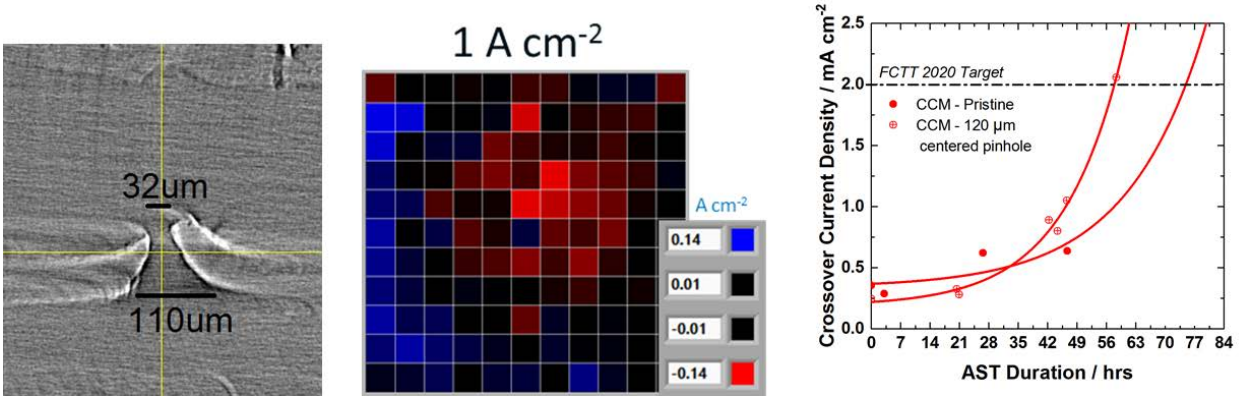

Figure 1. XCT imaging of the pinhole in the fabricated MEA (left), segmented cell data showing local performance variation resulting from the pinhole (center), and results from the AST test, showing measured hydrogen crossover current density as a function of AST hours (right)

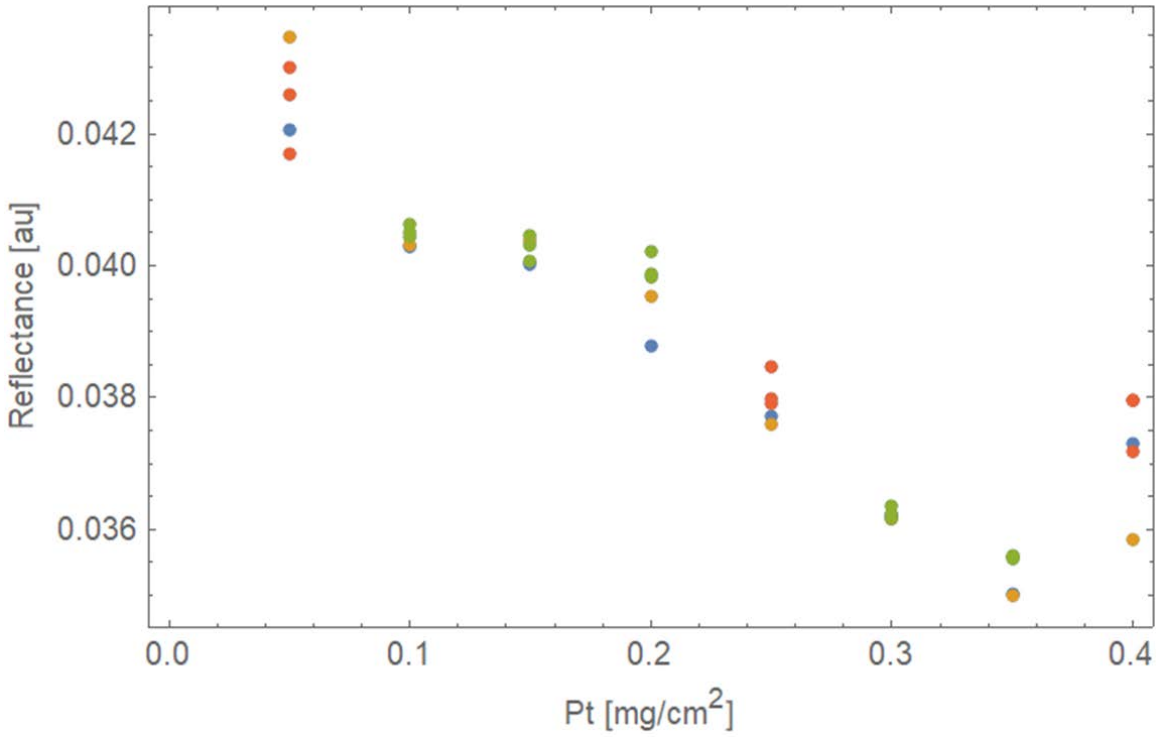

Figure 2. Optical reflectance signal as a function of Pt loading for CCM samples

With regard to our work on infrared methods, we demonstrated a moving-substrate configuration for TPRE using a web sample with individual catalyst-coated sections with pinholes in the membrane. Thermal responses due to the pinholes were detected; however, they were typically less than 1°C. Subsequent modeling at LBNL indicated that small increases in reactive gas hydrogen concentration results in significant increases in temperature rise, so a follow-on experiment is contemplated using such gas mixtures to further explore the potential for the technique. Other beneficial modifications to the equipment setup were also modeled. We also performed analysis of the thermal scanning data from the new series of half-cell (membrane on GDE) samples fabricated by GM. The analysis showed that the responses were statistically significant and proportional to thickness.

We initiated a study of the rheology and stability of unsupported catalyst inks in a 1:1 water/n-propanol solvent. Figure 3 shows rheology as a function of solids loading (left) and zeta potential as a function of ionomer-to-carbon (I:C) ratio (right). Similar to Pt/C inks, we see an increase in structure (agglomeration) and shear-thinning behavior with increasing solids loading. We also observe the change from shear-thinning to Newtonian behavior with the addition of ionomer. We also studied the rheology of Ni-C and Ni-Fe catalyst inks. Similar to the case of supported catalysts, we observe that water-rich inks have lower viscosity than alcohol-rich inks. However, we see the unexpected result that unsupported catalysts with high surface area do not always behave similarly to inks made with carbons of similar surface area.

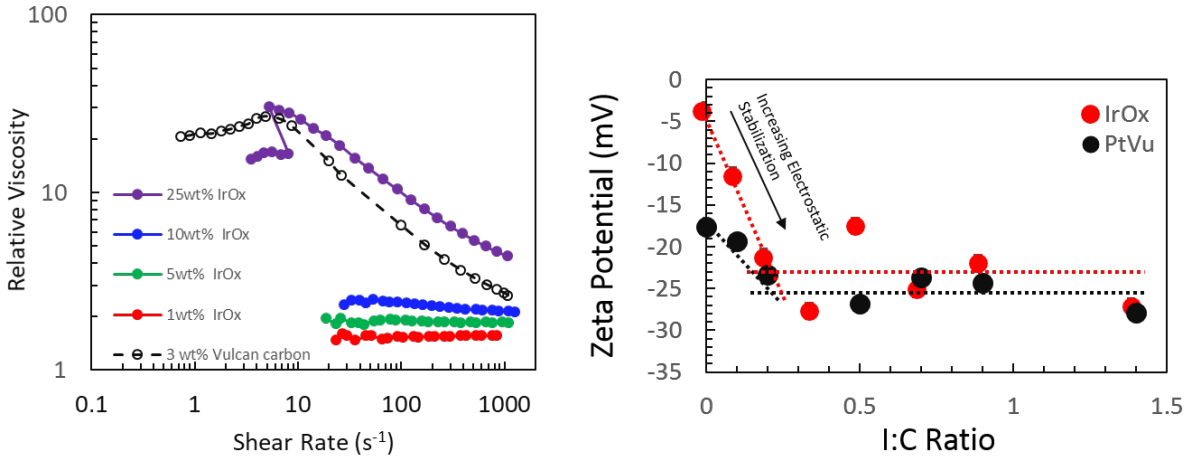

Figure 3. Relative viscosity of IrOx inks of different solids loading as a function of shear rate (left) and zeta potential of IrOx (red) and Pt/Vulcan (black) catalysts as a function of I:C

Finally, we characterized the influence of ink composition stability. We have also begun studying the physical stability of various catalyst inks and how different catalysts and formulations affect the rate of agglomeration and sedimentation of catalyst particles. For this work, we built a new measurement setup to continuously monitor the optical transmission of catalyst inks. Figure 4 shows results of an IrO_x catalyst ink, where initially the catalyst particles are well dispersed, and transmission is low. However, at around 20 minutes after cessation of ink mixing, the top of the vial has very high transmission, indicating that the catalyst particles have already sedimented out of this region.

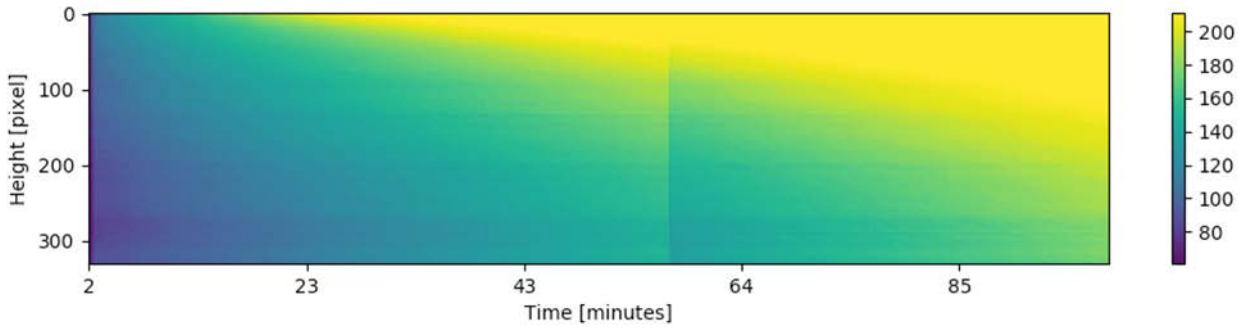

Figure 4. Temporal data for transmission of an IrOx ink from the ink stability testing device

CONCLUSIONS AND UPCOMING ACTIVITIES

- Perform ink development studies of unsupported LTE catalysts to understand the influence of solvent and catalyst materials on ionomer-catalyst interactions.
- Perform initial defect detection tests for LTE membranes using existing test beds.

- Perform studies to understand the impact of electrode coating irregularities and pinholes in membranes, with particular focus on how their effects are modulated by aspects of membrane architecture, e.g., thickness and presence of reinforcing material (in coordination with modeling and/or XCT characterization with project partner LBNL).
- Perform hyperspectral imaging of membrane thickness, exploring x-y resolution, z resolution, and percentage of coverage, and evaluate the effect of line speed, with milestone criteria: physical resolution of 100 µm or smaller, thickness ranges: 50–200 µm (LTE) and 12–50 µm (PEMFC), line speed of 2 ft/min or faster.
- Evaluate ink formulations, drying conditions, and substrates to reduce crack formation in fuel cell and electrolysis catalyst layers coated using scalable methods.

FY 2018 PUBLICATIONS AND PRESENTATIONS

1. P. Rupnowski and M. Ulsh. Thickness mapping using multispectral imaging. U.S. Patent Application no. 15/830,585, filed June 7, 2018.
2. A. Phillips, M. Ulsh, K.C. Neyerlin, J. Porter, and G. Bender. "Impacts of electrode coating irregularities on PEMFC lifetime using quasi in-situ infrared thermography and accelerated stress testing." *Int. J. Hydrogen Energy* 43 (March 22, 2018): 6390–6399.
3. A. Phillips, J. Mackay, N. Shrivastava, J. Porter, T. Harris, M. Ulsh, and G. Bender. "The Effect of Membrane Casting Irregularities on Initial Fuel Cell Performance." Oral presentation IO1C-1484 at the ECS Fall Meeting, National Harbor, MD, October 2017.
4. A. Phillips, J. Mackay, J. Porter, M. Ulsh, and G. Bender. "The Effect of Catalyst Layer Coating Irregularities on Fuel Cell Performance Over Time." Oral presentation IO1A-1412 at the ECS Fall Meeting, National Harbor, MD, October 2017.
5. S. Mauger, K.C. Neyerlin, A.C. Yang-Neyerlin, G. Bender, M. Ulsh, B. Green, and K. More. "Material-Process-Performance Relationships for Roll-to-Roll Coated Fuel Cell Electrodes." Oral presentation IO1B-1441 at the ECS Fall Meeting, National Harbor, MD, October 2017.
6. S. Mauger, S. Khandavalli, K.C. Neyerlin, J. Stickel, K. Hurst, and M. Ulsh. "Rheological Characterization of Interparticle Interactions in Fuel Cell Catalyst Dispersions." Oral presentation IO1A-1382 at the ECS Fall Meeting, National Harbor, MD, October 2017.
7. S.A. Mauger, S. Khandavalli, J. Stickel, K.E. Hurst, K.C. Neyerlin, and M. Ulsh. "Rheological Properties and Interparticle Interactions in Fuel Cell Catalyst Dispersions." Poster presentation at the 89th Annual Meeting of the Society of Rheology, Denver, CO, October 2017.
8. M. Ulsh. "Fuel Cell MEA Manufacturing R&D." Oral presentation at the Hydrogen and Fuel Cell Program Annual Merit Review and Peer Evaluation Meeting, Washington, DC, June 2018.
9. M. Ulsh and S. Mauger. "Material-Process-Performance Relationships in PEM Catalyst Inks and Coated Layers." Poster presentation at the Hydrogen and Fuel Cell Program Annual Merit Review and Peer Evaluation Meeting, Washington, DC, June 2018.
10. S. Khandavalli, J. Stickel, K. Hurst, N.N. Kariuki, J.H. Park, D.J. Myers, K.C. Neyerlin, M. Ulsh, and S.A. Mauger. "Rheological Investigation of Catalyst Inks for Roll-to-Roll Processing of Fuel Cell Electrodes." Poster presentation at the Fuel Cells Gordon Research Conference, Smithfield, RI, July 2018.
11. S. Khandavalli, J. Stickel, K. Hurst, N.N. Kariuki, J.H. Park, D.J. Myers, K.C. Neyerlin, M. Ulsh, S.A. Mauger. "Rheological Investigation of Catalyst Inks for Roll-to-Roll Processing of Fuel Cell Electrodes." Oral presentation at the International Symposium of Coating Science and Technology, Long Beach, CA, September 2018.

12. S.A. Mauger, K.C. Neyerlin, A.C. Yang-Neyerlin, K.L. More, and M. Ulsh. “Gravure Coating for Roll-to-Roll Manufacturing of Proton-Exchange-Membrane Fuel Cell Catalyst Layers.” *J. Electrochem. Soc.* 165.11 (September 11, 2018): F1012–F1018.