In-Line Quality Control of Polymer Electrolyte Membrane Materials

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Overall Objectives (SBIR Phase IIb)

- Identify types and sizes of defects that lead to stack failure.
- Detect defects in membrane, gas-diffusion layer (GDL), catalyst, and electrodes to 10 µm at 100 ft/min.
- Determine thickness to ± 0.5 µm at 100 ft/min.
- Demonstrate that the image analysis for thickness and defect detection can be performed in real time up to 100 ft/min.
- Identify defects optically with false-positive and false-negative rates less than 0.023% (5s) using the turnkey system.
- Create a turnkey prototype solution for quality control of all polymer electrolyte membrane fuel cell (PEMFC) materials on a full-speed roll-to-roll process.
- Deploy the prototype to three industry sites for customer demonstrations and data collection

Fiscal Year (FY) 2019 Objectives

- Transition the reflectance technique to a production system by selecting hardware needed to perform in-line, real-time reflectance measurements.
- Develop software that can handle the large amount of image data and perform real-time analysis.
- Test the system on a variety of relevant opaque fuel cell materials (e.g., reinforced membrane, GDL, catalyst).
- Prepare system for prototype demonstrations.

Technical Barriers

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

- Lack of improved methods of final inspection of membrane electrode assemblies (MEAs)
- Low levels of quality control.

Contribution to Achievement of DOE Milestones

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

- Milestone 1.6: Develop fabrication and assembly processes for PEMFC membrane electrode assembly (MEA) components leading to an automotive fuel cell stack that costs $20/kW at high volume (500,000 units/year). (4Q, 2020)
- 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 quality control device for PEMFC MEA materials based on National Renewable Energy Laboratory's (NREL) optical reflectance technology. (4Q, 2017)

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

- 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 5.8: Implement demonstrated in-line quality-control techniques on pilot or production lines at PEMFC MEA material manufacturers. (4Q, 2020).

FY 2019 Accomplishments

- Created a website to communicate all publications and new technologies: https://www.mainstream-engr.com/products/mantis-eye-optical-scanner/.
- Successfully installed reflectance test equipment that can be used for analyzing 12-inch by 12-inch samples and to develop software that operates at the target 100 ft/min roll speed.
- Developed software that can acquire and process reflectance images up to 20 ft/min and deployed it on an industrial computer.
- Implemented a plan for determining the minimum defect that impacts MEA performance. A gas-diffusion electrode (GDE) and a catalyst-coated membrane (CCM) with a 100 µm pinhole in a 50 µm thick membrane were tested, and data indicated that fabricating MEAs with CCMs reduces the impacts of defects. However, neither case led to initial failure.
- Measured optical catalyst loading on GDE to within ± 0.1 mg Pt/cm^2 for spot sizes of 0.03 cm^2, but error may be related to actual variation on the surface. Correlation between thickness and loading is underway.
- Established a quantitative relationship between optical imaging and catalyst loading on a CCM. Defects were seen and identified down to sub-25 µm. X-ray fluorescence (XRF) indicated that spot variation seen in optical images is real and correctly identified.

INTRODUCTION

Fuel cells stand on the cusp of commercialization for large-scale applications such as zero-pollution automotive systems. They are held back by high manufacturing costs and expensive catalysts. The membrane alone accounts for as much as 16% of the total stack cost of a 2020 auto system at 1,000 units/year and 8% at 500,000/year [1]. Moreover, manufacturing defects in the membrane not only lead to waste of expensive materials but they also cause cell failures that can cascade into complete stack failure. This requires additional labor to rework the stack and results in the loss of expensive catalyst- and gas-diffusion electrode materials. Current inspection methods can miss defects up to 200 µm in size, while defects down to 50 µm in size have been shown to lead to cell failure, with even smaller defects causing performance issues [2–6]. Furthermore, these inspection methods look for defects after batch production of the membrane, leading to delayed correction of issues with the membrane and membrane electrode fabrication process. Reaching the quality targets for fuel cell system manufacturing requires a new, high-efficiency, real-time quality control system that can provide 100% inspection of fuel cell materials at full production speeds. Mainstream Engineering developed a real-time optical quality control system, which we call the Mantis Eye, that provides increased resolution, improved accuracy, and increased detection speeds over current approaches for the examination of fuel cell and other membranes. In the sequential Small Business Innovation Research (SBIR) Phase IIb program, Mainstream will finalize a suite of instruments that provide a full turnkey inspection package for fuel cell production including CCMs and GDEs. Mainstream will also continue to commercialize the Mantis Eye technology developed in Phase II.

APPROACH

Mainstream's overall technical approach to create a turnkey inspection package is to rigorously validate the patent-pending optical techniques with a wide range of commercially available fuel cell materials, integrate the hardware and develop the software to allow automated real-time defect detection, conduct reliability testing, and productionize the prototype system. A variety of defects induced in membrane, CCMs, GDEs, and GDLs were examined to generate calibrations for catalyst loading as a function of the support material and composition. While the optical capabilities are being demonstrated, NREL is examining how different sized defects in each component impact the initial and lifetime performance of the fuel cell. The new optical techniques will then be integrated with the existing software for imaging samples, detecting defects, logging defects, tracking the defect location, and printing an identifying mark on the defect. The combined turnkey system will be deployed and tested on multiple material manufacturing lines. Many materials will be tested at actual production speeds. Alternative markets will be examined to leverage the unique technology developed on this program.

RESULTS

Sheet Test Stand

Mainstream's sheet sample imaging system is capable of performing real-time analysis of samples up to 12-inch by 12-inch in size. The system (shown in Figure 1) consists of a line-scan camera, a line-scan light, a linear encoder, a linear stage, and a stage controller, all mounted to an aluminum frame. The line-scan camera acquires single lines up to 8192 pixels in width at speeds up to 80 kHz. This corresponds to pixel dimensions of 37.2 µm by 37.2 µm for a 12-inch-wide sample or 18.5 µm by 18.5 µm for a 6-inch sample. Each line of the raw image is triggered by a pulse from the encoder that measures the position of a linear stage. The stage is controlled by a coil linear motor capable of 450 mm (17.7 inch) of translation at speeds up to 300 ft/min and an accuracy of 2.5 µm. The system can scan full-resolution images at 100 ft/min with an exposure time of 36.6 µs or less. After images are acquired, they are transferred to a computer via a camera link connection for real-time processing.

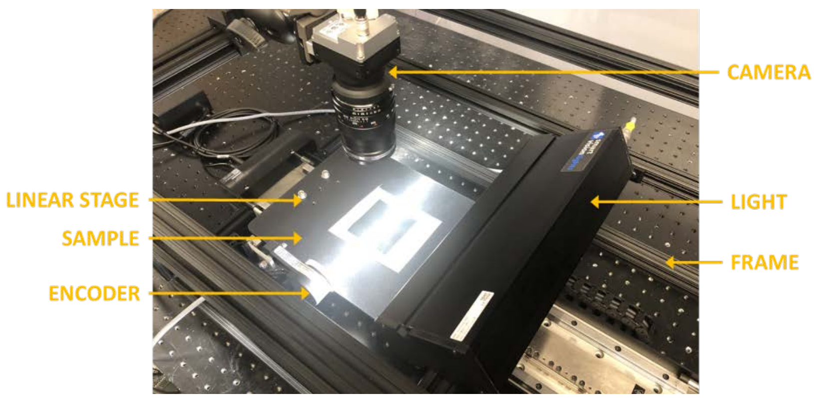

Figure 1. Sheet sample test stand for software test bed and prototyping small, fixed samples

Software

Mainstream's imaging software is a turnkey solution that offers real-time processing of images and implementation of user-selected machine vision algorithms for defect identification. The imaging software consists of three parallel loops. The acquisition loop receives pixel data from the camera based on settings selected by the user (e.g., image size, exposure time). Line data is buffered and passed to the main processing loop, which constructs a full image. For a maximum resolution image, each group of 128 lines is buffered in a single data packet, and 64 of these packets are assembled to form an image. The processing loop also interfaces with the encoder, which provides the camera with trigger pulses, and the linear stage, which controls the movement of the stage with respect to the camera. Once a full image is acquired and the initial processing is complete, the image is sent to a new buffer and passed to the second processing loop that executes the vision algorithm. The vision algorithm applies filters and morphological operations to identify defects. The defect data, original image, and processed image are all saved to the hard drive for analysis. The parallel loops are optimized for fast processing to enable real-time operation.

Impact of Defects on MEA Performance

NREL initiated a detailed study of the impact of pinholes on MEA performance and lifetime that examines different possible cases of how a defect in the membrane or catalyst appears after production of GDE by catalyst on the GDL or catalyst coated on the membrane. This enables different defect morphologies to be examined to identify which production method is impacted most by which defects. Pinholes of four different sizes are being tested in three different Nafion membranes (NRE211, NRE212, XL) with varying thickness and reinforcement. This set of samples was fabricated, and failure testing has begun. Test stations allow for in situ spatial detection of hydrogen crossover or measurement of distributed current density during operation of the cell.

Testing began with 100 µm pinholes in NRE212 that had been made by laminating catalyst-coated GDLs or by coating the membrane. Hydrogen crossover showed that the sample made with a GDE had an observable pinhole while that with the CCM did not. However, initial performance testing showed no observable effects caused by the 100 µm pinholes. This indicates that only during long-term testing would this pinhole lead to a quality failure for this setup.

GDE Testing

Several GDEs were prepared by spray-casting a Pt/C catalyst ink (nominally 60% Pt) with Nafion ionomer (Nafion D521 ionomer, 5 wt %) with an 85:15 ratio onto a GDL base material (Sigracet 29BC, 54 cm^2). The Pt/C catalyst loading was 0.05–0.25 mg/cm^2, as verified by mass. Optical reflectance testing was conducted on the GDEs using the sheet sample reflectance setup. All samples were imaged; the blank GDL was the brightest, or most reflective, and as catalyst was added, it became the darkest at 0.09 mg Pt/cm^2. The GDEs then became brighter until the highest loading at 0.24 mg/cm^2, as shown in Figure 2. The average pixel intensity ranged from 69 to 71 for the samples. This change is small but is outside the error bars shown for the deviation between spot sizes of 0.03 cm^2 (0.2% of an image). An improved optical setup and tuning of the vision parameters could improve precision and accuracy and will be tested. Images indicate bright spots, like a dust particle, could be detected to sub-50 µm.

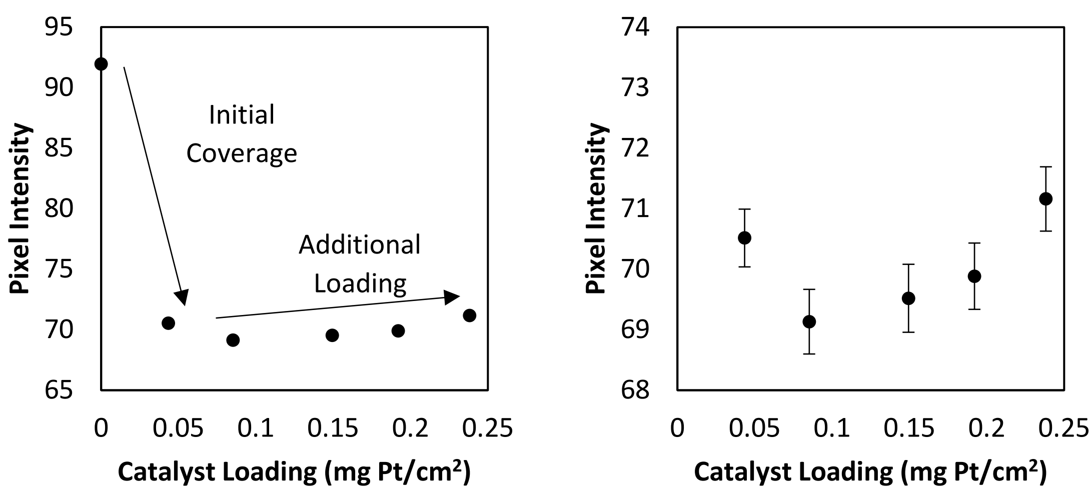

Figure 2. Average pixel intensity for different catalyst loadings on GDEs where the error bars show one standard deviation for sub-sampled spot sizes of 0.03 cm^2

The samples were analyzed with scanning electron microscopy (SEM) and showed changes in surface morphology as the Pt loading increased (Figure 3). Without Pt on the surface, large island structures approached 100 µm. As Pt was added from 0.04 to 0.15 mg Pt/cm^2, the surface was smoothed and the island structures were no longer observed; however, 300–500 µm cracks appeared. As Pt coverage increased from 0.19 to 0.24 mg Pt/cm^2, island features and cracking increased. The islands could be aggregated Pt based on their distribution and size (<10 µm). These SEM images indicate that the variance detected in the optical loading is a function of the actual surface changes and are not inherent error. The optical image therefore provides significantly more detail on possible catalyst aggregates and on the loading. This could also translate to the catalyst thickness.

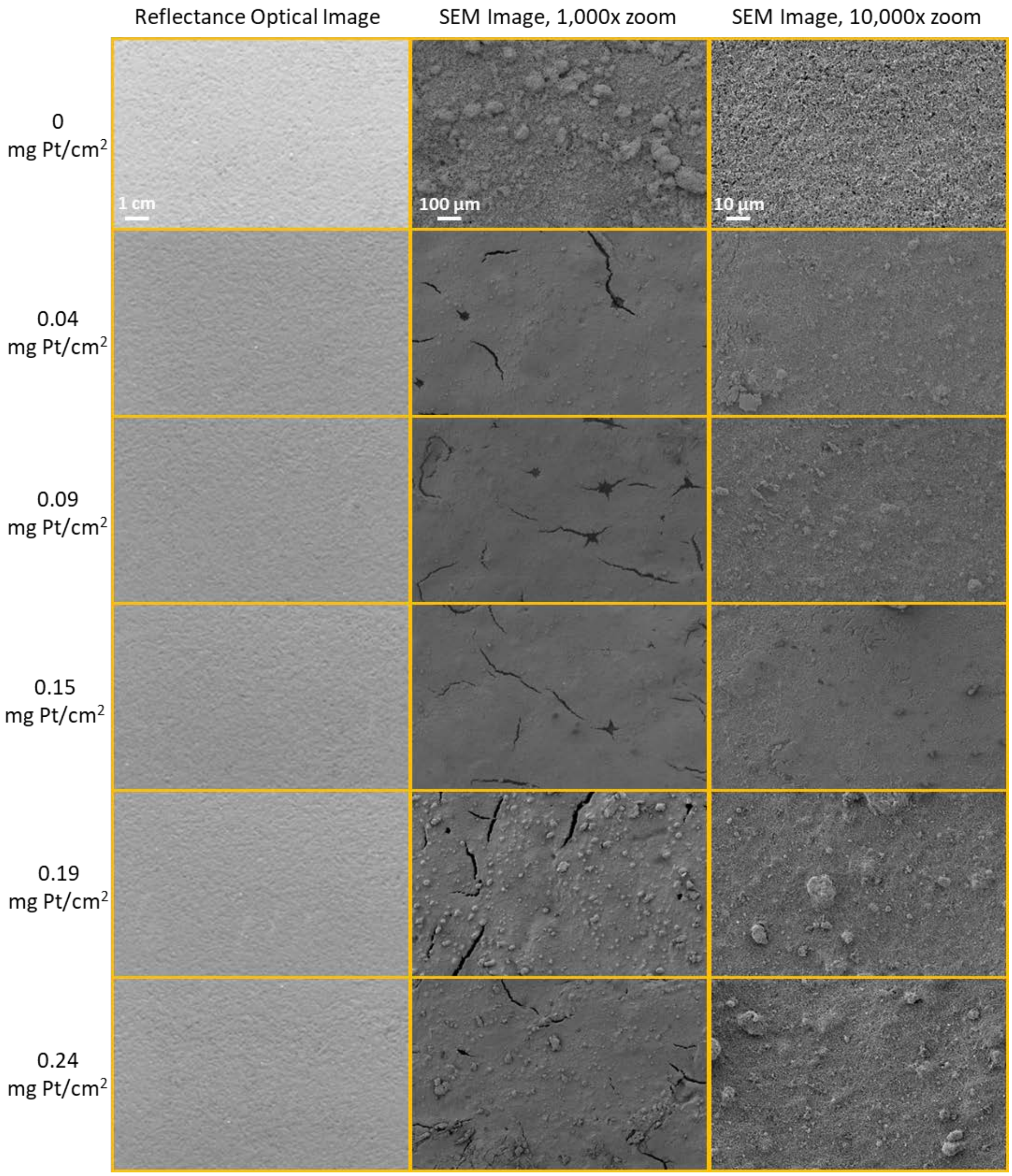

Figure 3. Comparisons of GDLs loaded with 0–0.24 mg Pt/cm^2 taken by optical reflectance and different magnifications of SEM to show the difference in observable surface features

CCM Testing

Several CCMs were prepared by spray-casting a Pt/C catalyst ink (nominally 60% Pt) with Nafion ionomer (Nafion D521 ionomer, 5 wt %) with an 85:15 ratio onto a Nafion base material (NRE115, 54 cm^2). The Pt/C catalyst loading was 0.05–0.25 mg/cm^2, as verified by mass. Images were collected in the same fashion as in the GDE setup. Defects can be seen down to sub-25 µm for bright spots (e.g., dust). A calibration was made for catalyst loading that indicated darker pixels showed increased loading (Figure 4). This is presumably because the membrane continues to have increased coverage as more catalyst is deposited. The variation from spot to spot was determined to be 10% on a 0.03 cm^2 spot size. The images show significant changes between small sub-millimeter sections. To identify if this “error” or change was real, XRF was used to measure an estimated 0.2 mg/cm^2 sample spatially every 3 mm. The 2-D loading map shows variations of up to 10% between these spots. This direct measurement indicates that the optical loading technique is showing real, discrete changes in loading (actual variation) and not necessarily error. The two aligned quite well—within 0.01 mg/cm^2—and showed similar trends through the sample. This positive result indicates the high accuracy and resolution capabilities of the optical technique.

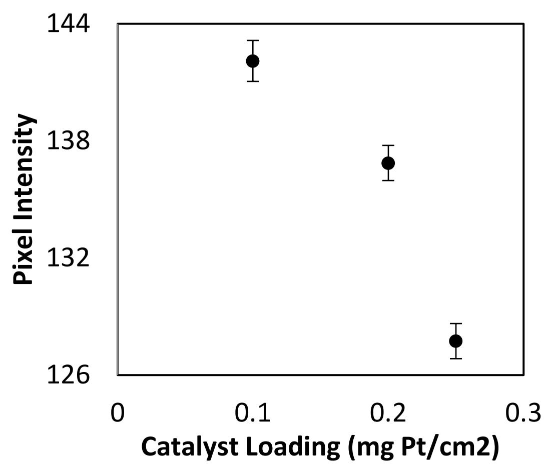

Figure 4. Optical calibration relating pixel intensity to catalyst loading

CONCLUSIONS AND UPCOMING ACTIVITIES

For the SBIR Phase IIb project, the overall goal is to develop and commercialize a suite of instruments that provide a full turnkey inspection package for MEA production, including analysis of CCMs and other opaque materials. Mainstream Engineering developed the Mantis Eye inspection system, which is a low-cost, real-time optical detector for quality control using continuous analysis of membranes for PEMFC MEAs. A reflectance-based technique has now been brought online for performing quality control of opaque fuel cell materials (e.g., GDEs and CCMs). A prototype system has been developed and tested on a variety of materials. Bright spot defects were detected down to 25 µm, and loading variation was identified to within 10% at 0.03 cm^2 spot size. For FY 2020, the goal will be to test the prototype system on as many materials as possible as well as on real production lines. This will be enabled by collecting calibration samples of GDEs, CCMs, and other fuel cell materials with defects and different thickness, loading, or catalyst properties. With these calibrations, the system will be tested while operating in-line at full speed and demonstrated at manufacturers' facilities. Mainstream will report positive and negative feedback from key industry demonstrations and use it to improve the inspection package. The full limits of detection will be characterized and false-positive and false-negative rates determined. NREL will identify the effects of different defects and the critical minimum defect size that leads to stack failure. These plans will enable the development of a suite of instruments that provides a full turnkey inspection package for MEA production.

FY 2019 PUBLICATIONS/PRESENTATIONS

1. A. Wagner, T. Lasko, and P.E. Yelvington, "In-line Quality Control of PEM Materials," DOE Hydrogen and Fuel Cells Program 2019 Annual Merit Review and Peer Evaluation Meeting, Washington, D.C., May 2019.

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