VI.6 In-line Quality Control of PEM Materials

Paul Yelvington (Primary Contact), Andrew Wagner, Philip Cox
Mainstream Engineering
200 Yellow Place
Rockledge, FL 32955
Phone: (321) 631-3550
Email: pyelvington@mainstream-engr.com

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

Contract Number: DE-SC0013774

Subcontractor:
National Renewable Energy Laboratory (NREL), Golden, CO (Phase II)

Project Start Date: Phase I – June 8, 2015, Phase II – August 1, 2016
Project End Date: Phase I – March 7, 2016, Phase II – July 31, 2018

Overall Objectives

- Identify membrane defect size that leads to cell failure.
- Create a fully packaged prototype (TRL 7) automated vision system to perform quality control and demonstrate it on a full-speed membrane web line.
- Detect defects down to 4 µm at 100 ft/min.
- Determine membrane thickness to 0.5 µm resolution.
- Achieve a 5σ false-positive and false-negative rate.

Fiscal Year (FY) 2016 Objectives

- Develop membrane rejection criteria, standard samples, and image evaluation methods.
- Develop software and processing algorithms to automate membrane thickness and defect image analysis and identification.
- Fabricate and test a prototype system at roll-to-roll membrane coating line conditions up to 60 ft/min.
- Apply real time processing methods to an array of membranes types and thicknesses to determine the breadth of applicability of the analysis methodology.

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.

(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 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 1.3: Develop continuous MEA manufacturing processes that increase throughput and efficiency and decrease complexity and waste. (4Q, 2017)
- Milestone 1.6: Develop fabrication and assembly processes for PEMFC MEA components leading to an automotive fuel cell stack that costs $20/kW. (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 QC device for PEMFC MEA materials based on NREL's optical reflectance technology. (4Q, 2017)
- 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 QC techniques on pilot or production lines at PEMFC MEA material manufacturers. (4Q, 2020)

FY 2016 Accomplishments

- Mainstream's lab prototype optical system successfully identified the following defects in Nafion® membranes: a 25-µm diameter pinhole (smallest tested), a 10-µm wide scratch, and a 100-µm wide fold.
- The system was successfully demonstrated on NREL's continuous roll-to-roll web line with Nafion-211 detecting 40 out of 40 100 µm pinhole defects in real time up to 30 ft/min. With post processing, all defects were successfully identified at web line speeds up to 100 ft/min.

- Nafion membrane thickness was measured autonomously in real time to ±1 µm.
- Successfully combined an encoder that measured roll speed/position and a printer that marked defects at the locations identified with the real-time optical analysis.
- Demonstrated broad applicability of our approach to eleven unique membranes for a range of applications, including polymer electrolyte membrane fuel cells (PEMFCs), reverse osmosis, electrolysis, anion exchange membranes, and hydrocarbon membranes.

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 45% of the total material cost of a commercial fuel cell system at low volume [1]. Moreover, manufacturing defects in the membrane not only lead to wasted expensive materials, they also cause cell failures that can cascade into complete stack failure. This requires additional labor reworking the stack as well as the loss of expensive catalyst and gas diffusion electrode materials. Current 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. Mainstream Engineering is developing a real-time optical quality control system that provides significant benefits with increased resolution, improved accuracy, and increased detection speeds for the examination of fuel cell and other membranes.

APPROACH

Mainstream's overall approach was to rigorously prove out the optical technique with a wide-range of commercially available membranes and select optimized hardware for Nafion, the primary initial target membrane. Ultraviolet–visible spectroscopy was used to demonstrate thickness measurement by absorbance and select the most applicable light source wavelengths and configuration. A wide range of typical defects were induced and examined in the Nafion membranes and characterized with Mainstream's sensor. Pinholes, scratches, and folds were selected for in-depth analysis in Phase I, and the limits of the hardware used to find these defects were identified. Software to perform automated image analysis for both defects and thickness was created and initially tested on a group of static membrane samples to validate the detection accuracy of the hardware and processing scheme. The prototype system was combined with a printer and encoder and demonstrated on NREL's web line at speeds up to 100 ft/min to validate the ability to identify and mark defects in a continuous process in real time.

RESULTS

Membrane Defect Types Evaluated by Mainstream's Prototype Quality Control System

The Phase I Small Business Innovation Research project evaluated three initial target defect types including pinholes, scratches, and folds (creases) that were identified as feasible from baseline ultraviolet–visible spectroscopy. A pinhole is defined as a small hole that penetrates completely through the membrane and is less than 1 mm in size, as shown in Figure 1. Pinholes commonly occur from mechanical damage to the membrane, the presence of bubbles in the coating that have subsequently burst, dirt or fibers that have been subsequently removed in the processing leaving a void, or dewetting spots in the membrane coating process. A scratch is a surface defect where part of the membrane has been eroded or removed, as shown in Figure 1. Scratches commonly occur due to mechanical damage in the coating line from the presence of dirt particles or rough surfaces on the rollers. A fold is a defect where the membrane has been creased or overlapped on itself causing surface as well as thickness abnormalities, as shown in Figure 1. Folds commonly occur due to issues in handling. Additional defects are possible in the membrane including bubbles, dirt or undissolved polymer particles and gels. These are easily detectable using our approach but were not present in significant and controlled numbers in the commercially available membrane samples used for validation of the process on the web line. In Phase II, Mainstream will obtain samples with controlled sizes of these defects for additional validation and optimization of our inspection equipment.

Demonstration on a Moving Roll-to-Roll Web Line

The Phase I prototype system was tested on NREL's 14-in wide web line with Nafion-211, the primary commercially

FIGURE 1. Membrane samples illustrating each of the main defect types including pinholes, scratches, and folds taken edge-lit with a compact camera

available membrane investigated (Figure 2). Forty 500 µm pinholes and forty 100 µm pinholes were induced randomly in the Nafion-211 membrane at a variety of locations across and down the membrane roll. The web line was run at speeds of 10, 30, 60, and 100 ft/min while the detector analyzed the membrane for the 80 induced defects. Figure 3 shows a time series of captured processed images taken during this experiment. The roll direction was to the left, while time progressed to the right. The defects were shown in white in the black analysis area and were outlined in red by the image processing software. Additionally, in the figure, a large colored circle was placed around the defect to further highlight the location. The time series continued through the next four images where the defects were moving with the roll to the left. The defects were highlighted before they entered the area of analysis and after they left to help track the passage of time through the images. They were detected in real time by the system as they passed through the black analysis area. The detector was able to find all the defects in real time up to 30 ft/min. At higher speeds, the computer processing speed and camera data transfer rate became an issue. When the video recorded by the detector was analyzed with post-processing, all defects could be detected up to the maximum speed of 100 ft/min. In the Phase II, the algorithm, processing speed, and camera hardware will be upgraded to allow the analysis in real time.

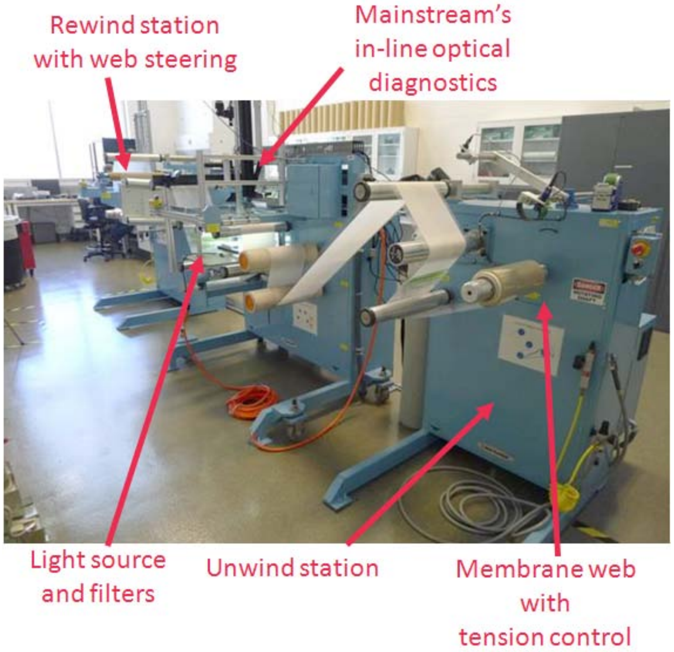

FIGURE 2. Mainstream's in-line quality control diagnostic system installed in the middle web transport zone of NREL's web line

Membrane Thickness Measurement

Membrane thickness was demonstrated with a sample of Nafion-115 processed to create areas of variable thickness as shown in Figure 4. The sample was nominally 132 µm and was processed to produce sample areas from 130 to 140-µm thickness across the sample surface. The thicknesses were mapped with a precision micrometer. The membrane was imaged with the sensor system, and the thickness was calculated from the optical image data. There was excellent agreement between Mainstream's optical method and the micrometer mapping with an error of ±1 µm, which is comparable to the micrometer error. Mainstream will perform additional optimization and automation of this method in Phase II, allowing the detection of membrane thin spots as well as membrane thickness with a variable membrane composition.

CONCLUSIONS AND FUTURE DIRECTIONS

Mainstream Engineering developed a low-cost real time optical detector for quality control using continuous analysis of membranes for PEMFC membrane electrode assemblies (MEAs). The inspection system samples, logs, and marks every location on the roll of material such that defects in MEA materials can be removed prior to assembly into complete cells. A prototype system was built and integrated into NREL's 14-in wide web line and successfully ran autonomously with real-time defect analysis. Mainstream's system was tested on NREL's web line with Nafion-211 and

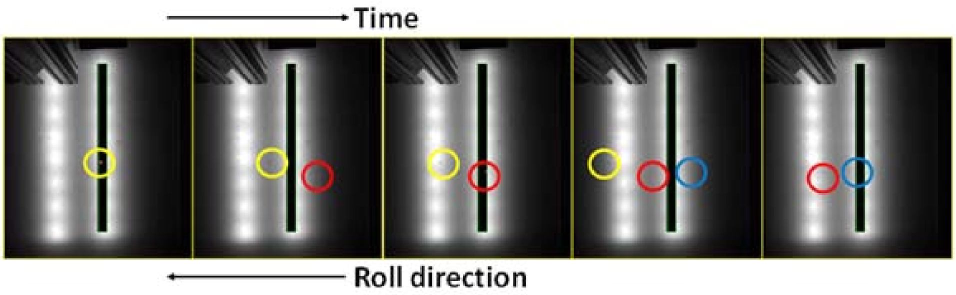

FIGURE 3. Stop frame time-series of images showing roll-to-roll defect detection in Nafion-211 where defects are detected as they pass through the central black band and colored circles indicate the defects as the roll progresses by the detector

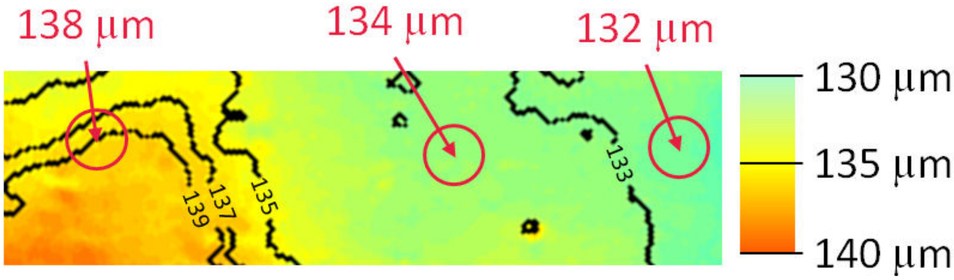

FIGURE 4. Colorized image of a Nafion-115 sample initially 132 µm that that has been processed to different thicknesses and measured by micrometer (highlighted in red on the image) as well as optically quantified (color scale on the right and contour lines on image)

able to find 40 out of 40 100 µm pinhole defects in real-time up to 30 ft/min. An encoder to independently measure roll-speed and printer to mark defects were successfully paired to the optical analysis system to mark defective membrane in real-time at speeds up to 30 ft/min.

The overall goal of the Phase II project is to research, develop, and commercialize an in-line quality control machine for roll-to-roll membrane manufacturing. The device will identify and mark defects as well as monitor membrane thickness in real-time to improve line efficiency and to reduce waste. For FY 2017, the main goals will be to produce defective membranes for use in determining defect size that leads to cell failure, design a prototype system for 24-in wide membrane, and assemble and test new components for enhanced resolution, including upgraded hardware and software.

SPECIAL RECOGNITIONS & AWARDS/ PATENTS ISSUED

1. Yelvington, P.E., and Wagner, A. 2016. “Apparatus and Method for Cross-polarized, Optical Detection of Polymer Film Thickness and Defects.” U.S. Patent Application Serial No. 15/170,360.

FY 2016 PUBLICATIONS/PRESENTATIONS

1. Wagner, A., Cox, P., Yelvington, P.E., “In-line Quality Control of PEM Materials,” poster, DOE 2016 Annual Merit Review, Washington, D.C., June 2016.

REFERENCES

1. Kleen, G.J., “Membrane Development in the U.S. DOE Fuel Cell Technologies Program,” Fuel Cell Seminar and Exhibition, Orlando, FL, 2011.