In-line Quality Control of PEM Materials

SBIR Phase II and IIb

DOE Annual Merit Review, Online Submission

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Contract No.: DE-SC0013774
PM: Nancy Garland

Overview

Timeline and Budget

SBIR Phase I/II/IIb

- June 2015 – August 2020
  - Phase II end: August 2018
- $2.15 MM
  - Total Project: $2.15 MM
  - Total recipient share: $0
  - Total DOE funds spent: $1.9 MM

Technical Targets

Demonstrate a turnkey system that simultaneously measures:

Phase II

- Defects in a moving web of membrane
- Membrane thickness over the full web width

Phase IIb

- Defects in a moving web of PEM materials
- Material thickness over the full web width

Barriers Addressed

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

Partners/Collaborators

- National Renewable Energy Laboratory: Michael Ulsh, Peter Rupnowski, Scott Mauger, Min Wang, Guido Bender, Brian Green

Relevance

- **<u>DOE Objectives</u>: Improved quality control to improve reliability and reduce automotive fuel cell stack costs to $20/kW by 2020 at 500,000 units/year**

- **<u>DOE Manufacturing R&D Activities</u>**
  - Develop in-line diagnostics for component quality control and validate performance in-line
  - Increasing the uniformity and repeatability of fabrication
  - Reduce labor costs and improve reproducibility by increasing automation
  - Identify cost drivers of manufacturing processes

- **<u>Mainstream Engineering Targets</u>**
  - Demonstrate real time automated in-line defect and thickness mapping
  - Improve manufacturing process by providing real time feedback on quality metrics
  - Scan the PEM materials with 100% coverage, marking and logging defective regions

In-line QC of PEM Materials

- **Mainstream is developing a suite of instruments to provide full turnkey inspection for MEA production including catalyst coated membrane and other opaque materials**
- **In the Phase II, we developed and commercialized the Mantis Eye™ machine vision system for automated, continuous monitoring of transparent films on coating lines and web converting equipment**
- **In the Phase IIb we will integrate technology for opaque material inspection into the Mantis Eye™ platform to provide a complete quality control solution**
- **Patent-pending optical design provides simultaneous thickness mapping and defect detection**
- **Guiding principle of our product design is to provide the finest defect and thickness resolution with reasonably priced camera hardware**

PhaseIIb Technical Approach

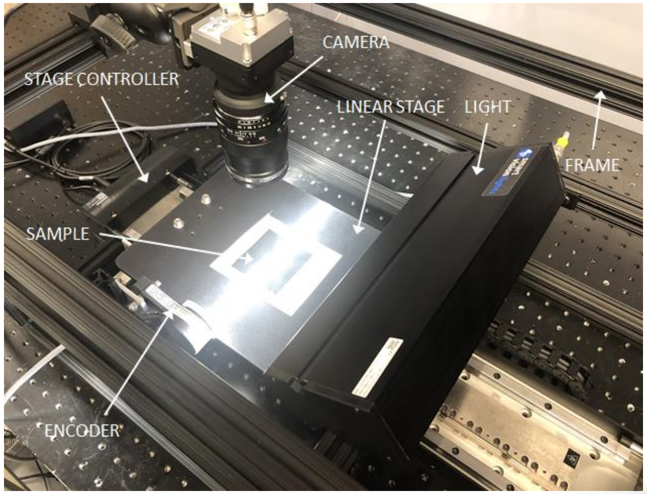
- Create defective membrane, GDLs, CCMs, and MEAs to identify defect size that leads to cell failure
- Transition technology from small-scale, offline use to real-time, full web analysis based on the Mantis Eye platform
- Determine defect and thickness limit of detection (LOD) with hardware for all PEM materials
- Develop hardware and automated software
- Test prototype system on partner's weblines
- Validate performance criteria in-house
- Demonstrate prototype system on industry weblines
- Expand technique to alternative membranes

Webline Measurements

- **Modular system can be installed in a variety of webline locations**
- **In-house Mantis Eye Inspection Station for Transmission or Reflectance**
  - 500 ft/min
  - Automated defect marking
  - Small test samples can be spliced into existing rolls for analysis
- **Sheet Reflectance setup**
  - Automated scanning up to 100 ft/min
  - Process single sheets up to 12" by 12"
  - Real-time analysis

Optional Light for Reflectance

Transmission Setup



Sheet Reflectance Setup

Analysis – Materials Examined

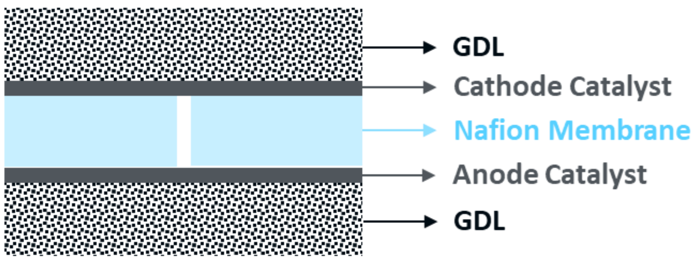
- **Examined three types of materials**
  - Membrane (Phase I/II)
    - Thicknesses from 17 – 250 microns
    - Nafion sheets and freshly cast
    - Supported and unsupported
    - A variety of alternative membranes for electrolysis and anion exchange
  - GDLs (PhaseIIb)
    - Base material
    - Pt/C catalyst ink in Nafion ionomer
  - CCMs (PhaseIIb)
    - Base membrane
    - Pt/C catalyst ink in Nafion ionomer

Analysis - Impact of Defect Size & Type on MEAs – NREL

- **NREL prepared a variety of pinhole samples and testing is ongoing to determine necessary QC detection limits and identify cost trade-offs**

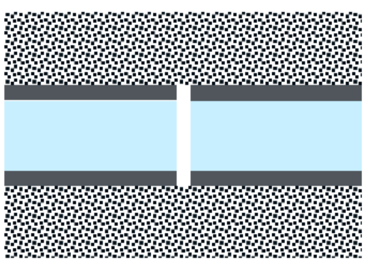
Pinhole configuration is related to the hole production step and the MEA fabrication procedure.

(a)



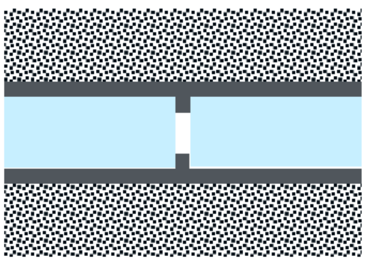
(1). Pinhole was produced during membrane casting
MEA fabrication: GDE without lamination

(b)



(2). Pinhole was produced through the CCM
MEA fabrication: CCM without lamination

(c)



(3). Pinhole was produced during membrane casting
MEA fabrication: CCM without lamination

(4). Pinhole was produced during membrane casting
MEA fabrication: CCM with lamination

(5). Pinhole was produced during membrane casting
MEA fabrication: GDE with lamination

(6). Pinhole was produced through the CCM
MEA fabrication: CCM with lamination

Milestones

Phase II Final 2018 Milestones	Results
Commercialize the Mantis Eye system for transparent film	-Mantis Eye system is currently being used to evaluate multiple samples from industry for capability demonstrations
Phase IIb Final 2020 Milestones	
Identify defect size and type that leads to MEA failure	NREL prepared a variety of pinholes in membrane CCMs, and GDEs and assembled for performance and life testing in MEAs
Detect defects down to 10 µm at 100 ft/min for all fuel cell materials (e.g., membrane, GDL, catalyst, electrodes)	-Pinholes down to 25 µm in both supported and unsupported membranes -Modified Mantis Eye found defects down to 25 µm in GDLs and CCMs -Smaller defect samples are being tested
Determine membrane thickness to 0.5 µm resolution	-Examined different GDEs and CCMs and determined catalyst loading from 0 – 0.4 mg Pt/cm^2, thickness testing ongoing
Create a turnkey prototype and demonstrate it on three weblines	-Prototype unit of both the reflectance and transmission hardware was made. We have conducted material testing for 10 different manufacturers of CCM, GDL, or membrane. Performed multiple in-person demonstrations for manufacturers. Additional webline demonstrations to follow
Achieve a 5σ false-positive and false-negative rate	-Mantis Eye software and winder can be used to compare runs and determine identification rate, testing has shown 5σ rates if vision parameters are optimized

Mantis Eye Commercialization Efforts

Mantis Eye Inspection Station

- www.mainstream-engr.com/products/mantis-eye-optical-scanner/
- **Integrated winder triggered from Mantis Eye inspection system**
- **Built-in polarized backlight and splice table**
- **Automatic tension control**
- **Forward and reverse winding**
- **Max web speed – 575 ft/min**
- **Max web width – 13.75 in.**
- **Hosted demos for several interested membrane manufacturers**
- **Tested several other membrane, GDL, GDE, and CCM materials for a variety of manufacturers**
- **System has been commercialized and is available for sale and for sample testing or analysis**

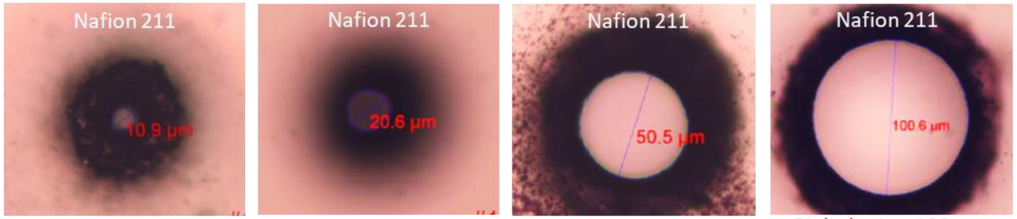
Cost-Benefit Analysis

- **Several Factors Involved In Cost-Benefit Analysis**
  - What is the required throughput (e.g. how much data/sec is processed)?
    - This determines how much it costs to perform QC, regardless of what is found
    - How small is the largest acceptable defect? (smaller defects = higher resolution = higher throughput)
    - How fast is the webline? (faster = higher throughput)
    - What is crossweb distance? (larger = higher throughput)
  - How costly is a false positive?
    - Detecting a defect that *doesn't* actually exist costs extra QC time, plus the cost of the discarded material
  - How costly is a false negative?
    - Missing a defect that *does* exist is potentially costlier, since it could lead to premature stack failure
- **Balancing these factors determines the economics of implementing a QC system**
  - Identifying defects that would otherwise be missed must be more valuable than the cost to implement and operate the QC system, plus the cost incurred from false positives
  - Largest cost is the initial investment in the QC equipment, benefits are realized over the life of the QC system
  - Biggest factors are scale of the operation and cost of manual QC

Membrane Pinhole Study – NREL

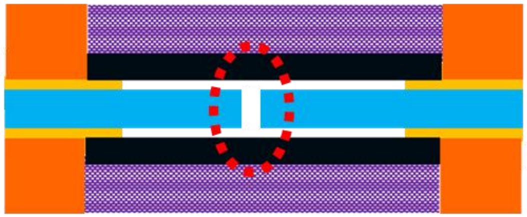
Objective: 1). Investigate the impact of membrane pinhole on performance and lifetime of GDE based MEAs
2). In-situ observation of membrane pinhole swelling behavior at different conditions

Nafion Membrane (NRE 211, 212, XL) with Laser Induced Pinholes



Pinhole size: 10 μm | Pinhole size: 20 μm | Pinhole size: 50 μm | Pinhole size: 100 μm

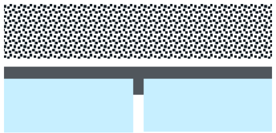
Laser Pinhole MEAs

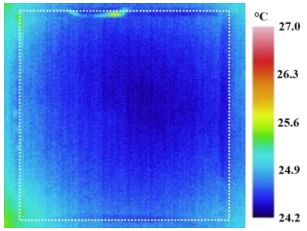


Preliminary study: impact of MEA configuration on pinholes

Half CCM-based MEA:

29BC + Cathode coated 212 with 100µm pinhole (Hot pressed)



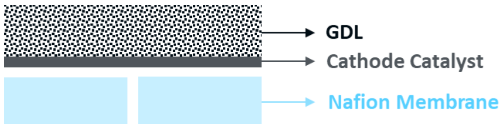


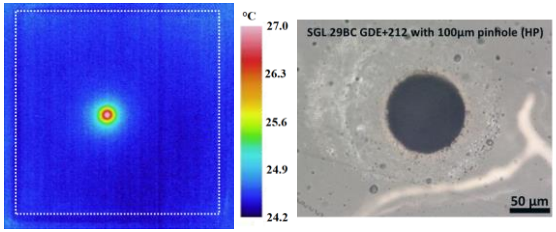
100 SCCM H_2; exposure time 200s

No thermal responses observed at this condition, suggesting the 100 µm pinhole was closed during spray coating

Half GDE-based MEA:

29BC GDE+212 with 100µm pinhole (Hot pressed)

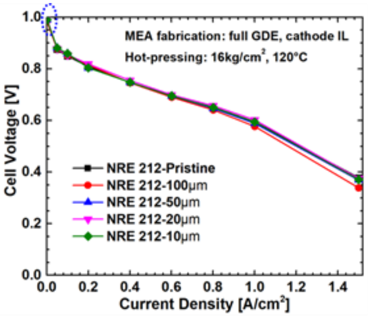


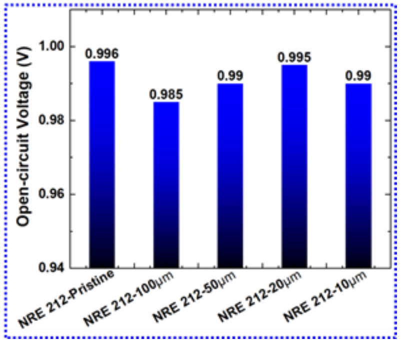


100 SCCM H_2; exposure time 200s

Pinhole was observed in both pinhole detector (PDA) and optical microscope, indicating 100 µm pinhole was significant in GDE

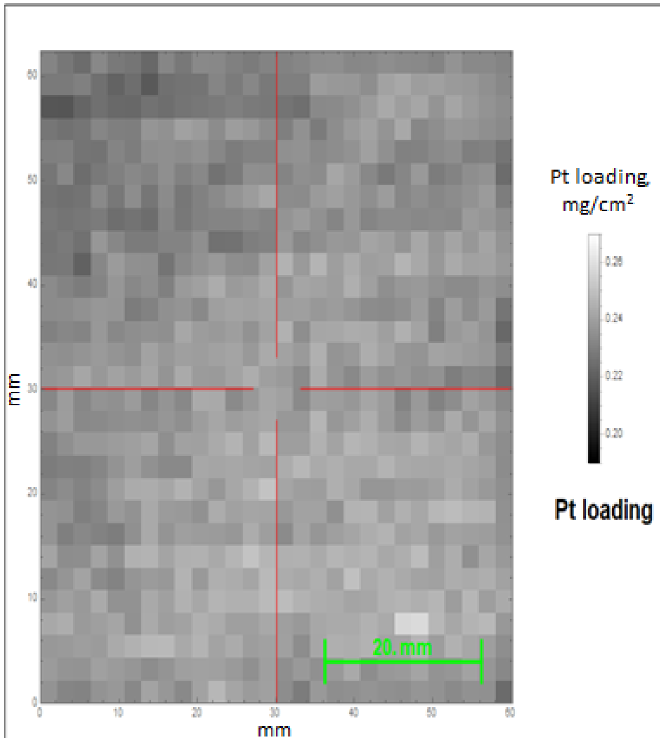
- **In-situ testing in single cell**: fabricated GDE-based MEAs and studied the impact of laser pinholes on PEMFC initial performance

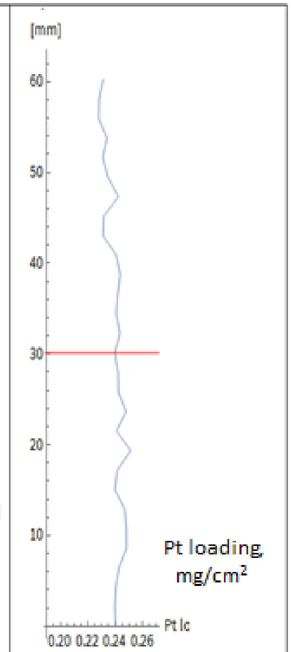




- **IR-AST**: will study the AST lifetime of MEAs with different membranes & laser pinholes, track the development of laser pinholes
- **In-situ testing in segmented fuel cell**: will perform drive cycle tests of laser pinhole MEAs in segmented cell to study the spatial performance over time

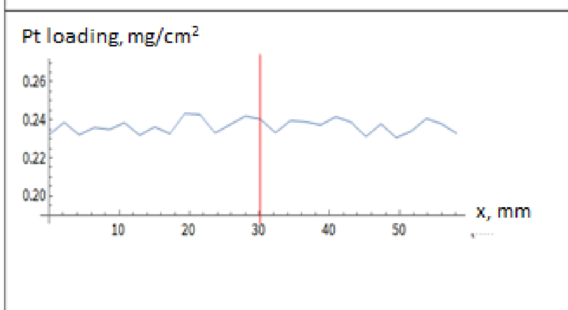
XRF Catalyst Comparison – NREL



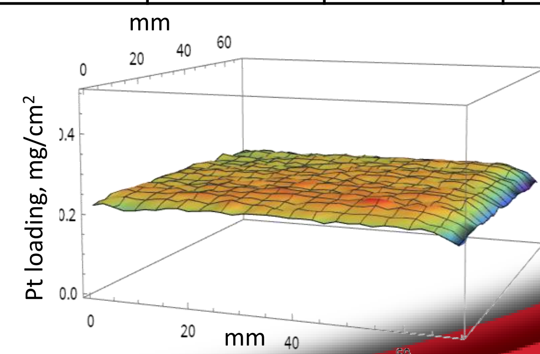


- **Objective:** Assess Pt loading uniformity by XRF mapping to verify optical loading measurements on GDEs and CCMs
- Loading was measured across the surface, significant deviation from expected was observed

GDE ID	Target loading, mg Pt/cm²	Measured loading, mg Pt/cm²	Percent difference from target	Standard deviation, % of measured
A	0.050	0.046	-8.9	1.3
B	0.100	0.104	4.4	6.1
C	0.150	0.180	20	4.4
D	0.200	0.235	17	2.4
E	0.250	0.249	-0.2	0.9
F	0.300	0.284	-5.1	1.7
G	0.350	0.337	-3.7	4.2
H	0.400	0.391	-2.2	2.6

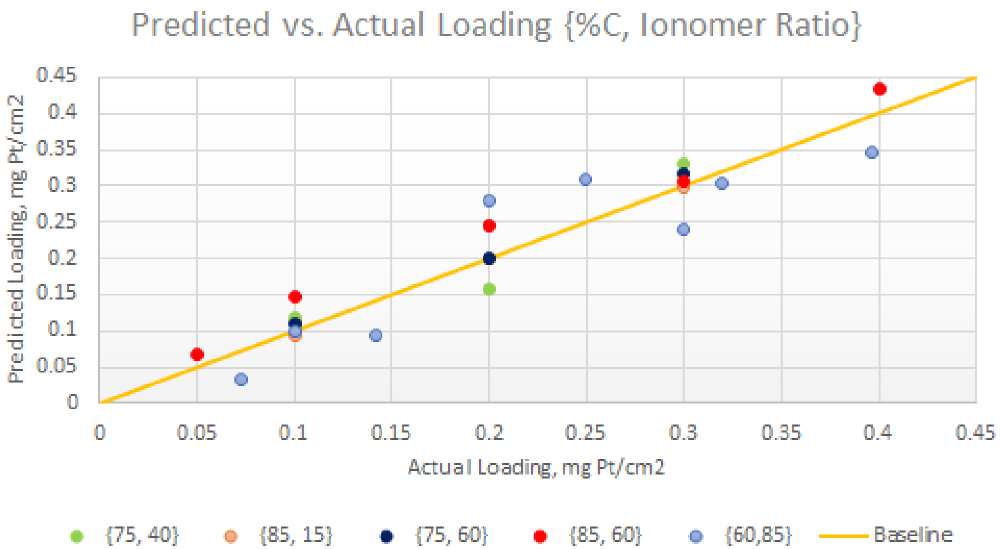


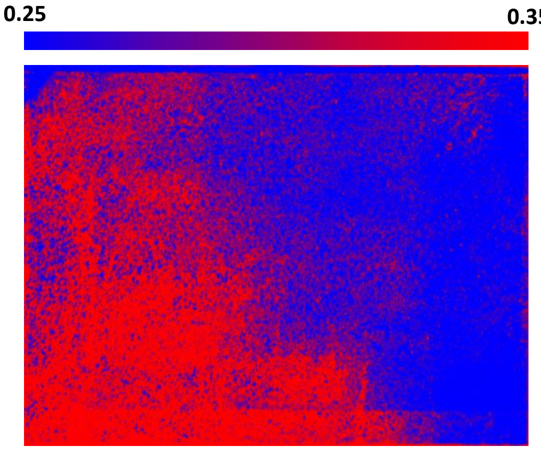
Gas diffusion electrode sample
Map density: 33 x 33=1089 measurement points
Point spacing: 2.15 mm
Beam spot diameter: 1.1 mm
Target loading: 0.200 mg/cm²,
Measured mean from map: 0.237 mg/cm².
Standard deviation = 2.5% over all points,
narrow distribution/high coating uniformity



Gas Diffusion Electrode Materials

- **Correlation developed to predict loading based on image data**
- **Average pixel value depends on Pt/C %, ionomer ratio, and catalyst loading**
  - Increase in Pt/C% or ionomer ratio results in darker pixels, catalyst loading has quadratic relationship with pixel value
  - Some corrections must be applied to correct for non-uniform lighting (up to 8% variation across sample)
- **Measurements well predict loading based on Pt/C % and ionomer ratio (R^2=0.88)**
- **System can detect changing concentration, pixel-to-pixel variation determines the smallest area a change can be seen on and samples loading can be spatially mapped**

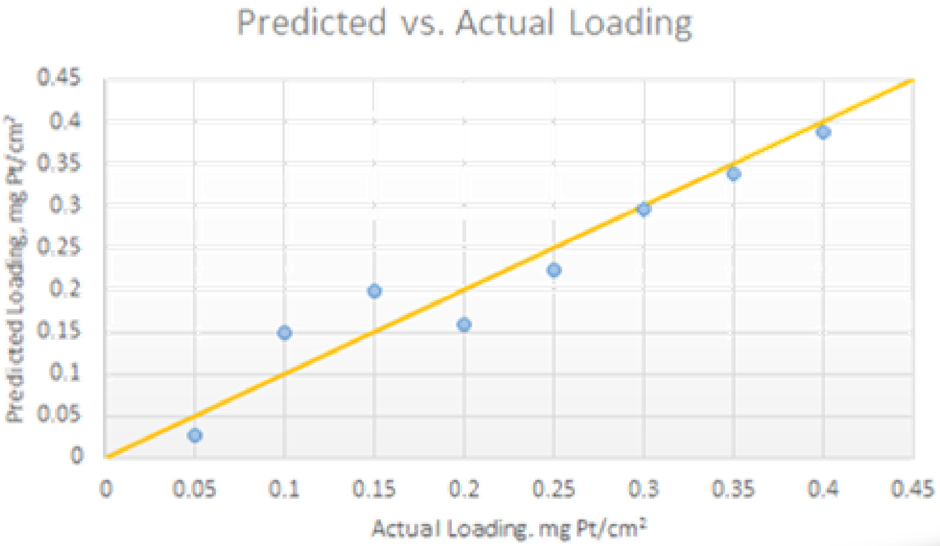




Sample Catalyst Loading (0.25-0.35 mg Pt/cm²) Using Optical Measurement Technique

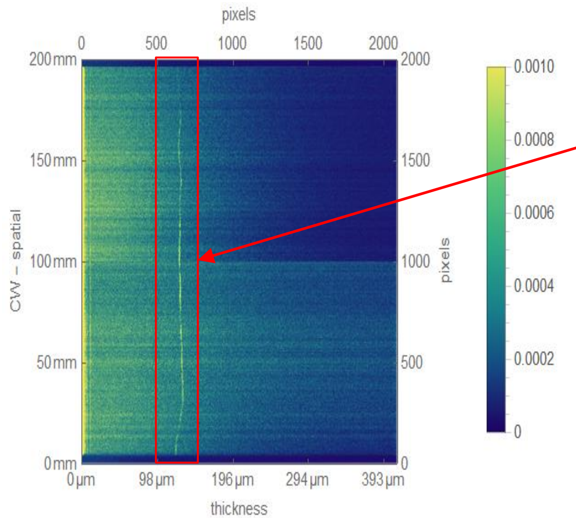
Catalyst Coated Membranes

- **Correlation developed to predict loading based on CCM image data of different concentrations of Pt/C catalyst applied to Nafion membrane**
- **Average pixel value depends on catalyst loading (Pt/C % and ionomer ratio held constant)**
  - Catalyst loading has quadratic relationship with pixel value
  - Pixels get darker up to 0.35 mg Pt/cm^2, then lighter up to 0.40 mg Pt/cm^2
- **Average error 0.027 mg Pt/cm^2 (20% of value)**
- **High correlation of predicted values and actual loading (R^2=0.93)**
- **Data at higher loading values has higher correlation**
- **System can detect changing concentration, but each material will require a calibration or known catalyst properties (e.g., Pt/C, ionomer ratio)**

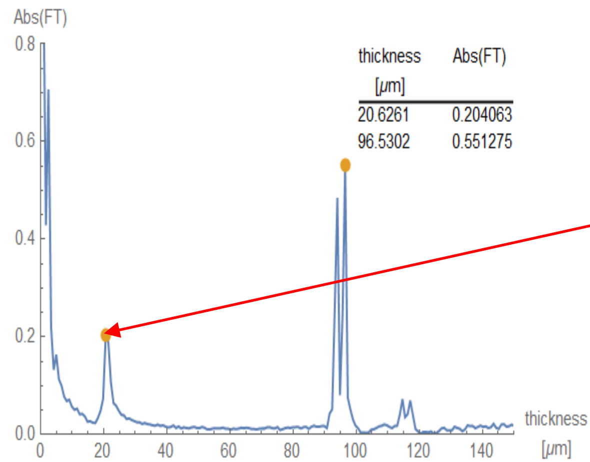


Membrane Thickness Mapping With NREL’s Hyperspectral Method – NREL

- **Motivation: Initial hyperspectral experiments using Si detectors have not produced expected thickness for Nafion N115, HP and XL membranes**
- **Objective: Investigate reasons for the unexpected results and improve the thickness mapping technique**
- **Accomplishments:**
  - All cases were further investigated using both experimental (single point spectroscopy) and modeling methods
  - A fundamental explanation for all three cases was given and mitigation strategies were successfully developed.
  - Hyperspectral technique provides a very accurate method of determining thickness across a wide variety of fuel cell membranes including reinforced membranes



N115 thickness signal is clearly visible despite the noise level



When InGaAs spectrometer was used to test HP membrane on a liner (top protective layer was removed), clear membrane thickness peak at 20.6µm was observed

Response to Reviewer Comments

Reviewer Comment	Response
• No basis to back critical parameters of needed defect size and cost. Without this, it is unclear how anyone can judge what is "good enough" or "fast enough." • The team should include the effect of the defect size on performance and durability.	• We have worked extensively with NREL to better understand size of defects that lead to cell failure and define required resolution • We have performed multiple industry demonstrations and gauged cost. • Based on these results our system can identify small defects that lead to cell failure
• The team should also investigate the two-dimensional spatial mapping, in particular for the loading mapping. • It would be good to add a range of catalyst thicknesses and types for electrolyzers as well as not platinum on both sides and are still at high loading.	• We have conducted 2-D spatial mapping using our optical technique and have performed 2-D XRF mapping for a secondary measurement to verify accuracy • We have examined different catalyst loadings and ratios and have a separate project with the University of Connecticut where we are examining IrOx as well as Pt
• The team should expand the project and funding to install equipment on an industrial production line and add a large-scale (3M or W.L. Gore) manufacturer to project.	• We are actively looking for large scale industrial partners and have a few possibilities that are being pursued.
• The cost of the equipment and the cost of using the QC process in a manufacturing process needs to be determined.	• Cost for the commercialized technology is known and starts in the tens of thousands and ranges up depending on size, scale, and complexity.
• It is not certain that the industry is ready for this. No commercial interest is demonstrated.	• We have now performed 10 material demonstrations and hosted multiple in-person demonstrations for both large and small manufacturers. The industry is still scaling to where automated QC is necessary. We are pursuing alternative markets in parallel.
• Investigate alternative markets (e.g., PEM electrolyzers)	• Have evaluated multiple alternative materials for companies in need of improved QC and commercialization is ongoing

Collaborations

Institution	Type	Extent	Role and Importance
National Renewable Energy Lab	National Laboratory	Major	Fabricate defect samples and conduct testing to determine the smallest defect to cause cell failure, develop small-scale advanced techniques for identification of MEA material properties of interest, and facilitate webline demonstrations

Remaining Challenges and Barriers

- **Remaining Objectives**
  - Finish software for continuous, autonomous operation
  - Demonstrate prototype system
  - Demonstrate the unit on industrial weblines
- **Key Barriers**
  - Relevant fuel cell materials with defects must be procured to develop and demonstrate the project to be relevant to manufacturers
  - **Cost of improved quality control must outweigh system cost**
  - **Manufacturers must be at scale where automated quality control outweighs man-hours**

Proposed Future Work

- **Proposed Work**
  - Demonstrate reliability of packaged system for defect detection on industrial weblines
  - Continue to refine and optimize software
  - Incorporate reflectance hardware on Mantis Eye with winder/unwinder
- **Methods to Mitigate Risk**
  - Demonstrate prototype system for industry customers
  - Focus on reducing cost at current defect targets
  - Disseminate results and find manufacturing partners
- **Key Milestones**
  - 10 μm defects in CCMs and GDL
  - Operating in real-time at 100 ft/min
  - Identifying catalyst loading and thickness to 0.5 μm
  - 5σ false-positive and negative rate
  - Customizable and packaged turnkey prototype able to be deployed
  - Prototype demonstration on industry webline

Technology Transfer Activities

- Mainstream is using SBIR Phase IIb funding to develop the system into a turnkey product and commercialize it
- While the PEM fuel cell market is the primary focus, the Mantis Eye technology is well-suited to many types of toll coating and other polymer films and we are conducting product demonstrations with multiple companies that are interested in the system
- Mainstream has a subcontract from UCONN to leverage this technology developed in the Phase IIb to build and deliver a quality control system as part of a project for improved catalyst design
- Mainstream has submitted two patents on this project
  - "Apparatus and Method for Cross-polarized, Optical Detection of Polymer Film Thickness and Defects." U.S. Patent Application Serial No. 15/170,360.
  - "Method and Apparatus for Cross-polarized, Optical Detection of Polymer Film Thickness and Defects Using Polarimetric Thickness Mapping." U.S. Patent Application Serial No. 15/894,172

Summary

- Mainstream is commercializing the Mantis Eye inspection system through industry demonstrations and a dedicated website for both the transmission and reflectance process for a full turnkey solution
- Reliability statistics can be used with a cost function to determine the benefit of improved quality control for each material and webline depending on hardware/software requirements, data throughput, and minimum defect size targeted
- NREL has prepared multiple pinhole defect samples in membrane, GDEs, and CCMs to evaluate impact on MEA performance
- Demonstrated ability to determine catalyst loading on GDLs and CCMs and make 2-D maps as well as identify defects and compared with XRF loading measurements
- Hyperspectral techniques can be used to more accurately determine thickness in multi-layered membranes
- We have performed in-person demonstrations of a prototype unit for several membrane, CCM, and GDE manufacturers