Development of Real-Time Characterization Tools and Associated Efforts to Assist Membrane Electrode Assembly Manufacturing Scale-Up

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Fuel Cell Technologies Office Webinar

August 22, 2018
Question and Answer

• Please type your questions to the chat box. **Send to: (HOST)**

![Chat interface](image)
Support

• This Early Stage R&D activity is funded as a lab core competency by FCTO
• Other funding has also been received from:
  – DOE: AMO, VTO, FE
  – Industry
Outline

• Overview of the manufacturing context and challenges for membrane electrode assembly (MEA) materials
• Detailed discussion of work to develop real-time in-line characterization techniques
• Overview of specialized in situ diagnostics developed to understand how defects in MEA materials affect cell performance and lifetime
• Overview of efforts to understand the foundational relationships between electrode materials (inks and coated layers), processing methods, and performance
Overview of the manufacturing context and challenges for MEA materials
Markets

- Markets for multiple applications are expanding
- Units, power output, revenue increasing
- Increased state activity

Estimated Costs from Techno-economic Analysis

- Stack and system cost analysis assumes the use of high-volume manufacturing methods for MEA materials
- The modeled manufacturing technologies are not in all cases proven out at scale

Roll-to-roll Manufacturing

High-volume roll-to-roll (R2R) manufacturing methodologies are relevant for:

- Gas Diffusion Media
- Electrode
- Membrane
- Assemblies w/gaskets

Premise for NREL Activity

- Membrane electrode assemblies (MEAs) for PEM fuel cells must be made using scalable processes to enable high volume and low cost.
- For PEM materials, these processes are typically atmospheric pressure and solution-based, given the heterogeneous polymeric and particle-based nature of the materials.
- These materials, when cast, coated, sprayed, extruded, laminated, aligned, etc., tend to have a variety of macro- and micro-scale defects that MAY affect performance and lifetime.
Challenges We Try to Address

• How can we detect defects in MEA materials in ways that are amenable to the fabrication process?
• How do we understand how defects formed during fabrication and handling affect performance?
• How do we understand how the parameters of the ink formulation and fabrication process affect performance?
Industry Collaborators

Approach: **Work with industry** to develop knowledge and techniques to improve quality and reduce manufacturing costs of MEA materials

- General Motors
- 3M
- W.L. Gore
- Proton OnSite
- Giner
- HyET
- Mainstream Engineering
- Pajarito Powders
- Umicore
- Ballard
- Altergy
- AquaHydrex
- Advent
- Ion Power
- BASF
- AvCarb
- Arkema
- UTC
- DuPont
Detailed discussion of work to develop real-time in-line characterization techniques
Why Worry About Quality?

• Preliminary analysis using Strategic Analysis Inc.’s well established automotive fuel cell cost model indicates that, even at 90% yield (vs. 100%), stack cost can increase close to 60%

• In their back-up power PEM cost analysis, LBNL (M. Wei, T. McKone, DOE Hydrogen Program Annual Merit Review, June 19, 2014) show a significant effect of stack yield on system cost
## Task 5: Quality Control and Modeling and Simulation

<table>
<thead>
<tr>
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<th>Milestone</th>
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<td>5.1</td>
<td>Establish models to predict the effect of manufacturing variations on MEA performance.</td>
<td>(4Q, 2016)</td>
</tr>
<tr>
<td>5.2</td>
<td>Demonstrate improved sensitivity, resolution, and/or detection rate for MEA inspection methods.</td>
<td>(4Q, 2016)</td>
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<tr>
<td>5.3</td>
<td>Validate and extend models to predict the effect of manufacturing variations on MEA performance.</td>
<td>(4Q, 2017)</td>
</tr>
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<td>5.4</td>
<td>Design and commercialize an in-line QC device for PEMFC MEA materials based on NREL's optical reflectance technology.</td>
<td>(4Q, 2017)</td>
</tr>
<tr>
<td>5.5</td>
<td>Develop correlations between manufacturing parameters and manufacturing variability, and performance and durability of MEAs.</td>
<td>(4Q, 2018)</td>
</tr>
<tr>
<td>5.6</td>
<td>Demonstrate methods to inspect full MEAs and cells for defects prior to assembly into stacks in a production environment.</td>
<td>(4Q, 2018)</td>
</tr>
<tr>
<td>5.7</td>
<td>Develop areal techniques to measure platinum (and other catalyst metals) quantitatively in an MEA.</td>
<td>(4Q, 2018)</td>
</tr>
<tr>
<td>5.8</td>
<td>Implement demonstrated in-line QC techniques on pilot or production lines at PEMFC MEA material manufacturers.</td>
<td>(4Q, 2020)</td>
</tr>
<tr>
<td>5.9</td>
<td>Develop imaging-based methods for 100% inspection of PGM loading in electrodes.</td>
<td>(4Q, 2020)</td>
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## Task 1: Membrane Electrode Assemblies

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<td>1.1</td>
<td>Develop processes for highly uniform continuous lamination of MEA components.</td>
<td>(4Q, 2017)</td>
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<td>1.2</td>
<td>Develop processes for direct coating of electrodes on membranes or gas diffusion media.</td>
<td>(4Q, 2017)</td>
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<td>1.3</td>
<td>Develop continuous MEA manufacturing processes that increase throughput and efficiency and decrease complexity and waste.</td>
<td>(4Q, 2017)</td>
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<td>Develop fabrication and assembly processes for PEMFC MEA components leading to an automotive fuel cell stack that costs $20/kW.</td>
<td>(4Q, 2020)</td>
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</table>

* MYR&D Plan Manufacturing Section currently being updated to reflect new office structure and milestones*
Enable Quality Inspection During R2R

Inspection Requirements:

• Rapid measurement and data processing
• Implementable in an in-line fashion
• Non-destructive
• Areal (100% inspection or nearly so)
## Overview of QC Techniques

<table>
<thead>
<tr>
<th>Material</th>
<th>Defects</th>
<th>Detection</th>
<th>Resolution (x-y)</th>
<th>Status</th>
</tr>
</thead>
<tbody>
<tr>
<td>Membrane</td>
<td>Pinholes, bubbles, scratches, agglomerates, etc.</td>
<td>Optical reflectance/transmission</td>
<td>micrometers</td>
<td>Demonstrated on web-line</td>
</tr>
<tr>
<td></td>
<td>Thickness variation (mapping)</td>
<td>Optical absorption</td>
<td>micrometers</td>
<td>Demonstrated on motion prototype</td>
</tr>
<tr>
<td></td>
<td></td>
<td>Optical reflectance (interference fringe)</td>
<td>millimeters</td>
<td>In development</td>
</tr>
<tr>
<td></td>
<td></td>
<td>Thermal scanning</td>
<td>millimeters</td>
<td>In development</td>
</tr>
<tr>
<td>GDL</td>
<td>Scratch, agglomerate, fibers</td>
<td>IR/direct-current</td>
<td>millimeters</td>
<td>Demonstrated on web-line</td>
</tr>
<tr>
<td>Electrode</td>
<td>Surface defects</td>
<td>Optical reflectance</td>
<td>micrometers</td>
<td>Demonstrated on motion prototype</td>
</tr>
<tr>
<td></td>
<td>Voids, agglomerates, cracks, thickness/loading indirectly</td>
<td>IR/direct-current (for CCMs or decals)</td>
<td>millimeters</td>
<td>Demonstrated on web-line</td>
</tr>
<tr>
<td></td>
<td></td>
<td>IR/reactive impinging flow (for GDEs or CCMs)</td>
<td>millimeters</td>
<td>Demonstrated on web-line</td>
</tr>
<tr>
<td></td>
<td>Loading (mapping)</td>
<td>Optical reflectance/transmission</td>
<td>millimeters</td>
<td>In development</td>
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<tr>
<td>Shorting</td>
<td></td>
<td>Through-plane IR/direct-current</td>
<td></td>
<td>Demonstrated on web-line</td>
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<tr>
<td>Membrane integrity</td>
<td></td>
<td>Through-plane reactive excitation</td>
<td>pinholes as small as 90 µm</td>
<td>Demonstrated on static test-bed</td>
</tr>
</tbody>
</table>
IR techniques for catalyst-coated membrane (CCM) electrode uniformity/defects and shorting
**IR/Direct-current (IRDC) Excitation Technique**

**Methodology:**
- Apply voltage across electrode layer
- Resulting current causes resistive heating
- Rapid (~sec), areal measurement of thickness uniformity

All samples: 25 cm² active area, 5 second excitation at 21V DC; % reduction of the thickness of the catalyst layer within the area of the defect

Aieta et al., *J. Power Sources*, **211** (2012), p.4-11.
Setup for IRDC on NREL Web-line

IR Camera

Excitation rollers with rotating electrical connectors

CCM
IRDC Defect Detection Examples

Carbon debris applied to GDE, under a laminated membrane

Simulated droplets from coating die

Electrode coating lumps on decal
We modulated excitation conditions to give equivalent detection over a range of line speeds.

*IRDC was demonstrated on an industry partner R2R CCM manufacturing line*
Through-plane IRDC Technique

Methodology

• Apply voltage to rollers on both sides of CCM or MEA
• Shorting pathways allow current, causing resistive heating
• Rapid, areal identification of shorting locations


Through-plane IRDC Defect Detection Examples

- **GDM fibers**
- **Catalyst layer lumps**
- **Slits in membrane made prior to laminating to GDE**
- **Carbon debris applied to GDL prior to electrode coating**
- **Filtered data analysis**
  - Agglomerates in catalyst layer and resulting thermal signature due to shorting
IR techniques for gas-diffusion electrode (GDE) electrode uniformity/defects, membrane integrity and measuring membranes in multi-layer constructions
Reactive Impinging Flow (RIF) Technique

Methodology

- Use a non-flammable reactive gas mixture to react on catalyst
- Use an array of jets (knife) to impinge reacting flow onto GDE
- Non-uniformities in electrode will result in differences in thermal response
- Rapid, areal measurement of thickness/loading uniformity
Setup for RIF on NREL Web-line

Gas knife over GDE web for reactive excitation

Web-line running GDE web
RIF on NREL R2R Coated GDE Web

- Created uniformity map of entire coated sample
- Temperature rise correlated well with small variation in loading

Single frame of RIF data from sample with very non-uniform coating

Thermal map of entire web, showing median temperature vs. loading (via XRF)
Through-plane Reactive Excitation (TPRE)

Methodology

• Expose membrane-containing assembly to hydrogen-containing gas
• Hydrogen advects through pinhole and reacts on catalyst, resulting in thermal response
• Rapid, areal detection of failure of membrane integrity
TPRE Pinhole Detection Examples

**MEA with 120 μm pinhole**

Thermal response with 0.5 lpm H₂ flow, 5 sec pulse: 1 °C temp rise achieved in 2 sec; Max temp rise > 2 °C

**90 μm diameter pinhole in 18 μm thick membrane,** tested with GDE (0.2 mg/cm² Pt)

**Half-cell with pinholes created using 25 μm tool (ΔT ≈ 0.2 °C)**
Thermal Scanning Technique

Methodology

- Use thermal excitation of active layer/substrate
- Measure peak/decay
- Link measurement to thermal model to back out physical properties, e.g. thickness, porosity

\[ R^2 = 0.957 \]
\[ t(\Delta T) = 11.5 - 0.64 \Delta T \]

Measured membrane thickness in half-cell (membrane on GDE) samples
Optical techniques for membrane defects, membrane thickness imaging, and electrode surface defects
Optical Defect Inspection

Methodology

• Use transmission and reflectance imaging in specular or diffuse modes

• Use flexible inspection apparatus on web-line
  – Easy control/repeatability of light and detector angles
  – Filtered hood to eliminate external light and minimize contamination

• Develop defect detection and classification algorithms

• Provide full width/full length high resolution product roll imaging (mapping)
Membrane Defect Detection Examples

- PFSA and other membrane chemistry
- Wide range of thickness
- Reinforced
- Discrete and areal defects
- Automated full-roll metrics

Example of full-roll defect metrics (simulated data)
Optical QC to detect defects in membrane material

Objective:
• Build and demonstrate a prototype system that simultaneously measures:
  • Defects in a moving membrane web
  • Membrane thickness over the full web width

Accomplishment:
• Scaled up NREL technique to detect pinholes in membrane material; defects detected down to 10 µm at 100 ft/min

Plans:
• Scale system to real-time measurements of thickness over 24-inch web
• Demonstrate reliability of packaged system for defect detection on two industrial weblines

The MantisEye film inspection station

Cross-polarized near-UV-Vis optical arrangement

Example Defects:
- Bubble
- Pinhole – white hole

R2R film inspection station with Automated Dynamics machine vision system commissioned February 28
Membrane Thickness Imaging

Methodology

- Use interference fringes in reflectance spectra
- Perform Fourier Transform to find thickness in each pixel
- Relevant for membranes
  - With and without reinforcement
  - While membrane is still attached to liners

Concept: interference fringes (right), Fourier Transform (below)

Scan of 4 samples of different thickness

Thickness image of 25 µm membrane taken at 5 foot per minute
Defects in Electrodes

- Detection of a variety of defect types in various electrode structures (10 ft/min)

Rupnowski et al., ASME PowerEnergy 2015-49212.
Overview of specialized in situ diagnostics developed to understand how defects in MEA materials affect cell performance and lifetime.
Example: Effects of Membrane Pinhole

- No observable impact in total cell initial performance (vs. pristine)
- However, we observe initial performance loss local to the pinhole (segmented cell), and
- Increased degradation in performance over time (drive cycle), and
- Earlier failure (accelerated stress test)

Optical image of mechanically punctured pinhole prior to spraying electrode (left), LBNL XCT image after MEA fabrication (right)

36 x 87 μm

Anode and cathode (0.2/0.2 mg Pt cm\(^{-2}\)) sprayed onto NRE212 membrane after pinhole is made
We need this suite of tools to fully understand the effects of electrode irregularities.
Example: Impact of Membrane Thickness

- Cathode centered bare spots
- Comparing effect on 25 µm vs. 50 µm membranes
- Not much difference in initial performance
- Impact during drive cycle much greater for thinner membrane
- Time to failure: NRE212 > NRE211 pristine > NRE211 with irregularity
Example: Effect of Electrode Thin Spots

- Compare effects of thin spots in the cathode to bare spots
- Irregularities are 2.5% of 5 cm² active area, 50% thickness reduction (vs. 100%)
- Thin spots cause similar performance degradation as bare spots
- Both thin and bare spots cause minor reduction in performance on 50 µm membrane
- Both thin and bare spots cause catastrophic loss of performance on 25 µm membrane

0.2 mg Pt/cm² nominal loading
Overview of efforts to understand the foundational relationships between electrode materials, processing methods, and performance
Study Transition from Lab-Scale to Scalable Electrode Production

Lab Scale – Ultrasonic Spray

Used to demonstrate new materials and for fundamental studies

Conditions
• Dilute ink (~0.6 wt% solids)
• Ultrasonic mixing
• Sequential build up of layers
• Heated substrate
• Vacuum substrate

Large Scale – Roll-to-Roll

Needed to demonstrate scalability of materials, MEA/cell designs, and industrial relevance

Conditions
• Concentrated ink (~4.5-15 wt% solids)
• Shear mixing
• Single layer
• Room temp. substrate
• Convective drying
Rheology of Carbon and Pt/C Inks

The influence of Pt appears to be dependent on the surface or internal location of Pt

- Addition of ionomer stabilizes carbon particles
- Transition from shear thinning to Newtonian
- Same trend for Pt/Vulcan
- However, ionomer does not stabilize Pt/HSC in same way
• Iridium oxide (IrOx) catalyst, without ionomer, displays similar agglomeration behavior to Pt/Vu, though at much higher weight fractions

• Addition of ionomer has the same stabilizing effect as for Pt/Vu
  • Only a small amount of ionomer is needed to stabilize the catalyst particles against agglomeration
# Gravure Coating Parametric Studies

- Studied the impact of roller volume factor and roller speed ratio on coatability, defect formation, and achievable loading.

## Gravure Cylinder Mesh and Volume Factor

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<td>80 lines/inch 67 cm$^3$/m$^2$</td>
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Gravure Cylinder Mesh and Volume Factor

- Achieved performance comparable to lab-standard spray coating.

- Gravure Coating Parametric Studies

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Pt/HSC, 50 wt% Pt, Nafion 1000 EW, 3.2 wt% PtC, 1.2 I:C, SGL 29BC

- Achieved performance comparable to lab-standard spray coating.

- Gravure Coating Parametric Studies

- Studied the impact of roller volume factor and roller speed ratio on coatability, defect formation, and achievable loading.
Contributors

• NREL
  – Peter Rupnowski
  – Brian Green
  – Guido Bender
  – Adam Phillips
  – Scott Mauger
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Question and Answer

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Thank you

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Technical Back-Up Slides
RIF Defect Detection Examples

10 fpm, 0.0625 cm², 50% electrode thickness reduction

10 fpm, 0.0625 cm², 25% electrode thickness reduction
Defects in Membranes on an Electrode

- Detection of a variety of defect types in electrode-containing structures and MEAs (10 ft/min)

Yellow boxes indicate automated detection
Pinhole images are at 10X magnification

Electrode on diffusion media with laminated membrane:
Detection of cuts, scratches

150 µm pinholes

Left: 50 µm debris (microscope); Right: specular reflectance imaging
Overview of In Situ Techniques

**Does an irregularity in an MEA component material impact:**
(a) initial performance, (b) performance over time, and/or (c) location or timing of failure?

**Initial performance (local and total cell)**
- PCB-based 50 cm$^2$ segmented cell with 121 segments
- Measure spatial and total cell performance at wet and dry conditions
- Analyze performance effects induced by irregularities using absolute and differential methods

**Prolonged performance**
- Use the “New European Drive Cycle”
- Measure total cell polarization data after every 72 cycles
- Analyze performance degradation induced by irregularities

**Onset of failure**
- Use a combined chemical/mechanical AST (based on DOE protocols)
- Use 50 cm$^2$ cell in NREL-developed test hardware for in situ testing and quasi-in situ spatial H$_2$ crossover
- Monitor failure development with OCV and H$_2$ crossover limiting current as indicators
- Determine “end of life” using 2020 FCTT crossover target as criteria
- Analyze impact of irregularity on location of failure(s) and lifetime
Effect of Solvent

- High water-content solvent causes stronger interparticle repulsion
- Stronger repulsion leads to smaller agglomerates in the ink and smaller particles in the coated electrode
- Smaller particle size leads to improved oxygen transport and performance

High water content in Pt/HSC inks appears to lead to a morphology that improves performance
RIF on R2R Screen-printed GDEs

- Demonstrated detection of thick and thin electrode defects
- Demonstrated detection of loading variations sample-to-sample
TPRE Web-line Experiment

• Use RIF with non-flammable gas to enable advection of hydrogen through pinhole and catalytic reaction

• Proved concept, but observed small thermal response

• Working on improved method