U.S. DEPARTMENT OF ENERGY

Office of ENERGY EFFICIENCY & RENEWABLE ENERGY

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

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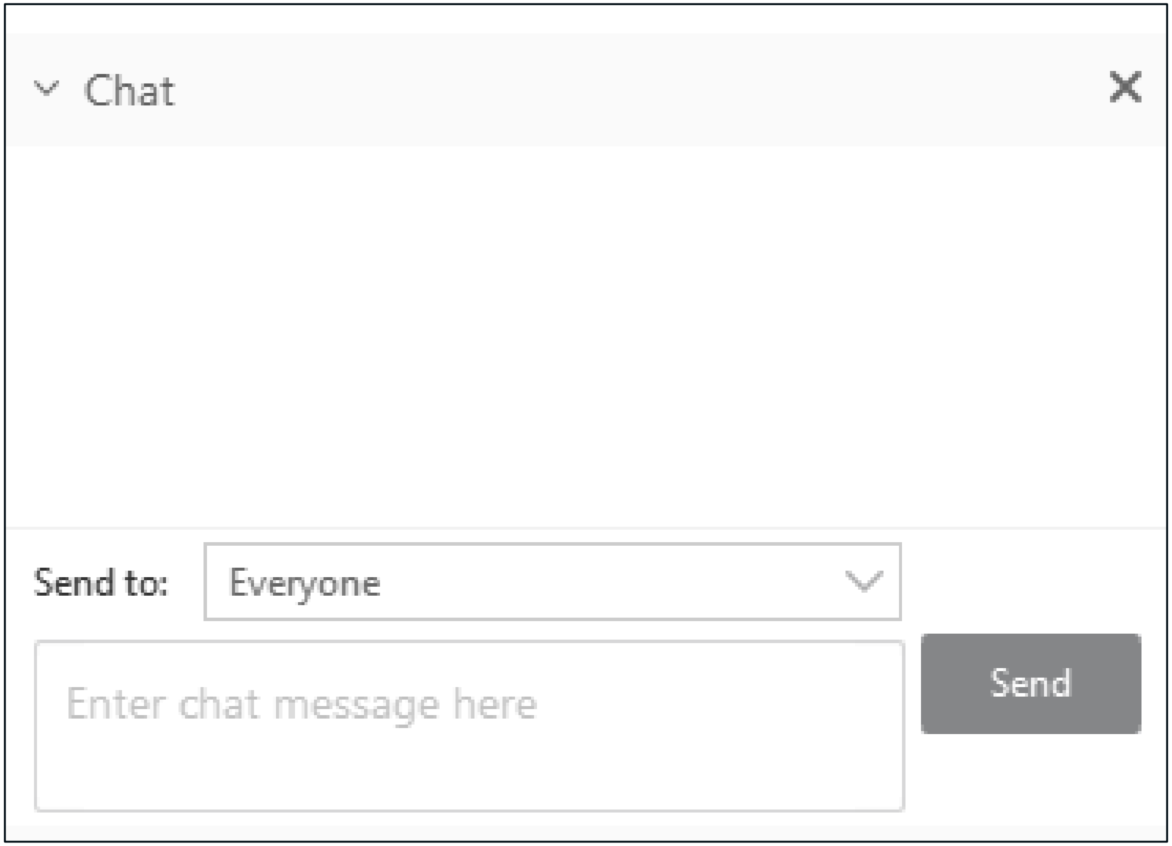
Fuel Cell Technologies Office Webinar

August 22, 2018

Question and Answer

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



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

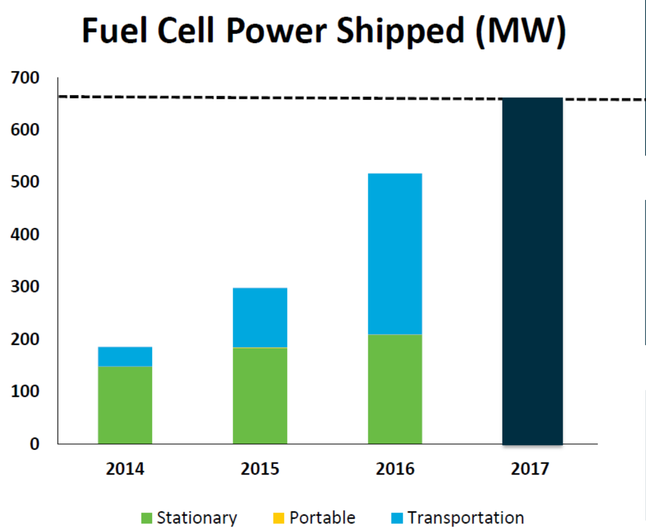
Outline

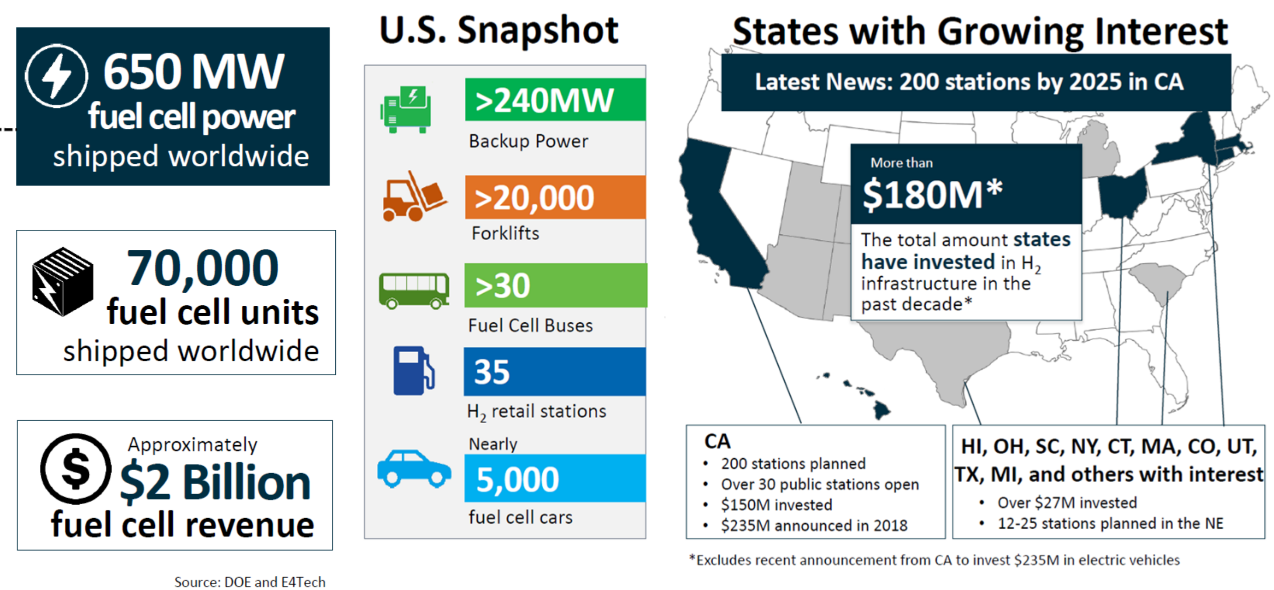
- Overview of the manufacturing context and challenges for membrane electrode assembly (MEA) materials
- Detailed discussion of work to develop real-time in-line characterization techniques
- Overview of specialized in situ diagnostics developed to understand how defects in MEA materials affect cell 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

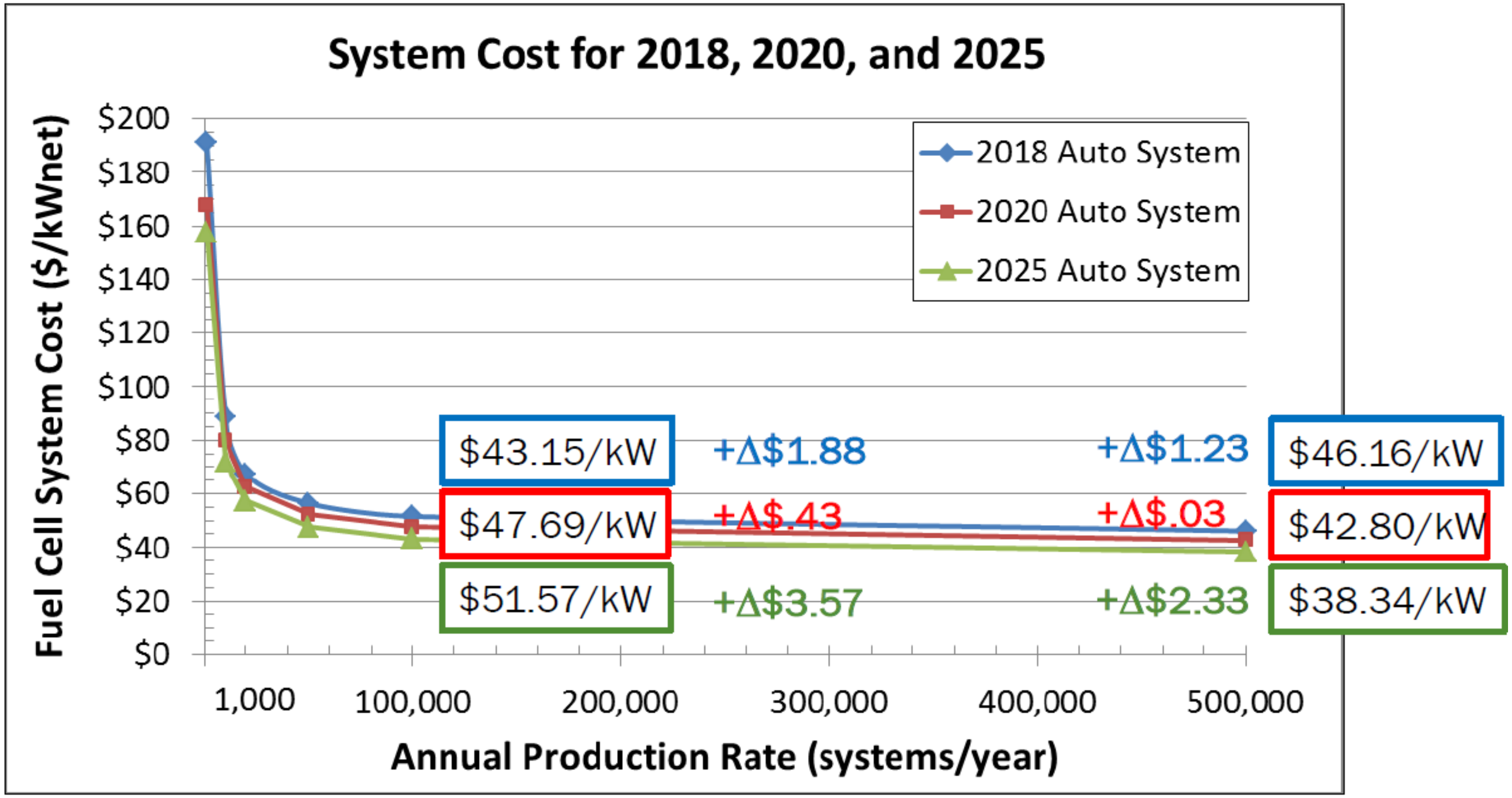
- Markets for multiple applications are expanding
- Units, power output, revenue increasing
- Increased state activity





S. Satyapal, "Hydrogen and Fuel Cell Program Overview," Hydrogen and Fuel Cell Program Annual Merit Review, June 13, 2018.

Estimated Costs from Techno-economic Analysis



B. James, "2018 Cost Projections of PEM Fuel Cell Systems for Automobiles and Medium-Duty Vehicles," FCTO Webinar, April 25, 2018.

- 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

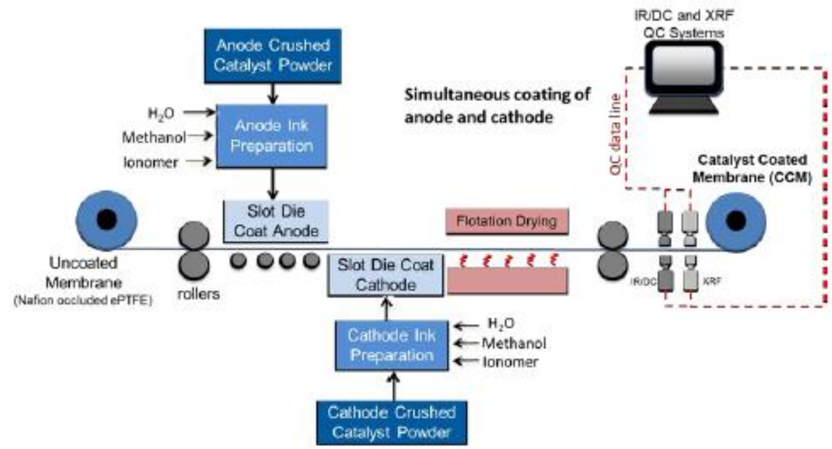


Figure 80. Horizontal dual-sided simultaneous slot die coating of de-alloyed $PtNi_3/C$ catalyst process flow diagram

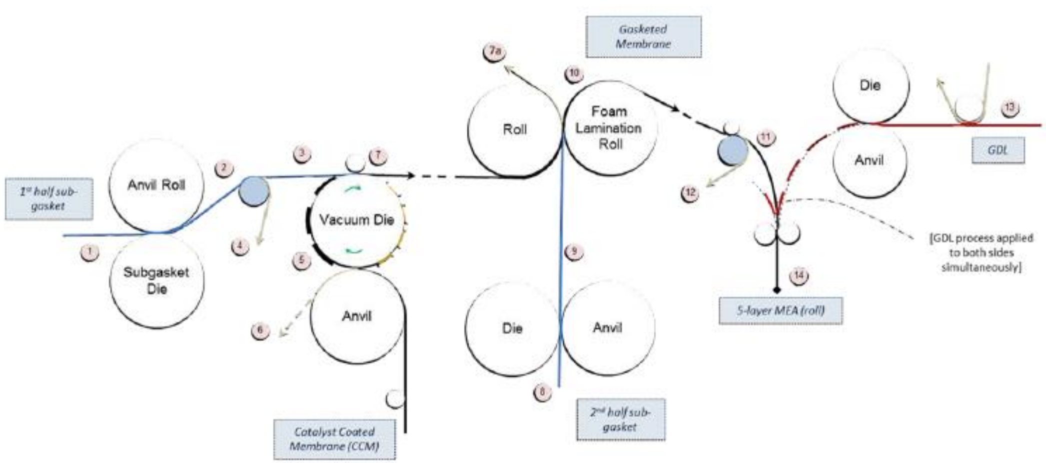


Figure 92. Roll-to-roll sub-gasket application process

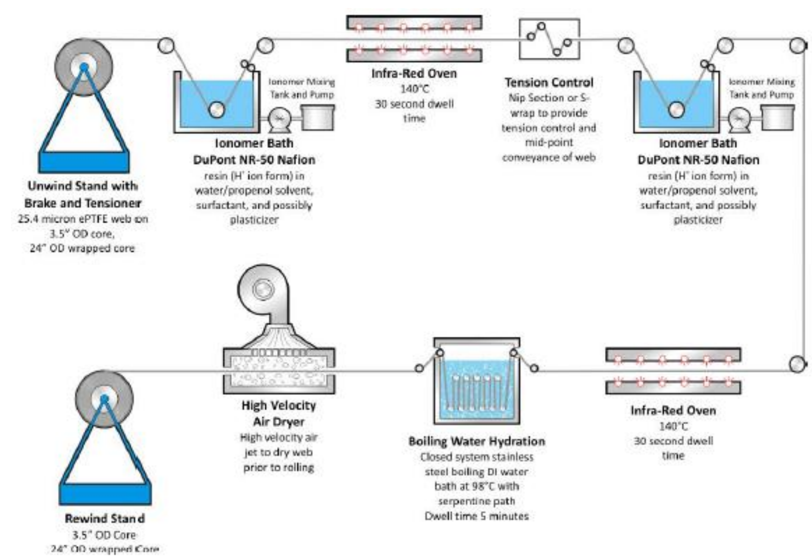
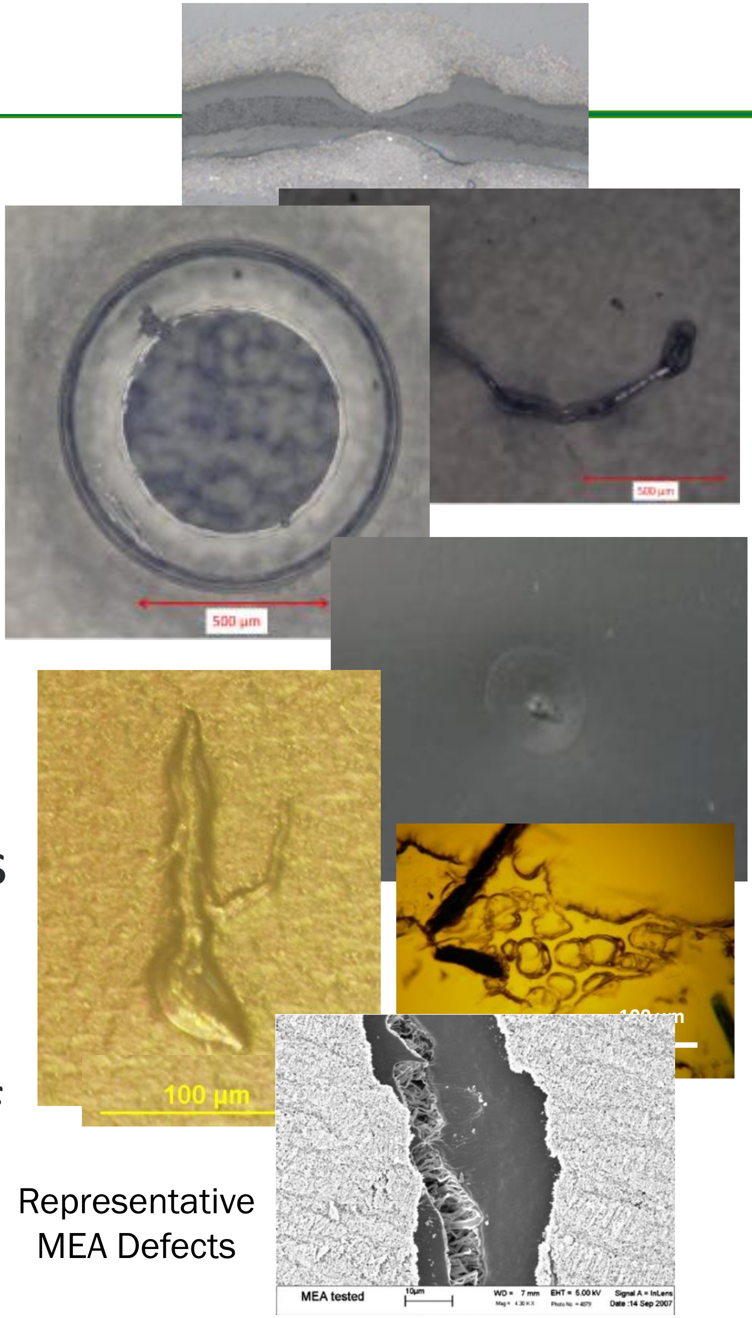


Figure 65. Membrane fabrication process diagram

B. James et al., "Mass Production Cost Estimation of Direct H2 PEM Fuel Cell Systems for Transportation Applications: 2016 Update ," January, 2017.

Premise for NREL Activity

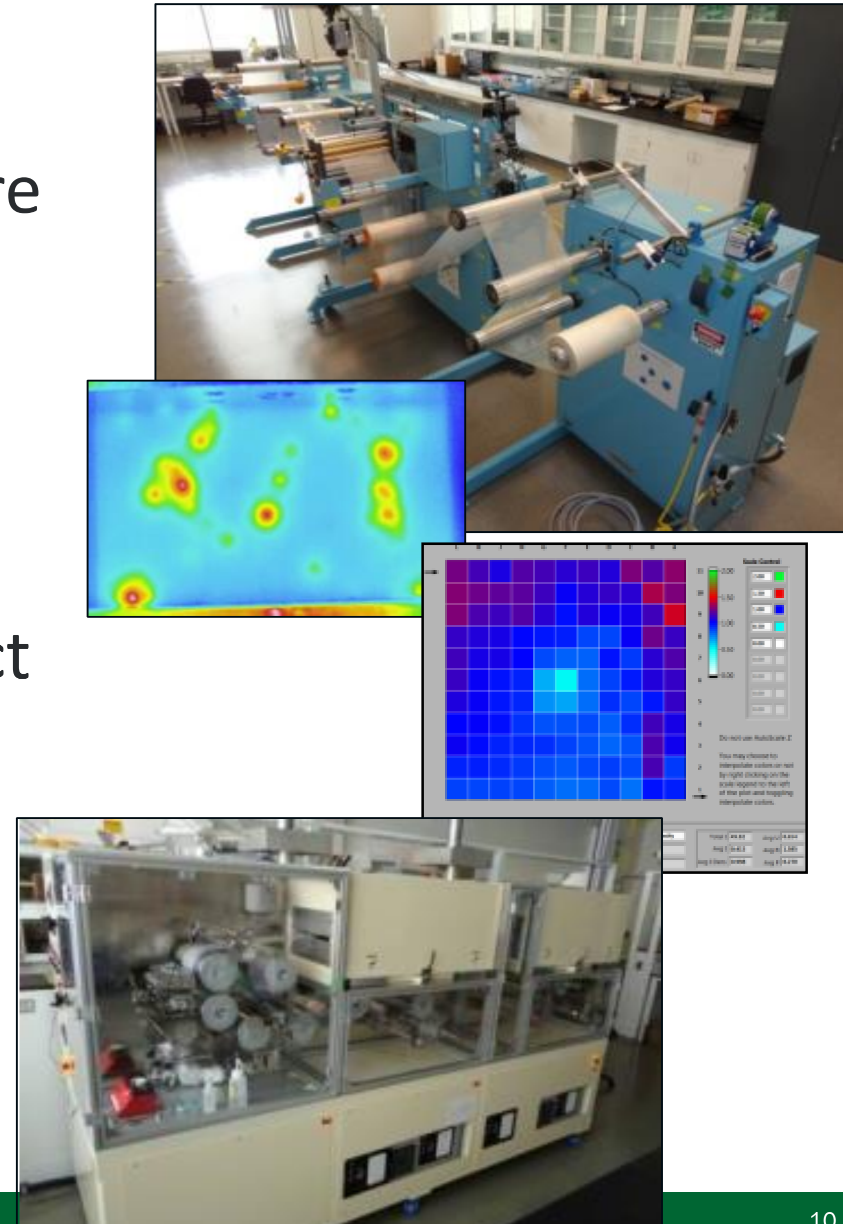
- Membrane electrode assemblies (MEAs) for PEM fuel cells must be made using scalable processes to enable high volume and low cost
- For PEM materials, these processes are typically atmospheric pressure and solution-based, given the heterogeneous polymeric and particle-based nature of the materials
-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



Representative MEA Defects

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

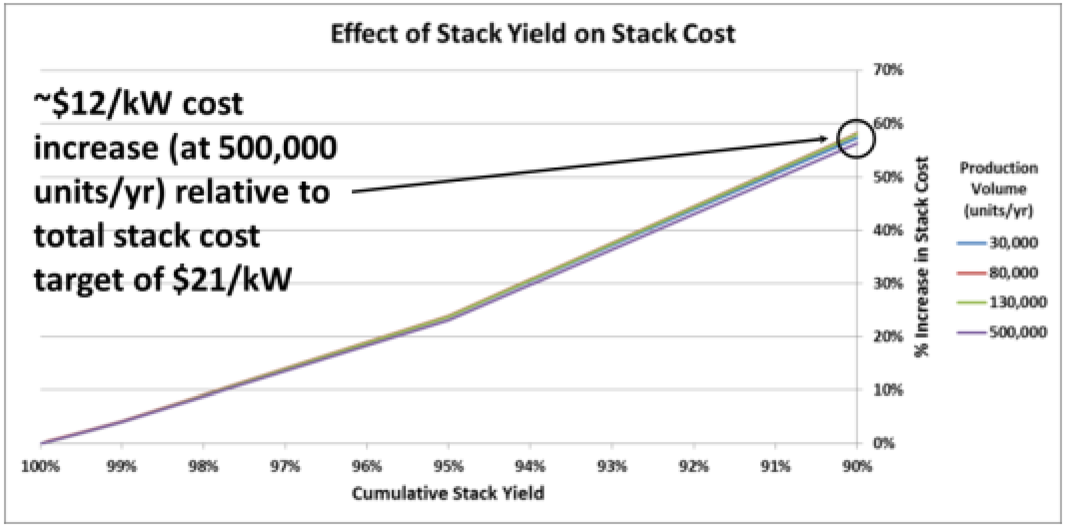
*Approach: **Work with industry** to develop knowledge and techniques to improve quality and reduce manufacturing costs of MEA materials*

- 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

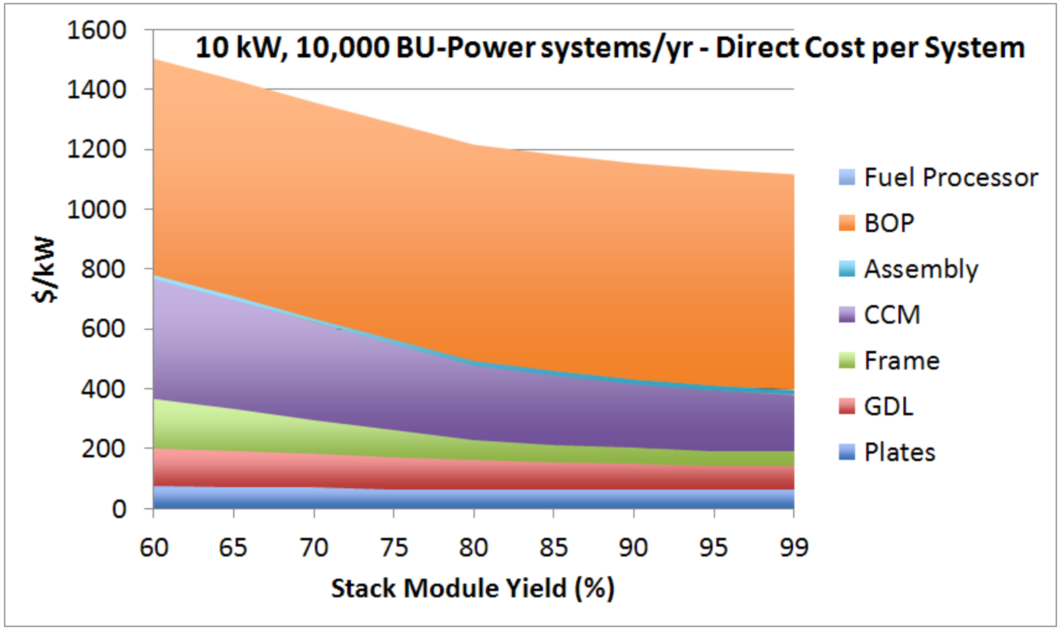
Detailed discussion of work to develop real-time in-line characterization techniques

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



Importance Reflected in FCTO MYR&D Plan

From the MYR&D Plan Manufacturing Section*

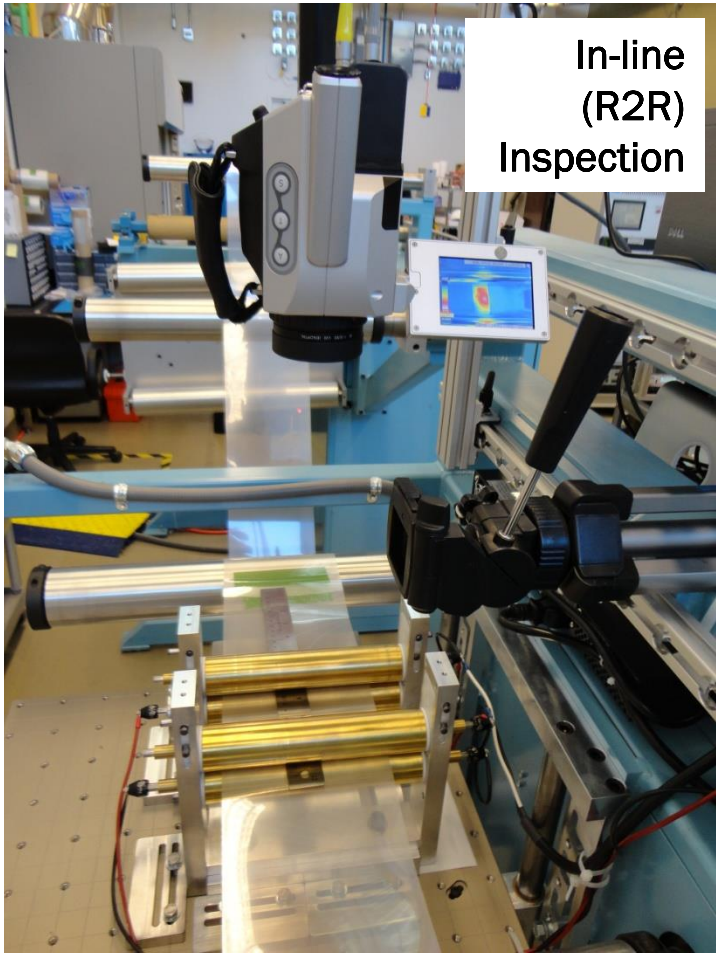
Task 5: Quality Control and Modeling and Simulation	
5.1	Establish models to predict the effect of manufacturing variations on MEA performance. (4Q, 2016)
5.2	Demonstrate improved sensitivity, resolution, and/or detection rate for MEA inspection methods. (4Q, 2016)
5.3	Validate and extend models to predict the effect of manufacturing variations on MEA performance. (4Q, 2017)
5.4	Design and commercialize an in-line QC device for PEMFC MEA materials based on NREL's optical reflectance technology. (4Q, 2017)
5.5	Develop correlations between manufacturing parameters and manufacturing variability, and performance and durability of MEAs. (4Q, 2018)
5.6	Demonstrate methods to inspect full MEAs and cells for defects prior to assembly into stacks in a production environment. (4Q, 2018)
5.7	Develop areal techniques to measure platinum (and other catalyst metals) quantitatively in an MEA. (4Q, 2018)
5.8	Implement demonstrated in-line QC techniques on pilot or production lines at PEMFC MEA material manufacturers. (4Q, 2020)
5.9	Develop imaging-based methods for 100% inspection of PGM loading in electrodes. (4Q, 2020)

Task 1: Membrane Electrode Assemblies	
1.1	Develop processes for highly uniform continuous lamination of MEA components. (4Q, 2017)
1.2	Develop processes for direct coating of electrodes on membranes or gas diffusion media. (4Q, 2017)
1.3	Develop continuous MEA manufacturing processes that increase throughput and efficiency and decrease complexity and waste. (4Q, 2017)
1.4	Demonstrate processes for direct coating of electrodes on membranes. (4Q, 2019)
1.5	Demonstrate processes for highly uniform continuous lamination of MEA components. (4Q, 2019)
1.6	Develop fabrication and assembly processes for PEMFC MEA components leading to an automotive fuel cell stack that costs $20/kW. (4Q, 2020)

** MYR&D Plan Manufacturing Section currently being updated to reflect new office structure and milestones*

Enable Quality Inspection During R2R

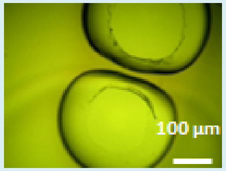
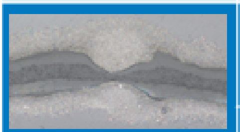
Manufacturing Fuel Cell Manhattan Project Presented by the Benchmarking and Best Practices Center of Excellence, ACI Technologies, 2012.



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

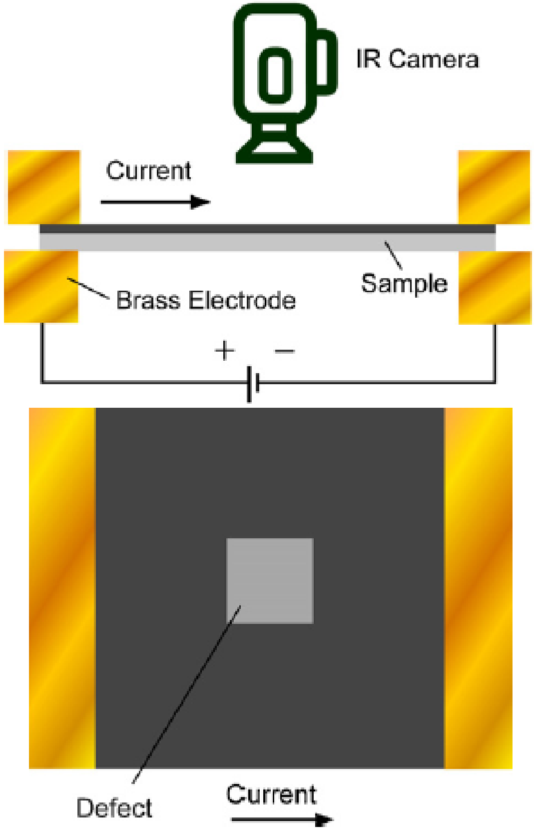
Material	Defects	Detection	Resolution (x-y)	Status
Membrane 	Pinholes, bubbles, scratches, agglomerates, etc.	Optical reflectance/transmission	micrometers	Demonstrated on web-line
	Thickness variation (mapping)	Optical absorption	micrometers	Demonstrated on motion prototype
		Optical reflectance (interference fringe)	millimeters	In development
		Thermal scanning	millimeters	In development
GDL	Scratch, agglomerate, fibers	IR/direct-current	millimeters	Demonstrated on web-line
Electrode 	Surface defects	Optical reflectance	micrometers	Demonstrated on motion prototype
	Voids, agglomerates, cracks, thickness/loading indirectly	IR/direct-current (for CCMs or decals)	millimeters	Demonstrated on web-line
		IR/reactive impinging flow (for GDEs or CCMs)	millimeters	Demonstrated on web-line
	Loading (mapping)	Optical reflectance/transmission	millimeters	In development
	Shorting	Through-plane IR/direct-current		Demonstrated on web-line
	Membrane integrity	Through-plane reactive excitation	pinholes as small as 90 μm	Demonstrated on static test-bed

IR techniques for catalyst-coated membrane (CCM) electrode uniformity/defects and shorting

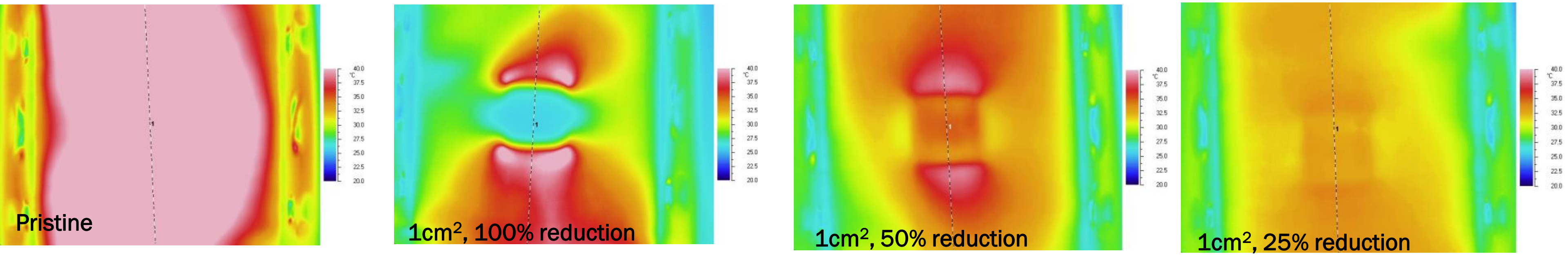
IR/Direct-current (IRDC) Excitation Technique

Methodology:

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

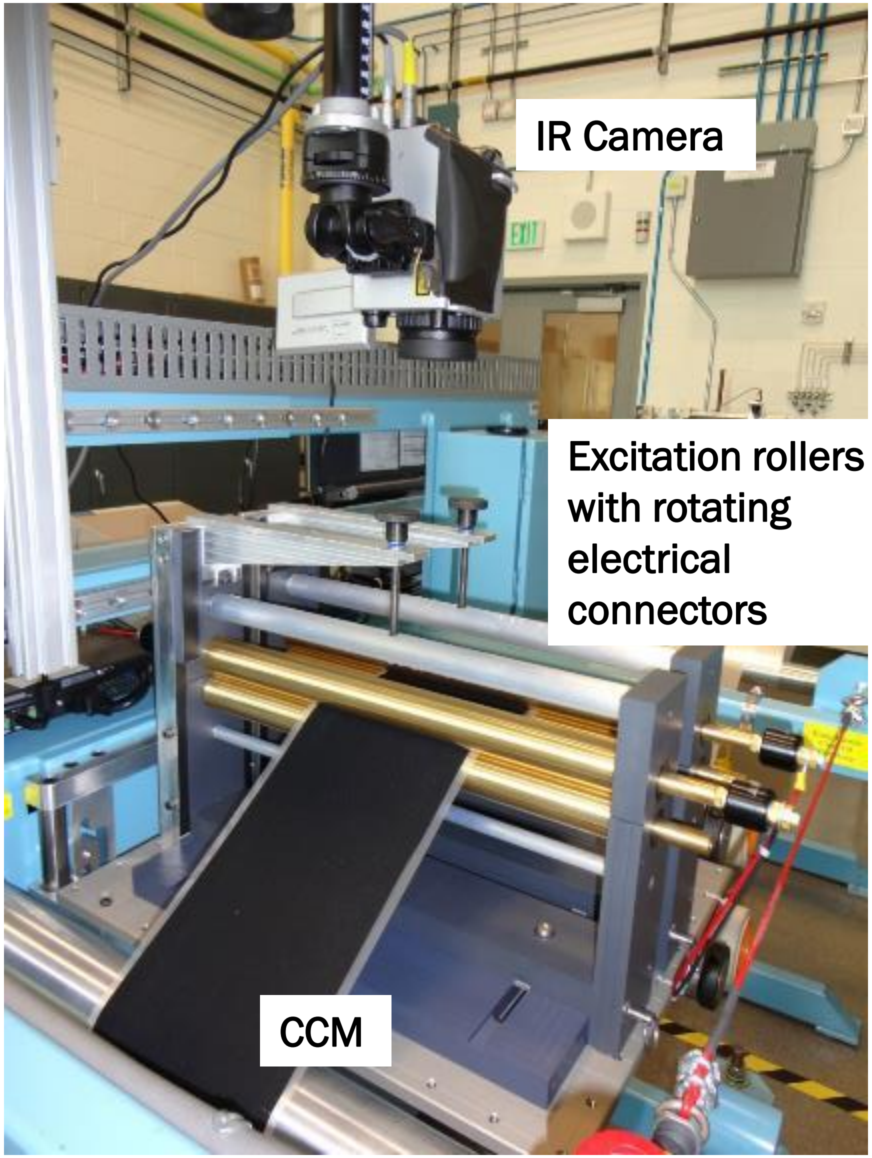


All samples: 25 cm^2 active area, 5 second excitation at 21V DC; % reduction of the thickness of the catalyst layer within the area of the defect



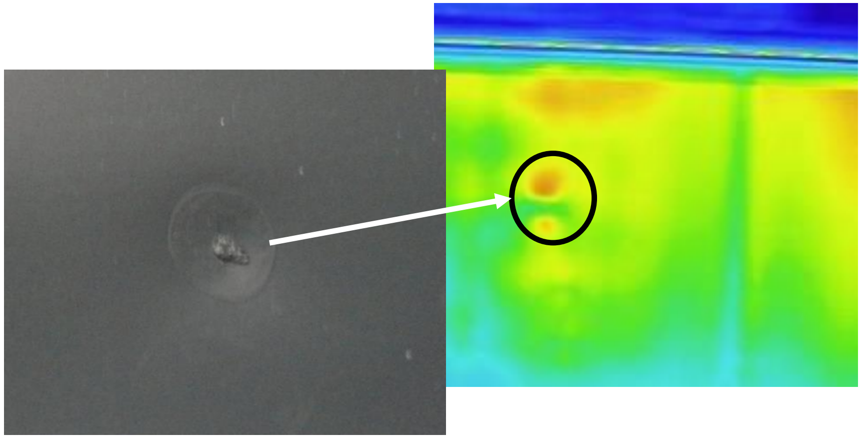
Aieta et al., *J. Power Sources,* **211** (2012), p.4-11.

Setup for IRDC on NREL Web-line

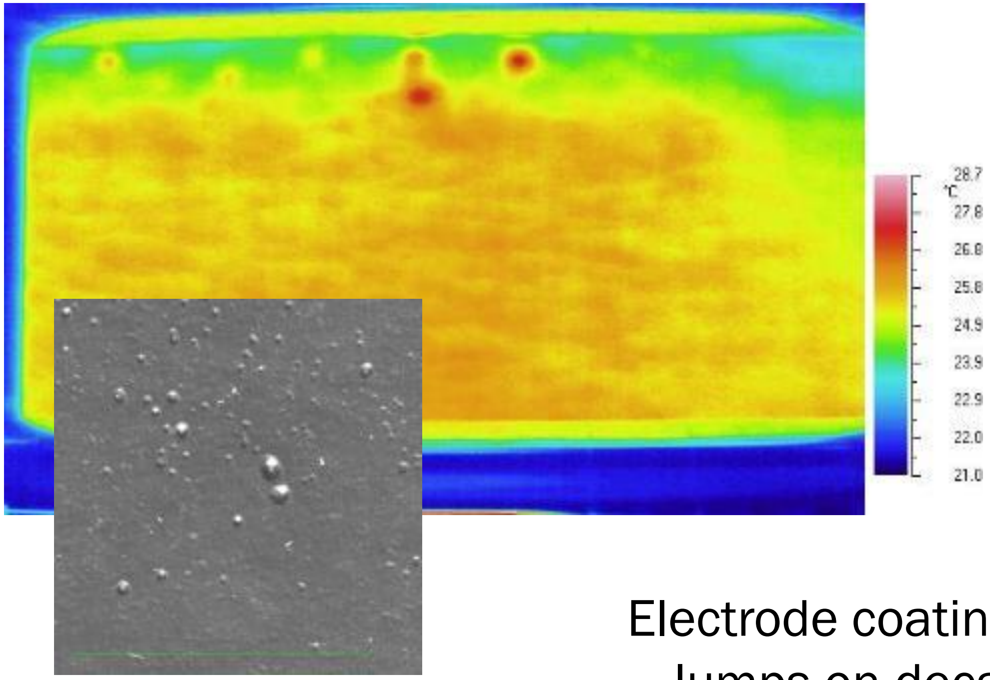


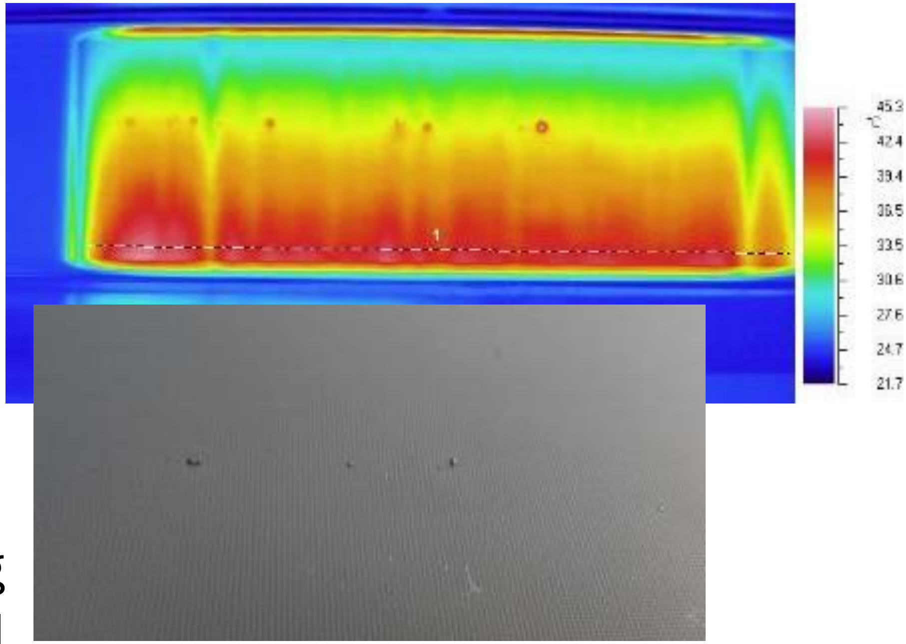
IRDC Defect Detection Examples

Simulated droplets from coating die



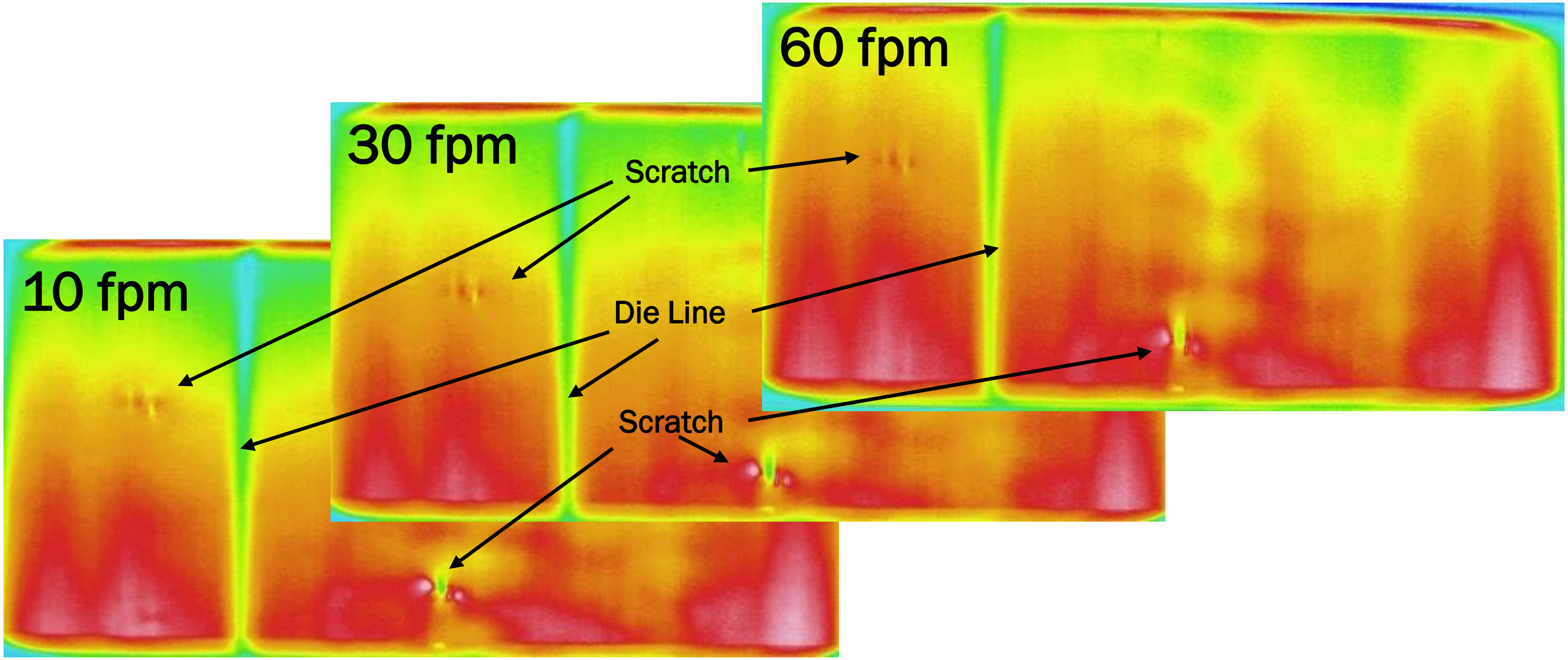
Carbon debris applied to GDE, under a laminated membrane





Electrode coating lumps on decal

IRDC Effect of Line Speed



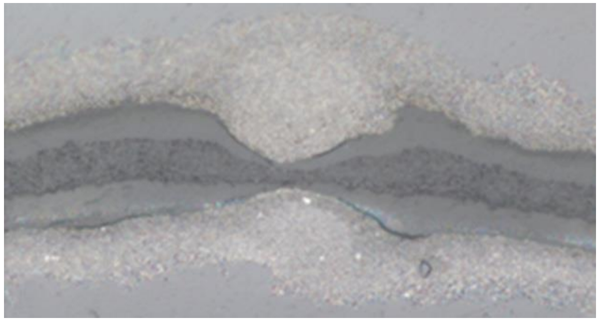
We modulated excitation conditions to give equivalent detection over a range of line speeds

IRDC was demonstrated on an industry partner R2R CCM manufacturing line

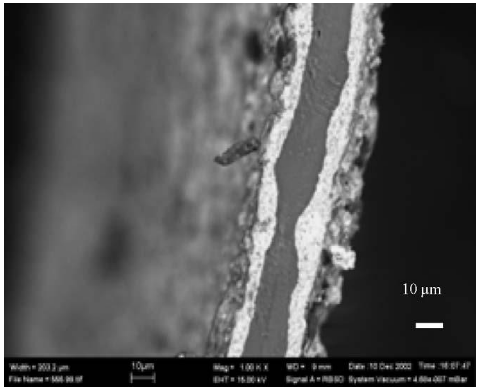
Through-plane IRDC Technique

Methodology

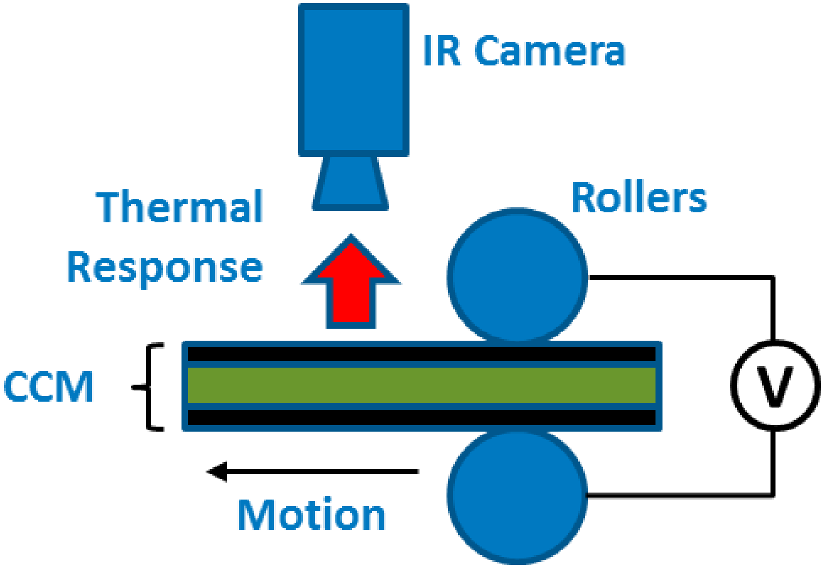
- Apply voltage to rollers on both sides of CCM or MEA
- Shorting pathways allow current, causing resistive heating
- Rapid, areal identification of shorting locations



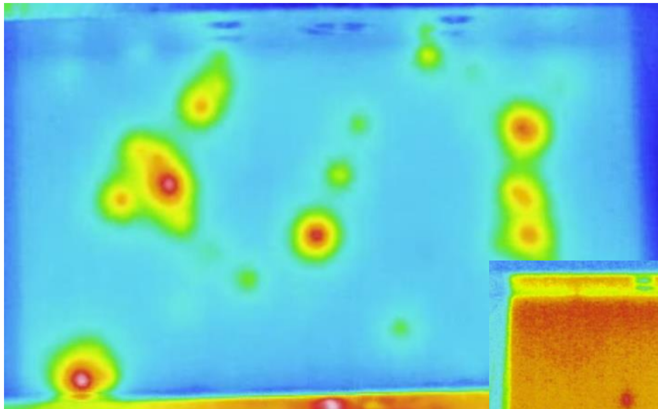
Gittleman et al., "Membrane Durability: Physical and Chemical Degradation", in *Modern Topics in Polymer Electrolyte Fuel Cell Degradation*, Elsevier, 2011, pp. 15-88.



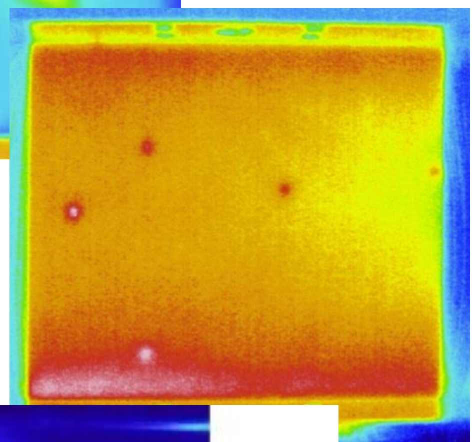
Kundu et al., *Journal of Power Sources*, **157** (2006) 650–656.



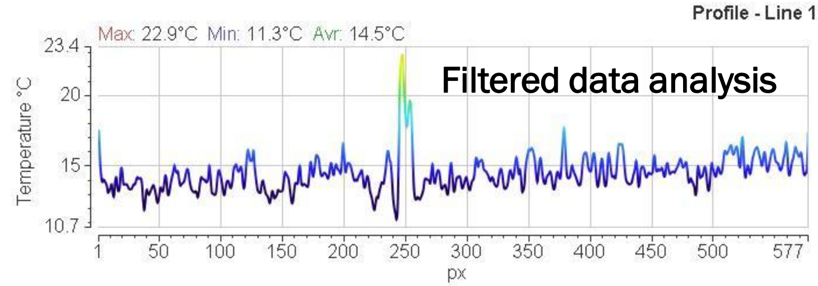
Through-plane IRDC Defect Detection Examples



GDM fibers

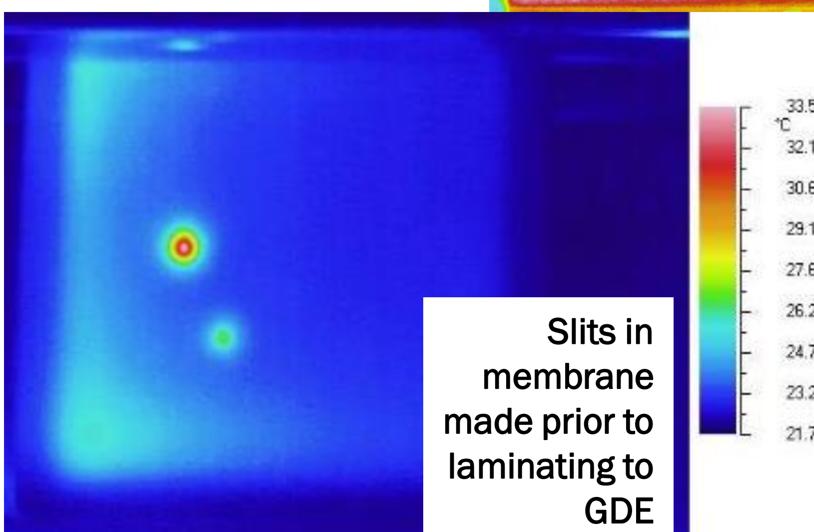


Catalyst layer lumps

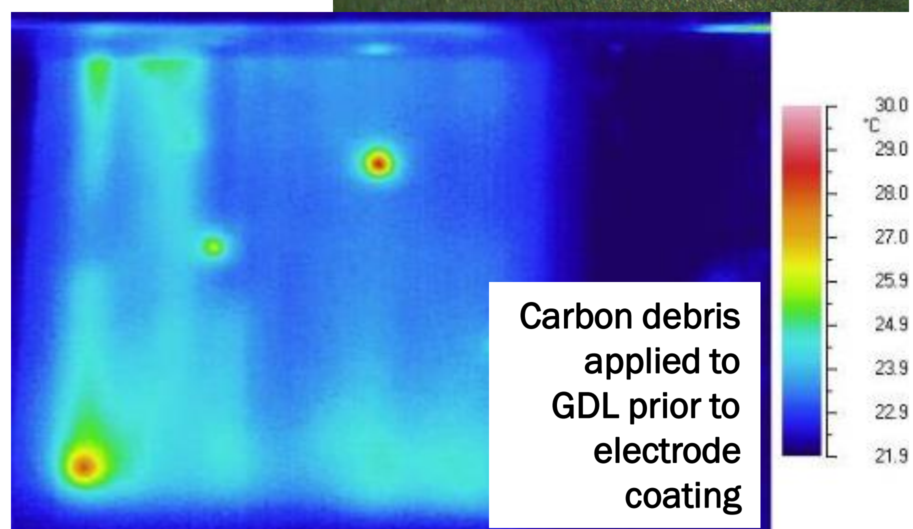


Filtered data analysis

Agglomerates in catalyst layer and resulting thermal signature due to shorting



Slits in membrane made prior to laminating to GDE



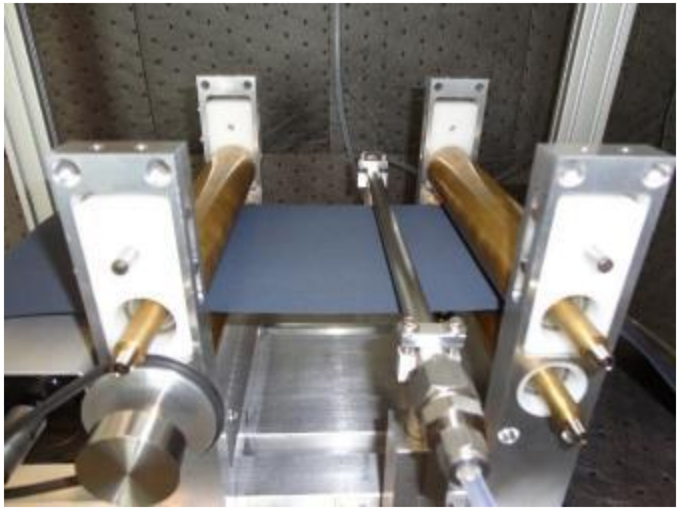
Carbon debris applied to GDL prior to electrode coating

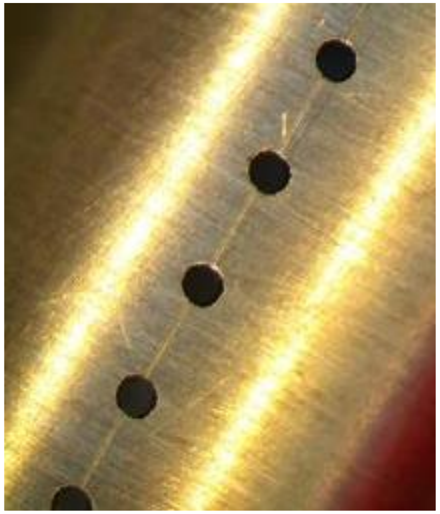
IR techniques for gas-diffusion electrode (GDE) electrode uniformity/defects, membrane integrity and measuring membranes in multi-layer constructions

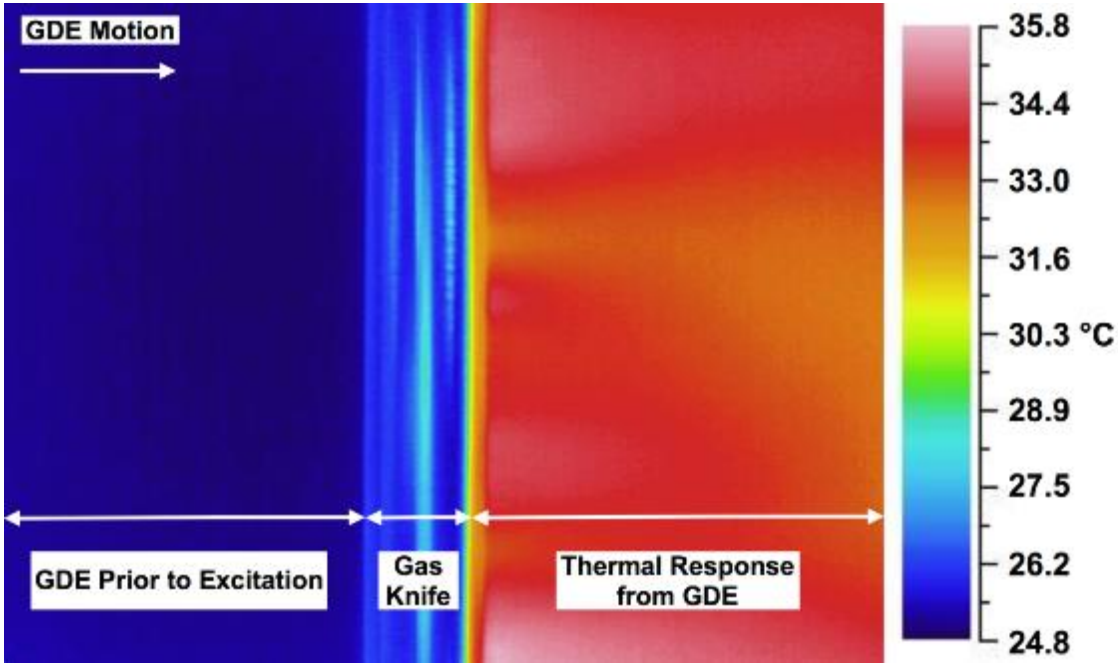
Reactive Impinging Flow (RIF) Technique

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



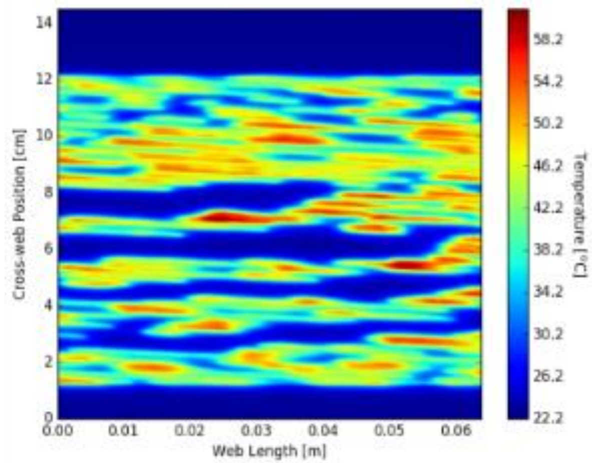




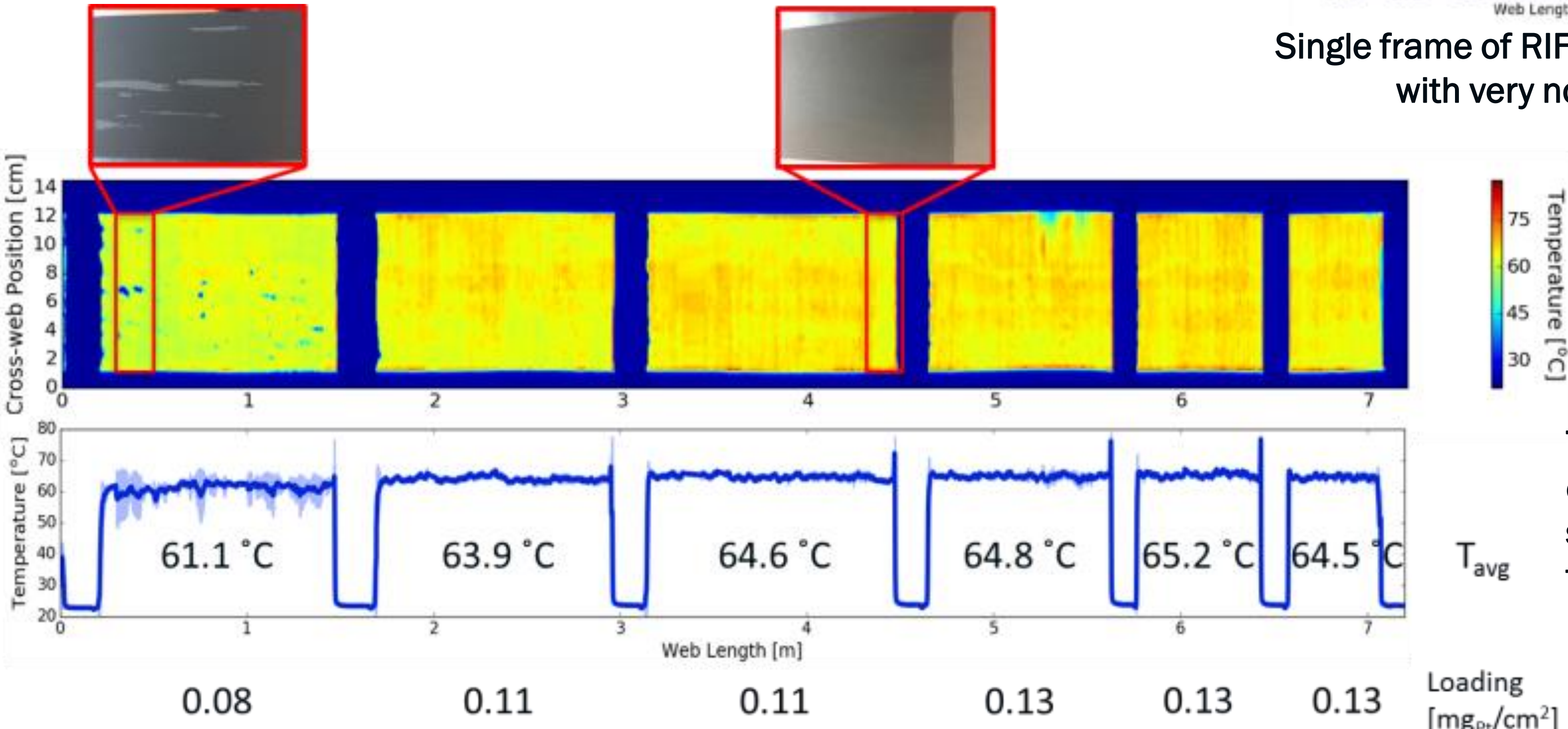
Setup for RIF on NREL Web-line

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

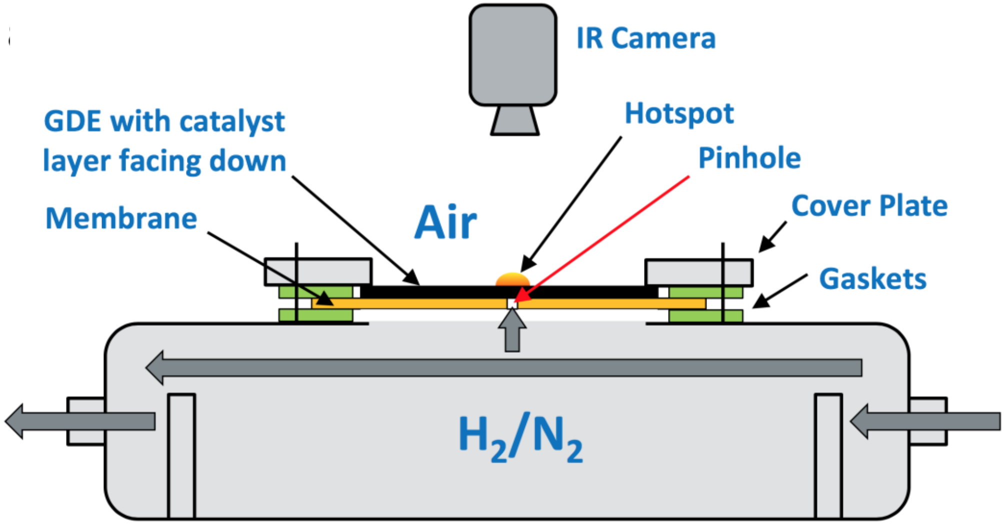


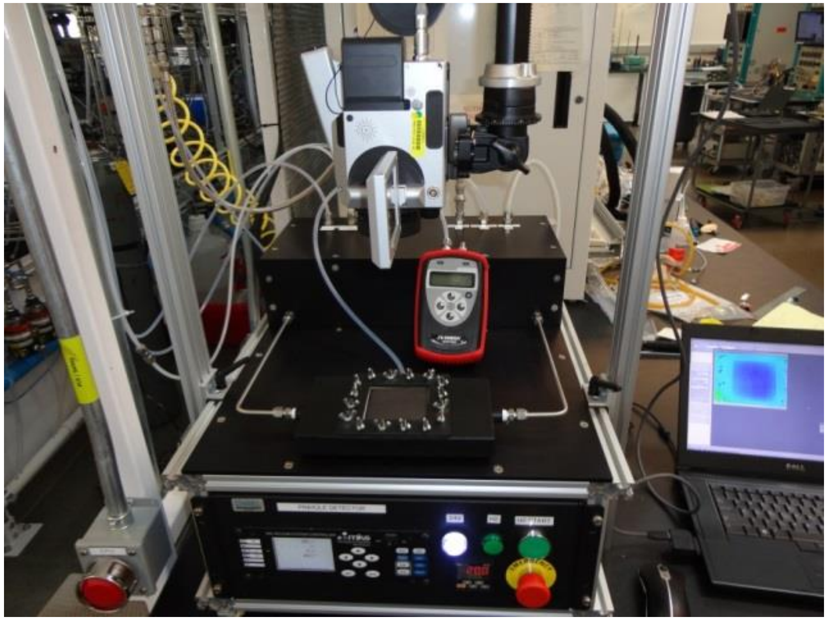
Thermal map of entire web, showing median temperature vs. loading (via XRF)

Through-plane Reactive Excitation (TPRE)

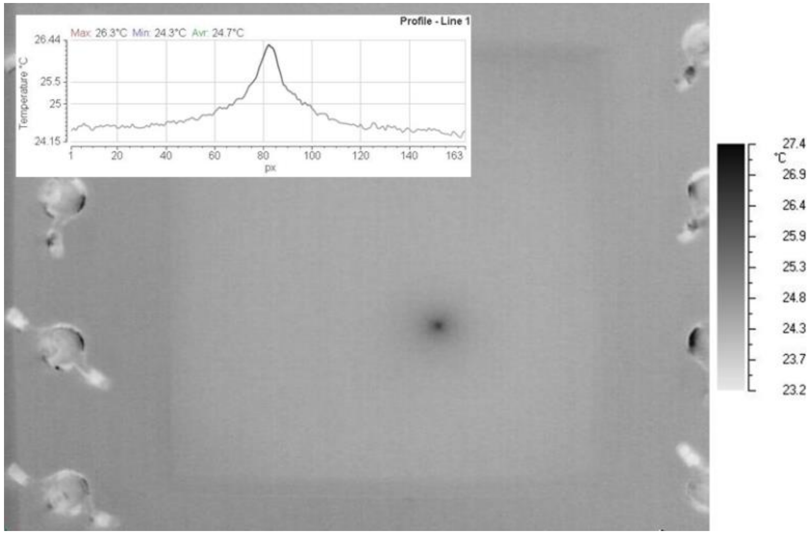
Methodology

- 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



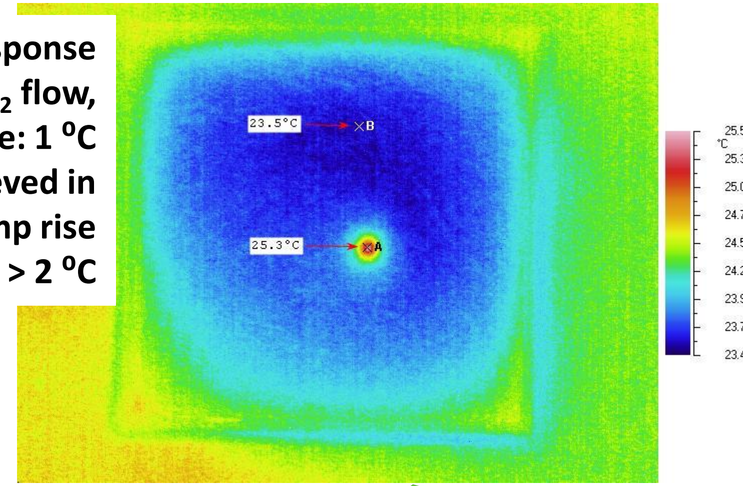


TPRE Pinhole Detection Examples

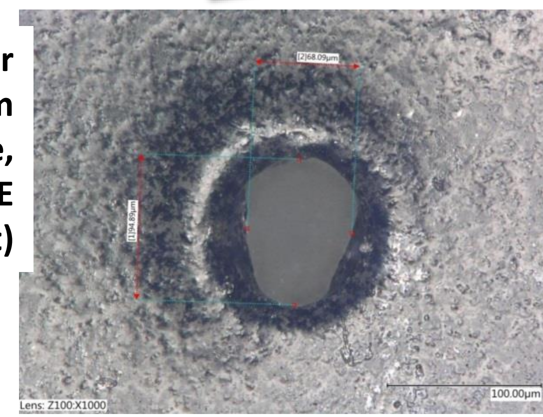


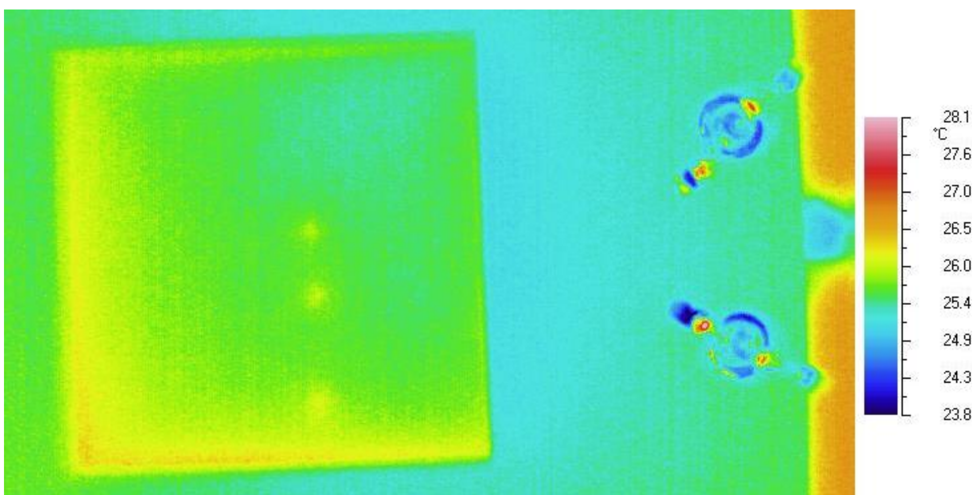
MEA with 120 µm pinhole

Thermal response with 0.5 lpm H_2 flow, 5 sec pulse: 1 ^oC temp rise achieved in 2 sec; Max temp rise > 2 ^oC



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



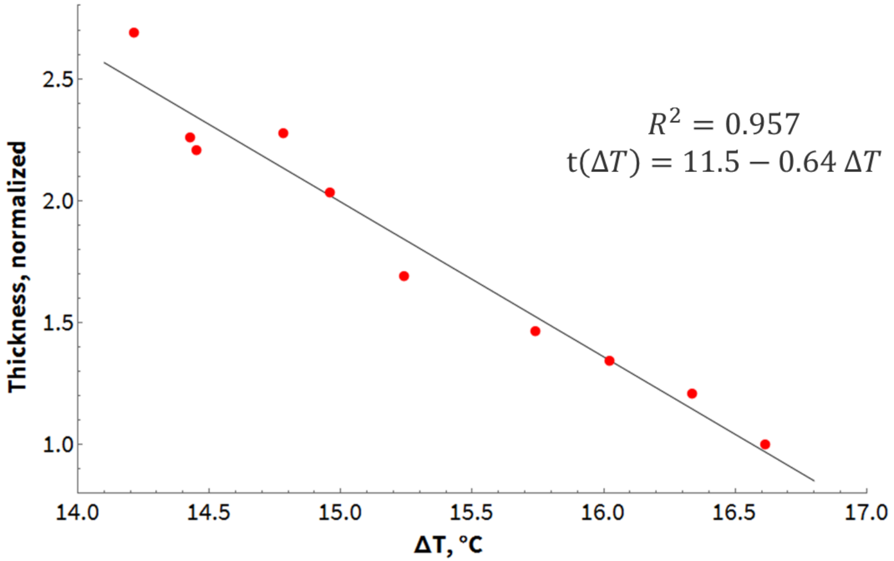


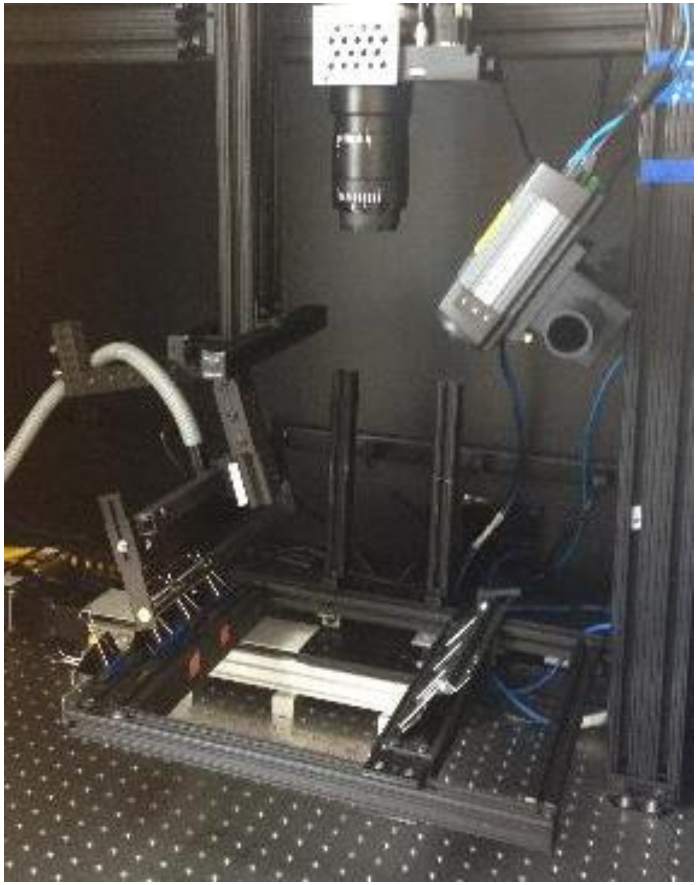
Half-cell with pinholes created using 25 µm tool ($\Delta T \approx 0.2$ °C)

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





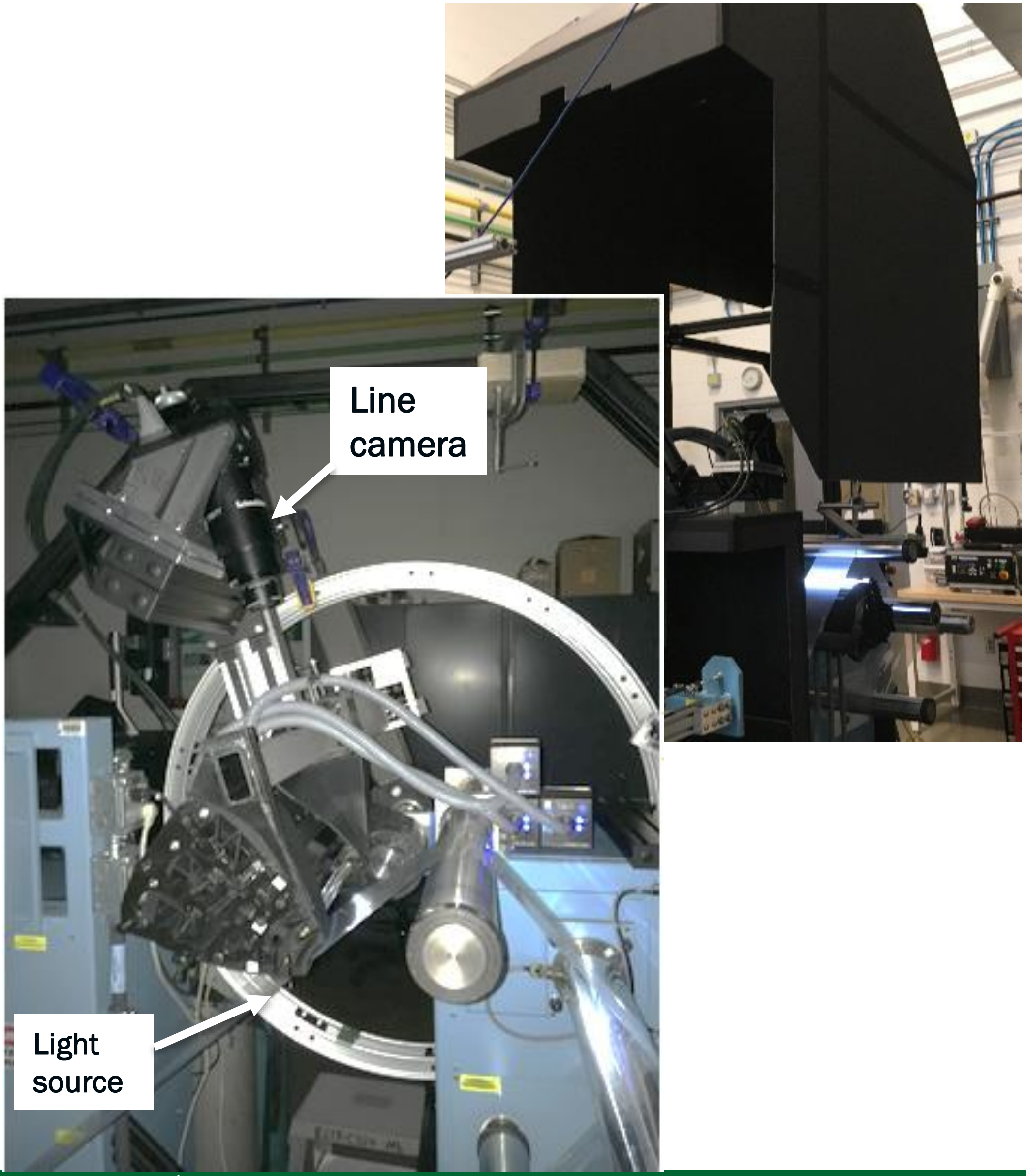
Measured membrane thickness in half-cell (membrane on GDE) samples

Optical techniques for membrane defects, membrane thickness imaging, and electrode surface defects

Optical Defect Inspection

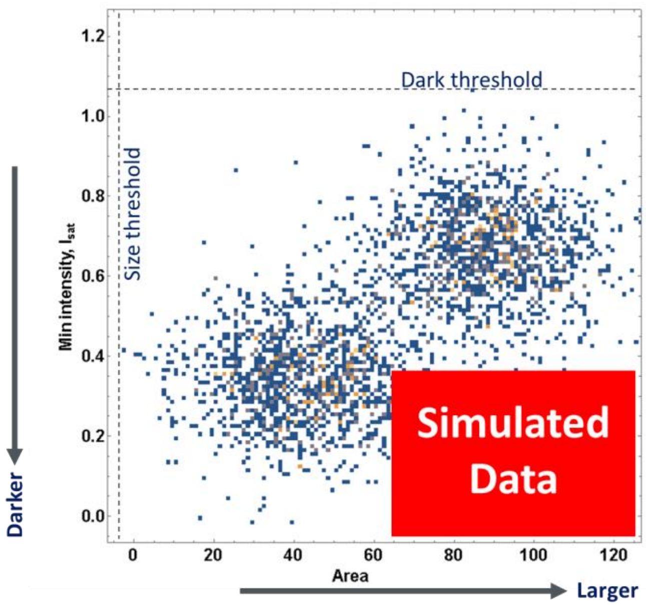
Methodology

- 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)



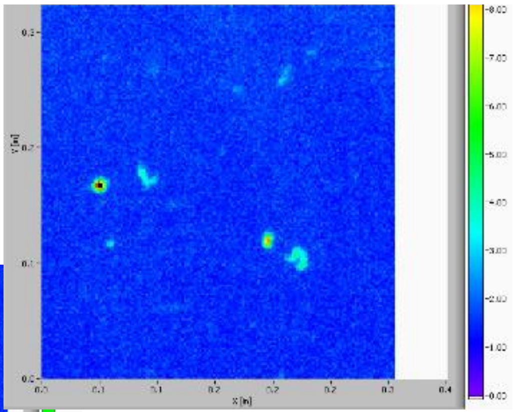
Membrane Defect Detection Examples

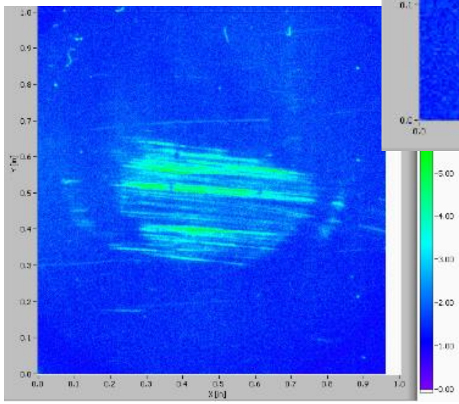
- PFSA and other membrane chemistry
- Wide range of thickness
- Reinforced
- Discrete and areal defects
- Automated full-roll metrics



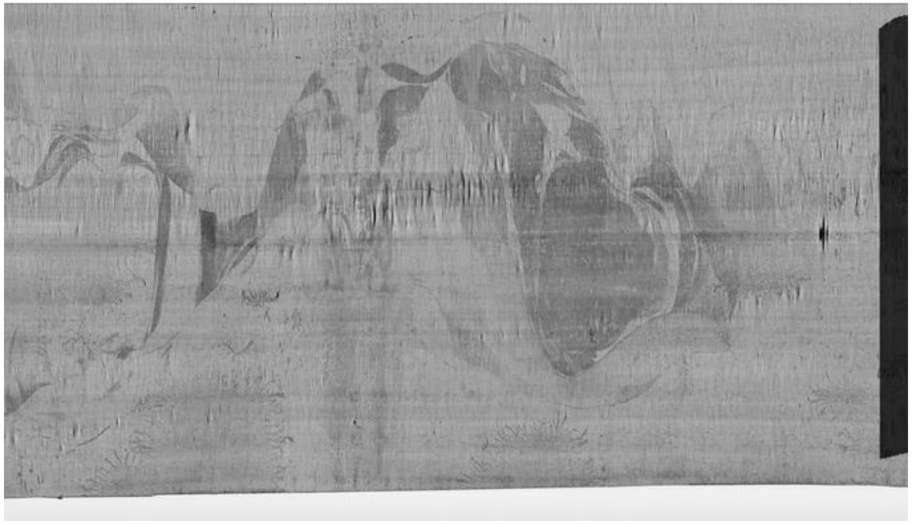
Example of full-roll defect metrics (simulated data)

Bubbles and scratches in PFSA membrane





Defects in composite membrane construction



Optical QC to detect defects in membrane material

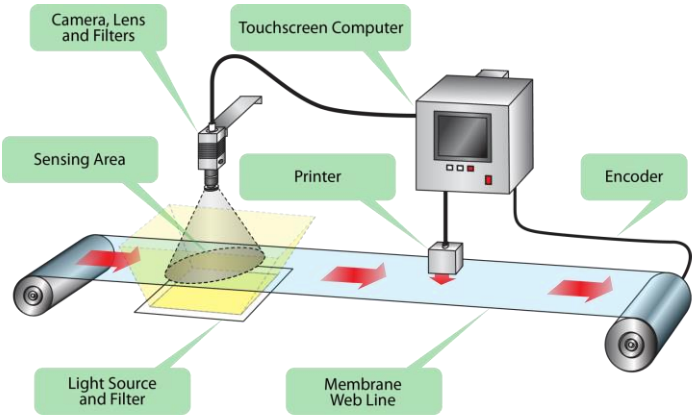
Objective:
- Build and demonstrate a prototype system that simultaneously measures:
  - Defects in a moving membrane web
  - Membrane thickness over the full web width

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

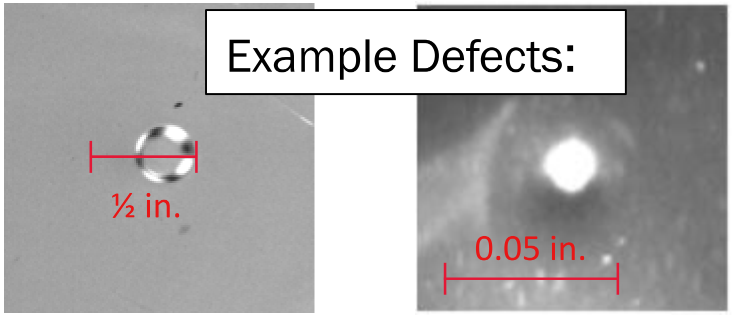
The MantisEye film inspection station

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



Cross-polarized near-UV-Vis optical arrangement

Example Defects:



Bubble

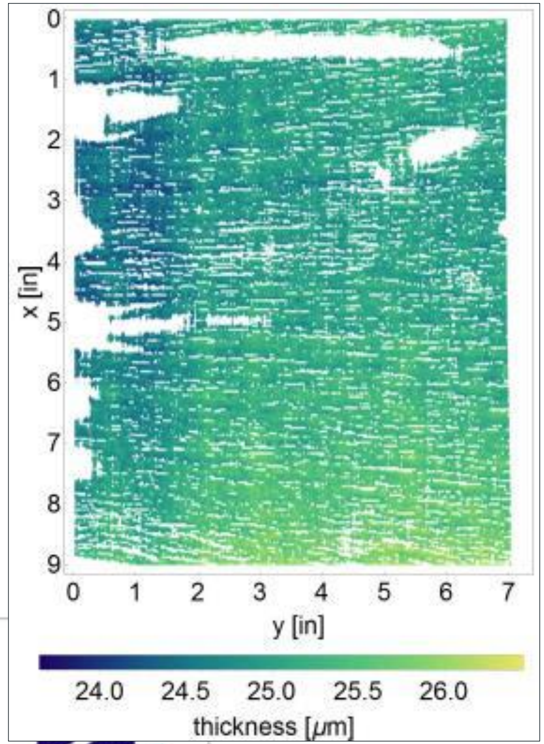
Pinhole – white hole

Membrane Thickness Imaging

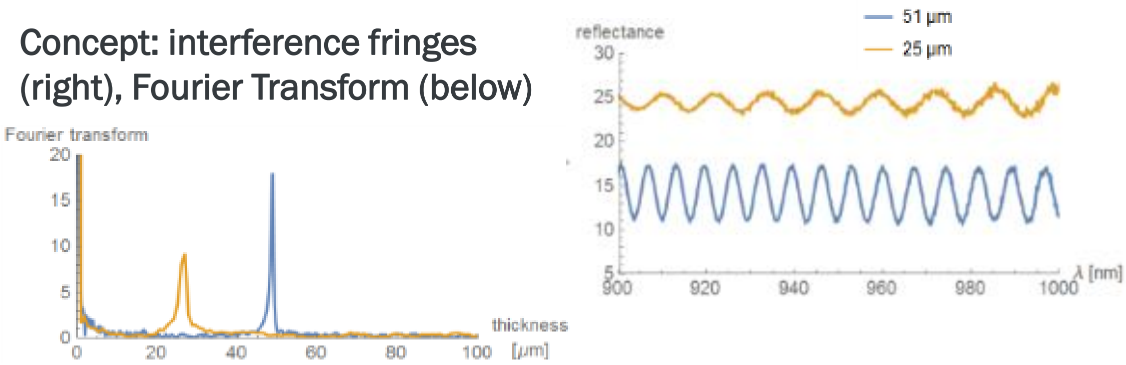
Methodology

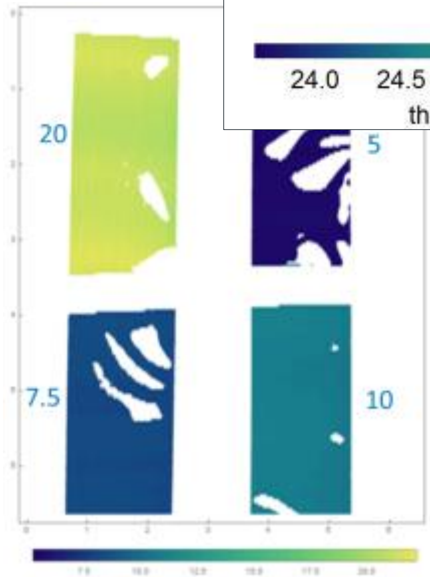
- Use interference fringes in reflectance spectra
- Perform Fourier Transform to find thickness in each pixel
- Relevant for membranes
  - With and without reinforcement
  - While membrane is still attached to liners

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



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

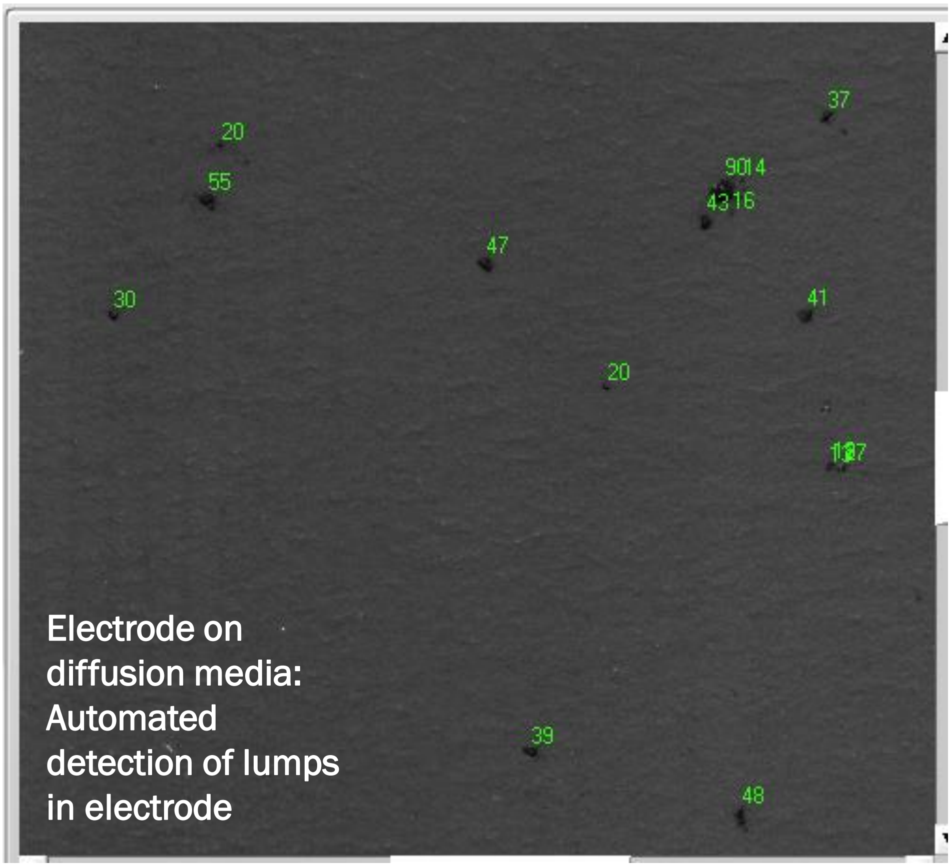


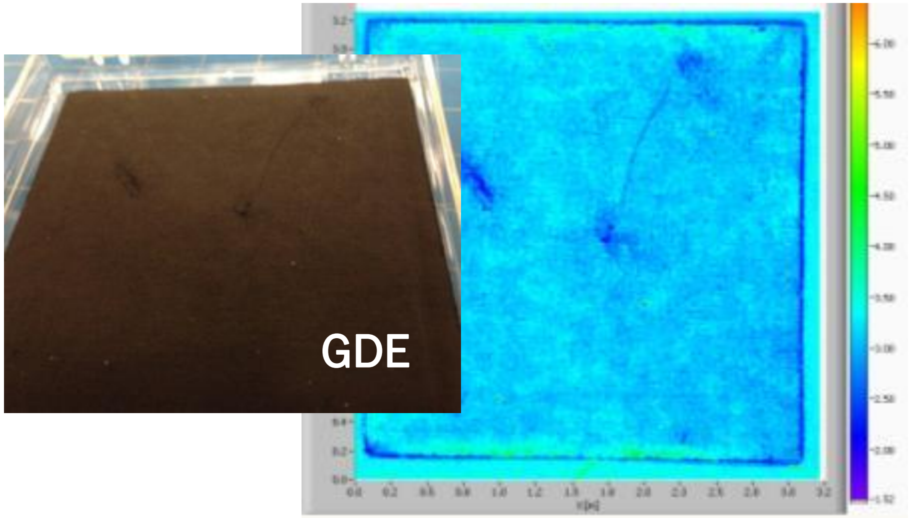


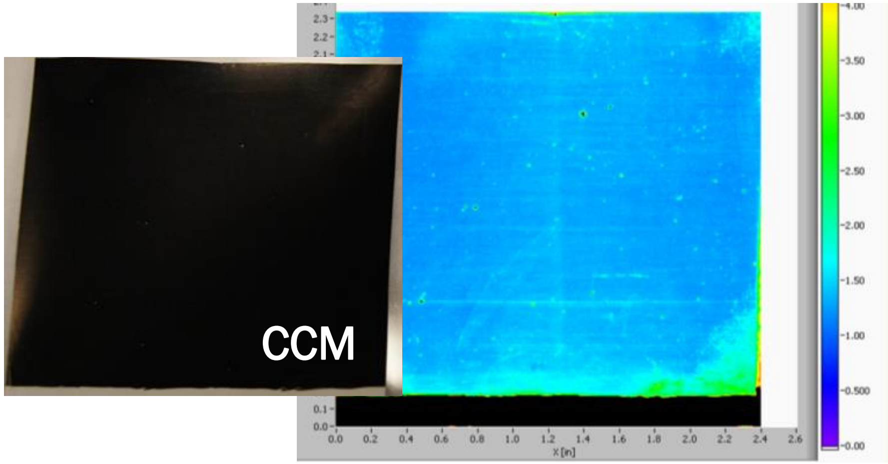
Scan of 4 samples of different thickness

Defects in Electrodes

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





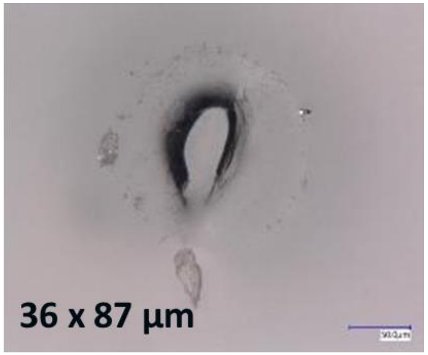


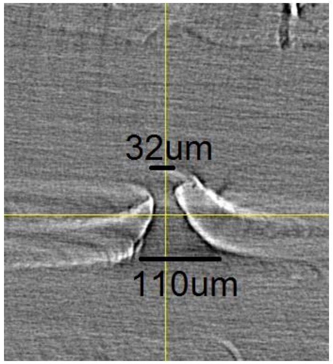
Rupnowski et al., *ASME PowerEnergy 2015-49212*.

Overview of specialized in situ diagnostics developed to understand how defects in MEA materials affect cell performance and lifetime

Example: Effects of Membrane Pinhole

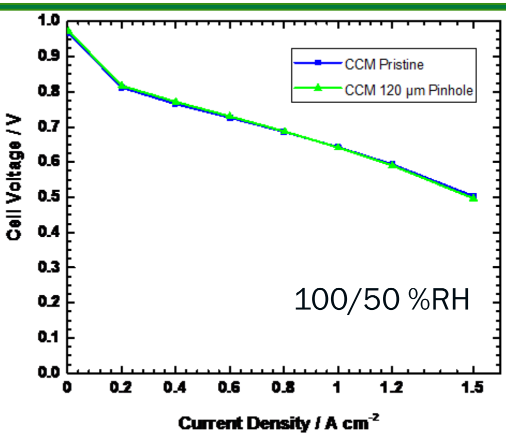
- No observable impact in total cell initial performance (vs. pristine)
- However, we observe initial performance loss local to the pinhole (segmented cell), and
- Increased degradation in performance over time (drive cycle), and
- Earlier failure (accelerated stress test)

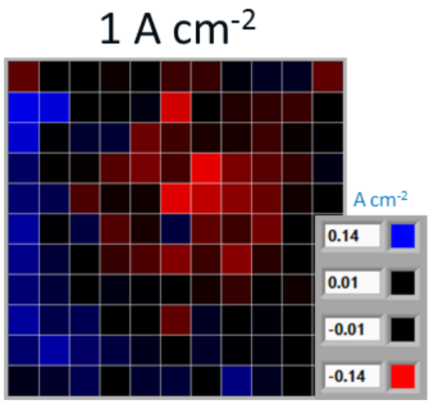




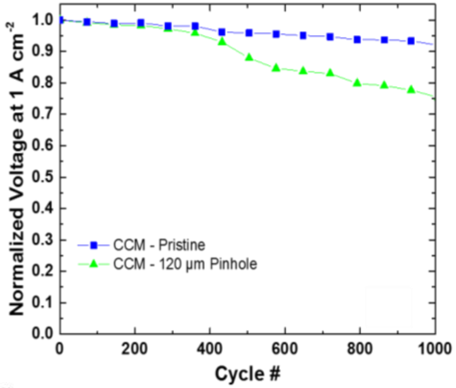
Optical image of mechanically punctured pinhole prior to spraying electrode (left), LBNL XCT image after MEA fabrication (right)

Initial performance



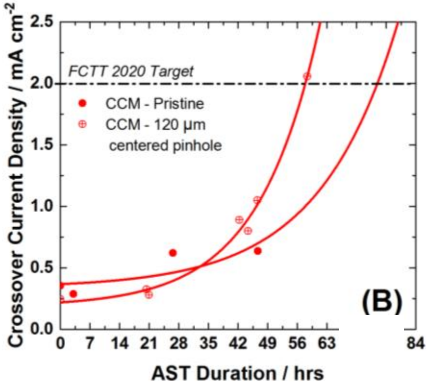


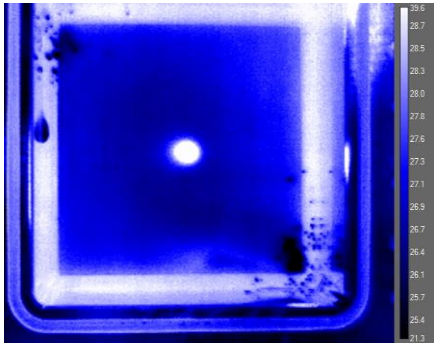
Drive cycle



Anode and cathode (0.2/0.2 mg Pt cm^{-2}) sprayed onto NRE212 membrane after pinhole is made

AST/IR/Failure





Status: Electrode Irregularity Studies

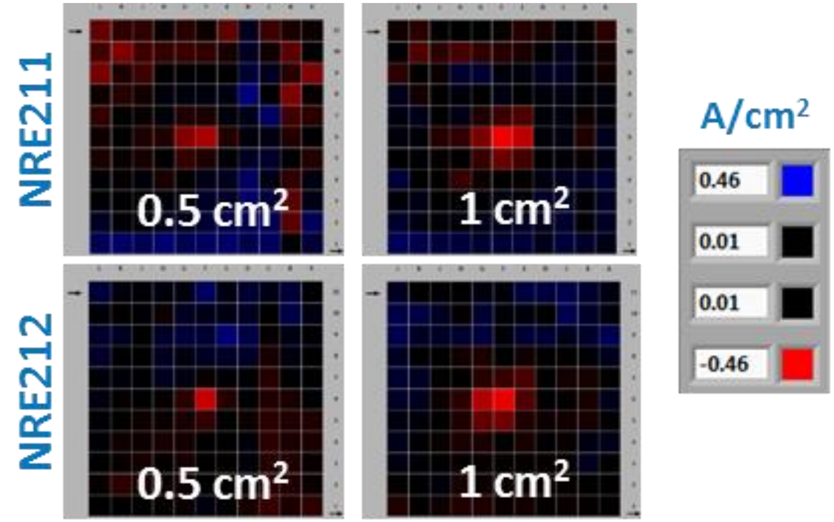
Parametric Study (Impact of XX on…)	Initial Performance: Total Cell	Initial Performance: Local	Prolonged Performance: Total Cell	Lifetime: Total Cell
Irregularity Size (0.125, 0.25, 0.5, 1 cm²)	Little/No Impact	Significant Impact	Moderate Impact	Little/No Impact
Membrane Thickness (25, 50 µm)	Little/No Impact	Significant Impact	Significant Impact	Moderate Impact
Irregularity Location (Inlet, Center, Outlet)	Little/No Impact	Significant Impact	Moderate Impact	Moderate Impact
MEA Configuration (GDE, CCM)	Little/No Impact	Significant Impact	Moderate Impact	Significant Impact
Catalyst Loading (0.15/0.15, 0.2/0.2 mg Pt/cm²)	Little/No Impact	Significant Impact	Ongoing Work	Ongoing Work
Irregularity Shape (Square, Rectangle, Circle)	Little/No Impact	Significant Impact	Ongoing Work	Ongoing Work
Catalyst Layer Thickness Variations (Thin, Bare Spots)	Little/No Impact	Moderate Impact	Significant Impact	Ongoing Work
Irregularity Aspect Ratio	Little/No Impact	Significant Impact	Ongoing Work	Ongoing Work
Slot Die Coating/Manufacturing Defects (Droplet, Scratch, Cut)	Little/No Impact	Little/No Impact	Significant Impact	Ongoing Work

Little/No Impact   Moderate Impact   Significant Impact   Ongoing Work

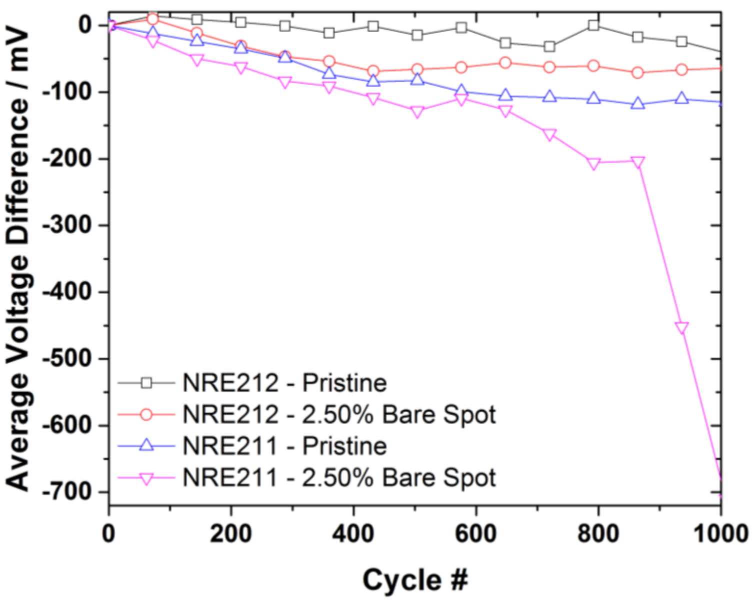
We need this suite of tools to fully understand the effects of electrode irregularities

Example: Impact of Membrane Thickness

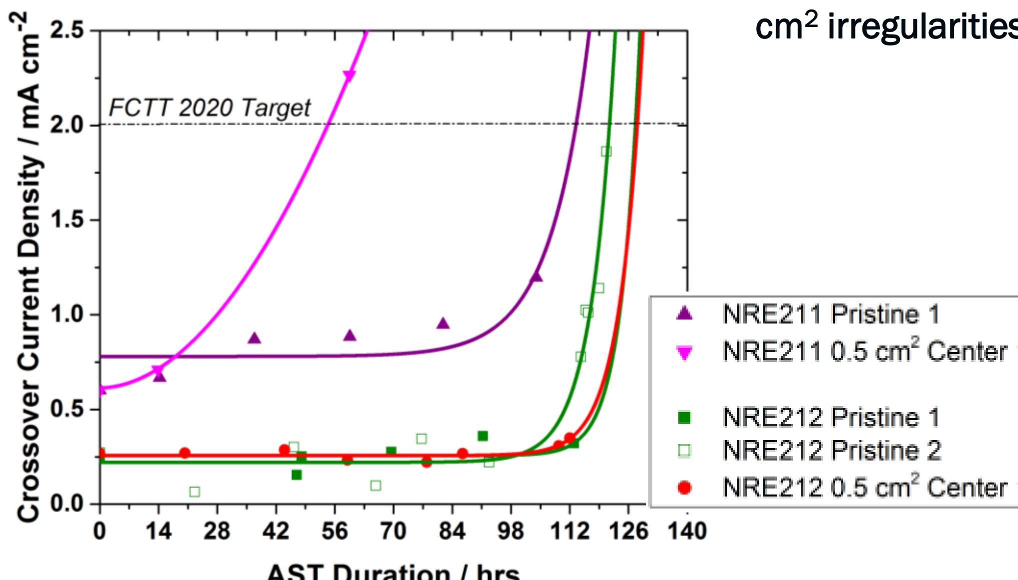
- Cathode centered bare spots
- Comparing effect on 25 µm vs. 50 µm membranes
- Not much difference in initial performance
- Impact during drive cycle much greater for thinner membrane
- Time to failure: NRE212 > NRE211 pristine > NRE211 with irregularity



Initial performance comparison for 0.5 and 1.0 cm² irregularities



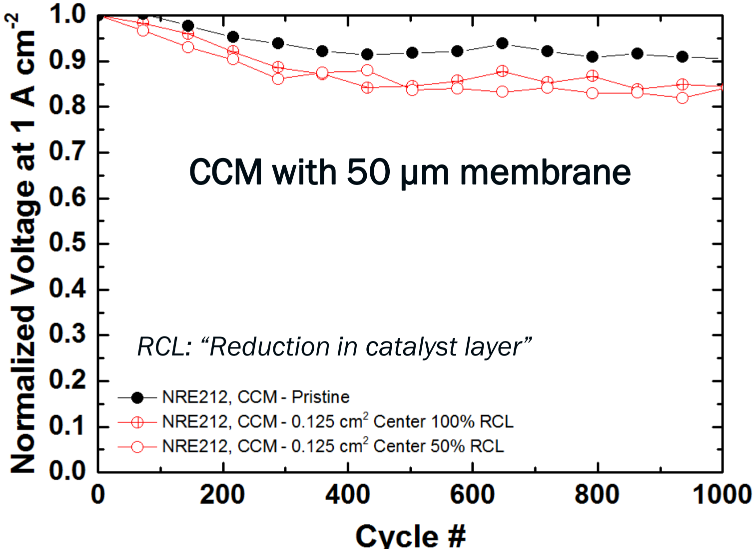
Irregularities of 2.5% active area

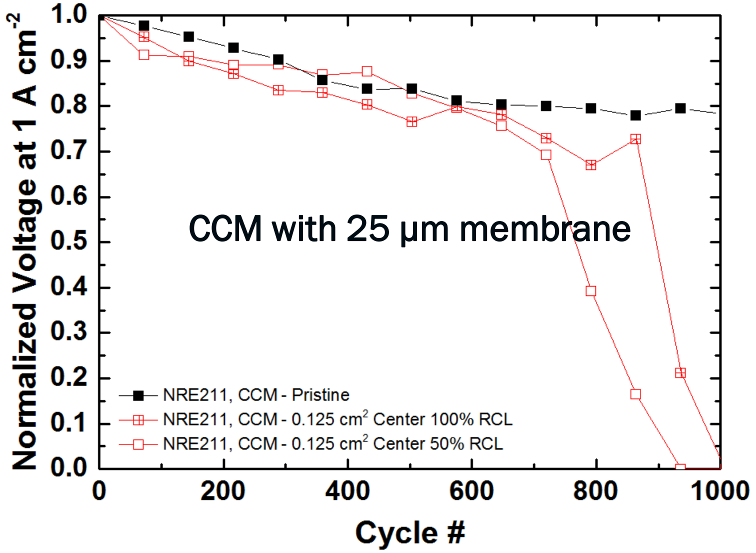


Irregularities of 1.25% active area

Example: Effect of Electrode Thin Spots

- Compare effects of thin spots in the cathode to bare spots
- Irregularities are 2.5% of 5 cm^2 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





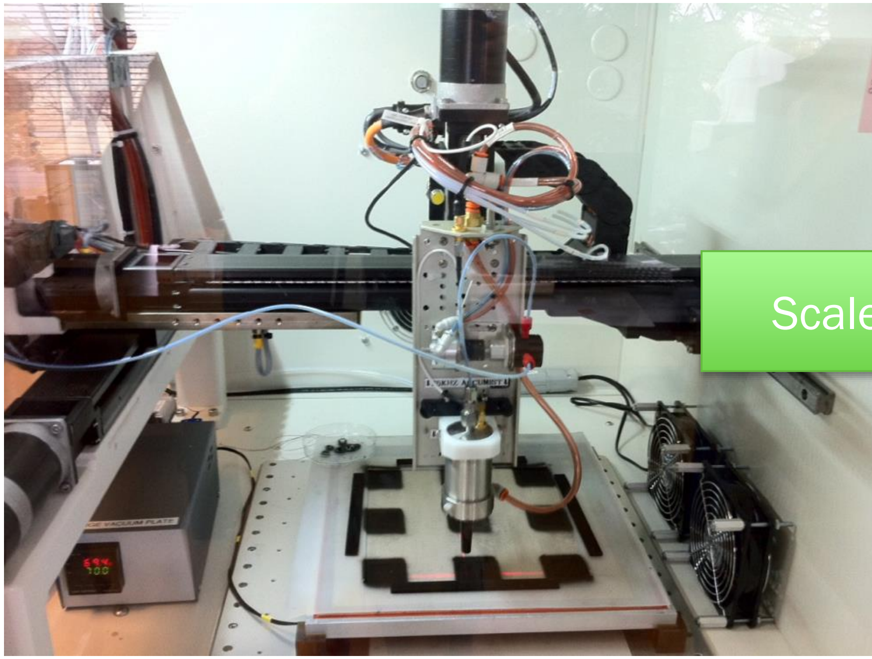
0.2 mg Pt/cm^2 nominal loading

Reduction in performance over time

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



Scale Up

Large Scale – Roll-to-Roll

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

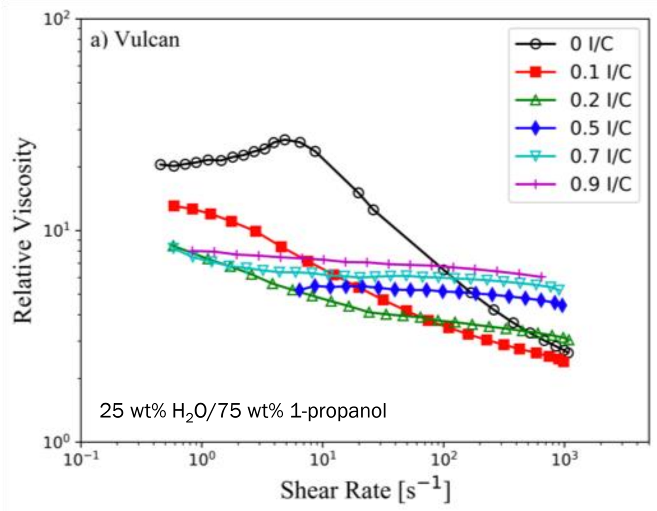
Needed to demonstrate scalability of materials, MEA/cell designs, and industrial relevance

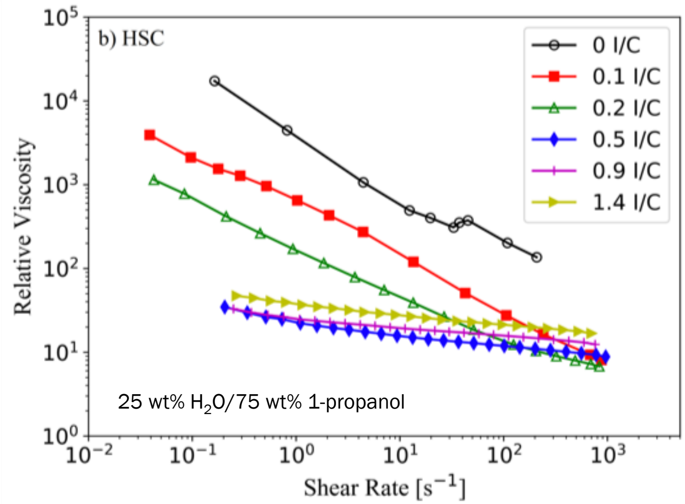
Conditions

- Concentrated ink (~4.5-15 wt% solids)
- Shear mixing
- Single layer
- Room temp. substrate
- Convective drying

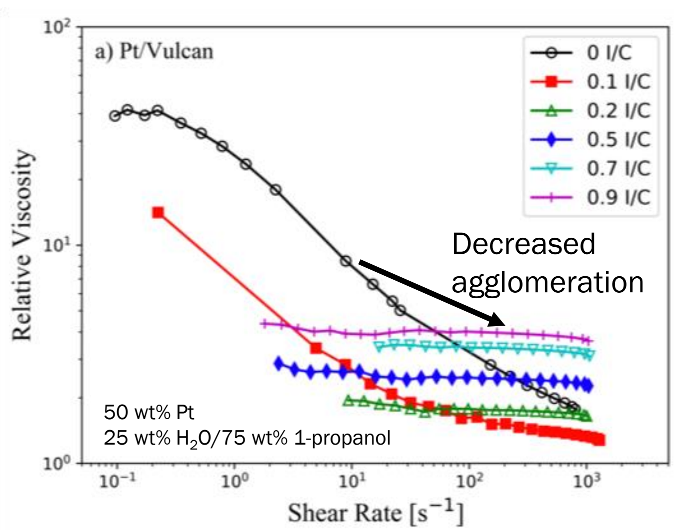
Rheology of Carbon and Pt/C Inks

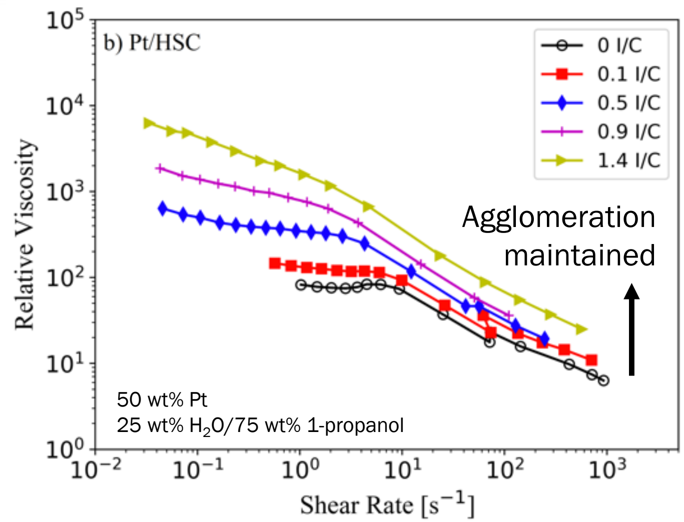
Carbon inks





Pt/Carbon inks

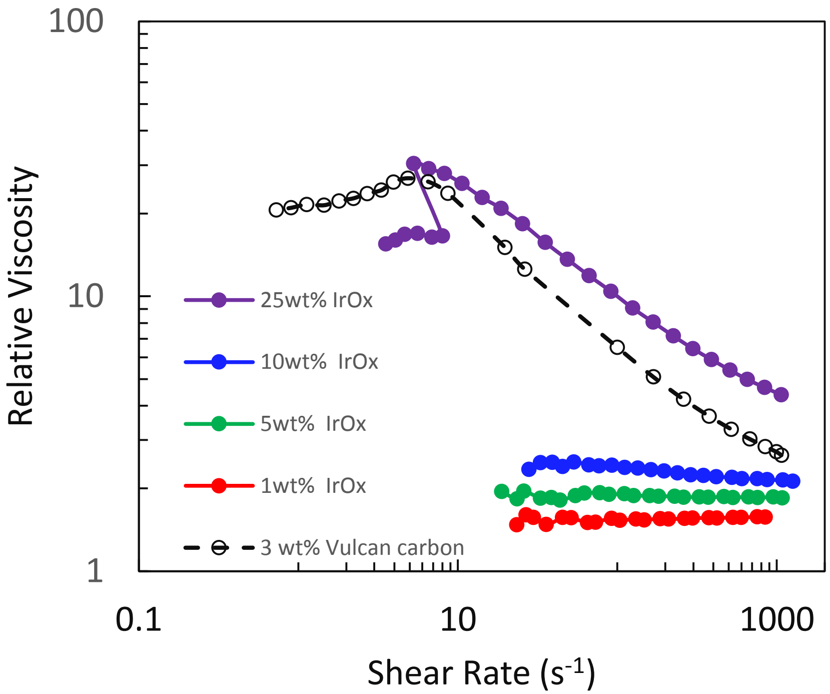


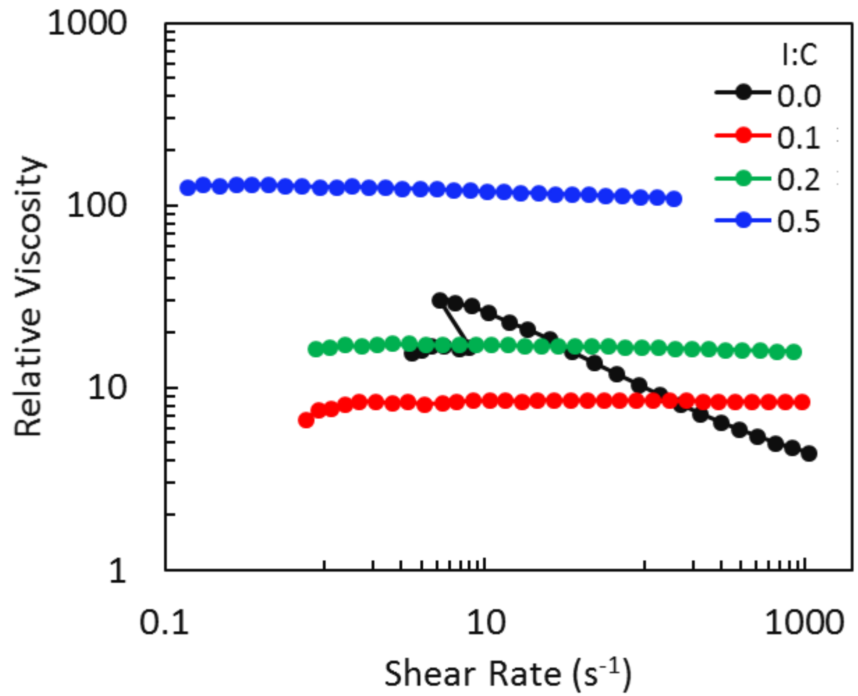


- Addition of ionomer stabilizes carbon particles
- Transition from shear thinning to Newtonian
- Same trend for Pt/Vulcan
- However, ionomer does not stabilize Pt/HSC in same way

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

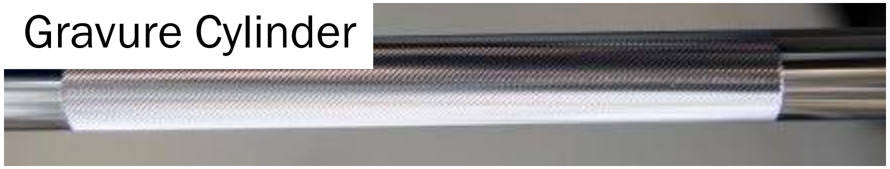
Rheology of Unsupported Low Temperature Electrolysis Catalysts

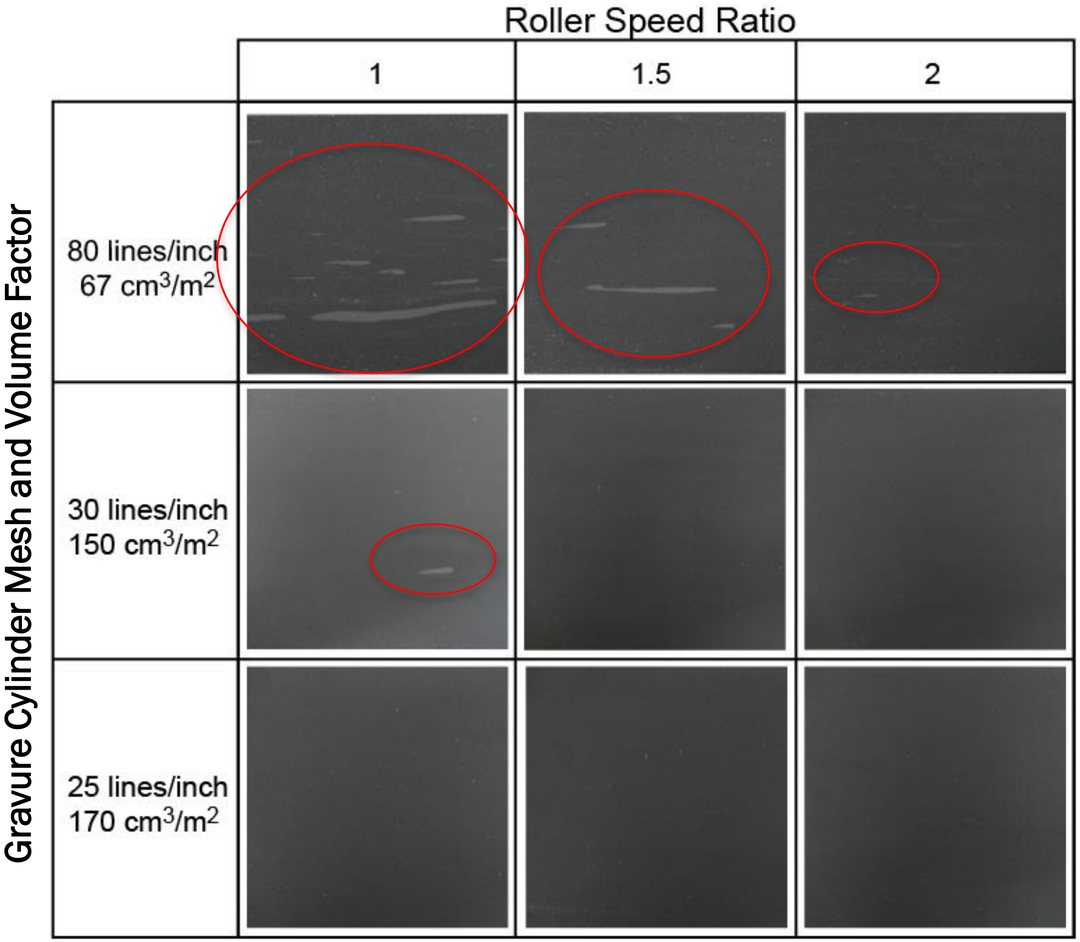




- Iridium oxide (IrOx) catalyst, without ionomer, displays similar agglomeration behavior to Pt/Vu, though at much higher weight fractions
- Addition of ionomer has the same stabilizing effect as for Pt/Vu
    - Only a small amount of ionomer is needed to stabilize the catalyst particles against agglomeration

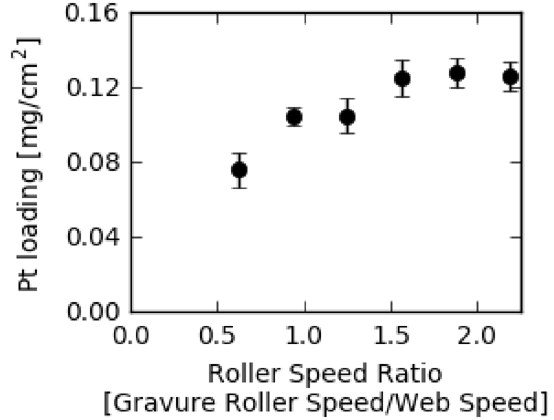
Gravure Coating Parametric Studies



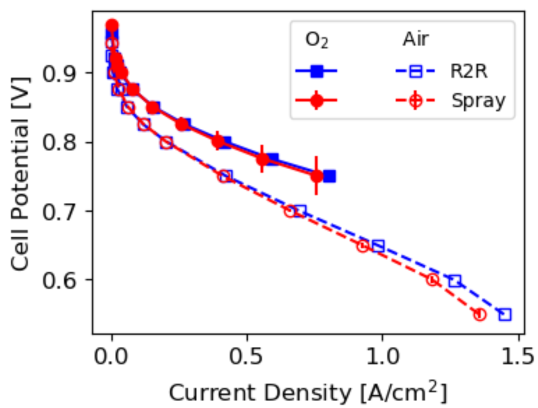


Pt/HSC, 50 wt% Pt, Nafion 1000 EW, 3.2 wt% PtC, 1.2 I:C, SGL 29BC

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



- Achieved performance comparable to lab-standard spray coating



$0.12\ mg_{Pt}/cm^2$
$50\ cm^2$
80 ˚C
100% RH
150 kPa
Anodic sweep

Contributors

- NREL
  - Peter Rupnowski
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- ANL
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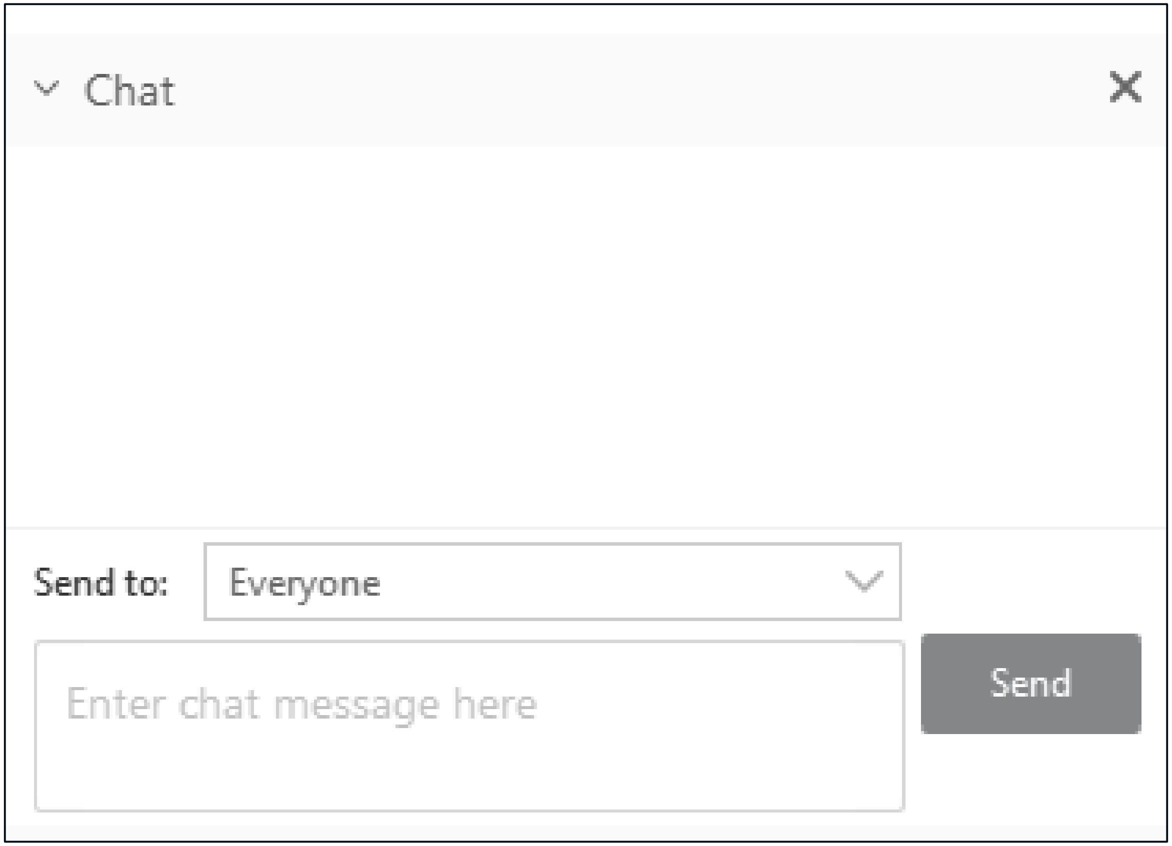
- Georgia Tech
  - Tequila Harris
- Colorado School of Mines
  - Jason Porter

Question and Answer

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



Thank you

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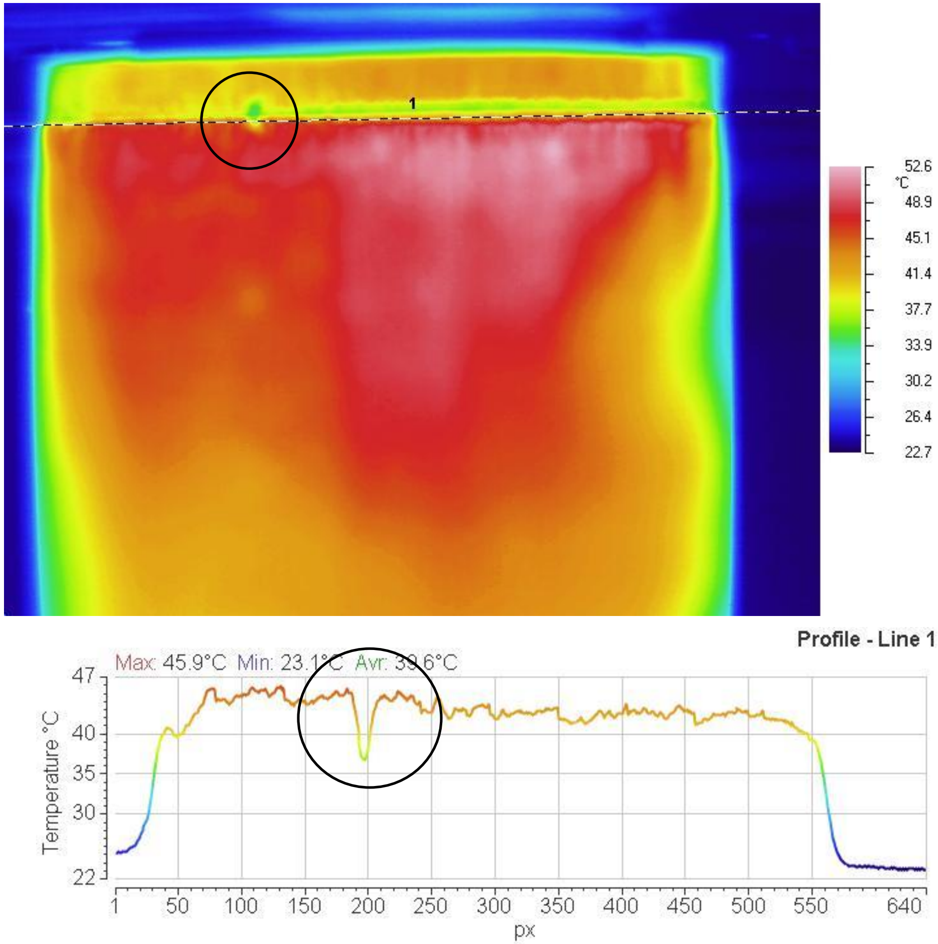
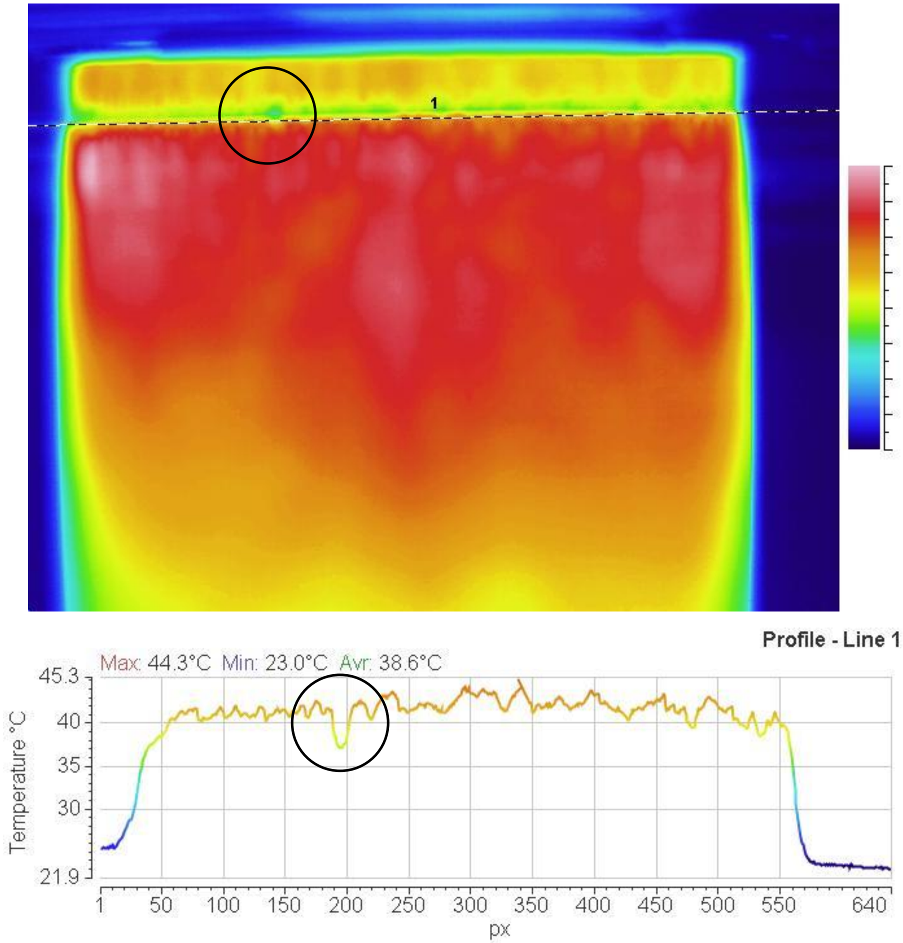
Technical Back-Up Slides

RIF Defect Detection Examples



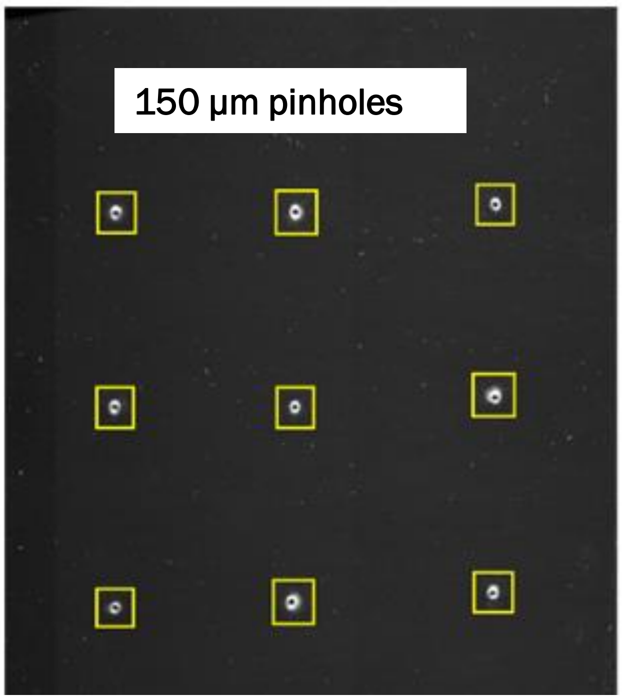
10 fpm, 0.0625 cm^2,
50% electrode thickness
reduction

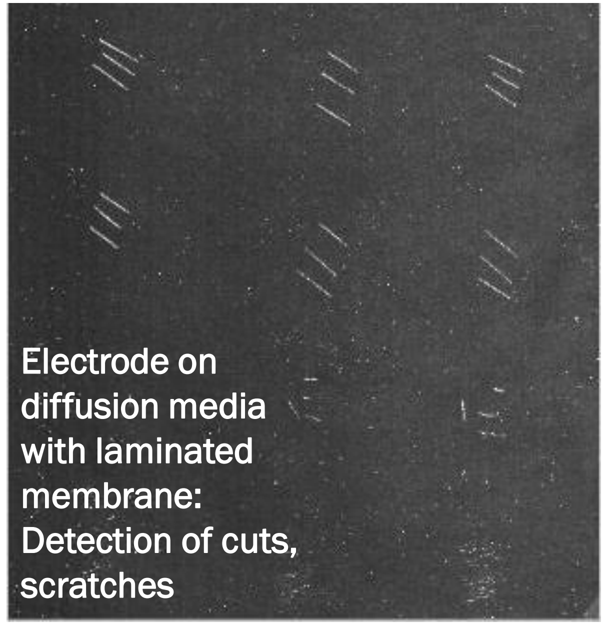


10 fpm, 0.0625 cm^2,
25% electrode thickness
reduction

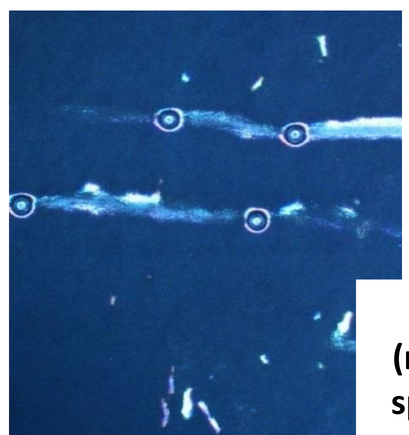
Defects in Membranes on an Electrode

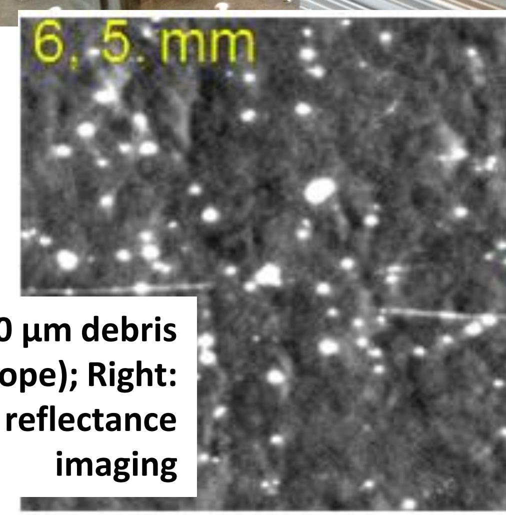
- Detection of a variety of defect types in electrode-containing structures and MEAs (10 ft/min)





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





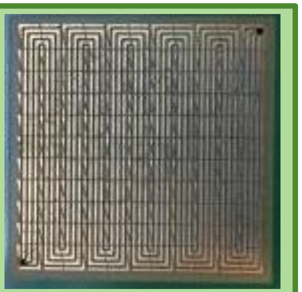
Left: 50 µm debris (microscope); Right: specular reflectance imaging

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

Overview of In Situ Techniques

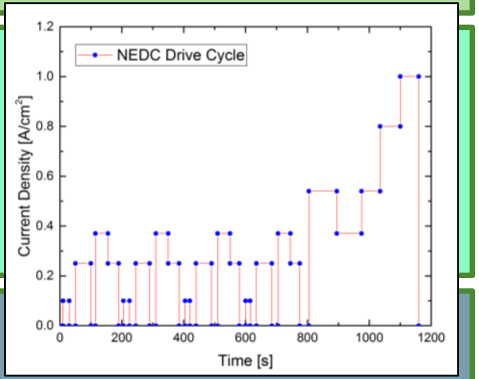
Does an irregularity in an MEA component material impact:
(a) initial performance, (b) performance over time, and/or (c) location or timing of failure?

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

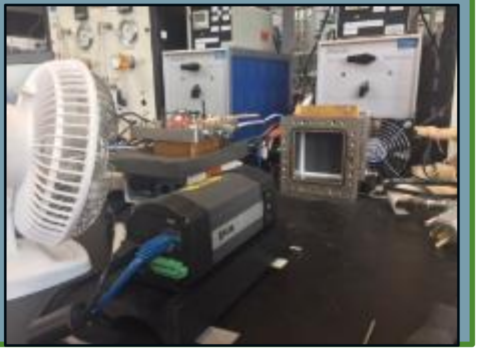
Prolonged performance



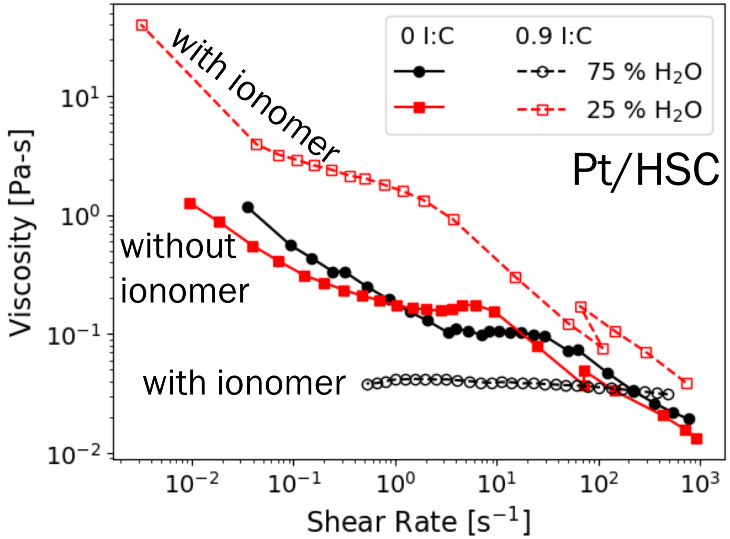
- Use the “New European Drive Cycle”
- Measure total cell polarization data after every 72 cycles
- Analyze performance degradation induced by irregularities

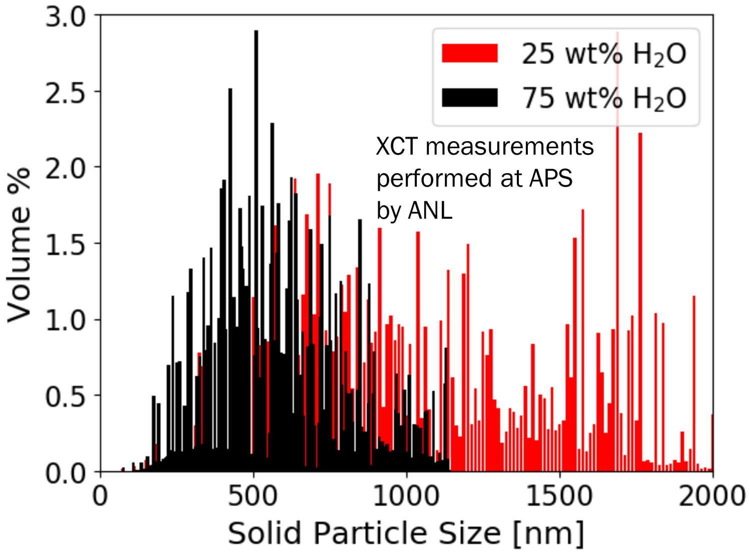
Onset of failure

- 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

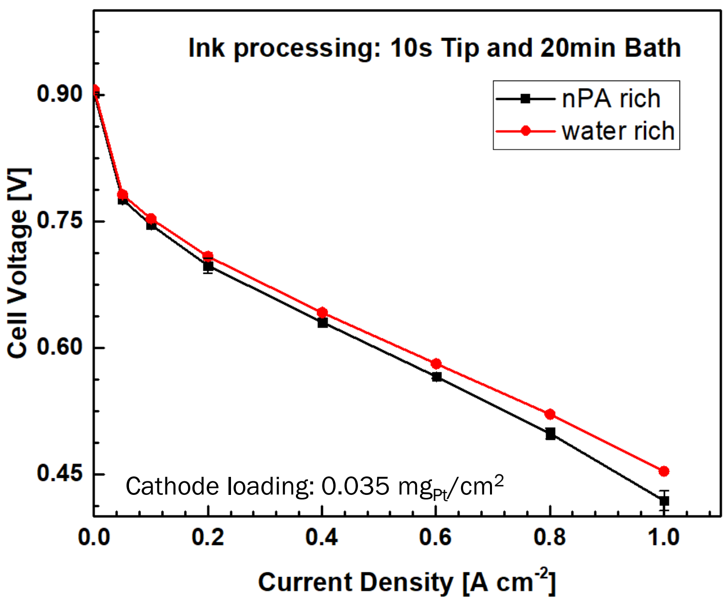


Effect of Solvent





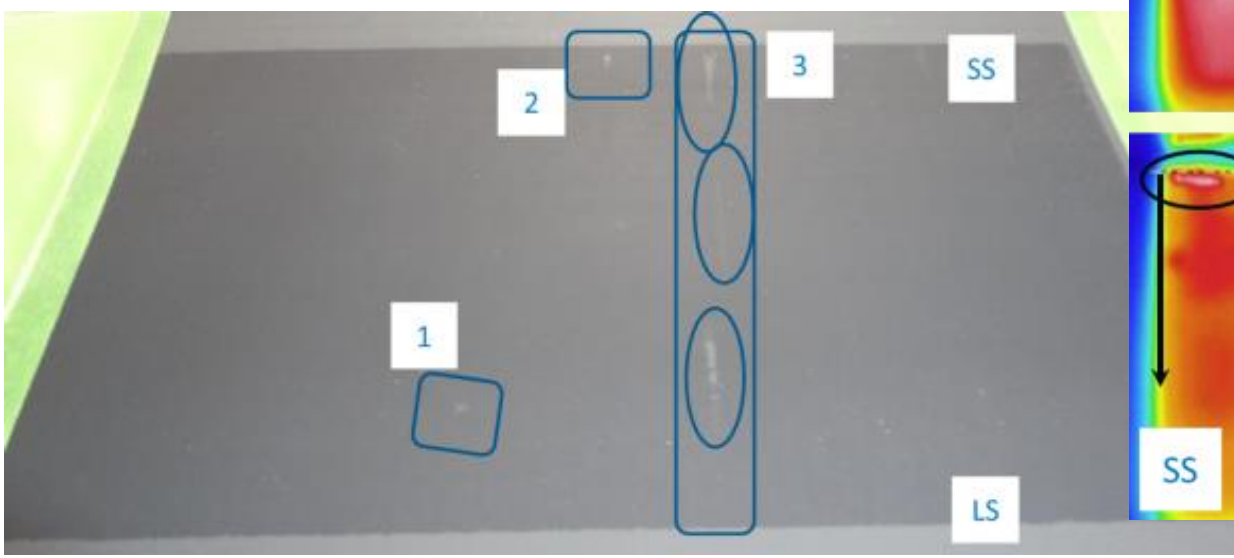
- High water-content solvent causes stronger interparticle repulsion
- Stronger repulsion leads to smaller agglomerates in the ink and smaller particles in the coated electrode
- Smaller particle size leads to improved oxygen transport and performance

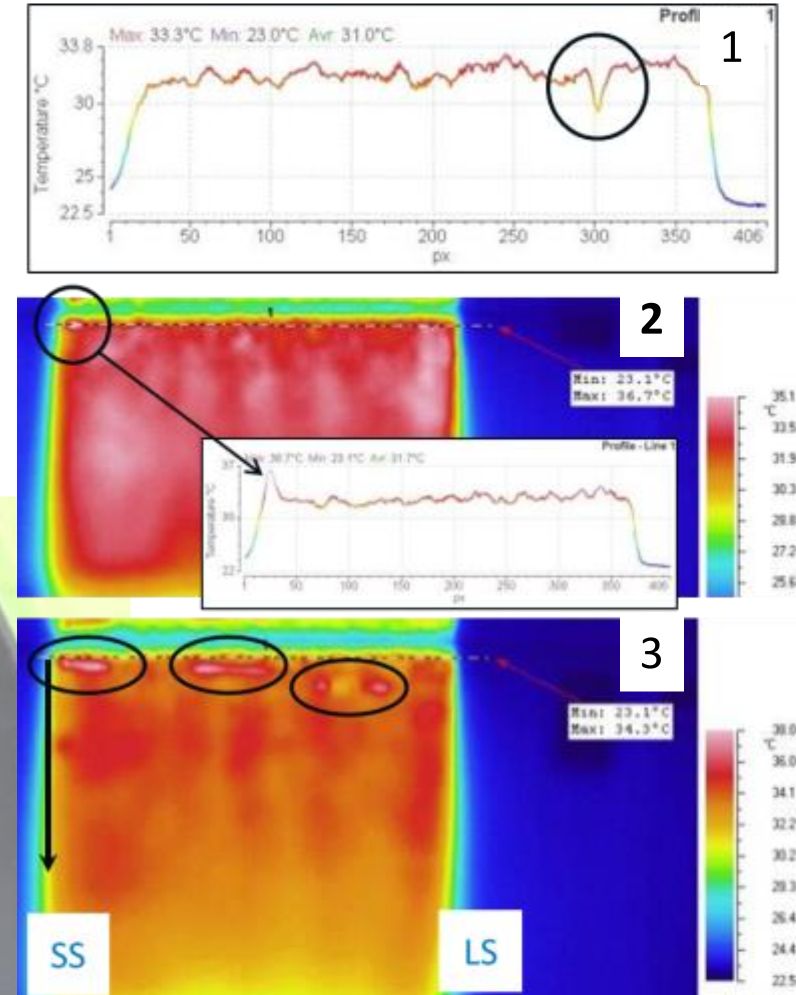


High water content in Pt/HSC inks appears to lead to a morphology that improves performance

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