NREL
NATIONAL RENEWABLE ENERGY LABORATORY

Fuel Cell MEA Manufacturing R&D

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MN001

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Overview

Timeline

Start: July 2007

End: Project continuation and direction determined annually by DOE

% complete: N/A

Barriers

Barriers	Target
E: Lack of Improved Methods of Final Inspection of MEAs	$20/kW (2020) at 500,000 stacks/yr
H: Low Levels of Quality Control	

Budget and Funded Partners

Fiscal Year	Total Funding*	LBNL	CSM	GaTech
2017 (received)	$1,056,000	$293,000	$103,000	$51,000
2018 (planned)	$550,000	$150,000	$66,000	$0

* Total funding is the sum of NREL and all funded partners; includes work shown in S. Mauger poster (MN019)

Relevance

- 2016 HTAC Annual Report
  - Despite progress, challenges remain, including: **"Improvements in manufacturing processes and yield rates for electrolyzer and fuel cell system manufacturing."**
- *Review of the Research Program of the U.S. Drive Partnership*, Fifth Report, The National Academies Press, Washington, DC, 2017.
  - *NRC Phase 4 Recommendation 3-3*. The DOE should increase the efforts related to the development of… membrane electrode assembly components… The **focus** should be on materials, performance, durability, **and, ultimately, on manufacturability**.
  - *NRC Phase 4 Recommendation 3-6.* U.S. DRIVE **should encourage projects that address the use of real-time, in situ electro-analytical quality-control methods** to assess membrane and electrode performance characteristics during the continuous manufacturing web-based process.
- Proton OnSite, "Working Together to Enable Gigawatt Scale Renewable Hydrogen Production: Solar Fuels and Large Scale Electrolysis"
  - "Not just about materials/performance: Manufacturing is its own science… **need to achieve cost and uniformity at scale**"
  - "**Manufacturing is the real cost issue** (catalyst ~10%)"

Approach

- Understand quality control needs from industry partners and forums
  - *Engage LTE/H_2@Scale community*
- Develop diagnostics
  - *Study underlying physics of excitation and material response*
  - *Use multi-physics modeling to guide development*
  - *Use a unique suite of in-situ testing capabilities to understand defect thresholds*
- Validate diagnostics in-line
- Transfer technology

Annual Milestone Go/No-go Criteria:

- Loading range: 0.05-0.4 mg Pt/cm^2
- Sensitivity of ± 0.1 mg Pt/cm^2
- Speed at least 1 in/sec

Date	Milestone/Deliverable (status as of 4/17/18)	Complete
9/17	Demonstrate an in-line configuration for through-plane reactive excitation	100%
9/17	Generate in situ failure study data for MEAs with electrode defects	100%
12/17	Complete in situ drive cycle testing on MEAs with membrane defects	100%
6/18	Determine the feasibility of using reflectance imaging to measure Pt loading (Go/No-go)	30%
9/18	Set up experimental test bed to study membrane thickness imaging	30%

Collaborations

Industry Collaborators

Objective: ensure we continue to get detailed input on manufacturing QC needs, prioritization of diagnostic development, feedback on technique capabilities, and pursue tech transfer

- **Gore (TSA):** understanding effects of membrane defects, in-line characterization of membrane production rolls
- **GM (CRADA):** development of in-line inspection techniques
- **Mainstream Engineering (CRADA):** demonstration of commercializable in-line QC device
- **Proton OnSite:** QC development for LTE MEA materials and structures

Labs and Academia

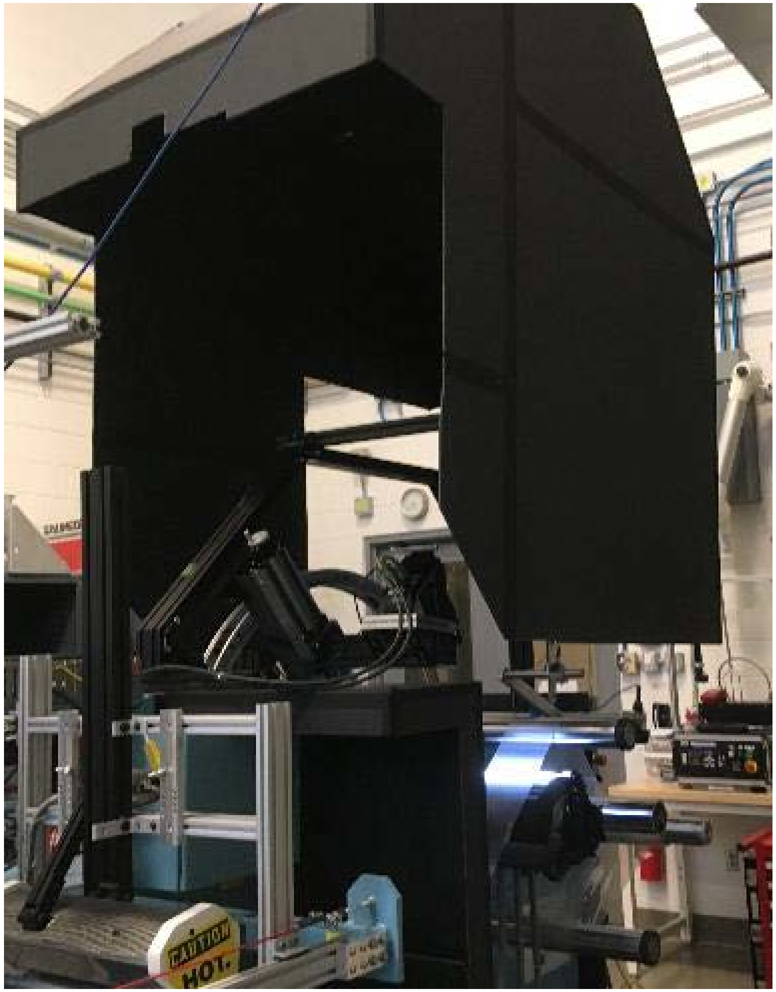
- **Lawrence Berkeley National Lab/Tufts University:** model development and integration, x-ray computed tomography
- **Colorado School of Mines:** cell fabrication and testing
- **Georgia Tech:** membrane casting
- **CEA-Liten:** R2R fabrication and quality inspection
- **National Research Council-Canada (NRC):** membrane inspection and coating

Technical Accomplishments

Expanded web inspection capabilities and scanned full product rolls

Gore collaboration: Gore-Select Membrane roll quality characterization

- Cost-shared project between Gore and FCTO
- Project Goals
  - Understand and optimize optical inspection setup/parameters
  - Develop defect detection and classification algorithms
  - Provide full width/full length high resolution product roll imaging (mapping)
- Developed new inspection apparatus on web-line
  - Easy control/repeatability of light and detector angles
  - Investigate transmission or reflectance, specular or diffuse modes
  - Fabricated filtered hood to eliminate external light and minimize contamination
- Scanned two full product rolls
  - ~15 µm x-y resolution
  - Automated full-roll defect density metrics (still optimizing)
  - Planning on multiple additional product rolls to scan



Web-line optical research apparatus, with hood

Technical Accomplishments

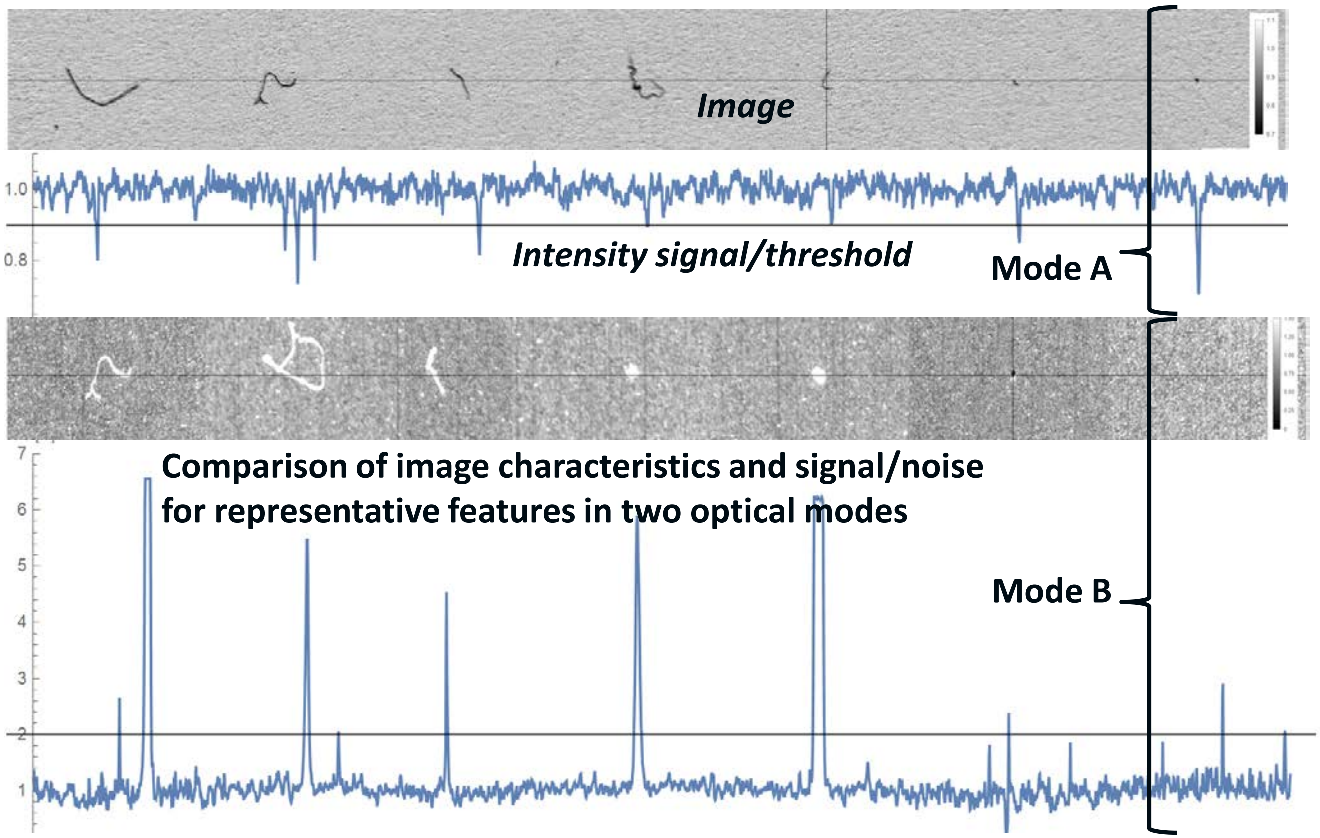
Determined the impact of optical mode on defect detection

Gore collaboration: Gore-Select Membrane roll quality characterization

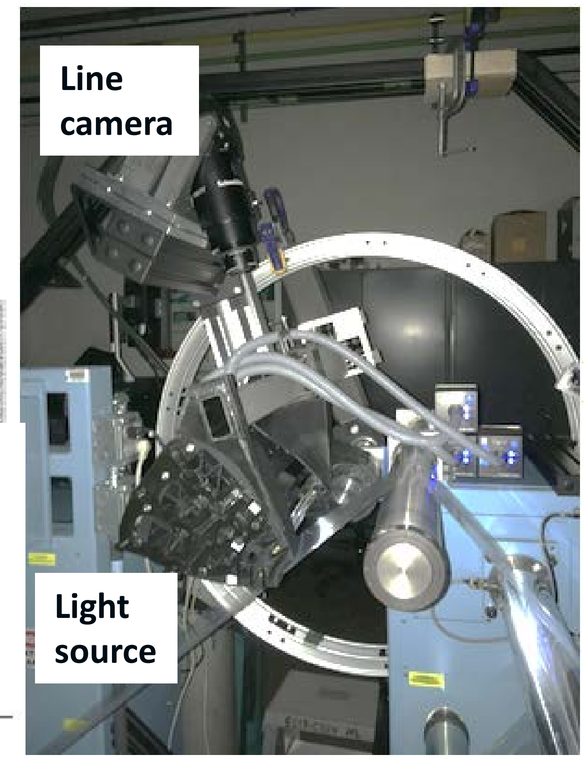
- Using the new research apparatus, performed a detailed study of optical mode
  - T vs. R, many camera/light angles
  - Understand sensitivity, level of noise, threshold

			camera angle from normal	mean lights angle from normal	diffuser
diffuse	T	1	12.	0.	N
		2	36.	0.	N
		3	60.	0.	N
	R	7	0.	65.	N
		8	0.	47.5	N
		9	0.	30.	N
		10	0.	47.5	N
specular	T	4	0.	0.	Y
		5	30.	30.	Y
		6	60.	60.	Y
	R	12	24.	24.	N

Optical mode test matrix



Comparison of image characteristics and signal/noise for representative features in two optical modes



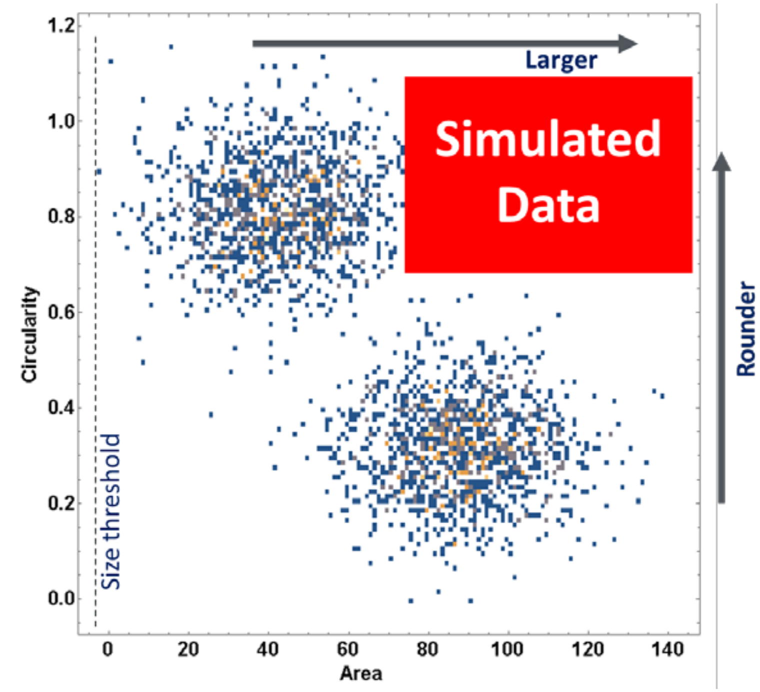
Optical research apparatus

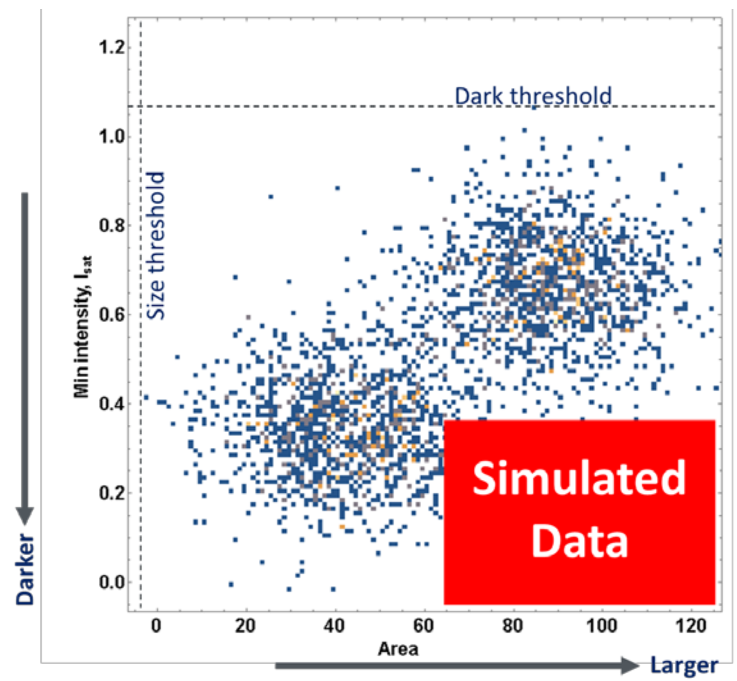
Developed automated defect detection and classification algorithm

Gore collaboration: Gore-Select Membrane roll quality characterization

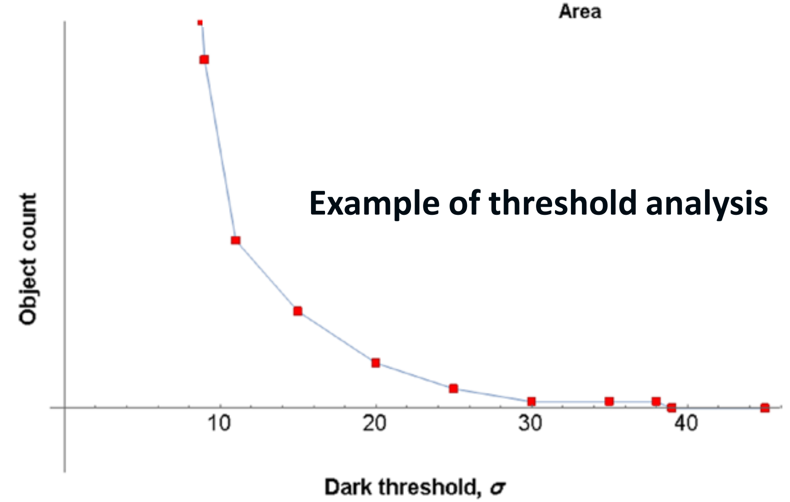
- Evaluated optical thresholding for defect detection
- Developing classification algorithms
  - Based on optical characteristics: size, shape, intensity
  - Validated by Gore proprietary information
- Implementing full-roll metrics

Example of full-roll defect metrics (simulated data)





Example of full-roll defect metrics (simulated data)

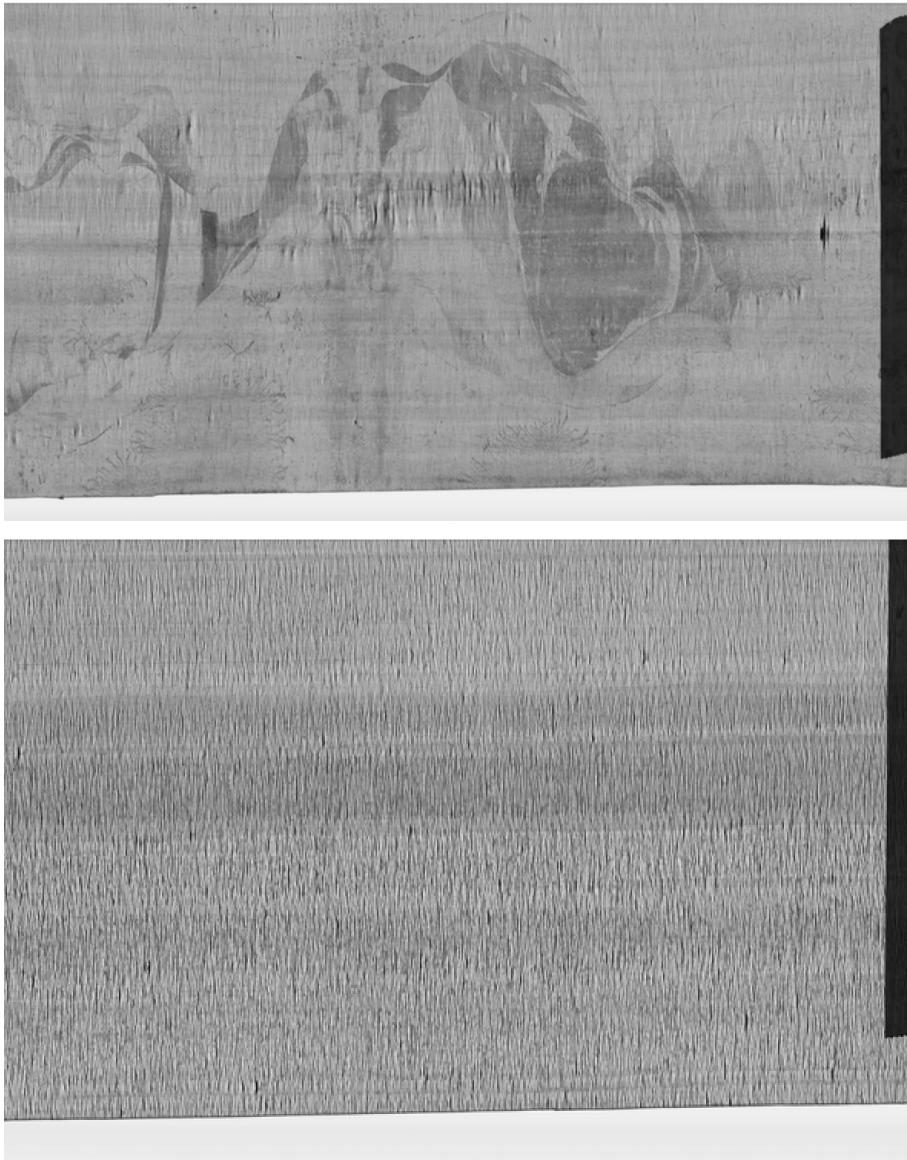


Technical Accomplishments

Performed optical scanning of 3-layer PFSA membrane sheets on web-line

NRC collaboration: initial optical scanning of melt-blown PFSA membrane

- New collaboration with NRC on their novel membrane, *which is still in development*
  - Membrane co-extruded with 2 PE skin layers (still attached during scanning)
- NREL roles:
  - QC development
  - Membrane coating
- Scanned several meter-length, 3-layer samples on web-line
  - Samples were 10-11.5 cm wide, 15-30 µm thick
  - Scanned in direct transmission
  - 13 µm/pixel physical resolution
  - Scanning at 2 ft/min
- Successful imaging of composite data from all three layers



Optical transmission scanning of NRC membrane sheets

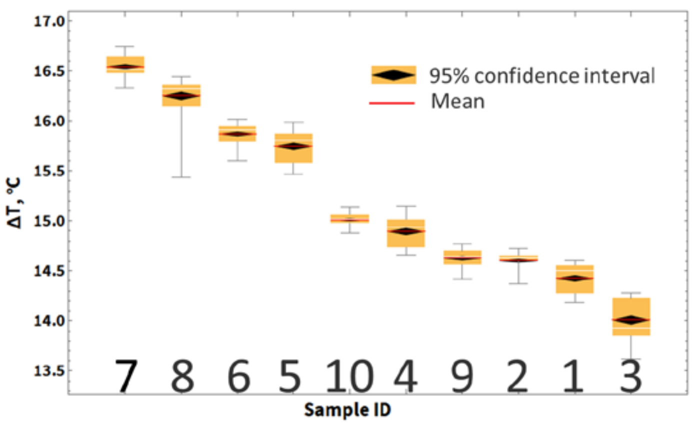
Technical Accomplishments

Demonstrated technique for measuring thickness of membrane on GDE

GM CRADA project

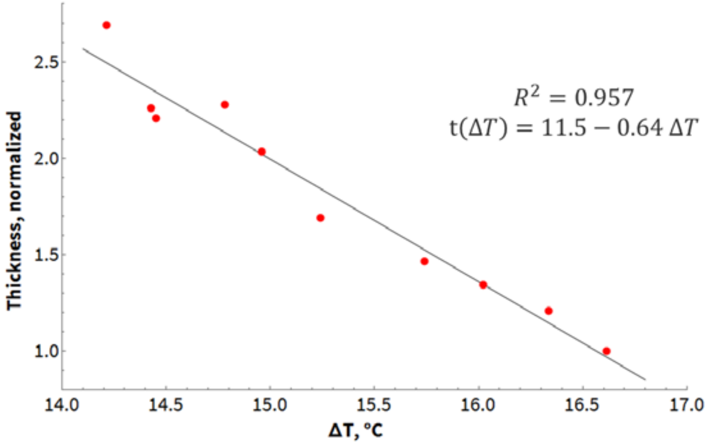
- Concept (presented last year)
  - Use thermal excitation of active layer/substrate
  - Measure peak/decay
  - Link measurement to thermal model to back out physical properties, e.g. thickness, porosity
- Blind study of membrane thickness in 10 half-cell (membrane on GDE) samples provided by GM
  - IR thermography of individual samples, heating by focused visible light, scanning speed 2.5 ft/min
  - Linear-fit calibration using GM thickness measurements
  - Initial sensitivity value of 0.26 °C/µm (1 std. dev. of the mean), estimated z-resolution of 1.40 µm

Thermal scanning configuration



Raw thermal data (statistics from ~220 data points per scan), taken at 2.5 fpm, 15 Hz, using 320x240 detector

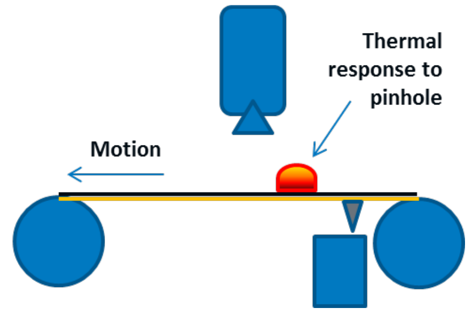
Calibration curve

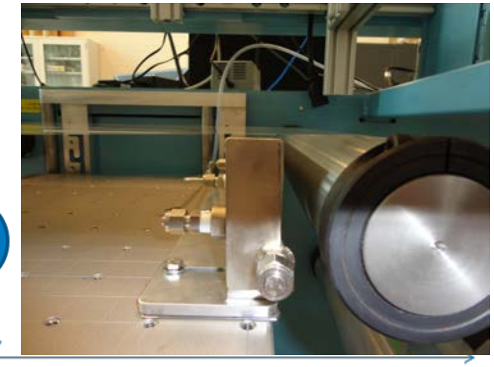


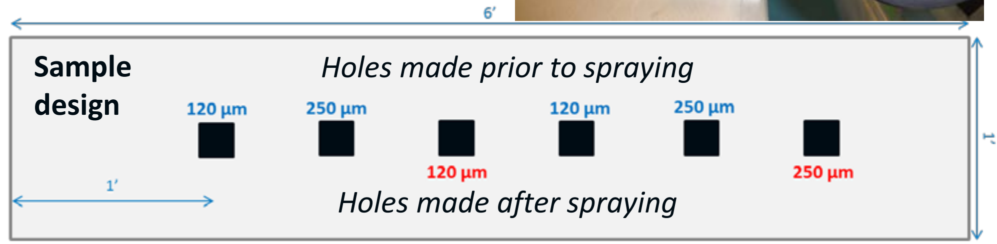
Demonstrated TPRE technique on web-line

Through-plane reactive excitation (TPRE) web-line experiment

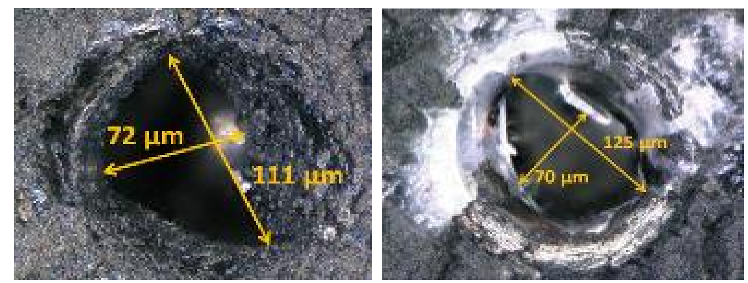
- Objective: in-line technique for pinhole detection in CCM
  - Impinging reactive flow
  - Advection of gas through pinhole
  - Catalytic reaction at electrode
- Sample
  - Pinholes made with 120 and 250 μm tools
  - 4x in membrane, then spray electrode
  - 2x poked through CCM
- Results
  - Explored flowrate, $[H_2]$
  - Detected pinholes, but very small (~0.1-0.4 °C) thermal response



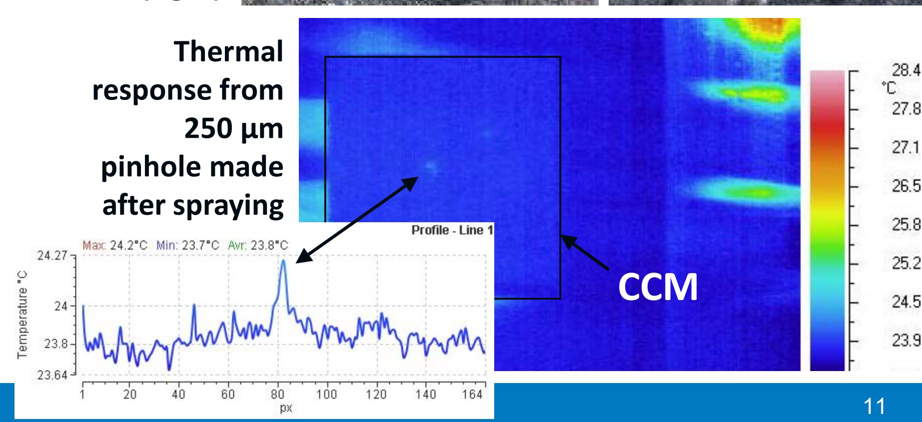




Pinholes made with 120 μm tool: prior to spraying (left), after spraying (right)



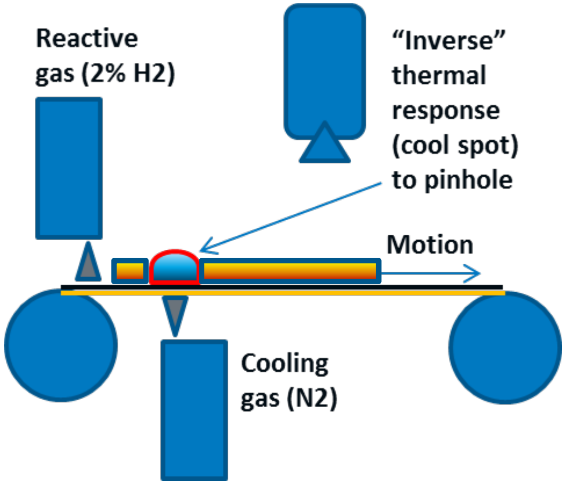
Thermal response from 250 μm pinhole made after spraying



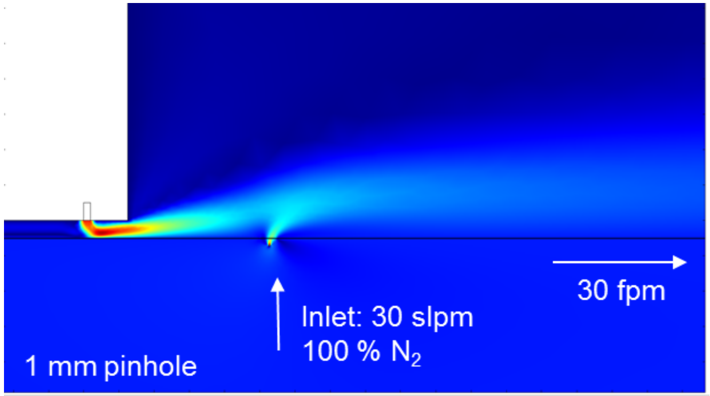
Predicted impact of possible improvements to TPRE configuration

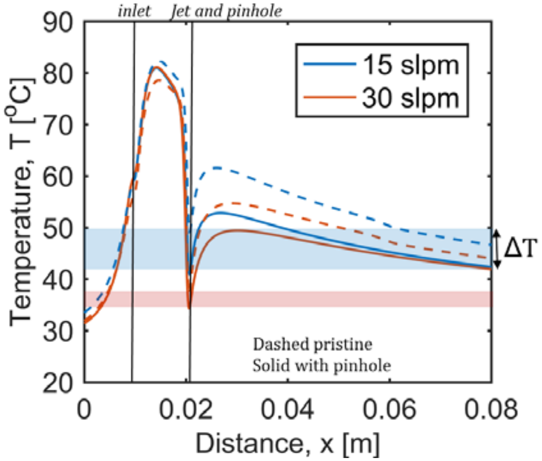
TPRE web-line development

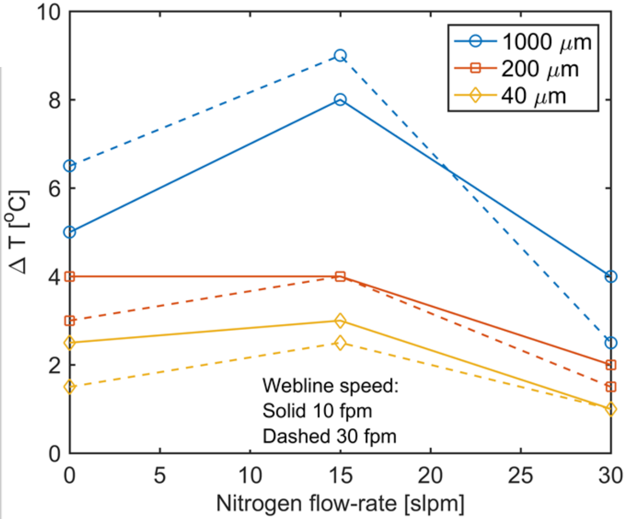
- Given the very small thermal response resulting from the initial web-line configuration, we developed some ideas for improvement
- Use reactive impinging flow (RIF) as previously described
  - Wide-area thermal response indicates electrode uniformity
- Use an opposed jet of N_2 to reduce the reaction at the location of a pinhole, creating "inverse" thermal response (cool spot)
- LBNL modeling predicts
  - Optimal combination of N_2 convection (bottom to top) and H_2 diffusion (top to bottom) through pinhole
  - Measurable (> 1°C) cool spot for pinhole diameter down to at least 40 µm



Revised TPRE concept with half-CCM



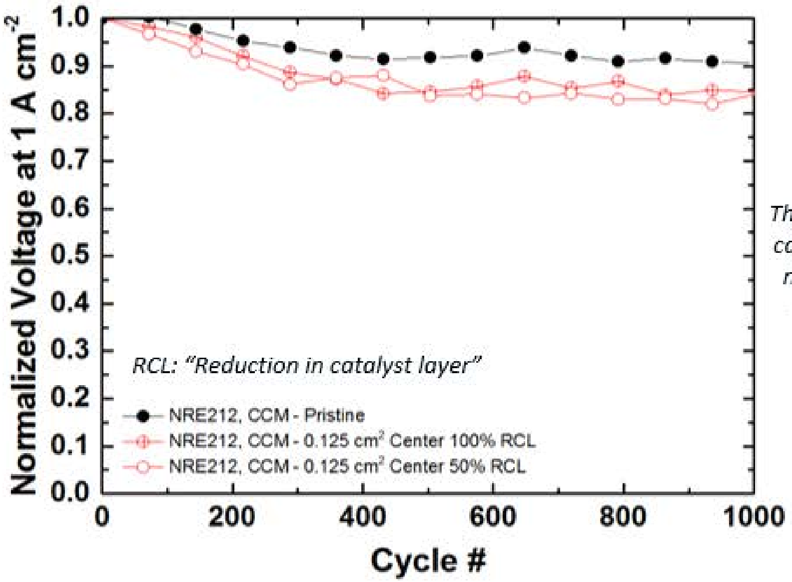




Proved detrimental impact of electrode thin spots, especially on thin membranes

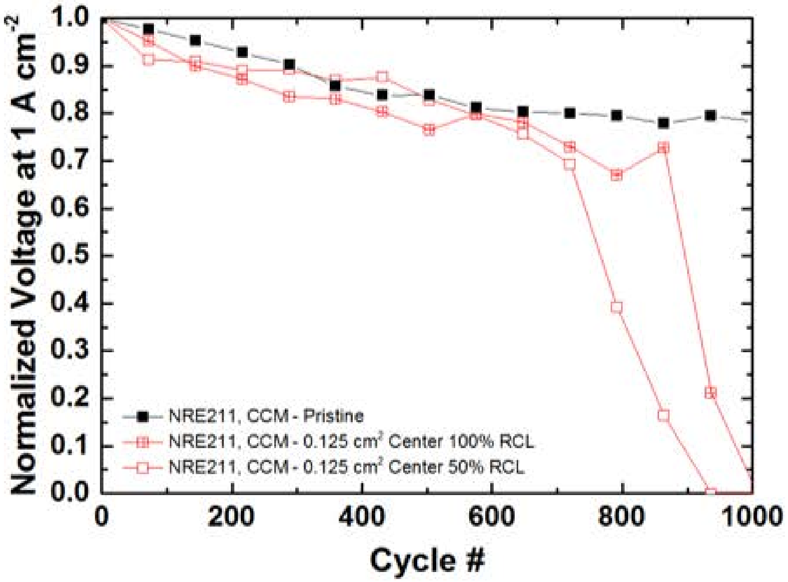
Effects of electrode thin spots

- Simulating known coating irregularities
- 2.5% of 5 cm^2 active area, 50% thickness reduction (created by masking during spray)
- Used previously described drive cycle testing
- 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



Reduction in performance over time for CCM with 50 µm membrane

Thin spots on cathode, 0.2 mg Pt/cm² nominal loading

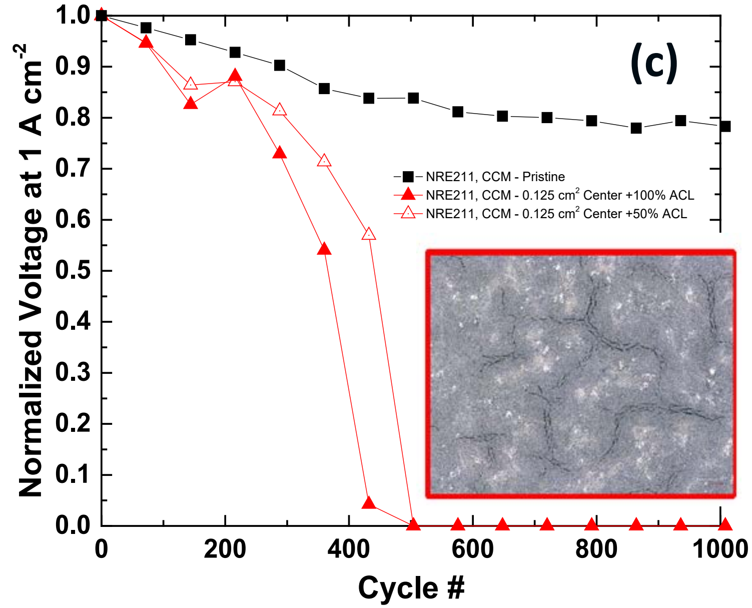


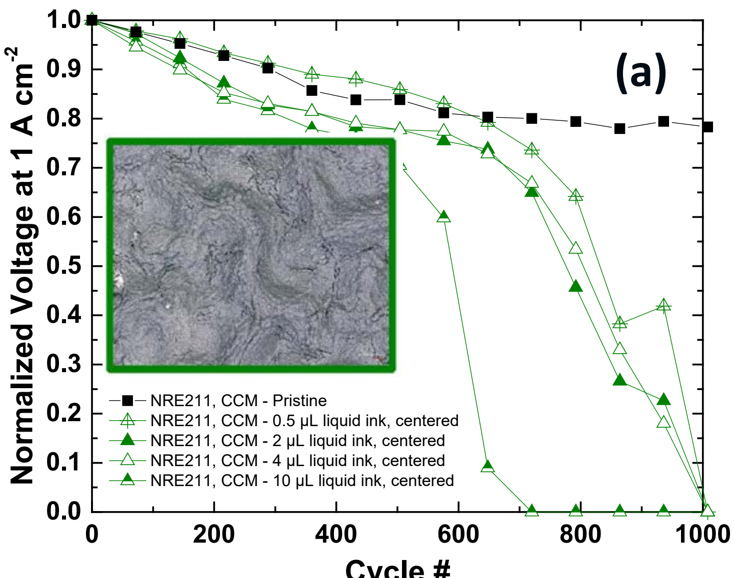
Reduction in performance over time for CCM with 25 µm membrane

Proved detrimental impact of electrode thick spots

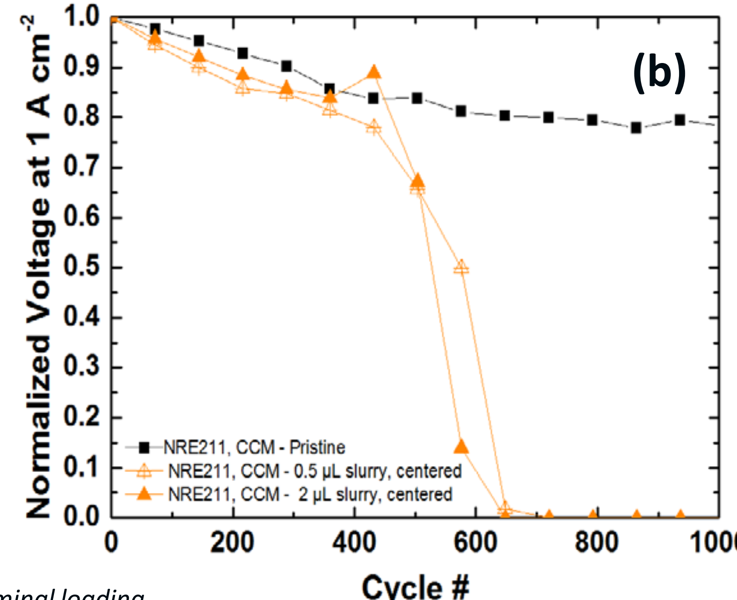
Effects of electrode thick spots

- Simulating known coating irregularities
- ~1.5-2.5% of 5 cm^2 active area, (intended to be same % of electrode volume as thin spots)
- Used previously described drive cycle testing
- Created by pipetting of low (a) and high (b) viscosity inks, and ultrasonic spray (c)
- All thick spots caused catastrophic loss of performance





Reduction in performance over time due to electrode thick spot (all on 25 μm membrane)



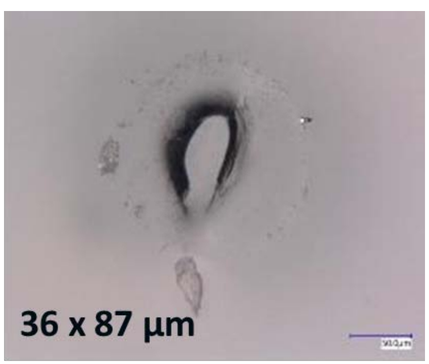
Thick spots on cathode, 0.2 mg Pt/cm^2 nominal loading

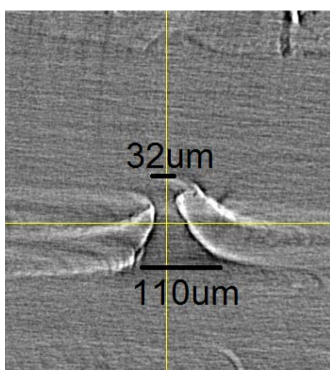
Technical Accomplishments

Proved detrimental impact of artificially created pinhole

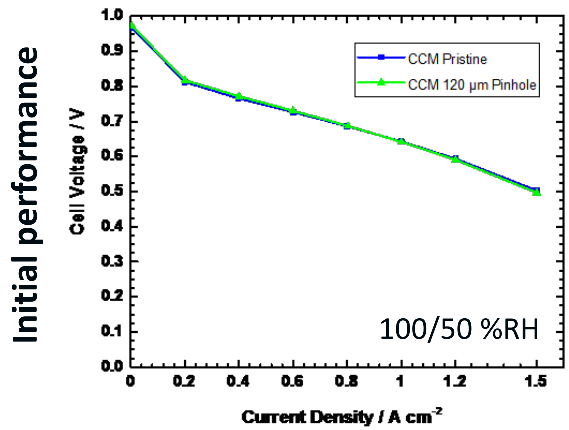
Effects of membrane pinhole

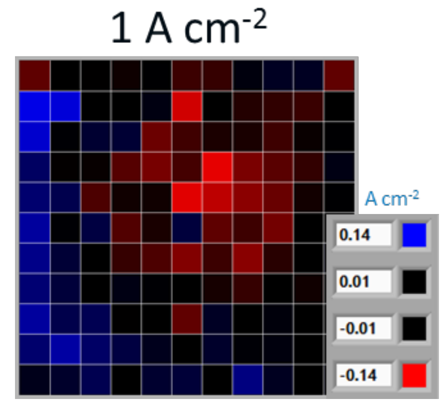
- Objective: more controlled follow-up to as-cast membrane study
- Used NREL-developed mechanical punching technique
  - 120 μm micro-needle
- Results in local initial performance loss, degradation in performance over time, earlier failure
- XCT of full MEA performed at LBNL to understand morphology of pinhole after cell fabrication

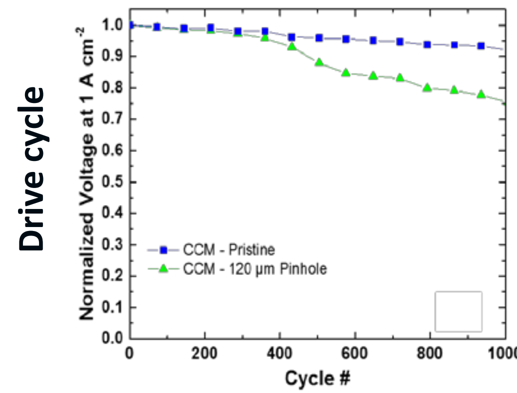




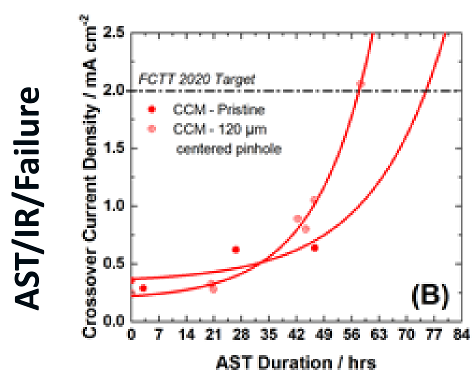
Optical image prior to spraying electrode (left), LBNL XCT image after MEA fabrication (right)

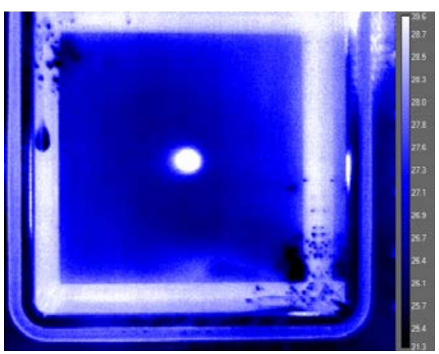






Anode and cathode (0.2/0.2 mg Pt cm-2) sprayed onto NRE212 membrane after pinhole is made

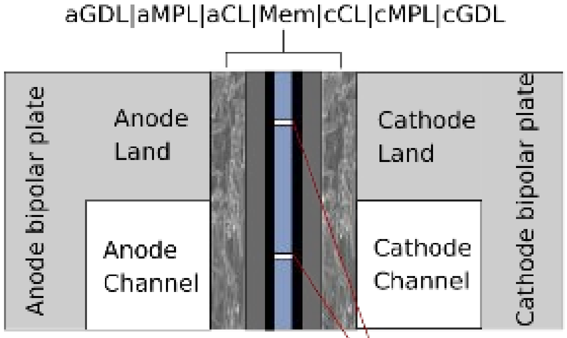




Developed COMSOL 2D MEA model to predict effects of pinholes

LBNL pinhole modeling

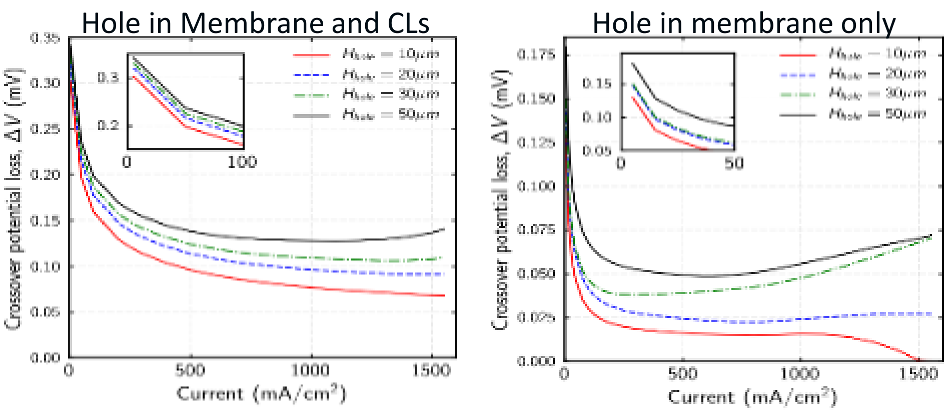
- Pinhole may be in membrane only, or both the membrane and catalyst layer (CL), depending on the mechanism of formation during MEA fabrication
- Results:
  - Crossover loss decreases at higher humidity -> liquid in pinhole
  - Higher crossover potential loss when pinhole in both membrane and CLs
  - H_2-O_2 reaction at edge of pinhole when pinhole in membrane & CLs leads to much higher current consumption and durability concern



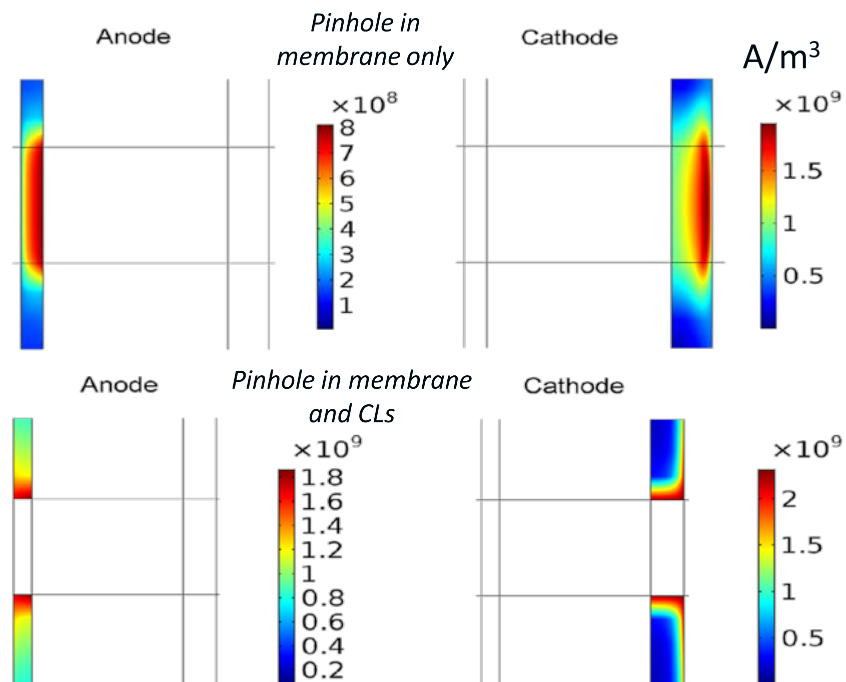
All data shown with pinhole under channel only

Pinhole modeling domain

RH 40%, 60 °C, Air



Potential loss due to crossover through pinhole



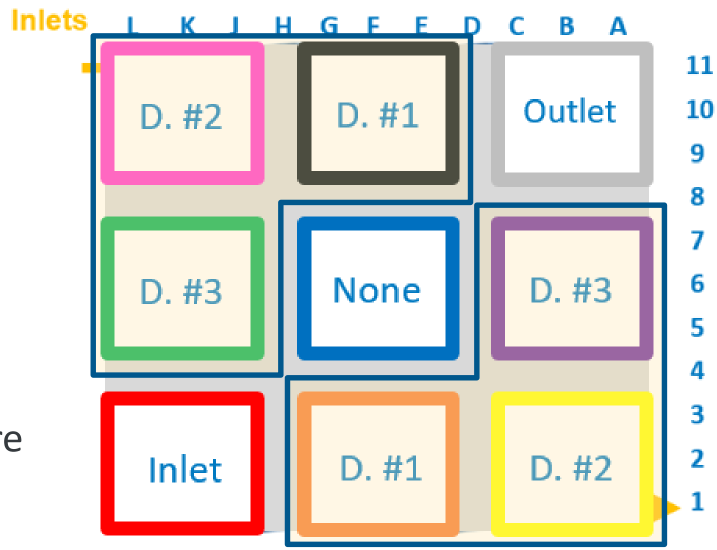
RH 40, 60C, 1550 mA/cm2, 30 µm hole

Comparison of two cases showing rate of reaction

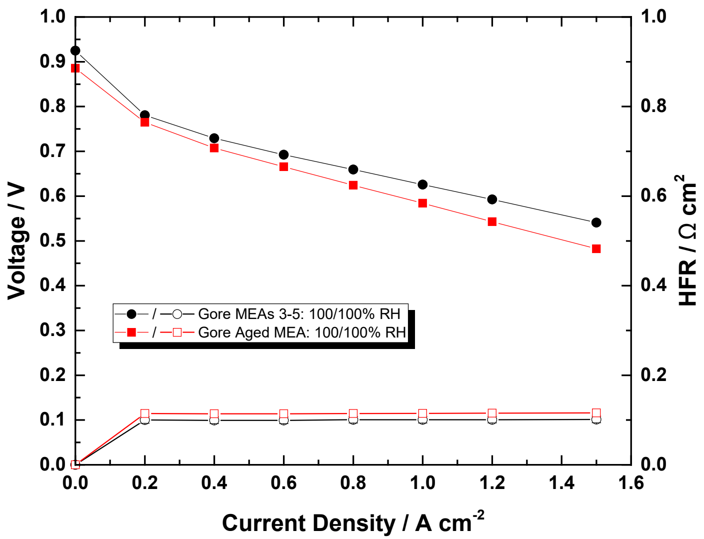
Completed exploratory in situ study of Gore MEA with defected membrane

Gore Collaboration: Understanding the impact of membrane irregularities

- Baselined performance with three pristine MEAs
- Tested first MEA with intentionally created membrane irregularities
  - Multiple irregularities arranged spatially (“D#1, #2, #3”)
  - MEA tested in Gore-proprietary AST for given time at Gore
  - Measured total cell and segmented performance
  - Performed spatial crossover with IR thermography

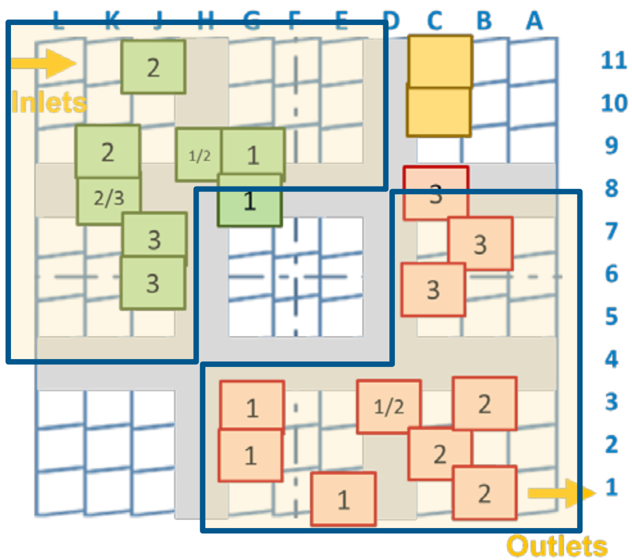


MEA irregularity design



Total cell polarization and HFR comparison between pristine MEAs and defected and aged MEA

Results of segmented performance analysis showing correspondence of defected regions and segments with largest drop in performance relative to nearest neighbors



Tech Transfer Activities

SBIR Phase II collaboration with Mainstream Engineering

- Advance QC prototype device to commercializable configuration
- NREL role
    - Technical assistance, baseline optical scanning
    - In situ testing of membrane defects
    - In-line demonstration on NREL web-line
- Georgia Tech role
    - Provide membranes (as-cast and EBL drilled) in sheet form for in situ testing and optical scanning
- Status
    - Performed in situ testing of effects of membrane defects
    - Hosted Mainstream for 2 demonstrations at NREL
        - Web-line: already made membranes
        - Coating line: during membrane casting

Opportunities for tech transfer

- SBIR/TTO (FCTO directed)
- R2R Consortium CRADA call
- Work for others

Additional activities

- Completed small business voucher (SBV) with Altergy
- Multi-lab R2R Consortium (AMO funded)
- New H_2@Scale CRADA with HyET

Barriers, Needs and Future Work

"Any proposed future work is subject to change based on funding levels."

Barriers and Needs

- General barriers and needs are documented in the MYRD&D Plan
  - Developing and demonstrating QC methods
  - Understanding how defects affect performance and lifetime
- We actively engage with partners to understand their needs, based on their specific processes, materials and MEA constructions
  - **H_2@Scale, HydroGEN, ElectroCat, FCPAD**, industry

Future Work

- Demonstrate a prototype system for in-line membrane thickness imaging
- Determine the feasibility of catalyst loading imaging
- Continue Gore and GM projects, initiate new work with Proton
- Apply multi-spectral techniques to MEA materials and constructions relevant to very-low Pt, Pt-alloy, **electrolysis, AEM, PGM-free etc.** materials
- Study the effects of relevant defects on cell performance and failure onset
  - Continue to expand spatial in situ testing capabilities
- Continue to develop and apply predictive models for diagnostics and defects
- Seek opportunities to demonstrate and **implement diagnostics in industry**

Summary

- Manufacturing R&D is highly relevant to
  - Continued scale-up of fuel cell applications
  - Newer, high priority FCTO activities
- Continued detailed information exchange with industry partners on QC priorities
  - Continued valuable Gore TSA and GM CRADA collaborations
- Optical diagnostics
  - Extensive efforts on membrane full-roll characterization and automated defect detection and classification
  - Completed installation of highly flexible in-line optical test-bed
  - Completed initial optical scanning study of developmental NRC membrane
  - Continued to assist Mainstream Engineering (CRADA for SBIR Phase II)
- IR/TPRE
  - Demonstrated in-line configuration & performed multi-physics modeling to improve
- Completed study of thermal scanning for half-cell membrane thickness
- Effects of defects studies
  - Performed performance and failure studies of electrode defects
  - Performed performance and failure studies of membrane defects and performed modeling of the initial performance effects of pinholes
- Focus on early-stage technique development for new material sets of interest
  - Multi-spectral imaging
  - Application of techniques to LTE, AEM, low-Pt/PGM-free
- *Technical Assistance: FCTO and State of Ohio fuel cell supply chain projects, Sub to SA, Inc.*

Response to Reviewer Comments

Comments: *"Some effort should be placed toward using "real" defects in accelerated tests to see whether failure occurs similarly to manufactured defects." "A study of "real" defects, their identification, and the effect on life should be conducted."*

Response: We certainly agree. This was the point of our study of membrane defects with Georgia Tech. Other defects are ubiquitous, like voids and thin spots in electrodes. Also, now that we are studying process impacts of fabricating electrodes, and to a smaller extent membranes, using relevant high-volume processes, we should have a steady stream of "real" defects.

Comments: *"The results from duPont's N211 and N212 membranes might not be relevant to state-of-the-art membranes. The addition of Gore and development of techniques specifically for advanced membranes is a big step in the right direction."*

Response: We are certainly excited about the interaction with Gore. To be clear, we may not always be able to use Gore membranes for these kinds of studies, however. To a large extent, they typically want us to use their materials for their studies. In addition, while the un-reinforced Nafion membranes are not state of the art, it remains that there is a large body of work performed across the community using these membranes, and as such, their use facilitates comparison. We would like to include DuPont's XL and/or HP membranes in future work, at least as being representative of reinforced state of the art membranes.

Comments: *"The goals beyond automotive fuel cells are not really defined at the manufacturing level yet."*

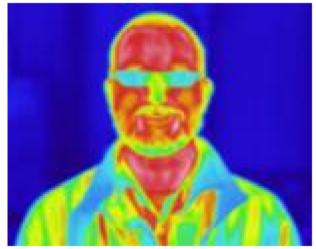
Response: This is an interesting comment. We have certainly focused on automotive fuel cells because of FCTO's focus on such. However, we believe that most if not all of our activities, or at least capabilities, are just as relevant to non-automotive PEM applications. We'd welcome an opportunity to learn what needs are different for non-automotive applications.

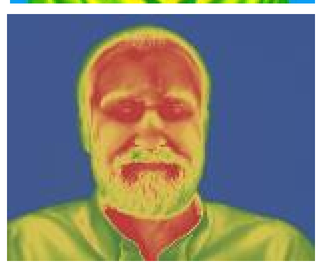
Comment: *"The largest focus has been on platinum catalyst layers; there was some preliminary work on other materials, but it would be good to keep up with the work on electrolysis catalysts and non-platinum-group-metal fuel cell catalysts as these two areas gain momentum to further leverage this capability."*

Response: We fully agree, and with FCTO support, will do so. We already have new work related to QC development for electrolysis/H_2 compression under the AMO R2R Consortium and H2@Scale, as well as process work related to electrolysis and PGM-free catalysts (in the third part of our project, which is presented via a separate poster) under HydroGEN and ElectroCat. These materials will constitute an increasing fraction of our work effort in this project.

Acknowledgement

NREL
- Guido Bender
- Peter Rupnowski
- Brian Green
- Derek Jacobsen





Tufts
- Prof. Iryna Zenyuk

LBNL
- Adam Weber
- Lalit Pant

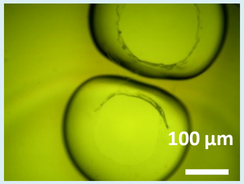
CSM
- Prof. Jason Porter
- Adam Phillips

Georgia Tech
- Prof. Tequila Harris

DOE
- Nancy Garland

Technical Back-Up Slides

Overview of diagnostic techniques

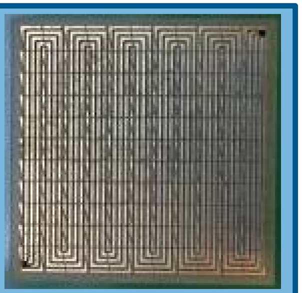
Material	Defects	Detection	Resolution (x-y)	Status
Membrane 	Pinholes, bubbles, scratches, agglomerates, etc.	Optical reflectance	micrometers	Demonstrated on web-line
	Thickness variation (mapping)	Optical absorption	micrometers	Demonstrated on motion prototype
		Optical reflectance (interference fringe)	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 imaging	millimeters	In development
MEA 	Shorting	Through-plane IR/direct-current		Demonstrated on motion prototype
	Membrane integrity	Through-plane IR/reactive excitation		Demonstrated on web-line

Methods for in situ effects of defects studies

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

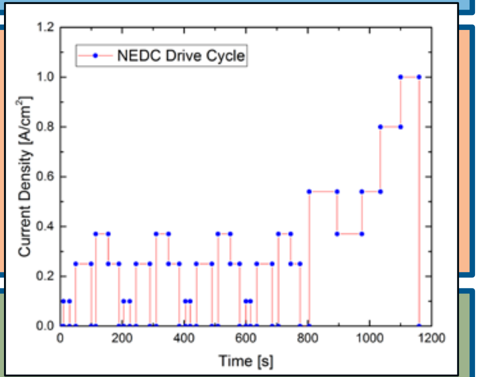
Initial performance (local and total cell)

- 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



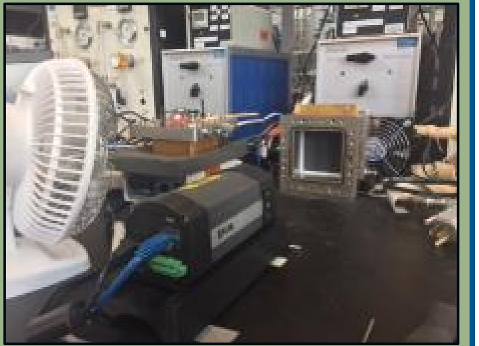
Prolonged performance

- 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



Breadth of capabilities needed to fully determine defect impacts

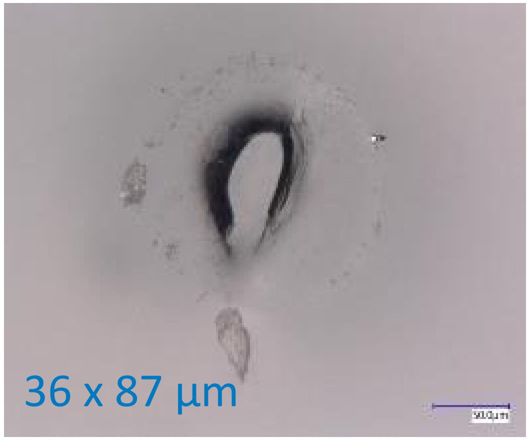
Summary of electrode irregularity studies to date

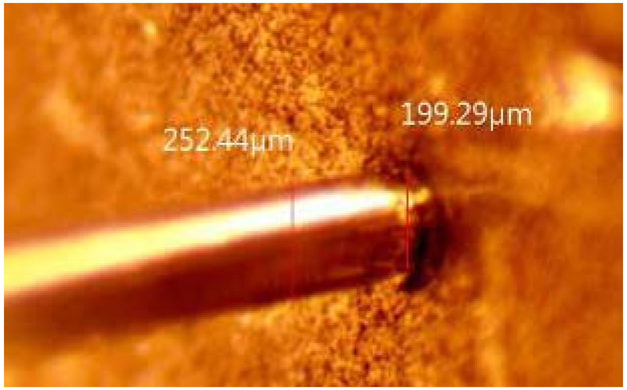
Parametric Study (Impact of XX on…)	**Initial Performance: Total Cell**	**Initial Performance: Local**	**Prolonged Performance: Total Cell**	**Lifetime: Total Cell**
Irregularity Size (0.125, 0.25, 0.5, 1 cm^2)				
Membrane Thickness (25, 50 µm)				
Irregularity Location (Inlet, Center, Outlet)				
MEA Configuration (GDE, CCM)				
Catalyst Loading (0.15/0.15, 0.2/0.2 mg Pt/cm^2)				
Irregularity Shape (Square, Rectangle, Circle)				
Catalyst Layer Thickness Variations (Thin, Bare Spots)				
Irregularity Aspect Ratio				
Slot Die Coating/Manufacturing Defects (Droplet, Scratch, Cut)				

New work

Little/No Impact **Moderate Impact** **Significant Impact** **Ongoing Work**

Fabrication process for pinhole samples via micro-tool





- Intentionally introduced pinhole into commercial Nafion membrane
- Pinholes created by use of a micro needle (i.e., a precise durable tool used for microscopy applications)
- Needle is mounted into cone tool and driven into sample; sample and needle position are carefully controlled by 3 linear translation stages
- Pinholes are optically measured with digital microscope for morphological shape and dimensions

Methods of sample fabrication for electrode thick spots

- Ultrasonically sprayed
  - Created in a similar fashion to thin spot samples, i.e., via SonoTek spray station
  - Size of thick ultrasonically sprayed defects were comparable to that of the thin spot defects
  - Spray pristine catalyst layer of desired loading
  - Mask off entire catalyst layer minus the defect location, i.e., only allow the defect location to get catalyst ink dispersion
- In the non-sprayed cases, ink volume was calculated to be approximately the same volume as the ultrasonically sprayed thick spots
- "Liquid Ink" = same catalyst ink used for ultrasonic spray (i.e. low viscosity)
  - Load liquid ink into a pipet
  - Slowly disperse ink onto catalyst layer, after the pristine catalyst layer was sprayed
    - Performed while the sample was under vacuum, at 80°C
- "Slurry mixture" = catalyst + solvents (i.e., not ultrasonically mixed, higher viscosity)
  - Same deposition method as liquid ink