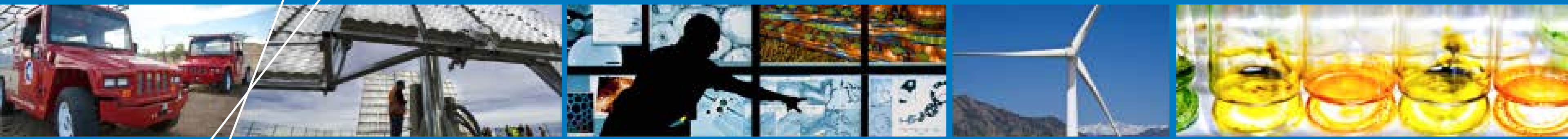
Fuel Cell MEA Manufacturing R&D



National Renewable Energy Laboratory

Michael Ulsh

June 8, 2016

MN001

NREL is a national laboratory of the U.S. Department of Energy, Office of Energy Efficiency and Renewable Energy, operated by the Alliance for Sustainable Energy, LLC.

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	NJIT	CSM	GaTech
2015 (received)	\$1,112,000	\$150,000	\$26,000		
2016 (planned)	\$919,000	\$150,000	\$5,900	\$76,700	\$59,000

Relevance: Project addresses MYPP milestones

From MYPP Section 3.5: Manufacturing R&D

Completed
Ongoing
Assisting industry

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)

Approach

- Understand quality control needs from industry partners and forums
- Develop diagnostics
  - Use modeling to guide development
  - Use in-situ testing to understand the effects of defects
- Validate diagnostics in-line
- Transfer technology

Go/No-go Criteria:
- **Detect pinhole of < 150 µm**
- **At an exposure time of < 5 s**

Date	Milestone/Deliverable (as of 4/8/16)	Complete
9/15	Go/No-go decision for development of in-line through-plane reactive excitation concept	100%
12/15	Complete evaluation of new segmented cell test board	100%
3/16	Complete single-point fast optical spectroscopic membrane thickness measurements	100%
6/16	Spatially resolved performance measurements of MEAs with electrode defects	80%
9/16	Demonstrate improved RIF performance, based on LBNL predictive modeling	25%

Collaborations

Industry Collaborators

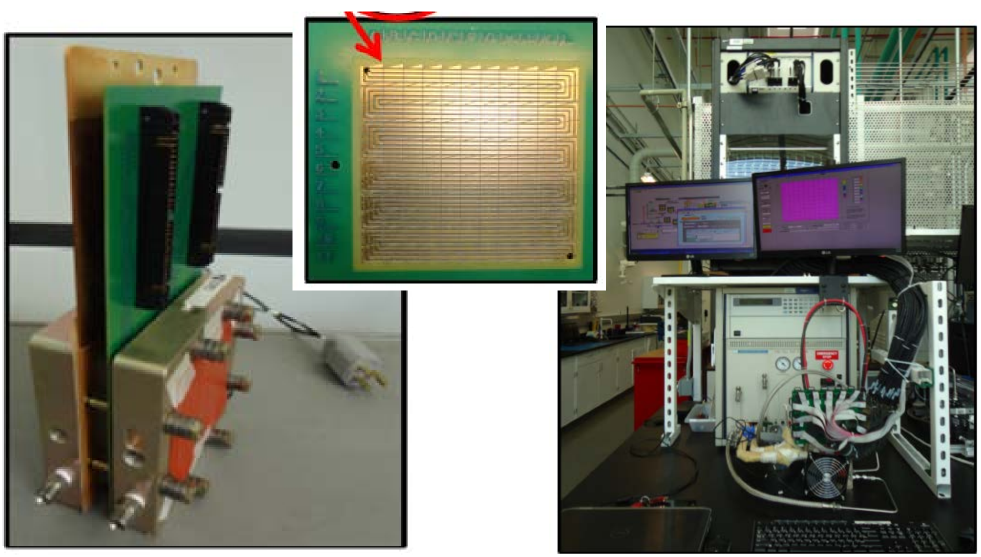
- **GM, 3M, Mainstream Engineering:** detailed input on manufacturing QC needs, prioritization of diagnostic development, feedback on technique capabilities, defect selection and sample fabrication; demonstration of commercializable in-line QC device

Labs and Academia

- **Lawrence Berkeley National Lab:** model development and integration
- **NREL National Center for Photovoltaics:** diagnostics development
- **Colorado School of Mines:** cell testing
- **Georgia Tech:** fabrication and characterization of as-manufactured defect samples

Technical Accomplishments: Continued in situ effects of defects studies: Performance studies

- **High resolution spatial performance studies**
  - Local and total cell effects
  - “Defects” created to simulate relevant process variations
  - Materials with actual as-manufactured variations
- **Objective is to determine:**
  - What defects actually effect performance or lifetime?
  - What do diagnostics have to detect?

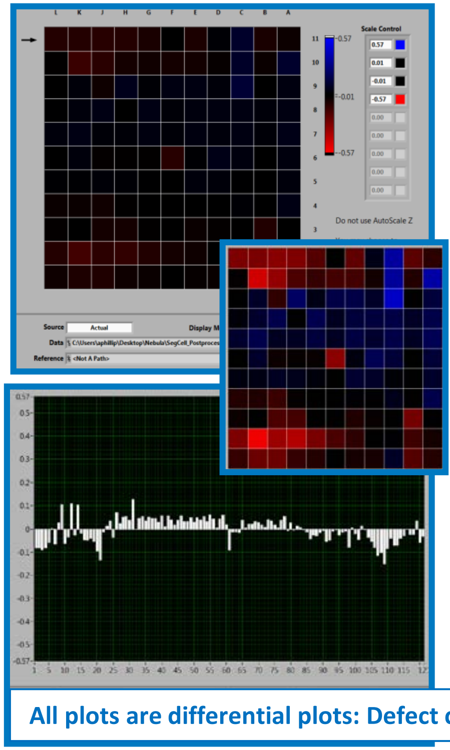


Studies of electrode defects:

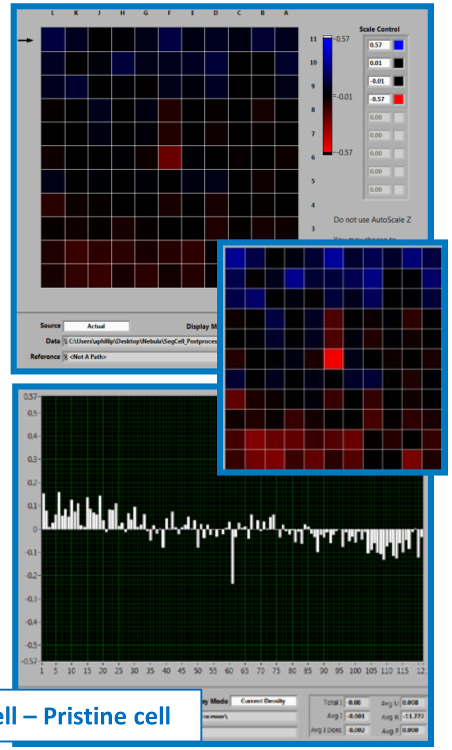
- Cathode centered bare spots
  (0.0625 to 1 cm^2)
- Defect on anode vs. cathode
  (0.5 cm2, 100% reduction, centered)
- Inlet vs. center vs. outlet
  (0.5 cm2, 100% reduction)
- Shape
  (0.5 cm2, 100% reduction)
- 1 mil vs. 2 mil membrane
  (0.5 & 1 cm2, 100% reduction)
- Nominal catalyst loading
  (0.5 & 1 cm2, 100% reduction, centered, 0.15/0.15 vs. 0.2/0.2 mg Pt/cm2)
- Reduction vs. addition
  (1 cm2, centered)
- CL total volume reduction
  (1% area reduction, 50% vs. 100% thickness reduction, square vs. rectangle)
- CCM vs. GDE
  (0.5 cm2, 100% reduction, inlet vs. center)
- GDE-specific defects
  (0.5 cm2, 100% reduction of catalyst, interface ionomer, or both)

Technical Accomplishments: Continued in situ effects of defects studies: Example study

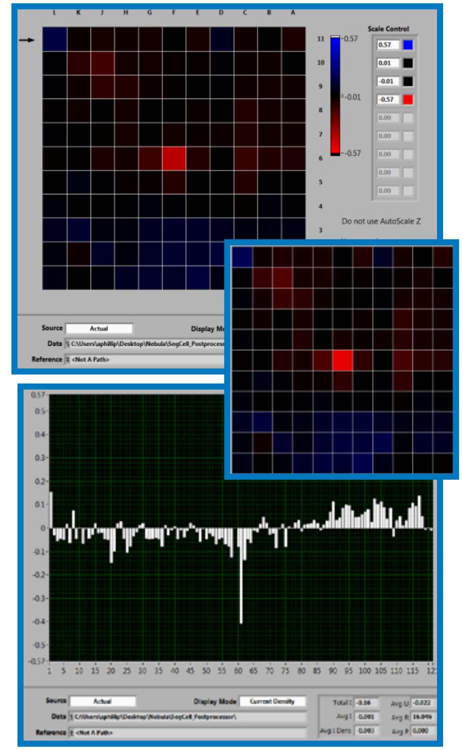
0.125 cm^2



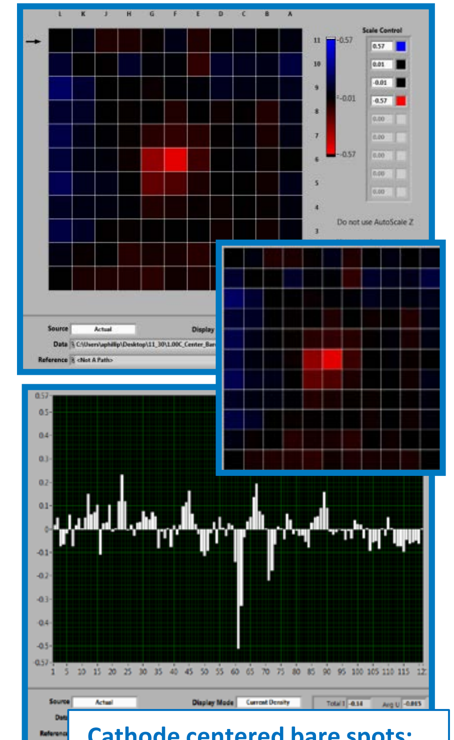
0.25 cm^2



0.5 cm^2



1 cm^2

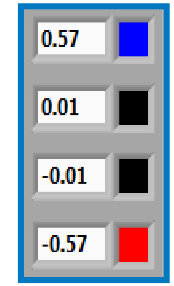


All plots are differential plots: Defect cell – Pristine cell

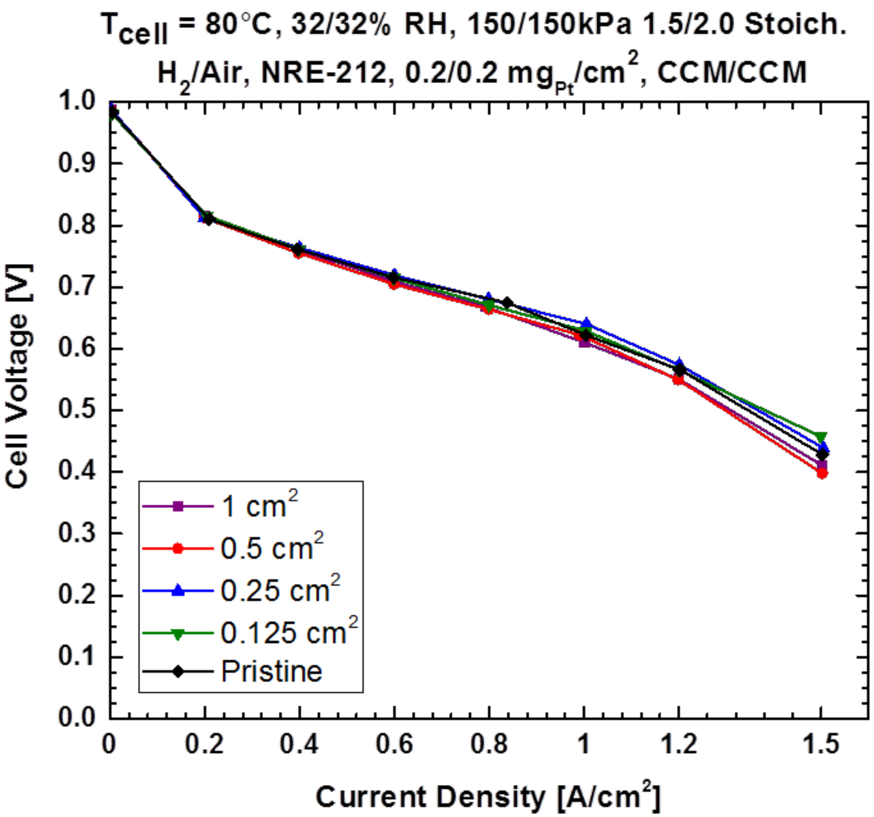
Cathode centered bare spots: 1.2 A/cm^2, 32/32% RH, NRE-212, 0.2/0.2 mg$_{Pt}$/cm^2

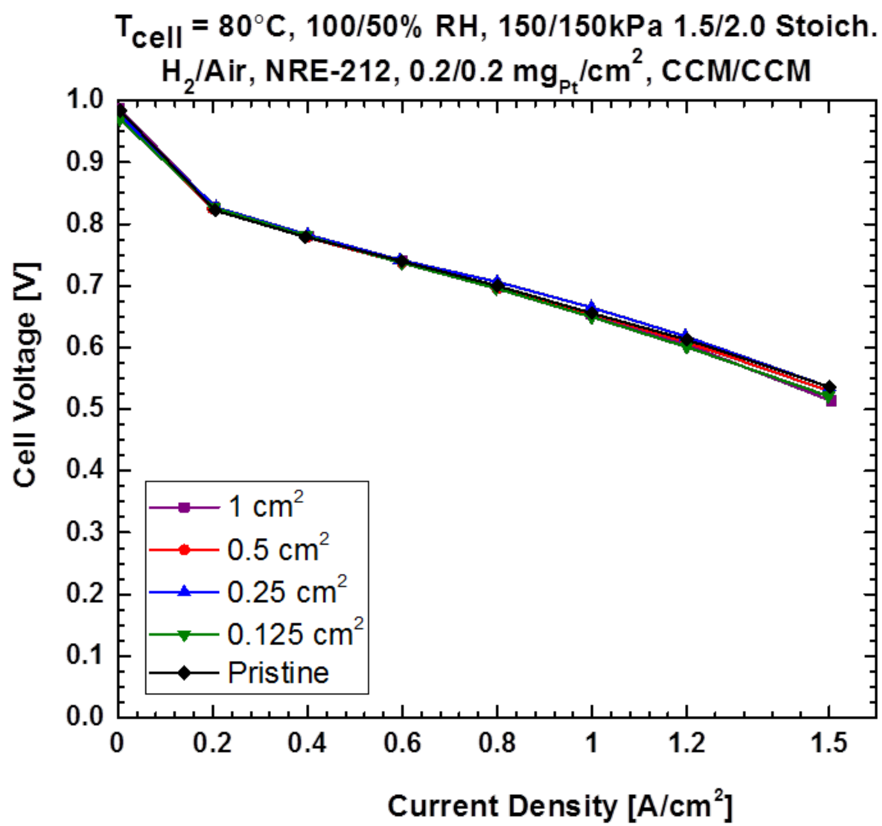
- Fixed-scale intensity graphs (top): local performance effects are clearly detected for 0.25, 0.5 and 1 cm^2 defects
- Auto-scaled graphs (insets) shows the effect of the defect relative to along-the-flowfield performance variations in the pristine base case
- Performance effects increase with defect size and current density

A/cm^2



Technical Accomplishments: Continued in situ effects of defects studies: Example study

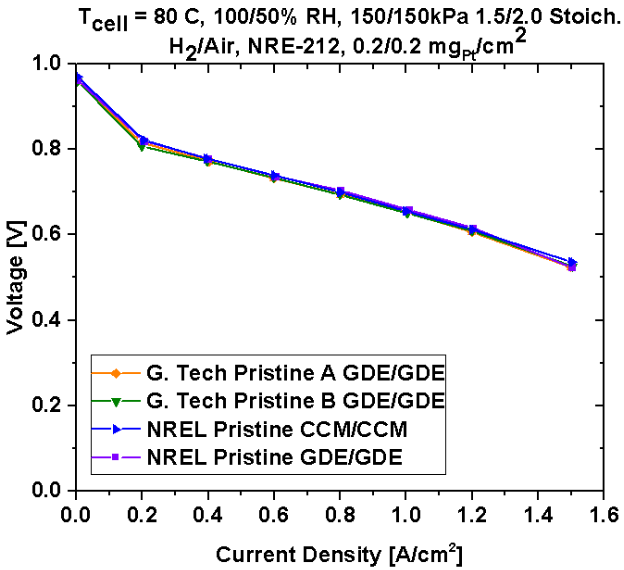


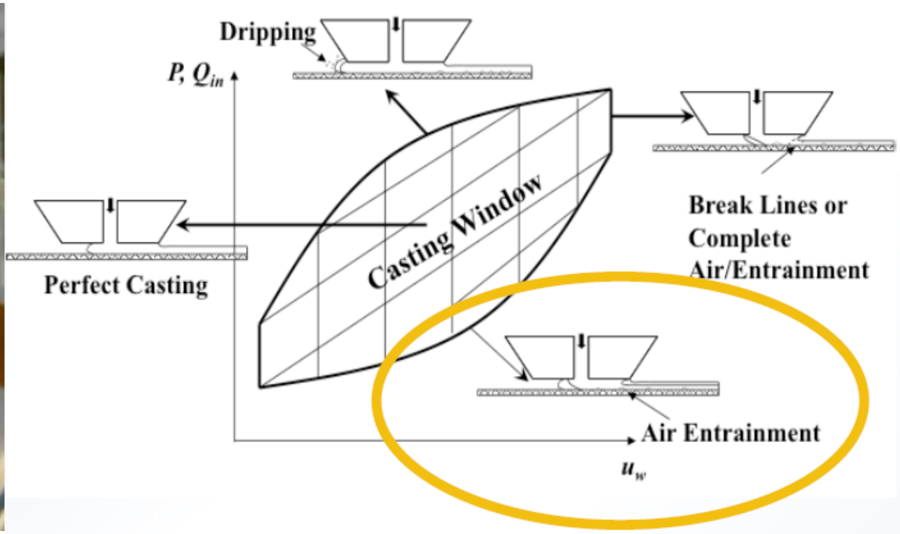


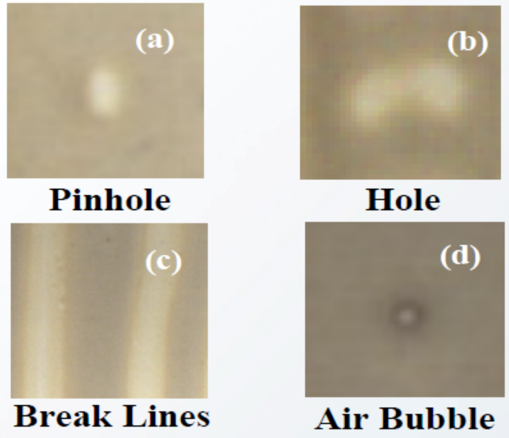
- Minor total cell performance effect at dry (32/32%) condition observed for the 0.5 and 1.0 cm^2 defects
- No effect at wet (100/50%) condition

Technical Accomplishments: Continued in situ effects of defects studies: New collaboration

- **New collaboration with T. Harris group at Georgia Tech**
- **Leverage their expertise to fabricate membranes with real, as-manufactured defects**
  - Specially instrumented R2R casting line
  - Experimental and numerical process-window studies for Nafion casting
- **Established GDE-based MEAs with comparable performance to CCM, including with GT pristine Nafion membranes**

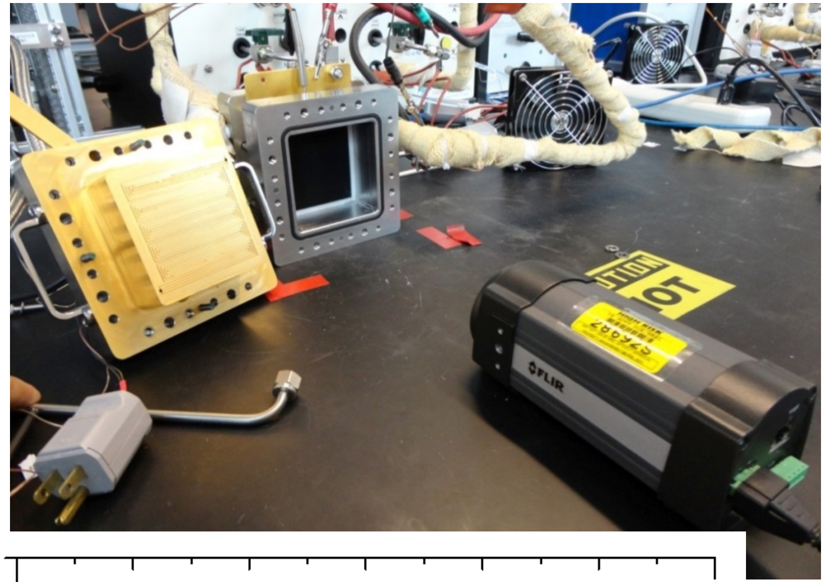




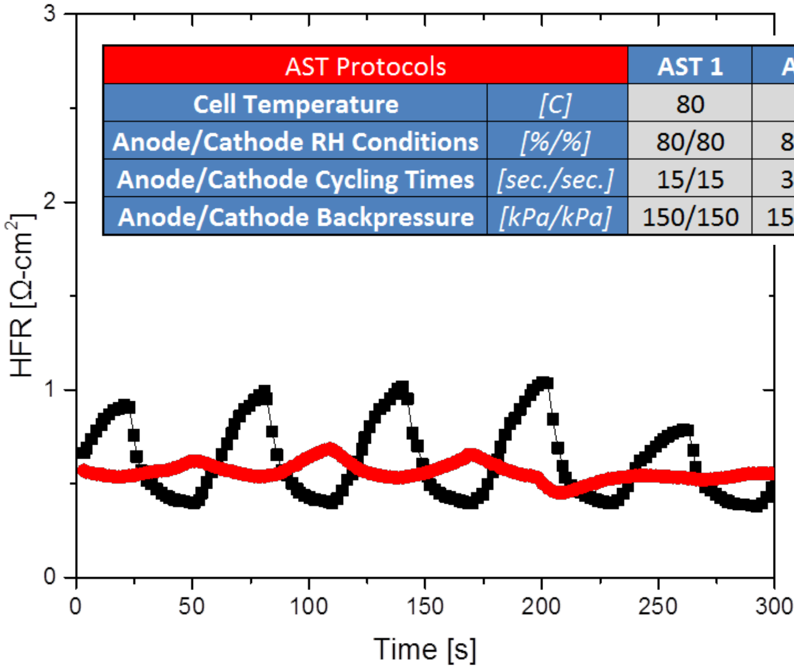


Technical Accomplishments: Continued in situ effects of defects studies: Failure studies

- **Objective: does a variation cause a failure…**
  - Faster than a pristine?
  - At the location of the defect?
- **Accelerated stress test:**
  - Combined mechanical and chemical degradation
  - Verified constant HFR cycle amplitude per LANL findings
  - Chose specific conditions to allow capture of failure onset
- **Specialized cell hardware with removable cathode flowfield:**
  - Allows all standard in situ diagnostics
  - Enables periodic quasi- in situ IR imaging (cell does not need to be removed from hardware)

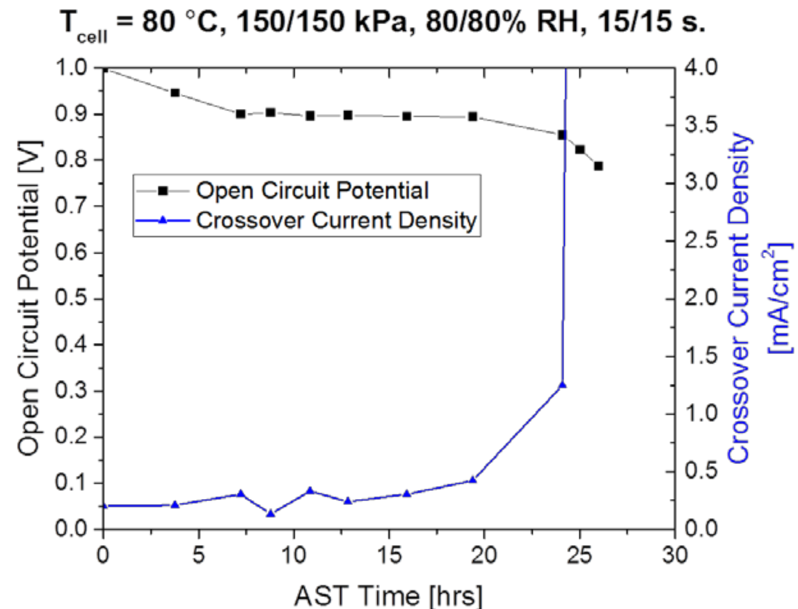


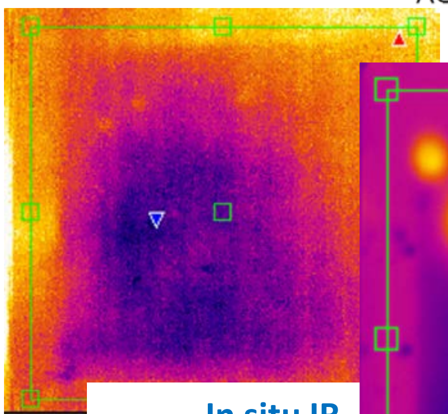
AST Protocols		AST 1	AST 2
Cell Temperature	[C]	80	80
Anode/Cathode RH Conditions	[%/%]	80/80	80/80
Anode/Cathode Cycling Times	[sec./sec.]	15/15	30/30
Anode/Cathode Backpressure	[kPa/kPa]	150/150	150/150

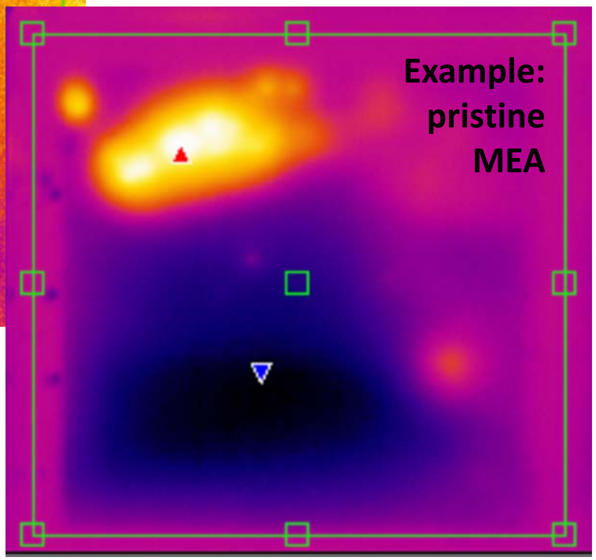


Technical Accomplishments: Continued in situ effects of defects studies: Failure studies

- **In situ diagnostics as indicators of failure onset**
  - Primary: continuously monitored open circuit voltage (OCV) decay rate
  - Secondary: periodically measured hydrogen crossover current density
- **As indicated by in situ diagnostics, periodically perform IR imaging to capture the development of failure within the MEA**



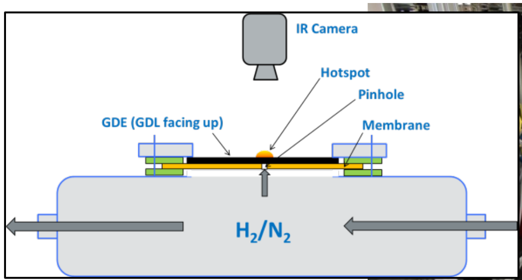


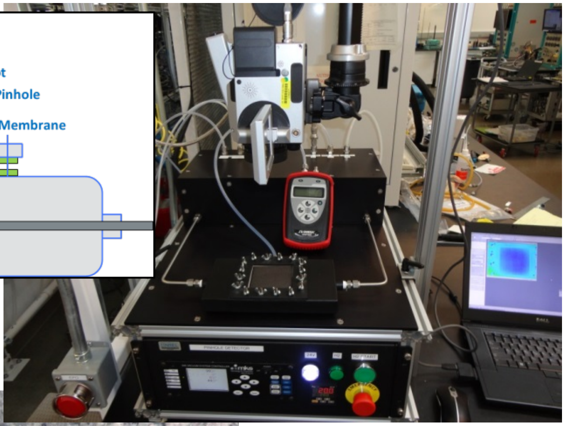


In situ IR imaging: beginning of test (above), failure (right)

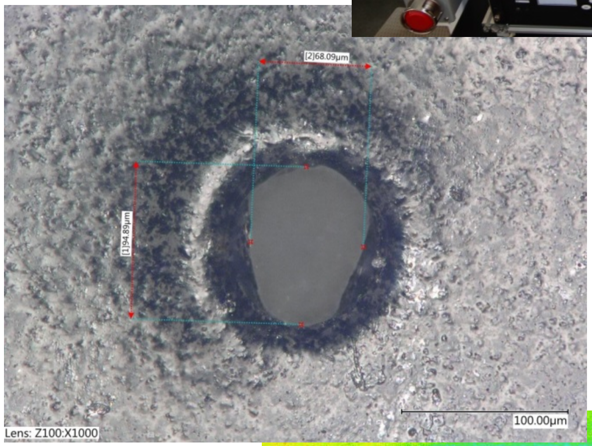
Technical Accomplishments: Demonstrated TPRE for pinhole detection on static test-bed

- **Through-plane reactive excitation (TPRE) detects:**
  - Failure of membrane integrity in CCMs, half-cells or full MEAs
  - Location & severity of failure
- **Successfully detected milestone criteria defect**
  - < 150 µm, < 5 sec exposure time
  - Used samples from GM and NREL
  - Studied effects of reactive gas exposure time, H_2 concentration, flow rate to understand feasibility for in-line implementation

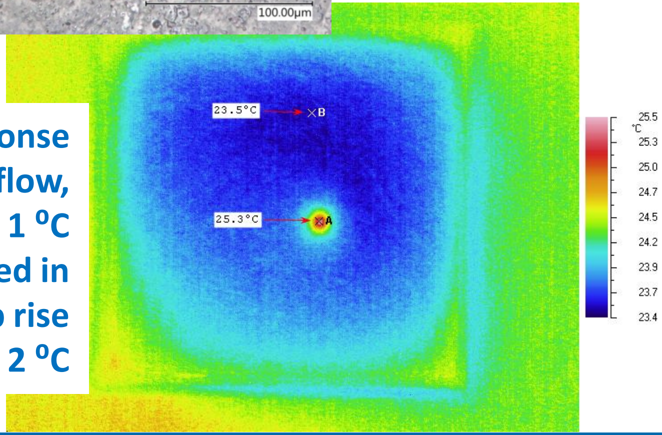




Pinhole detection apparatus



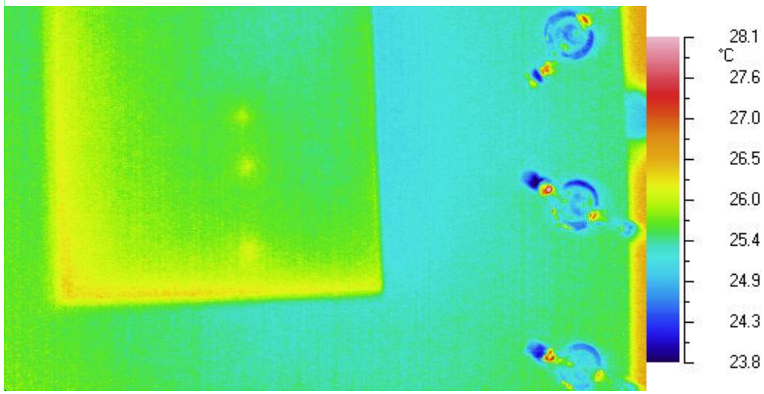
90 µm diameter pinhole in 18 µm thick membrane, tested with GDE (0.2 mg/cm² Pt)

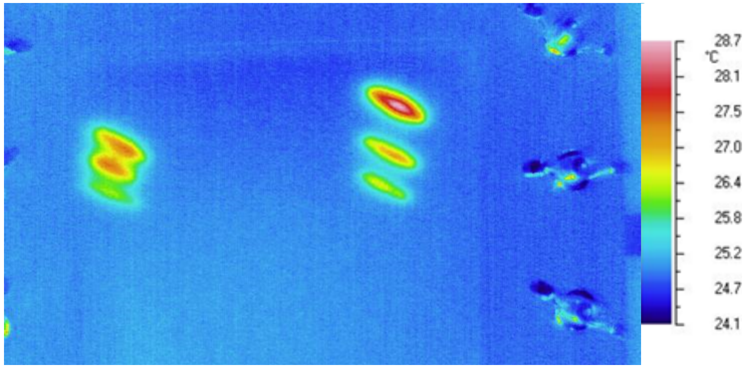


Thermal response with 0.5 lpm H_2 flow, 5 sec pulse: 1 ^oC temp rise achieved in 2 sec; Max temp rise > 2 ^oC

Technical Accomplishments: Developed multi-physics models for static and future in-line TPRE

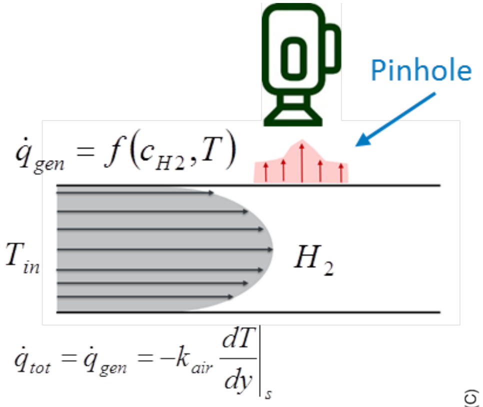
GM GDE + membrane half cell with three 25 µm pinholes: ~0.2 ^{o}C temperature rise => proves feasibility

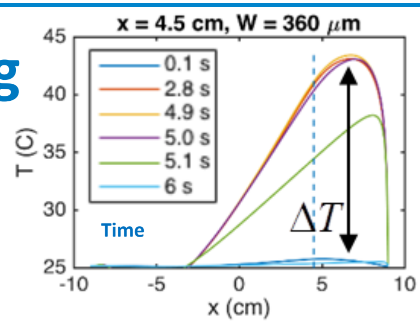




GM GDE + membrane half cell with cuts in membrane prior to lamination, tested at 0.5 lpm H_2 and 5 sec pulse: 3 ^{o}C temperature rise

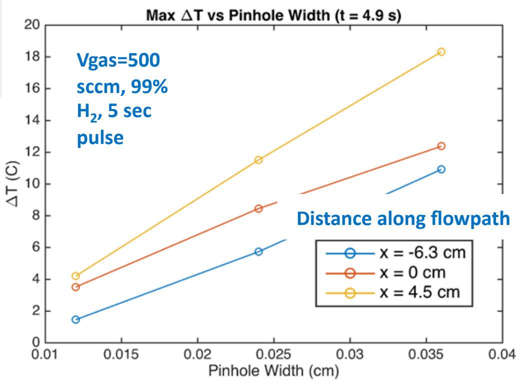
LBNL TPRE modeling

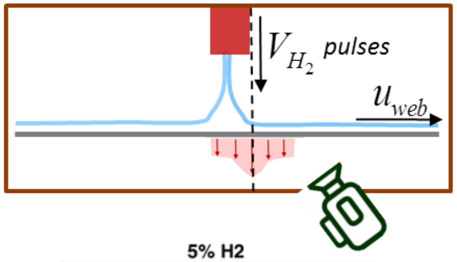


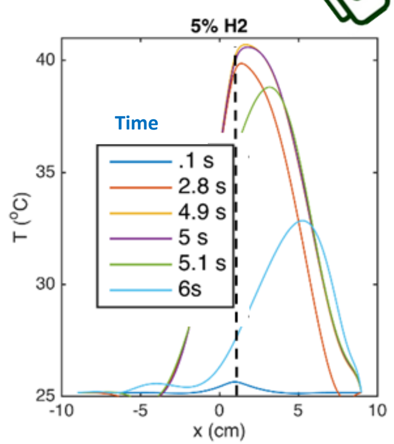


Static configuration:

- ΔT fn(pinhole size)
- ΔT fn(location relative to flow)

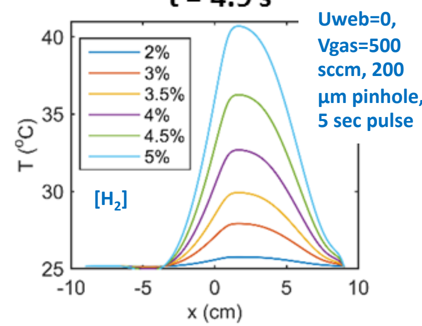






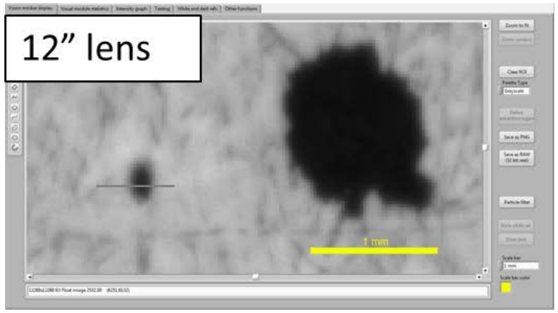
In-line (impinging flow) configuration:

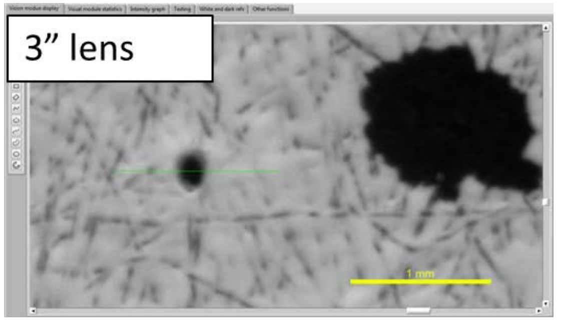
- Can achieve ΔT within ~secs
- Can achieve ΔT with a low (<LFL) H_2 concentration



Technical Accomplishments: Demonstrated higher resolution optical reflectance imaging

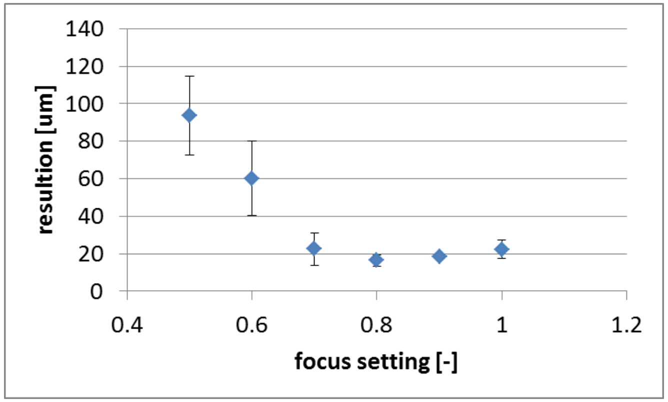
- **New linear lens with 3” field of view**
- **Reflectance imaging of membranes at 10 fpm**
    - 3M, Nafion



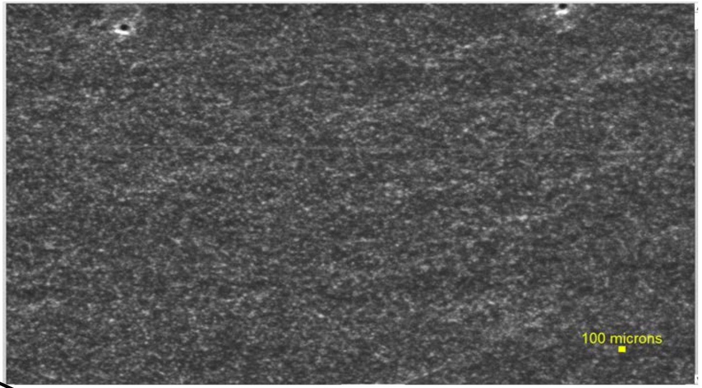


FOV	Pixel resolution	Optical resolution
12”	25 µm	62.5 µm
3”	6.25 µm	16 µm

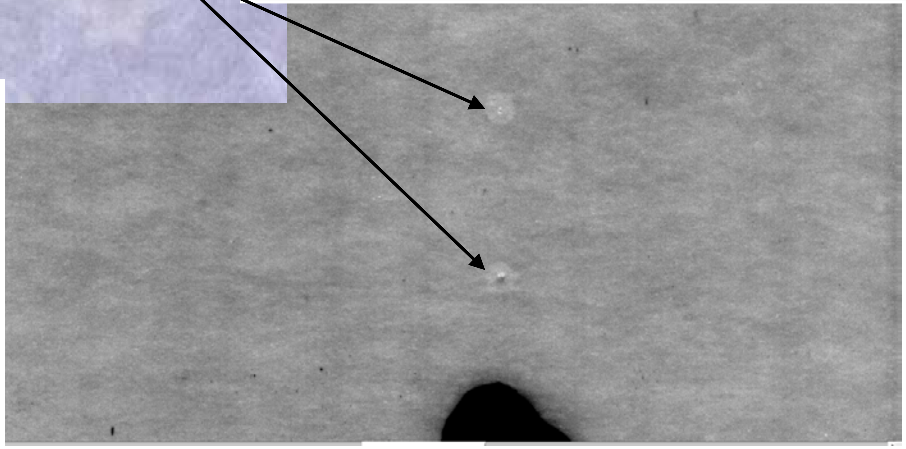
Opt. res. measured via 1951 USAF Resolution Test



Resolution optimization study



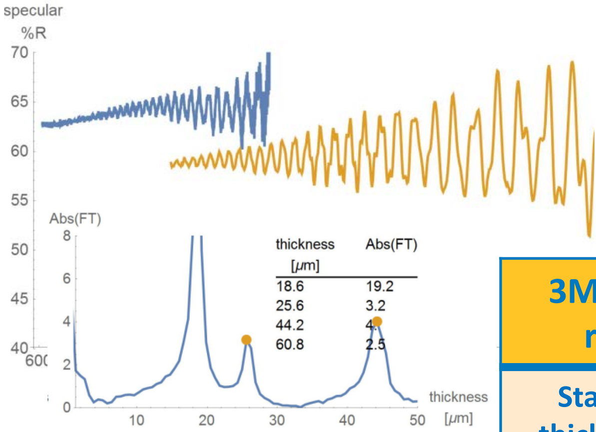
Optical microscopy of 25 µm pinhole



Reflectance imaging of 2 different 14 µm 3M reinforced membranes with <u>intentionally created</u> pinholes at 10 fpm

Technical Accomplishments: Measured single-point membrane thickness with reflectance spectroscopy

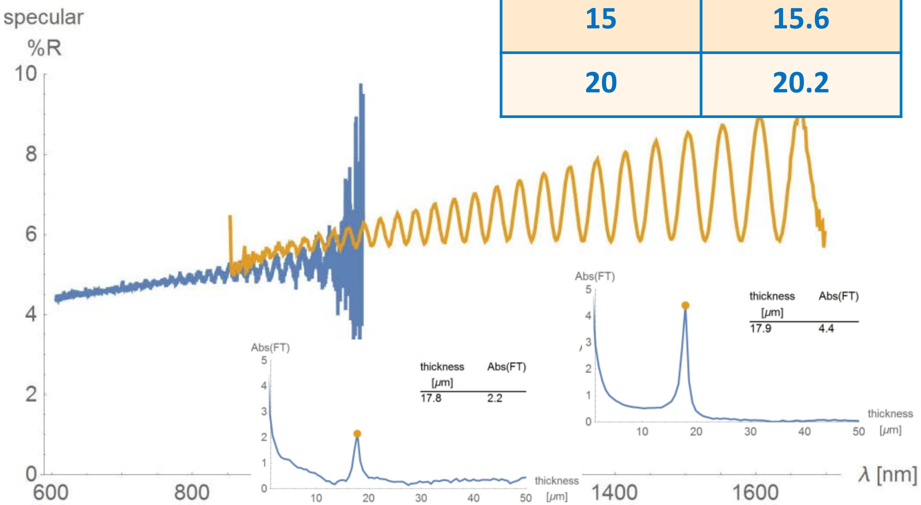
- **Tested a range of relevant membranes**
  - 3M membranes with and without reinforcement
  - Nafion and other commercial PFSA membranes
  - Range of thickness from 6 to 50 µm
- **Methodology**
  - Well-known film interference fringe method
  - Used optical and IR spectroscopy
  - Used reflectance and transmission modes
  - Used Fourier Transform to process spectra and identify thickness peaks
- **Demonstrated thickness measurement with and without protective layer**
- **Preliminary step to thickness imaging effort**



Visible and IR reflectance spectroscopy for 25 µm Nafion with 2 protective layers

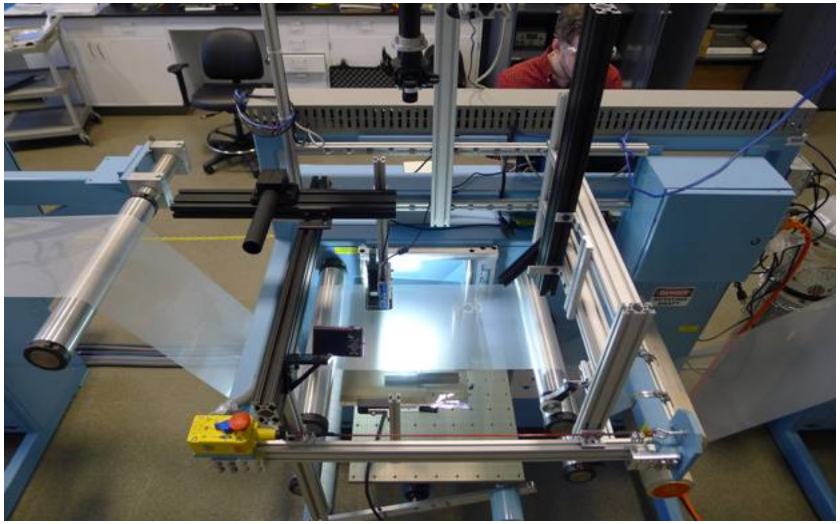
3M membranes (no reinforcement)	
Stated thickness (µm)	Measured thickness (µm)
5	5.2
7.5	7.9
10	10.4
15	15.6
20	20.2

Visible and IR reflectance spectroscopy for 18 µm PFSA membrane

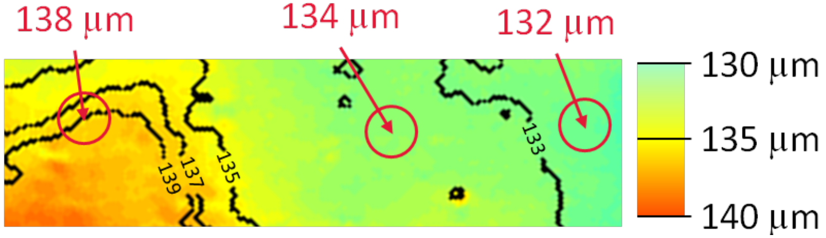


Technical Accomplishments: Supporting SBIR tech transfer project

- **Collaboration with Mainstream Engineering**
  - SBIR project awarded for design of commercializable device based on NREL's optical inspection patents
  - Mainstream performed demonstration of prototype device at NREL
    - Used web-line and roller systems
    - Used rolls of commercial and industry partner membrane materials



Mainstream's Phase I prototype on the NREL web line with optical system, encoder, printer, and data analyzer

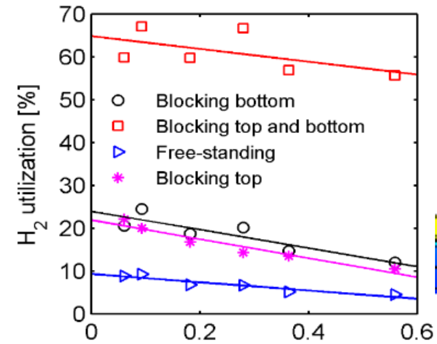


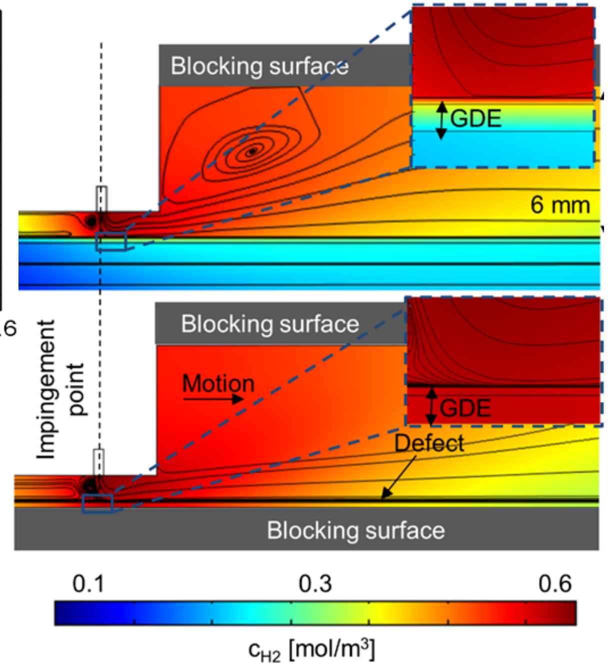
Thickness map of a deformed Nafion®-115 sample (Mainstream result)

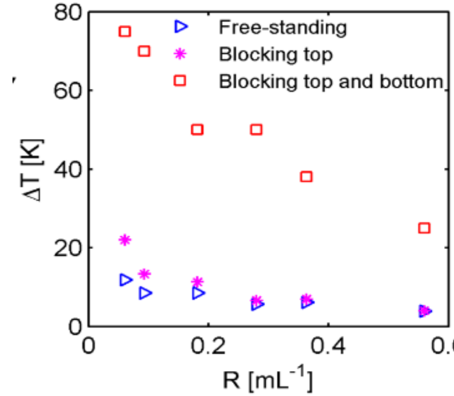
Technical Accomplishments:

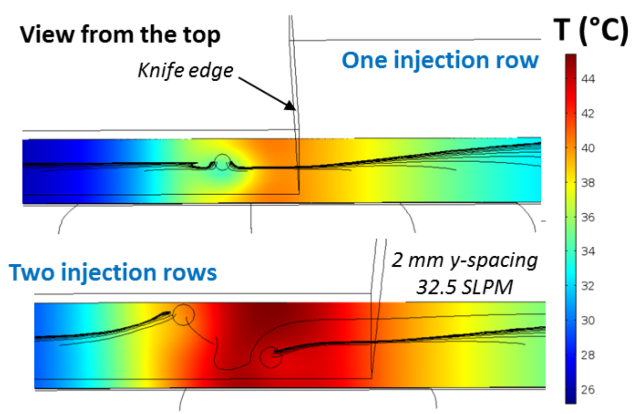
Extended IR/RIF models to predict technique improvements

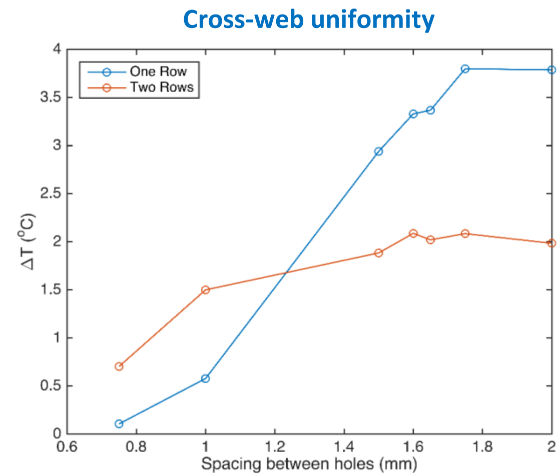
- **Improvement in H_2 utilization/ΔT via addition of blocking surfaces**
- **Improvement in cross-web uniformity and temperature rise via jet design**
  - Decreased jet spacing
  - Addition of second row of jets





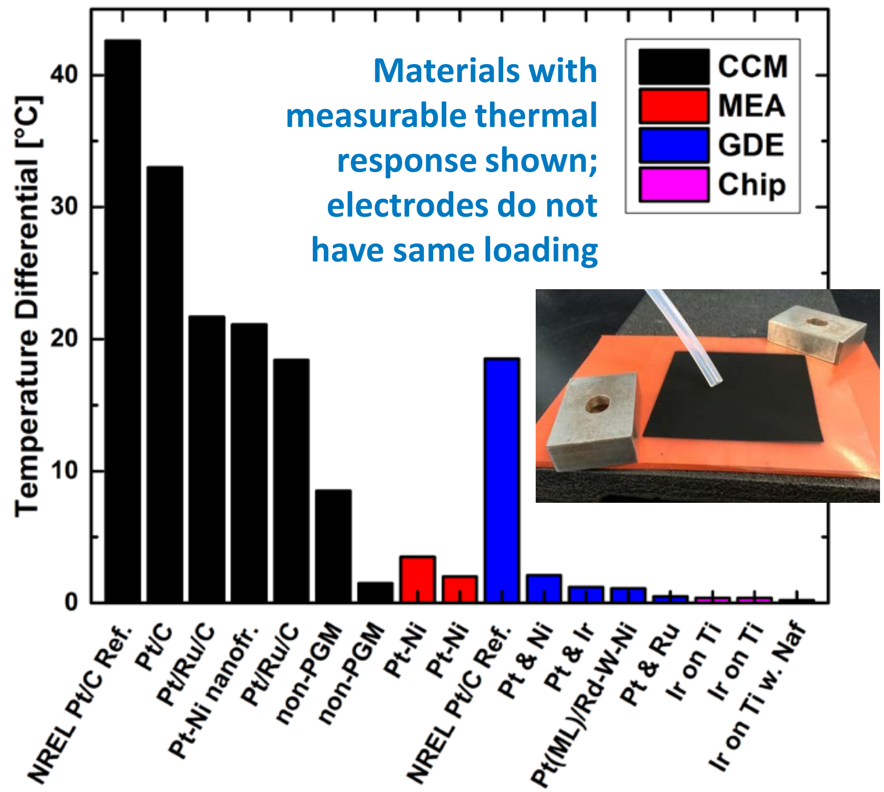


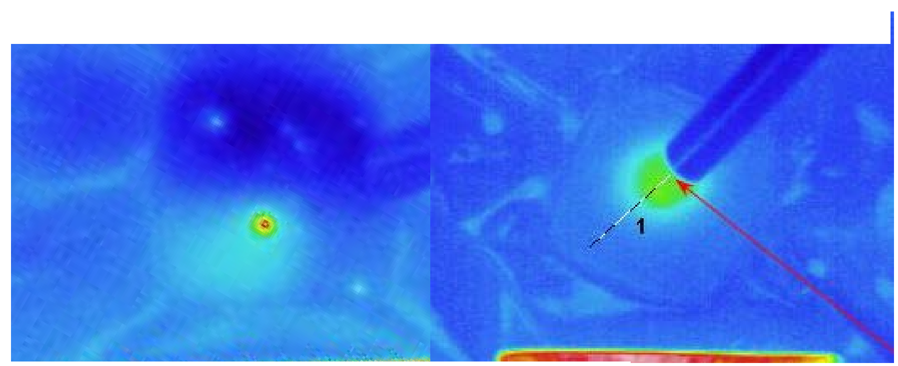




Technical Accomplishments: Expanded IR/RIF applicability to alternate catalysts

- **Objective: Understand the applicability of reactive impinging flow (RIF) to measure electrode uniformity in non-Pt-only catalyst systems**
  - Materials: Pt+X, Ir, Co, Ni, Fe, TiOx, Mo, Mn, Ag, NPGM
  - Structures: core-shell, nano-frames, other
- **LANL, ANL, BNL, and Proton OnSite provided electrode samples**
- **Generally successful for:**
  - PGM-containing
  - Some PGM-free





Barriers, Needs and Future Work

Barriers and Needs

- General barriers and needs are documented in the MYPP (slide 3)
  - Developing and demonstrating QC methods
  - Understanding how defects affect performance and lifetime
- We actively engage with industry to understand their needs, based on their specific processes, materials and MEA constructions

Future Work

- Demonstrate improvement in RIF detectability based on LBNL modeling
- Demonstrate a prototype system for in-line membrane thickness imaging
- Develop a concept, using modeling and experimentation, for in-line TPRE
- Explore optical methods for catalyst loading imaging
- Study the effects of relevant defects on cell performance and failure onset
  - Relevant electrode and as-manufactured membrane defects
  - Develop and prototype new expanded-capability segmented cell hardware
- Continue to develop and apply predictive models for diagnostics and defects
- Apply optical and infrared techniques to relevant industry MEA constructions, including fuel cell, electrolysis and non-PGM materials

Summary

- **Addressing many of the MYPP milestones**
- **Continued detailed information exchange with industry partners on QC priorities**
- **Effects of defects studies:**
  - **Performed high resolution spatial performance studies of electrode defects**
  - **Initiated new collaboration with Ga Tech to test as-manufactured membrane defects**
  - **Established methods and initiated failure onset studies of defected MEAs**
  - ***Completed testing of new segmented hardware concept board***
- **IR/TPRE:**
  - **Demonstrated pinhole detection on static testbed, met Go/No-go milestone criteria**
  - **Developed multi-physics model to predict detection limits and pathways for in-line implementation**
- **Optical Reflectometry:**
  - **Demonstrated reflectance imaging at higher resolution**
  - **Demonstrated single-point membrane thickness measurement by reflectance spectroscopy**
  - **Assisted Mainstream Engineering in demonstrating their optical QC prototype**
- **IR/RIF:**
  - **Used multi-physics model to expand predictions to improve detectability**
  - **Studied the applicability of RIF to electrodes with non-Pt-only catalysts**
- ***Technical Assistance: DOE and State of Ohio fuel cell supply chain projects, SBIR QC Project, Sub to SA Inc. on automotive FC cost analysis, Supported AMO R2R activities***

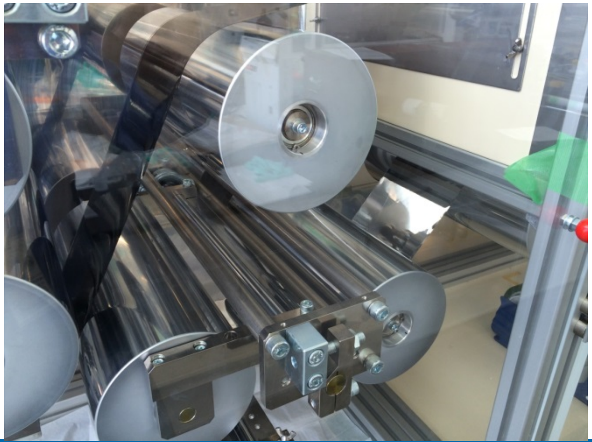
Tech Transfer Activities

"Manufacturing QC auto OEM Road Show"

- Activity: Focus on auto OEMs to ensure information about QC development capabilities is understood
- Impact:
  - Fine-tune existing QC techniques per OEM requirements
  - Technology transfer
  - New joint projects
- Accomplishments:
  - Coordinated interactions with GM through CRADA
  - Initiated NDAs with AFCC & Ballard; visit to Burnaby
  - Hosted and held discussions with Toyota Mirai staff
  - Collaborated with Mainstream on QC device development

MEA scale-up

- Emerging core competency
- Synergistic with NREL's MEA Integration and Manufacturing core competencies
- Demonstrate scalability of new catalysts, materials & structures
- Assist small businesses in scale-up studies
- Process-material-performance studies
- Currently have R2R membrane, electrode coating capability
- Exploring MEA fabrication



Response to Reviewer Comments

Comment: *"It would be nice to see a thrust toward gauge R&R. An effort to run large lengths or areas of materials for each of the inspection methods with "normal" materials is needed to demonstrate the robustness of the measurement methods. What are the rates of false positives, false negatives, repeatability, etc." (as well as several other comments similar to this)*

Response: We agree with the comments and have begun to put more emphasis, with small and sheet samples from industry partners, to seek and acquire sets of samples to be able to assess repeatability properly. In regards to roll materials, while it is still difficult for us to acquire long lengths, we have begun to pursue this type of activity in the Mainstream collaboration.

Comments: *"It is still not clear what detection limits are needed for quality assurance and what the correlation between defect size and frequency and performance are." "The proposed future work to predict the performance effects of defects is very important to this work." (as well as several other comments similar to this)*

Response: This topic continues to be a large part of our effort. We have completed a range of studies of the performance effects of electrode defects and have established methods for studies of failure resulting from defects. Our new collaboration with Georgia Tech enables us to pursue the study of realistic membrane defects. We agree that increased input from industry on this topic would be very useful, and while difficult because of confidentiality, we continue to pursue it.

Comments: *"It seems necessary to associate with this existing global community, and to acquire data about what particular measurements provide highest value for quality control in manufacturing."*

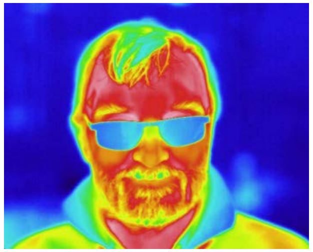
Response: Coincidentally, we are visiting (May, 2016) three laboratories in Europe that have PEM MEA manufacturing efforts, and are active with the European PEMFC manufacturing base. As suggested, we hope to gain from these exchanges.

Comments: *"It would be good to add quality manufacturing firms as part of this QC effort, as that makes sense." "…apply the diagnostic tools also on MEA components (CCMs & GDEs) for PEM water electrolysis." "NREL should move into tasks that address stack engineering."*

Response: We think all of these are interesting and relevant suggestions for future directions. The Mainstream collaboration is a step in the direction of more interaction with QC device developers. Also note that we have interacted with Proton OnSite for some time now on these topics, and have been seeking opportunities to work with them as they increasingly consider PEMFC-like MEA materials and manufacturing processes.

Acknowledgement

NREL
- Michael Ulsh
- Guido Bender
- Peter Rupnowski
- Bhushan Sopori
- Jocelyn Mackay (SULI)



LBNL
- Adam Weber
- Iryna Zenyuk

CSM
- Prof. Jason Porter
- Adam Phillips

Georgia Tech
- Prof. Tequila Harris

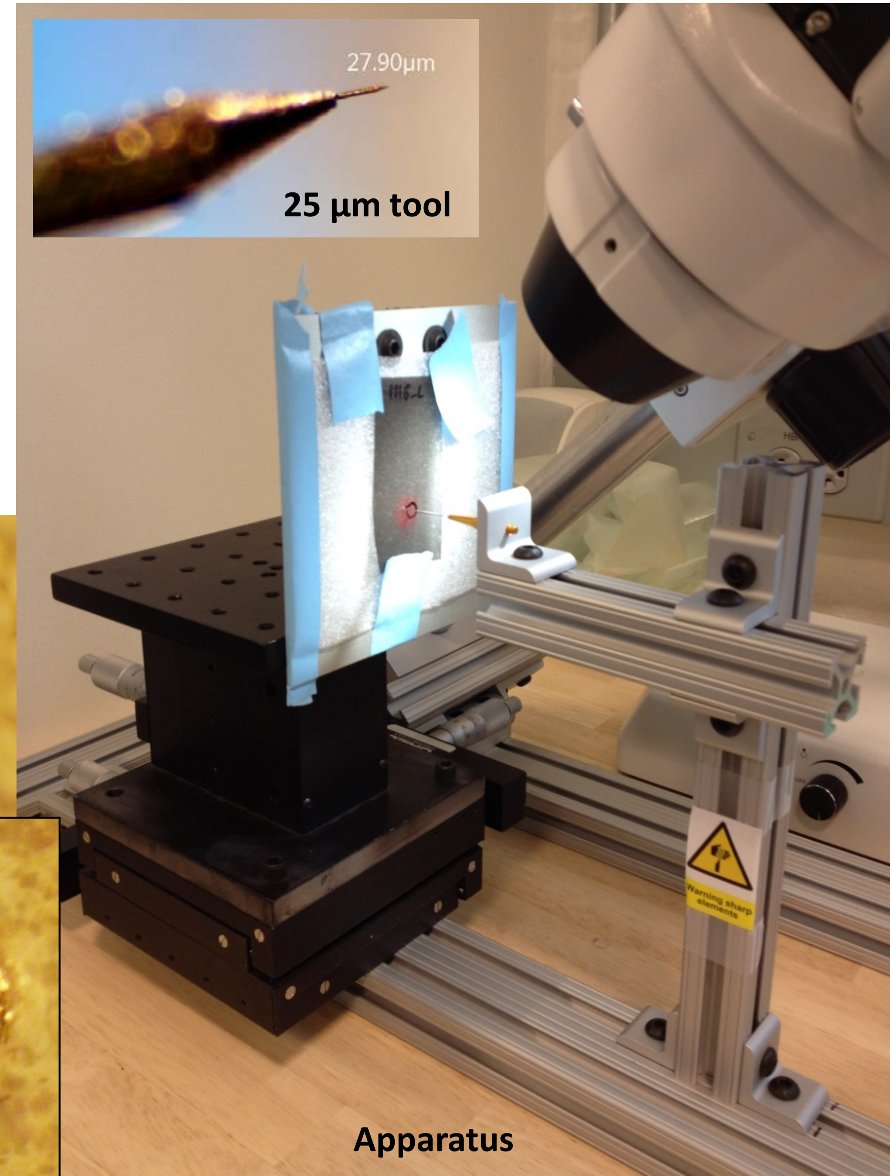
DOE
- Nancy Garland

NREL
NATIONAL RENEWABLE ENERGY LABORATORY

Technical Back-up Slides

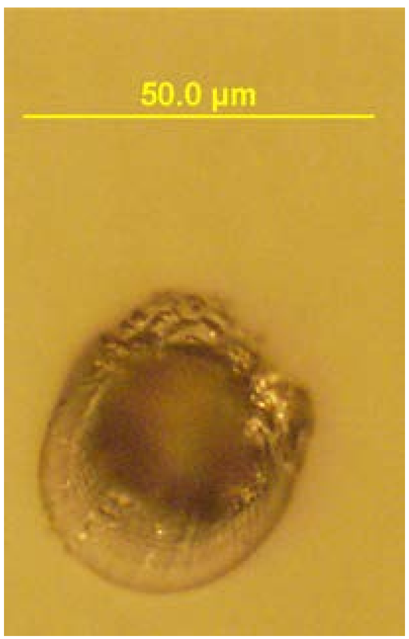
Technical Accomplishments: Developed repeatable method for pinhole fabrication

- **Developed apparatus and methods to fabricate pinholes**
  - Membranes, half-cells, MEAs
  - 25, 120, and 250 µm micro-tools
  - Apparatus on microscope stand for “real-time” control

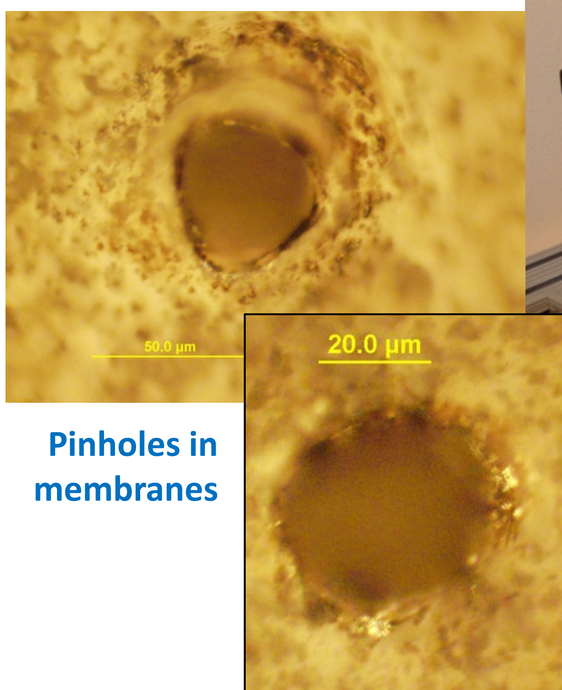


25 µm tool

Apparatus

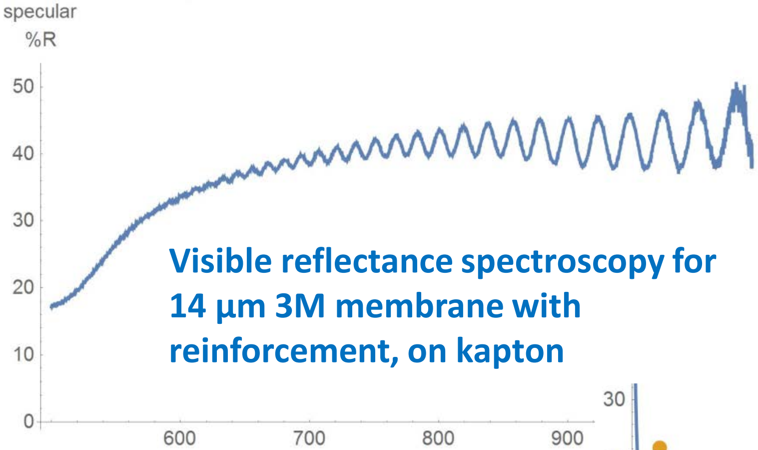


Pinhole in half-cell

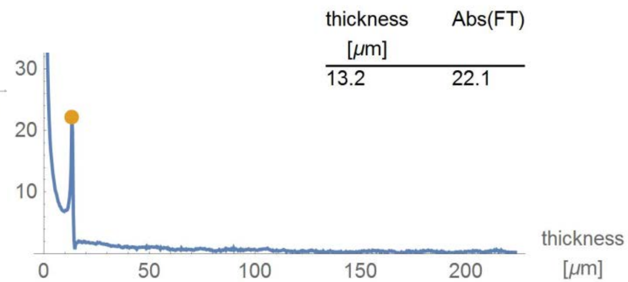


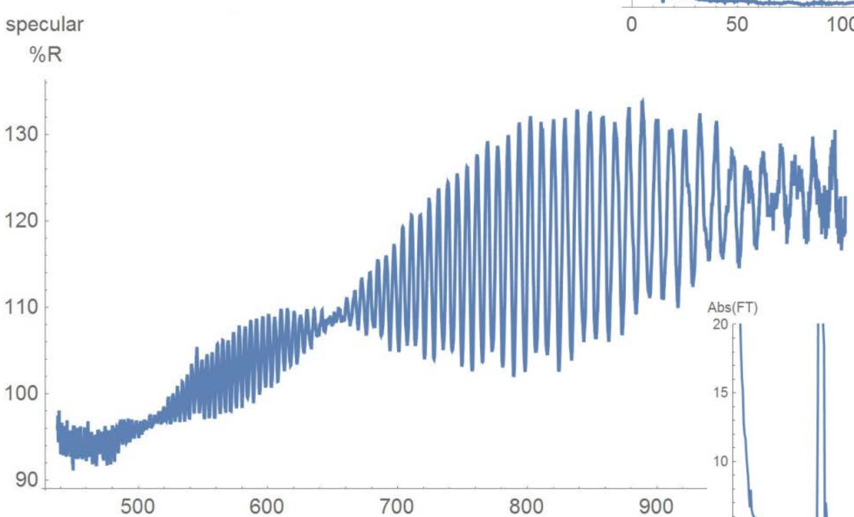
Pinholes in membranes

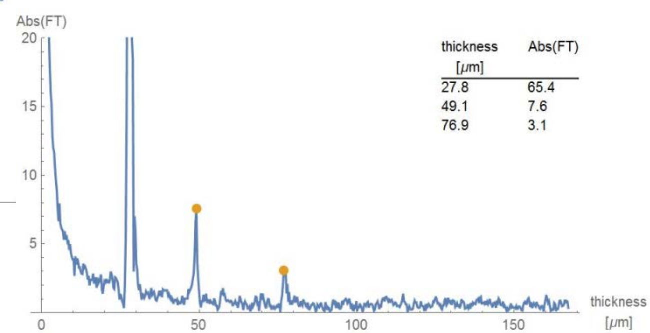
Technical Accomplishments: Measured single-point membrane thickness with reflectance spectroscopy



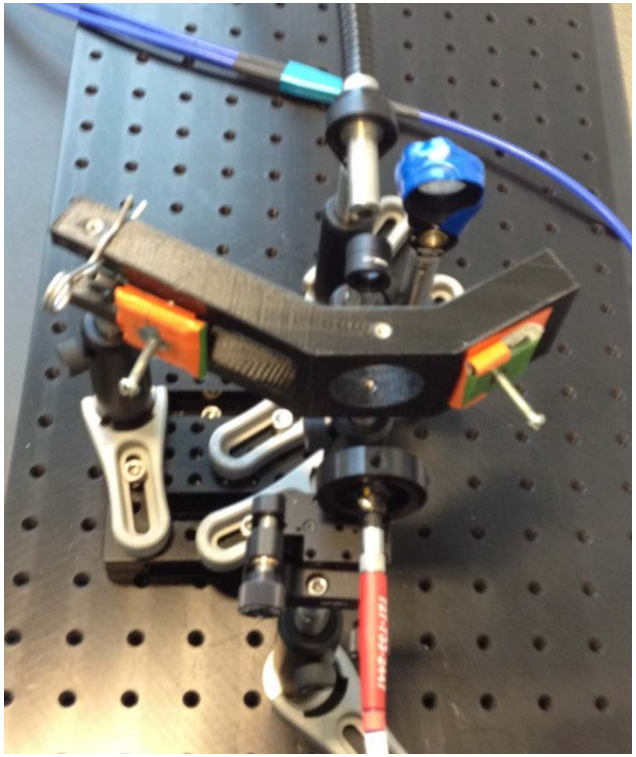
Visible reflectance spectroscopy for 14 µm 3M membrane with reinforcement, on kapton







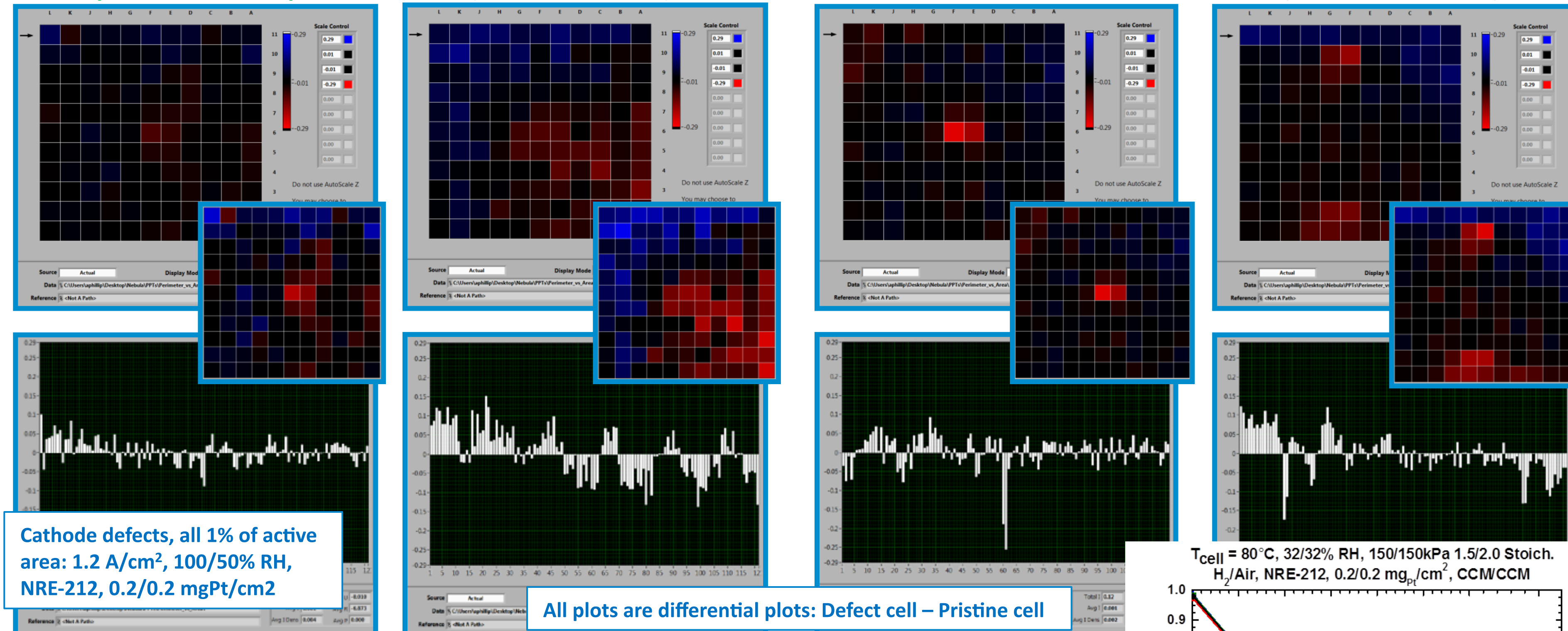
Visible reflectance spectroscopy for 50 µm Nafion with protective layers



Single-point fast spectroscopy test-bench with broadband light source, focusing optics, specimen holder, receiving optical fiber and Si and InGaAs spectrometers (not shown); Spot size: ~10 mm^2

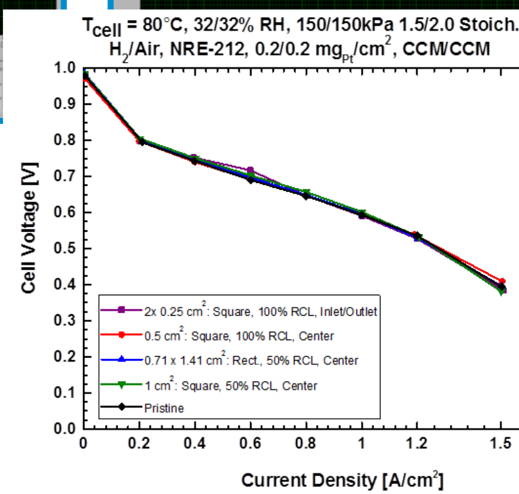
Technical Accomplishments: Continued in situ effects of defects studies

1 cm^2 Square (50% reduction)	0.71 x 1.41 cm^2 Rect. (50% reduction)	0.5 cm^2 Square (100% reduction)	2x 0.25 cm^2 Squares (100% reduction)



Cathode defects, all 1% of active area: 1.2 A/cm², 100/50% RH, NRE-212, 0.2/0.2 mgPt/cm2

All plots are differential plots: Defect cell – Pristine cell

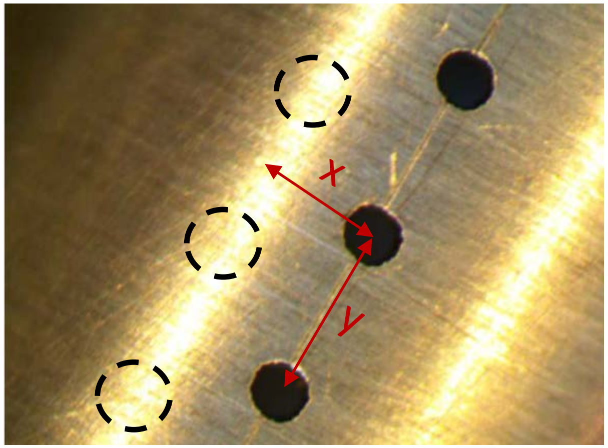


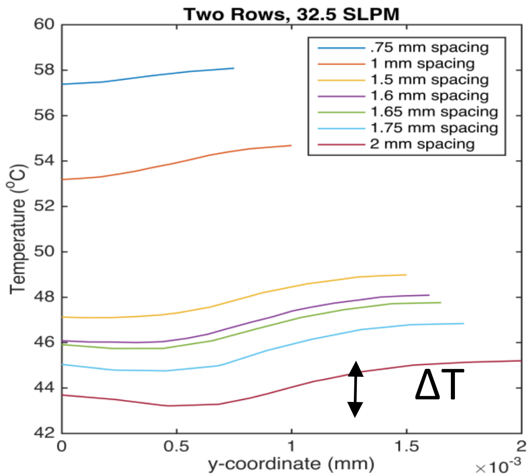
- All defects detected; bare spots have the largest impact
- 1% catalyst loading reduction
  - Does not result in total cell performance change
  - Does result in a wide range of local performance variation

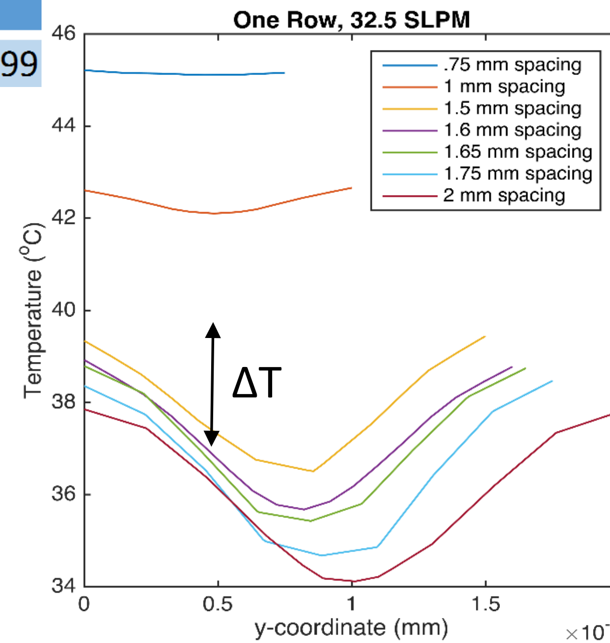
Technical Accomplishments: Additional details of LBNL RIF modeling

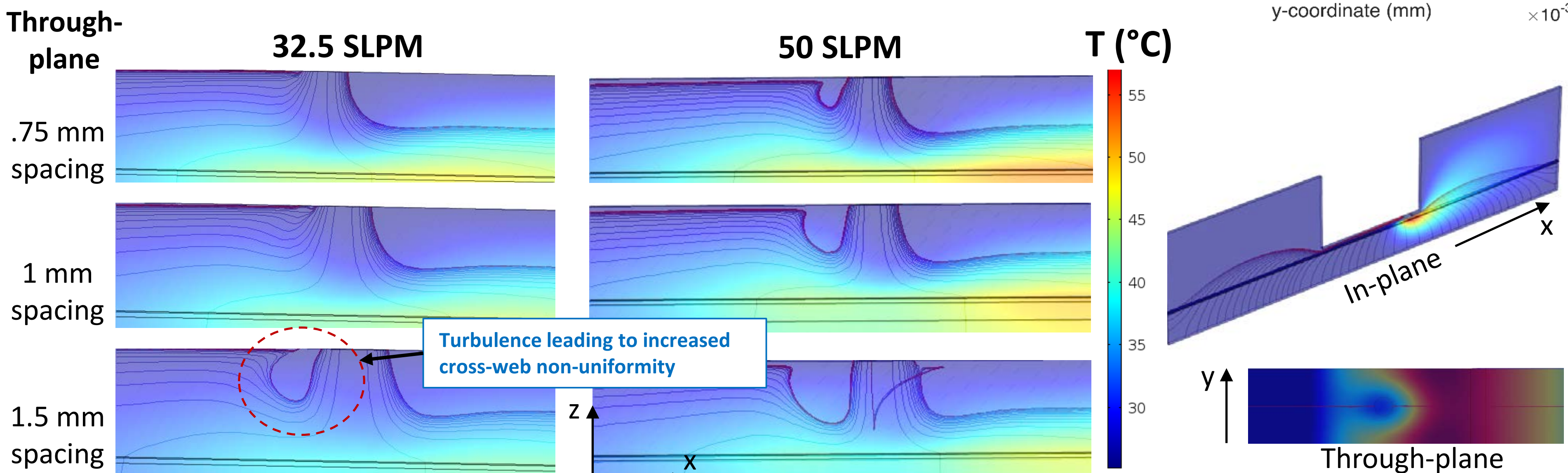
x-Spacing (mm)	1 mm	1.5 mm	2 mm	2.5 mm	3 mm
ΔT	2.15	2.36	2.21	2.18	1.99

Knife view from underneath



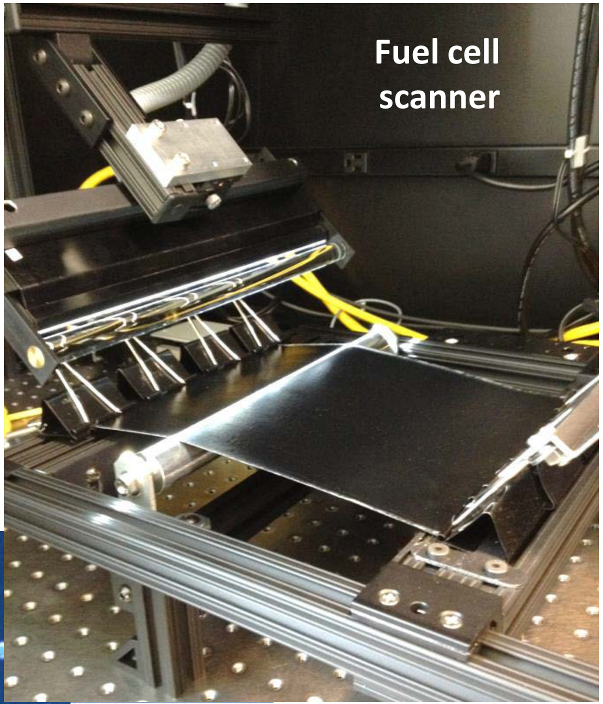


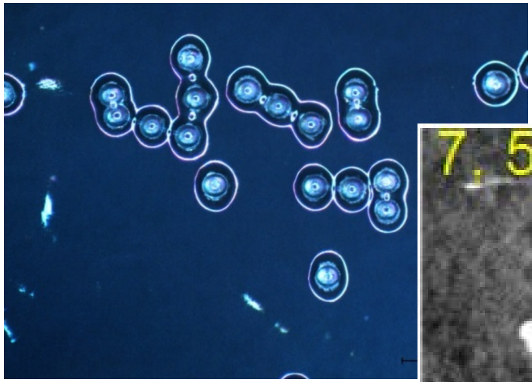


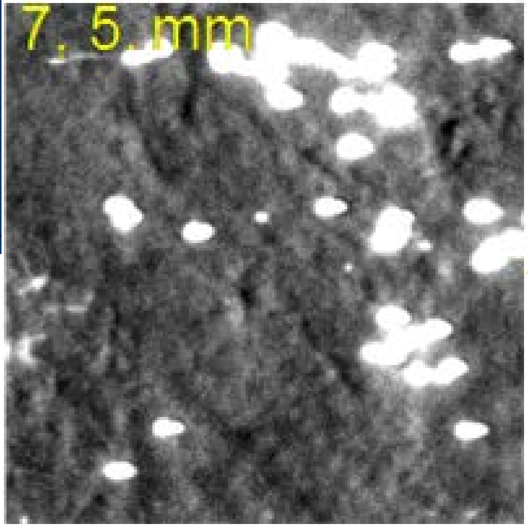


Technical Accomplishments: Explored catalyst debris defects with optical reflectance imaging

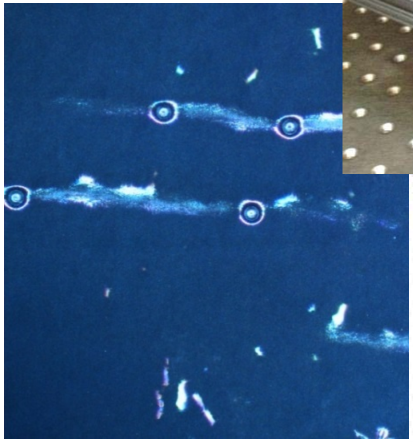
- **Scale-up relevant materials**
  - GDE with membrane
- **Intentionally created defects**
  - Debris of <u>well-defined</u> (50 & 100 μm) size deposited between electrode and membrane
- **Scanning system operated on sheet materials at 10 fpm**

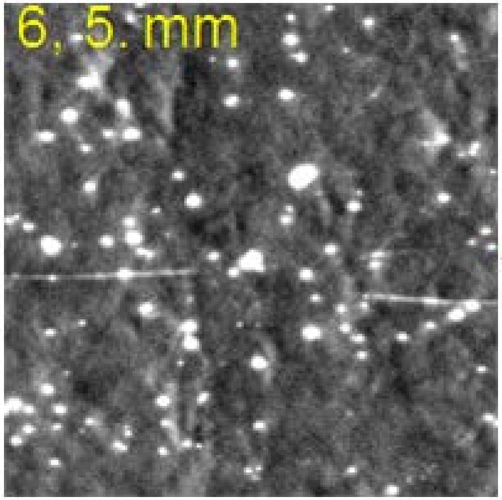






Above: 100 μm debris (microscope) and specular reflectance imaging (FC scanner) result: <u>viewing membrane side</u>





Above: 50 μm debris (microscope) and specular reflectance imaging (FC scanner) result