Fuel Cell MEA Manufacturing R&D

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June 6, 2017

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
2016 (received)	\$779,000	\$150,000	\$64,000	\$45,000
2017 (planned)**	\$780,000	\$150,000	\$67,000	\$49,000

* Total funding is the sum of NREL and all funded partners

** FY2017 planned funding is subject Congressional language

Relevance: Project addresses MYRD&D milestones

From MYRD&D Plan 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
  - *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:

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

Date	Milestone/Deliverable (status as of 4/10/17)	Complete
9/16	Validate LBNL model predictions for RIF process improvement	100%
12/16	Evaluate thermal scanning technique for membranes and electrodes	100%
3/17	Generate spatial performance data for cells with as-cast membrane defects	100%
9/17	Demonstrate an in-line configuration for through-plane reactive excitation	20%
9/17	Generate in situ failure study data for MEAs with electrode defects	50%
9/17	Go/No-go to determine the feasibility of using reflectance imaging to measure Pt loading	25%

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

- **GM (CRADA):** development of in-line inspection techniques
- **Gore (TSA):** understanding effects of membrane defects, in-line characterization of membrane production rolls
- **Mainstream Engineering (CRADA):** demonstration of commercializable in-line QC device

Labs and Academia

- **Lawrence Berkeley National Lab:** model development and integration, x-ray characterization
- **Colorado School of Mines:** cell fabrication and testing
- **Georgia Tech:** fabrication and characterization of as-manufactured defect samples
- **Tufts:** x-ray computed tomography modeling
- **CEA-Liten:** R2R fabrication and quality inspection

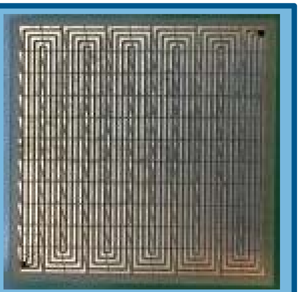
Technical Accomplishments

Applied multiple in situ methods to fully understand defect impacts

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

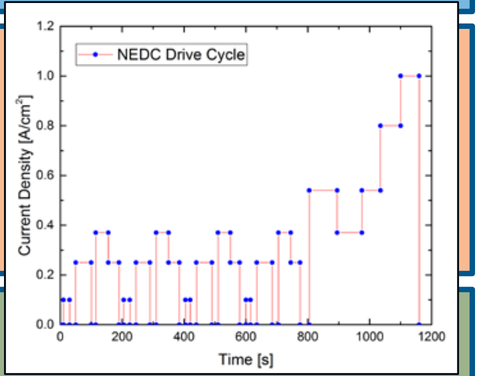
Initial performance (local and total cell)

- 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

Technical Accomplishments

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 cm²)	🟩	🟥	🟨	🟩
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/cm²)	🟩	🟥	⬜	⬜
Irregularity Shape (Square, Rectangle, Circle)	🟩	🟥	⬜	⬜
Catalyst Layer Thickness Variations (Thin, Bare Spots)	🟩	🟨	⬜	⬜
Irregularity Aspect Ratio	🟩	🟥	⬜	⬜
Slot Die Coating/Manufacturing Defects (Droplet, Scratch, Cut)	🟩	🟩	⬜	⬜
Ionomer Coating Thickness Variations	🟩	🟩	⬜	⬜

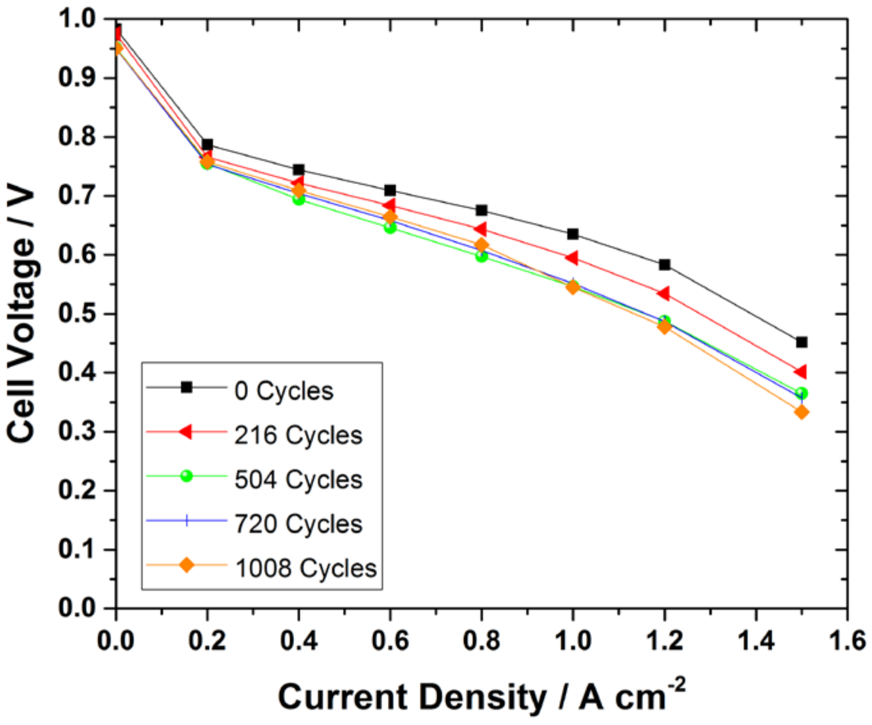
🟩 **Little/No Impacts** 🟨 **Moderate Impacts** 🟥 **Significant Impacts** ⬜ **Ongoing Work**

Technical Accomplishments

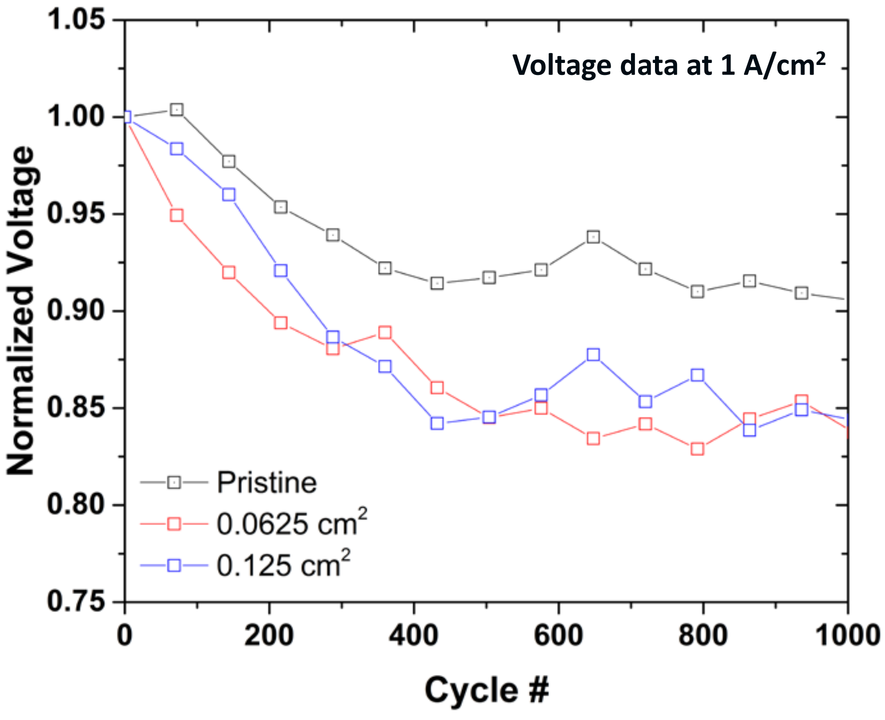
Continued in situ effects of defects studies: Example study

Effect of defect size on performance degradation over time

- Bare spots centered in cathode (2.5% and 1.25% of active area)
- No significant impact on initial performance
- All samples: performance degradation due to cycling
- Samples with irregularities: increased performance degradation over first 500 cycles



Reduction in performance over time due to irregularity of 2.5% of active area

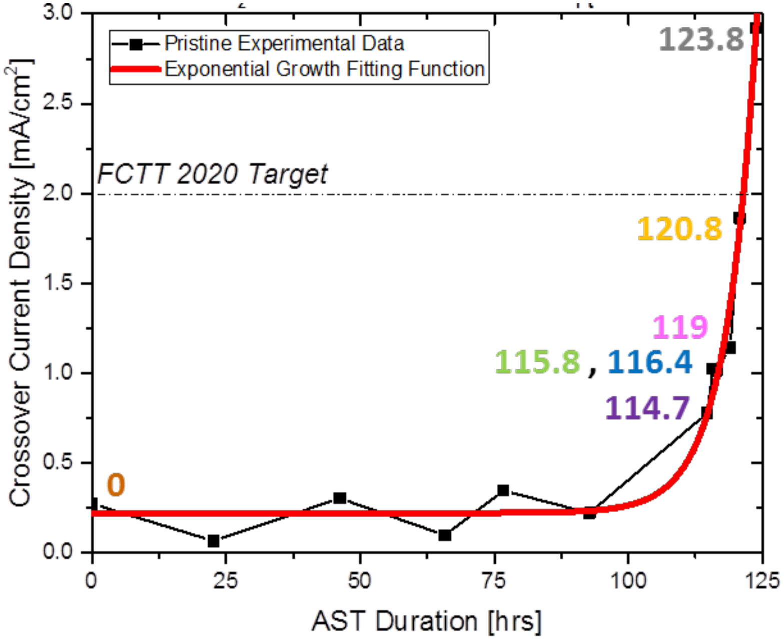


Comparison of performance degradation over time between pristine MEA and MEAs with irregularities

Technical Accomplishments

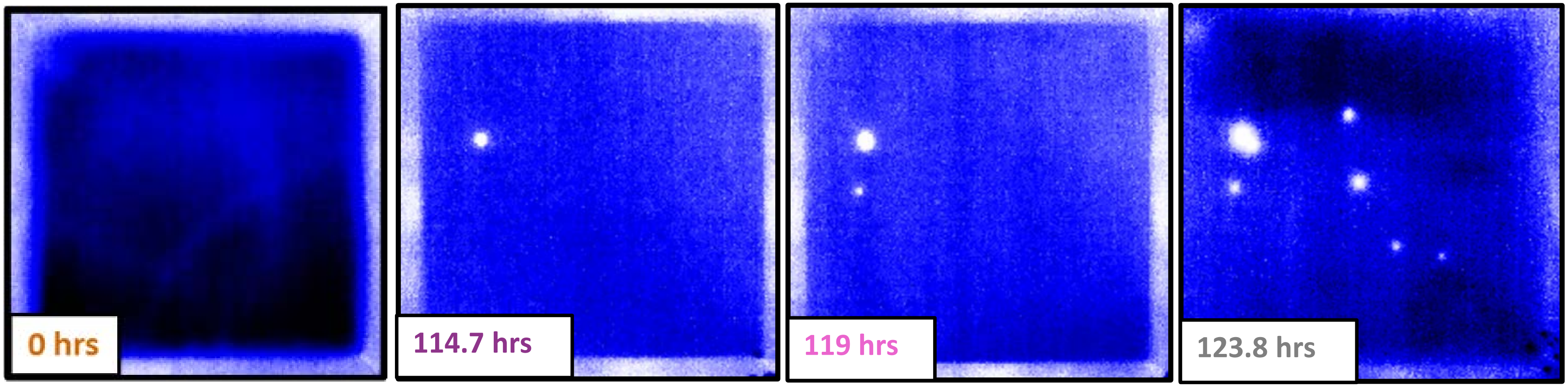
Captured onset of failure of pristine cell using unique capabilities

- Focus on failure point development and location of failures related to location of irregularities
- OCV and total H_2 crossover values trigger more frequent measurement and spatial H_2 crossover
- Curve fitting used for consistent end of life determination, i.e. AST time to 2.0 mA/cm² H_2 crossover limiting current density
- We observe the onset and growth of failures at various locations in the cell as a function of AST time



Hydrogen crossover vs. AST time showing onset of failure and failure time determination

Quasi-in situ IR imaging of the development of failure points

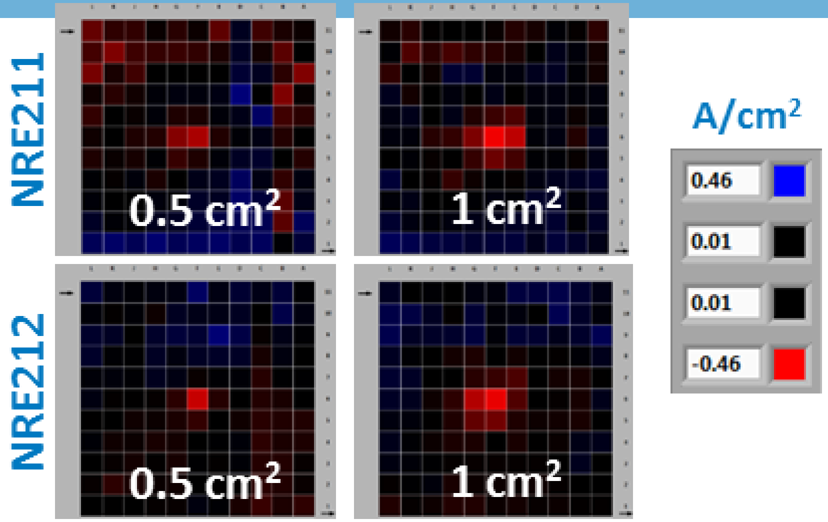


Technical Accomplishments

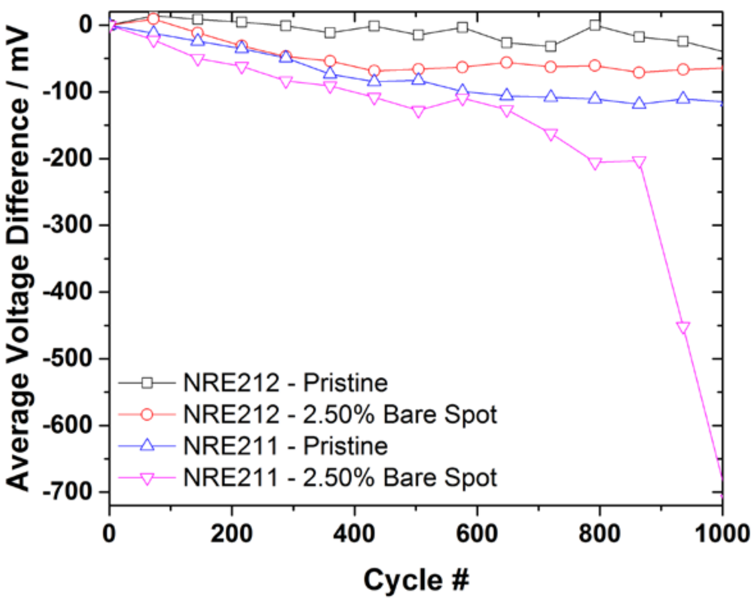
Continued in situ effects of defects studies: Example study

Effect of membrane thickness on performance and lifetime

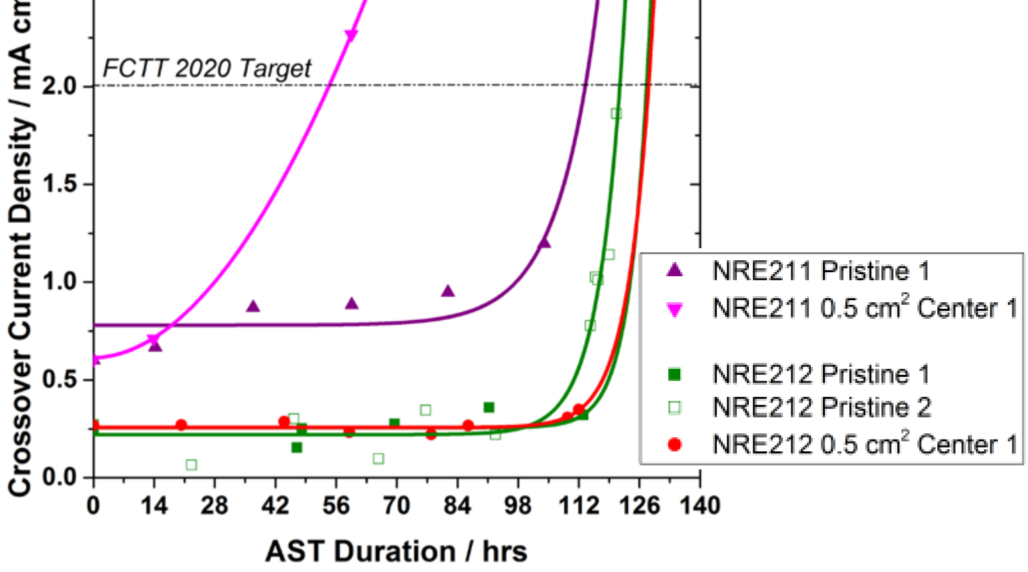
- Cathode centered bare spots
- Not much difference seen in initial performance
- Irregularity impact during cycling much greater for thinner membrane
- Time to failure: NRE212 > NRE211 pristine > NRE211 with irregularity



Initial performance comparison for 0.5 and 1.0 cm² irregularities



Performance over time for irregularity of 2.5% active area

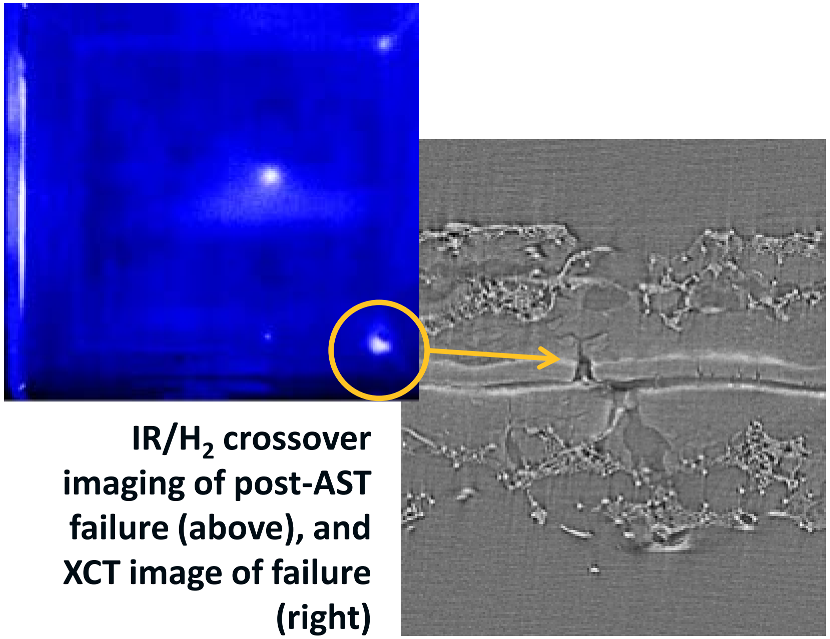


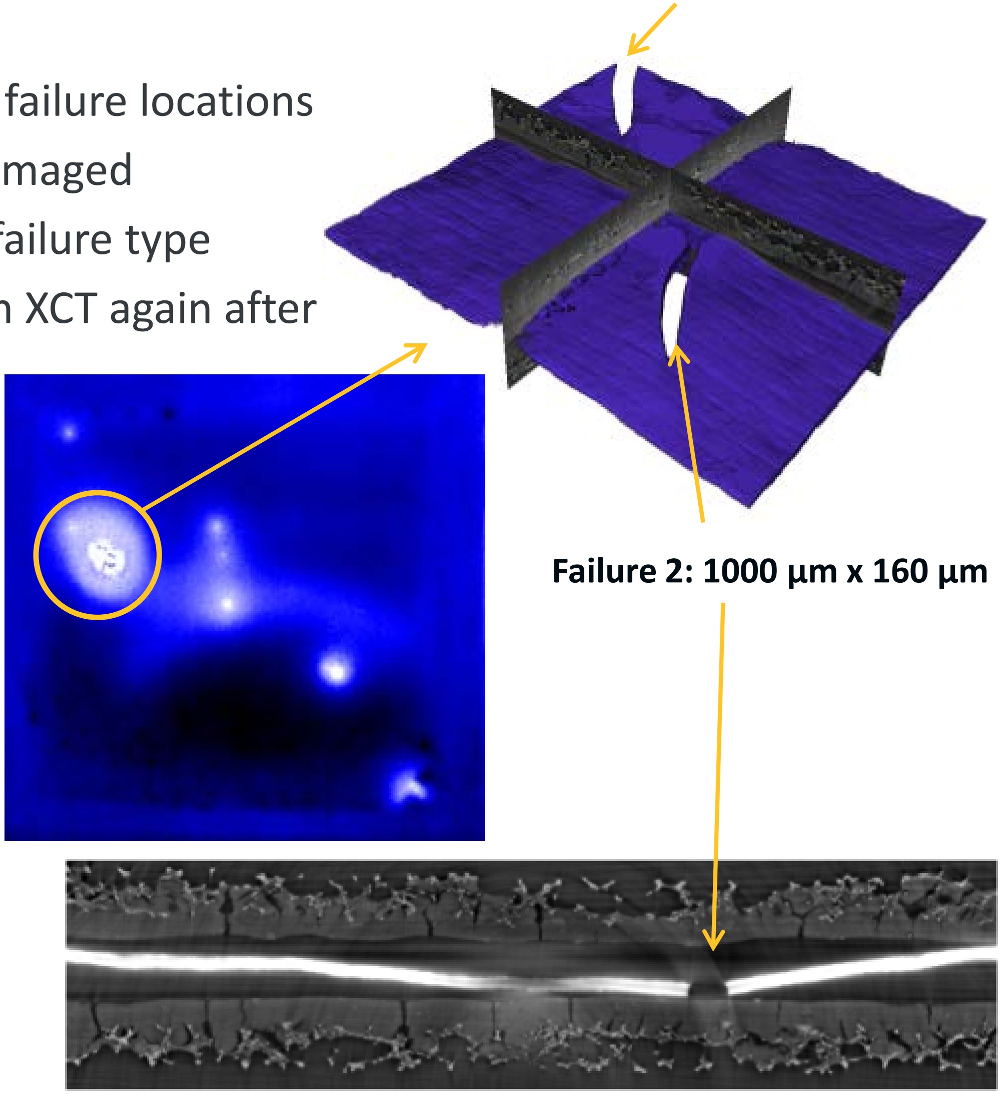
Time to failure comparison for 0.5 cm² irregularities

Technical Accomplishments

Used x-ray computed tomography (XCT) for characterization of failures

- Exciting new area of collaboration with LBNL & Tufts
- NREL identified failures after AST testing
- Entire MEA sent to partners with map of failure locations
- XCT performed and failures successfully imaged
- Provides fundamental understanding of failure type
- Future: XCT of defect before testing, then XCT again after testing



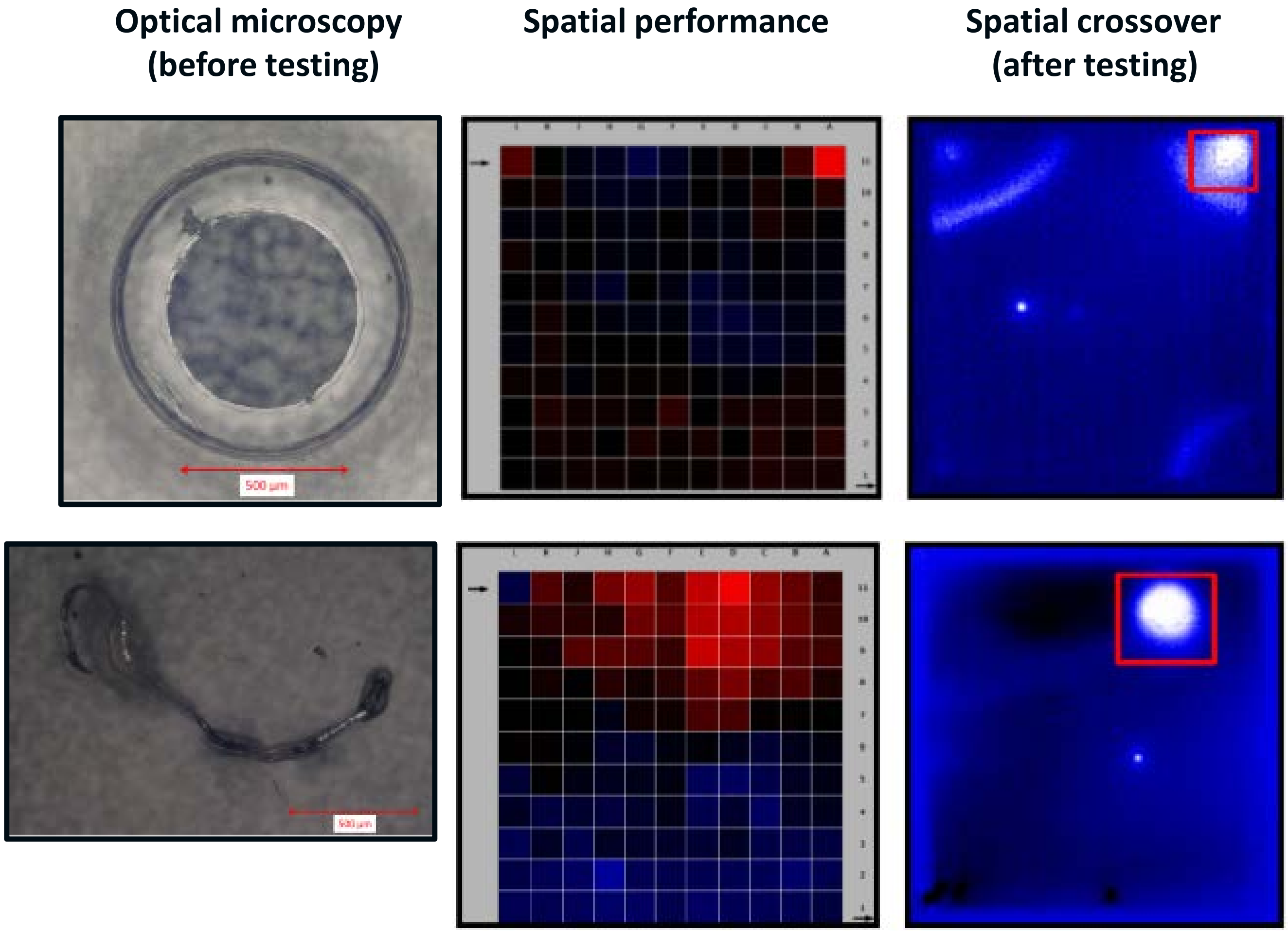


IR/H_2 crossover imaging of post-AST failure (above), and XCT image of failure (right)

Technical Accomplishments

Spatial performance testing of as-cast membrane irregularities

- Georgia Tech cast Nafion membranes with process-induced irregularities
    - 300-1000 µm pinholes, bubbles, cracks
- NREL used these membranes to assemble cells with in-house sprayed GDEs
- We have been able to correlate optical microscopy, spatial performance, and spatial H_2 crossover imaging


Optical microscopy (before testing)

Spatial performance

Spatial crossover (after testing)

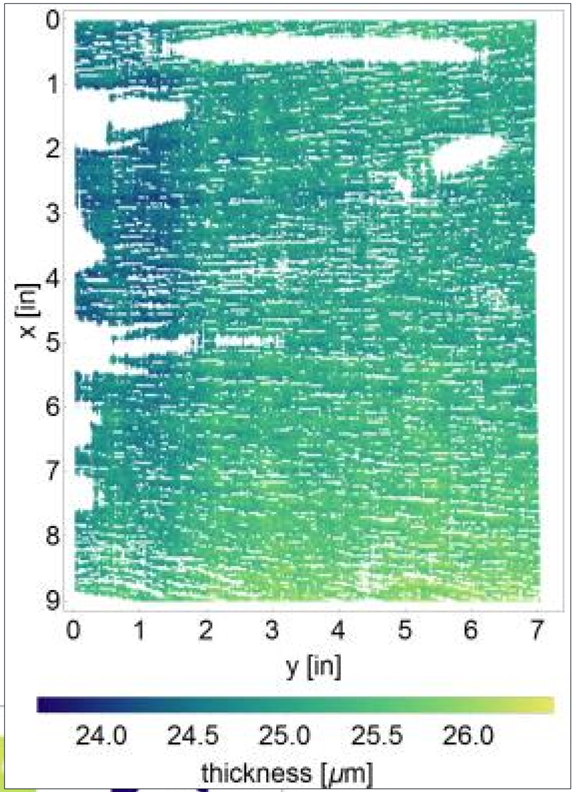
Results at 32/32% RH, 1.2 A/cm^2

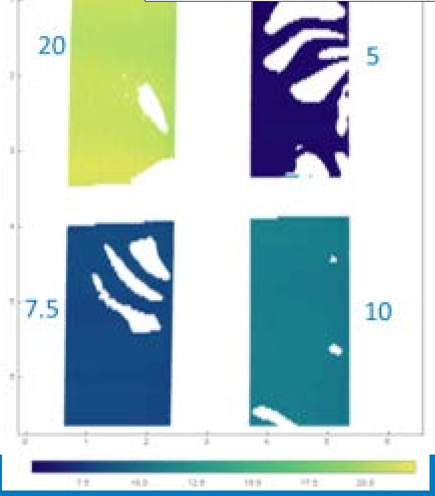
Technical Accomplishments

Demonstrated feasibility of membrane thickness imaging

- Concept:
  - 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
- Measurement requires visible (in many cases) or near IR spectra, depending on material properties
- Filed provisional patent

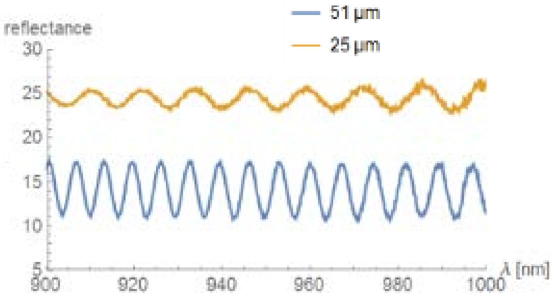
Thickness image of 25 µm membrane taken at 5 foot per minute

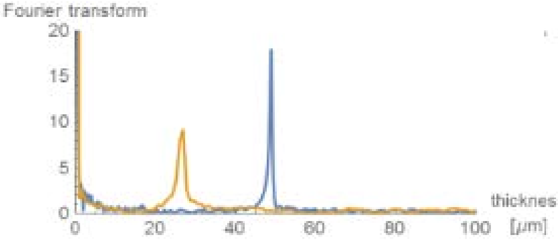




Scan of 4 samples of different thickness

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



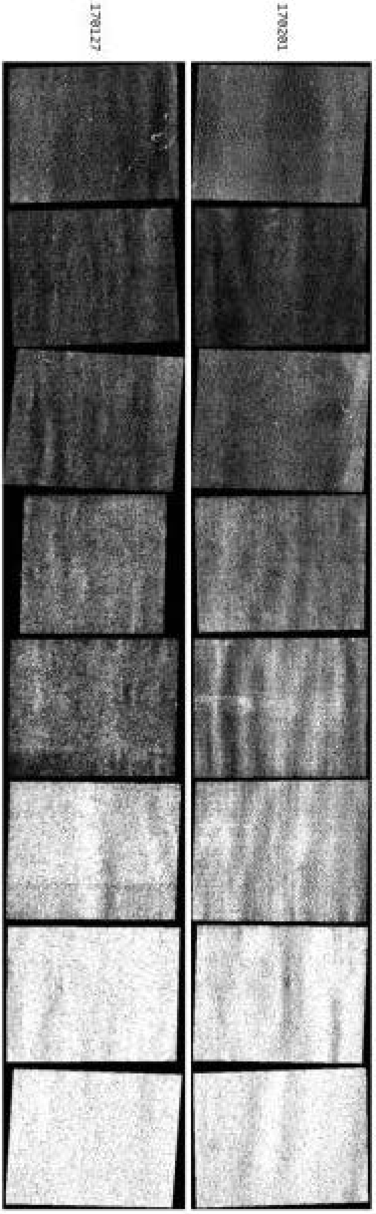


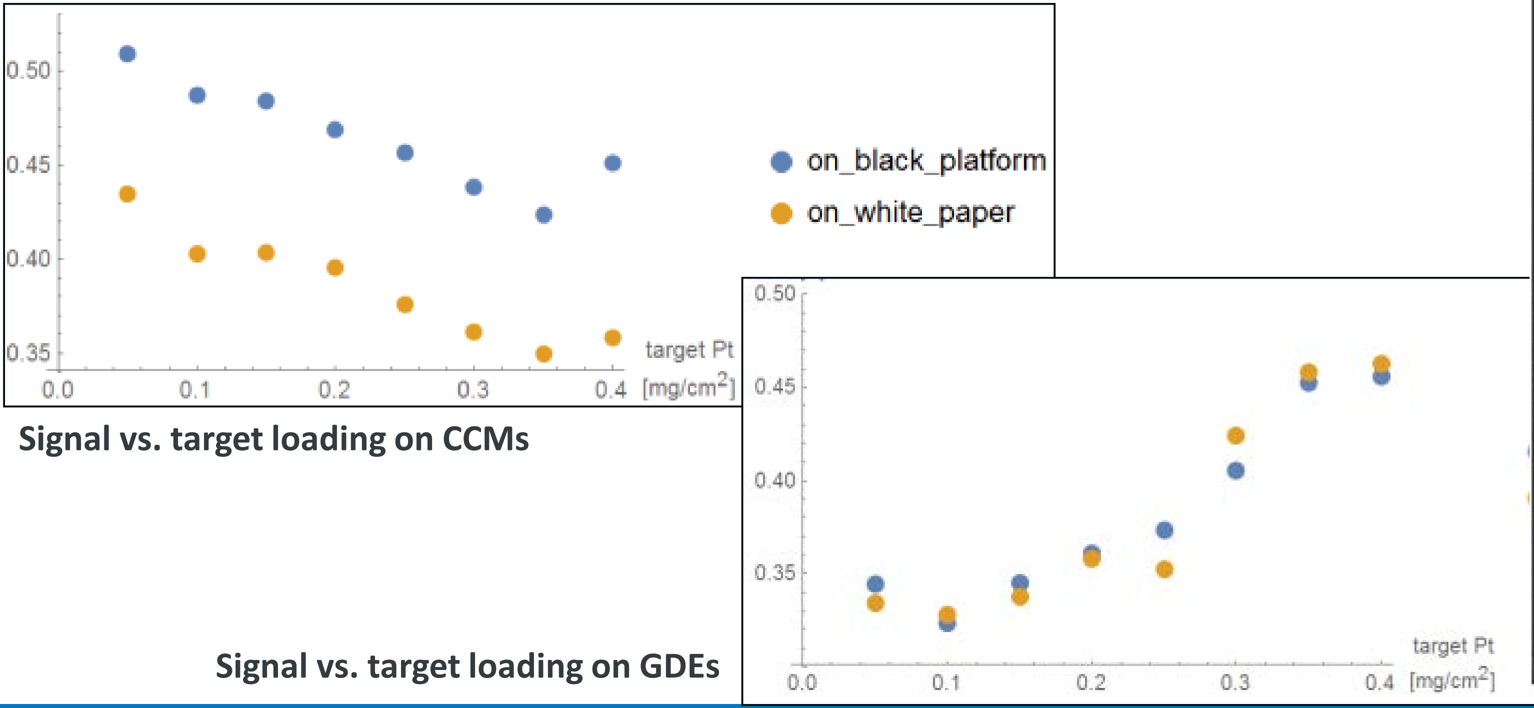
Technical Accomplishments

Exploring feasibility of imaging Pt loading

- Goal: develop a real-time, high-resolution, 100% inspection technique for Pt loading
- Early experiments using NREL-fabricated GDEs and CCMs
- We observe mainly monotonic relationships, but need to continue data analysis and gather more data to understand noise, sensitivity, and repeatability

Imaging of GDEs: lowest loading (top) to highest (bottom)





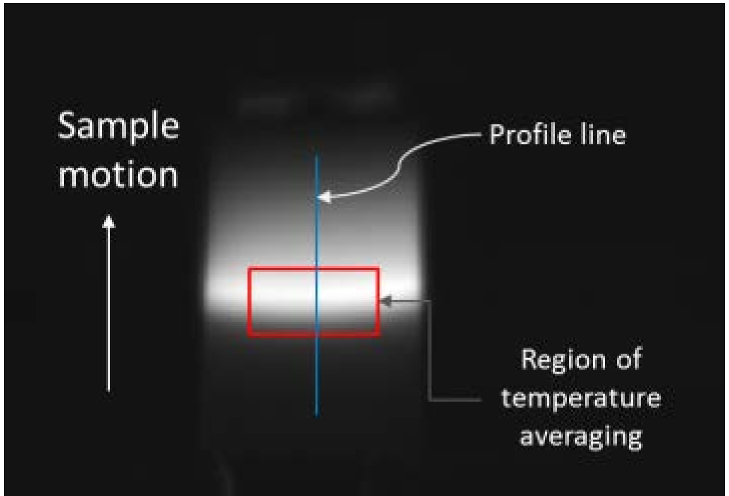
Signal vs. target loading on CCMs

Signal vs. target loading on GDEs

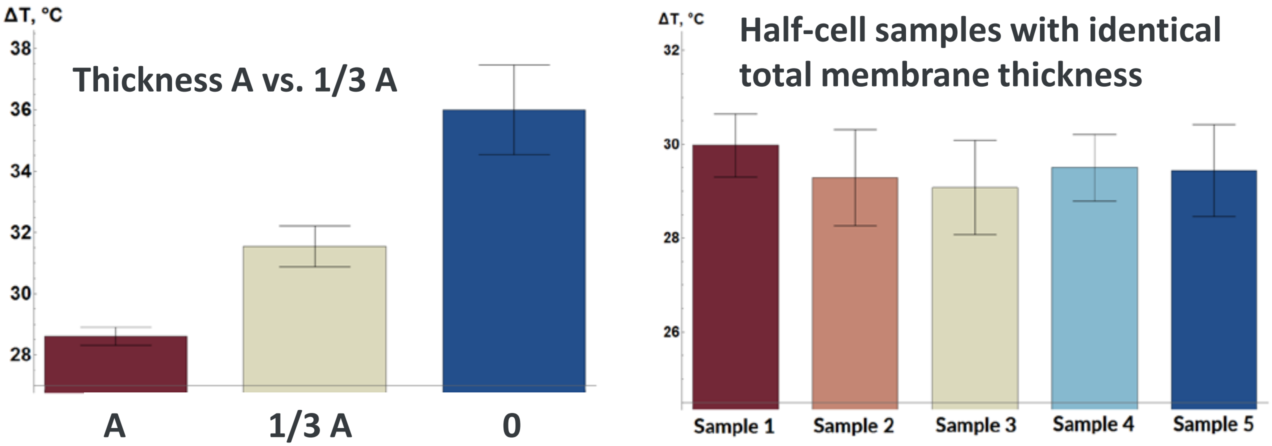
Technical Accomplishments

Exploring feasibility of thermal scanning for layer properties

- Concept:
    - Use thermal excitation of active layer/substrate
    - Measure peak/decay
    - Link measurement to thermal model to back out physical properties, e.g. thickness, porosity
- Leveraging ORNL/VTO battery electrode porosity project (patent application)
- Initial study of membrane thickness in half-cells: we observe monotonic response and good repeatability



Example thermal scanning data



Thermal response vs. membrane thickness in half cells

Thermal scanning configuration on optical testbed

Technical Accomplishments

Developing in-line through-plane reactive excitation (TPRE) concept

- Previous work done on stationary samples
- Considering a modification to the RIF configuration we have previously demonstrated
- LBNL modeling ongoing to assist in understanding process and configuration parameters
- Experimental hardware fabricated
- Need to fabricate appropriate sample, e.g. one-side coated CCM sheet with pinholes in the membrane

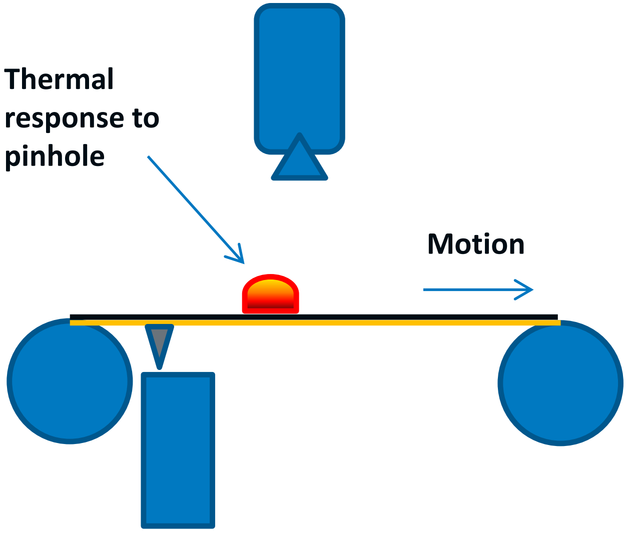
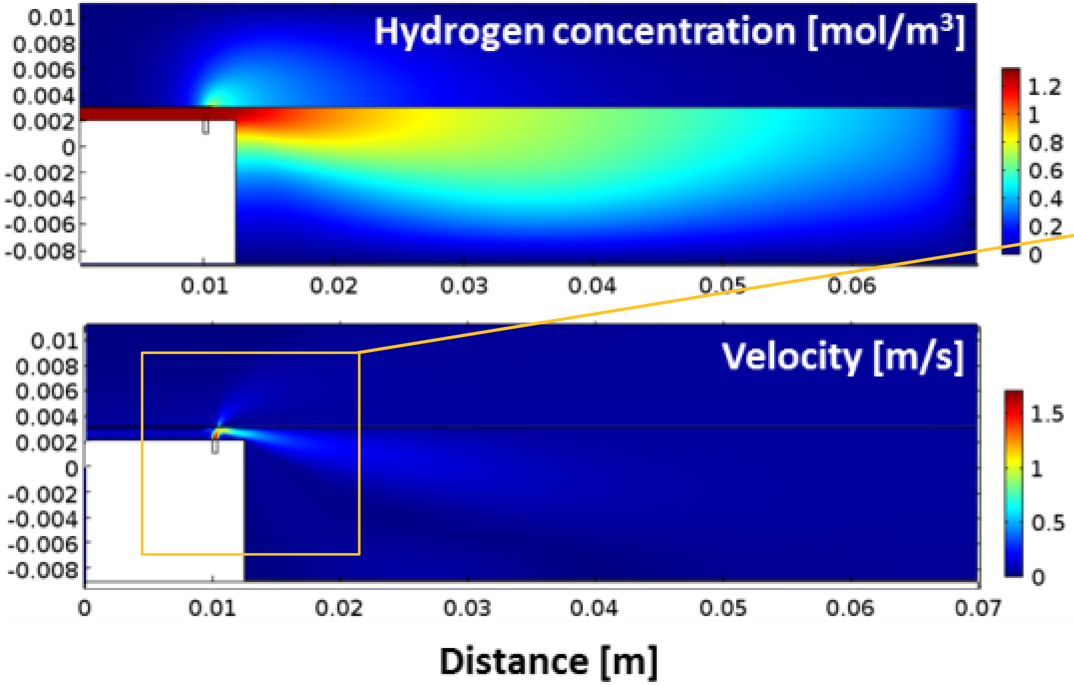
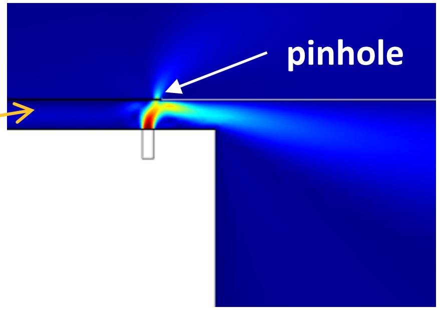


Diagram of in-line TPRE concept configuration



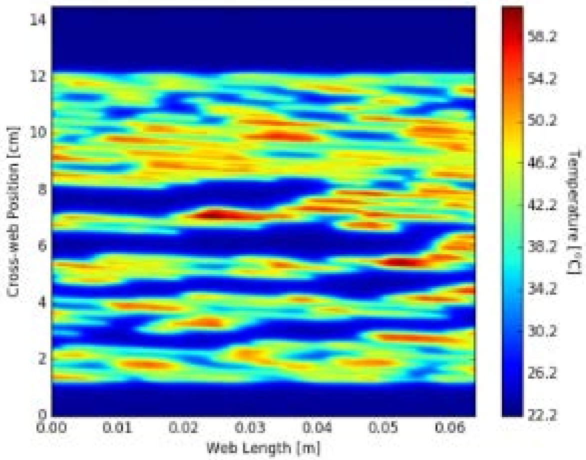


Model assumptions: 32.5 slpm flowrate, 10 fpm web speed, 200 µm pinhole, 45 µm membrane, 4% H_2 / 2% O_2 in N_2 reactive gas

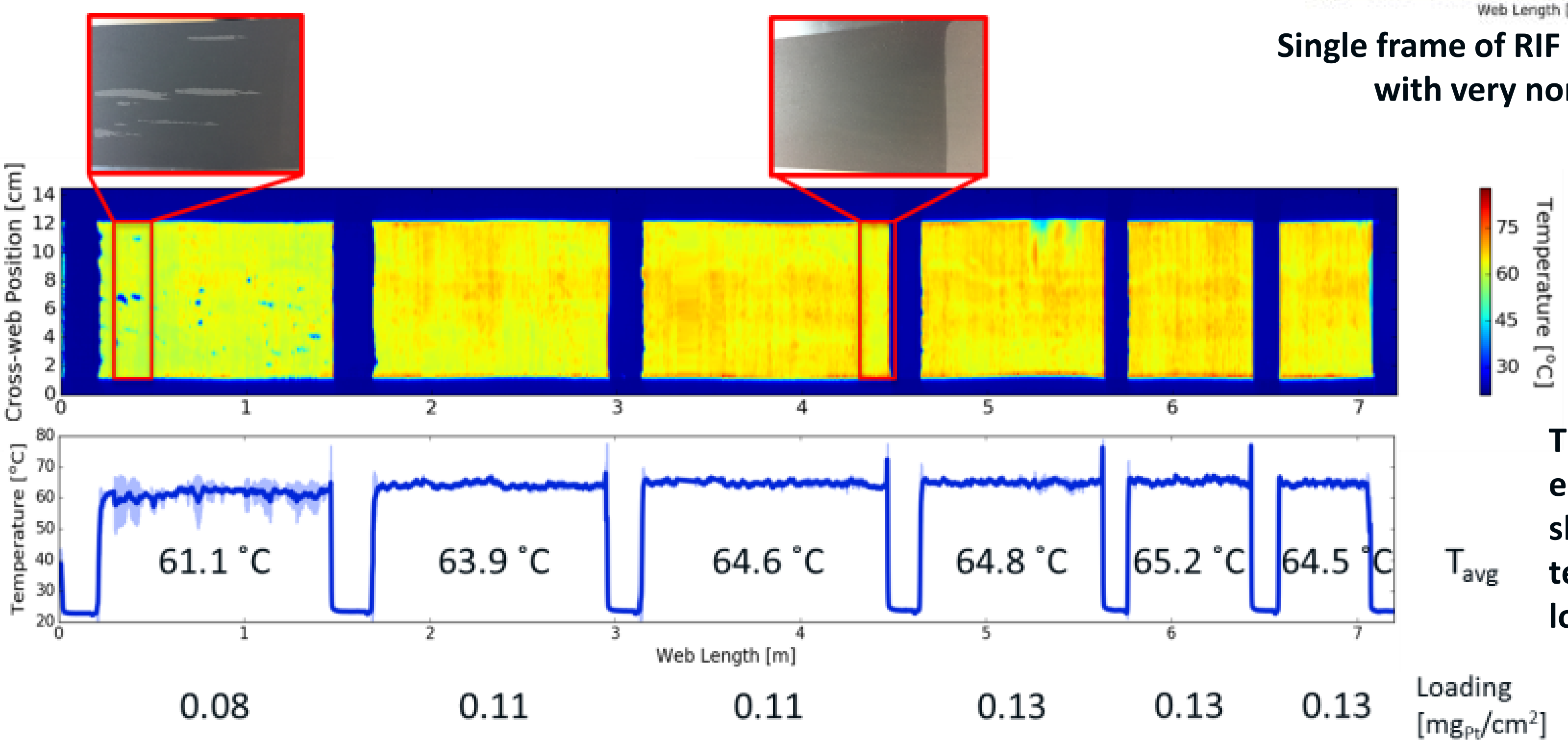
Technical Accomplishments

Demonstrated reactive impinging flow (RIF) on NREL R2R coated GDE web

- Leveraging web samples made for process-performance studies to continue to validate diagnostic techniques
- Ran continuous, several meter long sheet of coated GDL/MPL
- Clearly detected uncoated defects
- Created surface 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

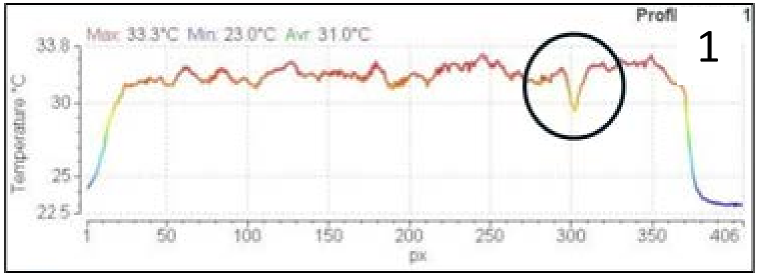


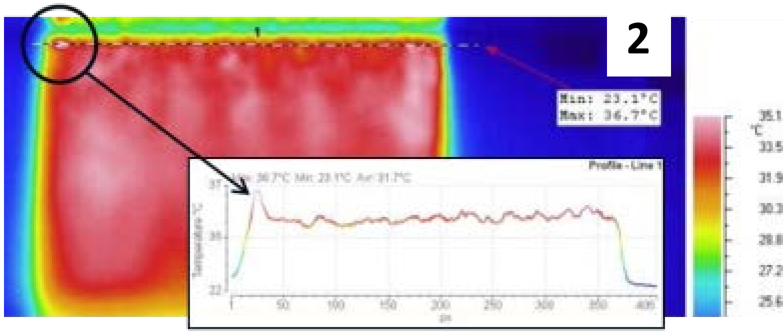
Thermal map of entire web, showing median temperature vs. loading (via XRF)

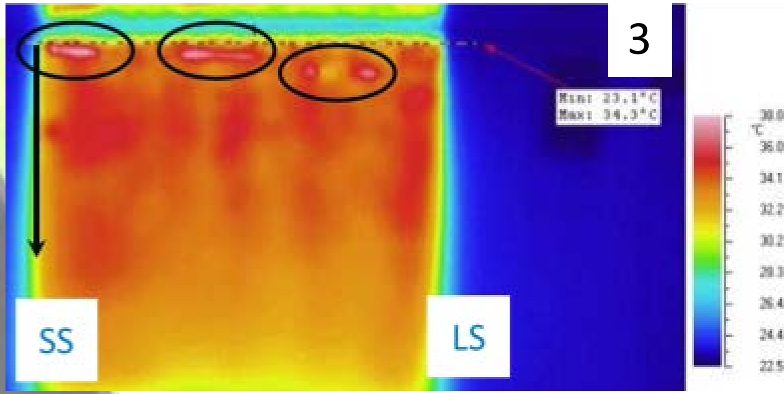
Technical Accomplishments

Demonstrated RIF on CEA-Liten R2R screen-printed GDEs

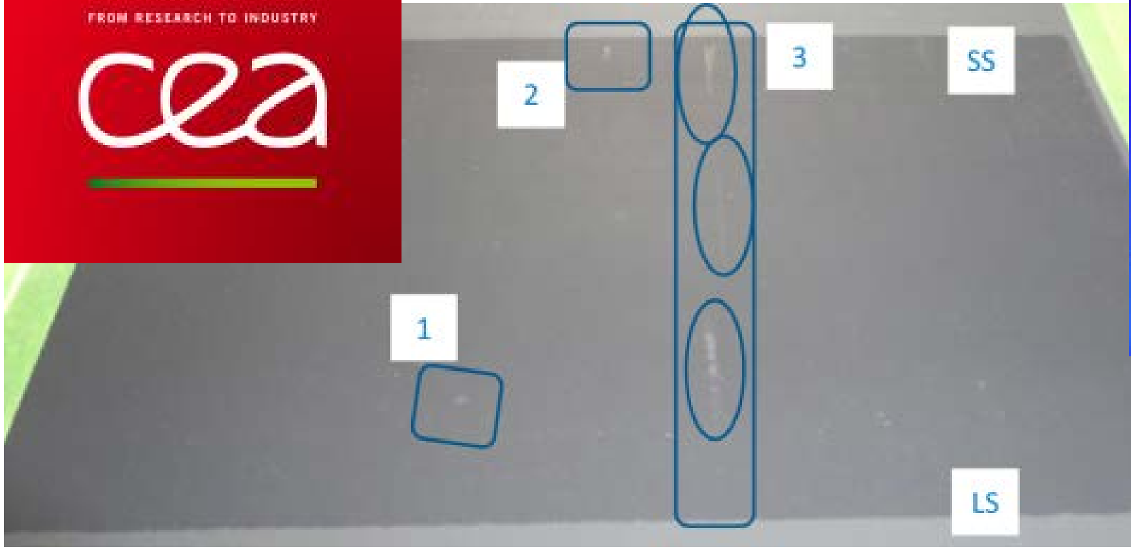
- Made splice roll with 10 GDE samples fabricated on CEA's continuous production line
- Ran RIF at 10 fpm
- Demonstrated detection of intentionally created defects
- Demonstrated detection of loading variations within samples, and sample-to-sample
- Further work identified at both NREL and CEA for additional characterization of the samples







Examples of defects detected



Tech Transfer Activities

SBIR Phase II collaboration with Mainstream Engineering

- Advance QC prototype device to more 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
  - Leveraging FCTO-funded GT collaboration for baseline in situ testing of effects of membrane defects
  - GT working on fabrication of sheet samples; first set delivered to Mainstream and NREL

Opportunities for tech transfer

- SBIR/TTO (FCTO directed)
- Technology Commercialization Fund
- SBVs
- AMO FOAs and R2R Consortium
- Work for others

Additional activities

- Small business voucher (SBV) with Altergy
- Multi-lab R2R Consortium (sponsored by AMO)
  - Ongoing cost-shared industry call to enable collaboration and tech transfer
- Synergy with our new process-performance project (see Ulsh/Mauger poster)

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 (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

- Develop a concept, using modeling and experimentation, for in-line TPRE
- Demonstrate a prototype system for in-line membrane thickness imaging
- Determine the feasibility of catalyst loading imaging
- 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
- Apply optical and infrared techniques to relevant industry MEA constructions, including fuel cell, electrolysis and non-PGM materials
- Further study data acquisition, storage, and processing requirements
- Seek opportunities to demonstrate and implement diagnostics in industry

Summary

- Addressing many of the MYRD&D Plan milestones
- Continued detailed information exchange with industry partners on QC priorities
  - Established important new collaborations with Gore, CEA-Liten, and Tufts
  - Continued valuable GM CRADA collaboration
- Effects of defects studies
  - Performed spatial performance and failure studies of electrode defects
  - Performed spatial performance studies of as-cast membrane defects
  - Established methods to evaluate defect impact on performance degradation over time
- Optical diagnostics
  - Demonstrated feasibility of membrane thickness imaging
  - Continued to assist Mainstream Engineering (CRADA for SBIR Phase II)
- IR/TPRE
  - Continued multi-physics modeling to predict pathways for in-line implementation
  - Developed hardware for in-line demonstration
- IR/RIF
  - Demonstrated defect and loading variation detection on R2R screen-printed and micro-gravure coated GDEs
  - *Validated modeling predictions of process improvements*
- Exploring imaging of Pt loading
- Completed initial exploration of thermal scanning for membranes and electrodes
- *Technical Assistance: FCTO and State of Ohio fuel cell supply chain projects, Sub to SA Inc. on automotive FC cost analysis, NREL lab-lead on new AMO R2R Consortium*

Response to Reviewer Comments

Comments: *"The evolution of defects during operation needs more consideration." "…most important, the effects of defects will be included."*

Response: In addition to spatial performance and failure in situ testing, we have added capabilities to evaluate the effects that defects have on cell performance over time and to resolve in time the onset of cell failure. We have also put a critical new industry partnership in place that, in part, aims to address this topic. We continue to see adding to the publicly available basis of knowledge in this area as a critical need and a critical part of the project.

Comments: *"The team would be enhanced by the addition of cell component manufacturers." "There may be room to identify and include custom membrane electrode assembly (MEA) suppliers."*

Response: As noted above, we have a new collaboration with a membrane supplier that will enable us to continue to get detailed and relevant input on industry needs. We also have a new collaboration with CEA-Liten (France), who have a more applied role with their European collaborators, and are working on MEA component production. We continue to reach out to component suppliers, especially related to funding opportunities, as noted on our Tech Transfer Activities slide.

Comments: *"The pathway to industry adoption of the manufacturing tools needs more explanation, it is not clear how the resulting improvements in manufacturing bring down the costs or performance." "…technology transfer should have a more detailed plan and include more than collaborators."*

Response: We agree that this is an important question for DOE and the community with respect to this project. It is the intent of this project to develop and validate new technologies, but it is always up to the decisions of industry to adopt them. From a more general point of view, we and others have shown the very strong impact that stack yield has on stack cost (see slide in Reviewer Only section), which we feel clearly shows the need for and potential impact of these kinds of technologies. Also, see our Tech Transfer Activities slide for further details of the mechanisms we have and continue to attempt to use to help improve industry uptake of this work.

Comments: *"It would be helpful to see a summary chart of all the methods being developed and considered for development under this project."*

Response: Thanks for the prompt! We had a slide like this in previous years, and have updated and included it (see slide in Technical Backup section).

Acknowledgement

NREL

Guido Bender
Peter Rupnowski
Brian Green
Jocelyn Mackay (SULI)

Tufts

Prof. Iryna Zenyuk

LBNL

Adam Weber
Pratiti Mandal

CSM

Prof. Jason Porter
Adam Phillips

Georgia Tech

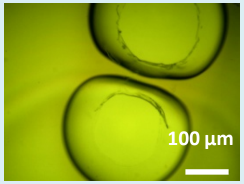
Prof. Tequila Harris

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)		millimeters	In development
MEA 	Shorting	Through-plane IR/direct-current		Demonstrated on motion prototype
	Membrane integrity	Through-plane IR/reactive excitation	pinholes as small as 90 µm	Demonstrated on static testbed

Technical Accomplishments

Modeling assists optimization of through-plane reactive excitation

- LBNL modeling to further understand the static through-plane reactive excitation (TPRE) results
- Studies explored the impact of:
    - $H2$ concentration in the reactive gas
    - Reactive gas pulse length
    - Membrane thickness

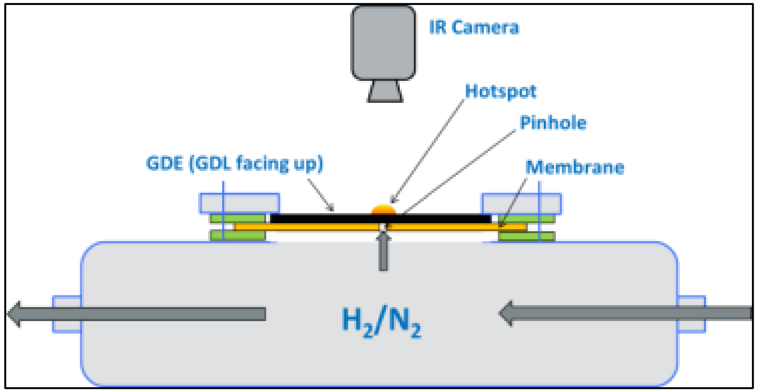
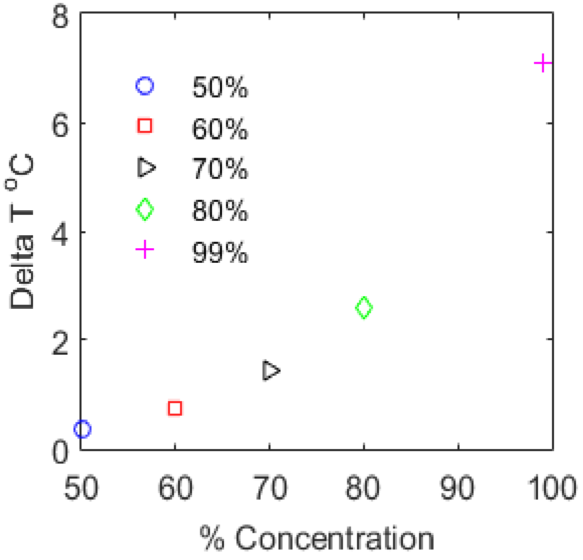
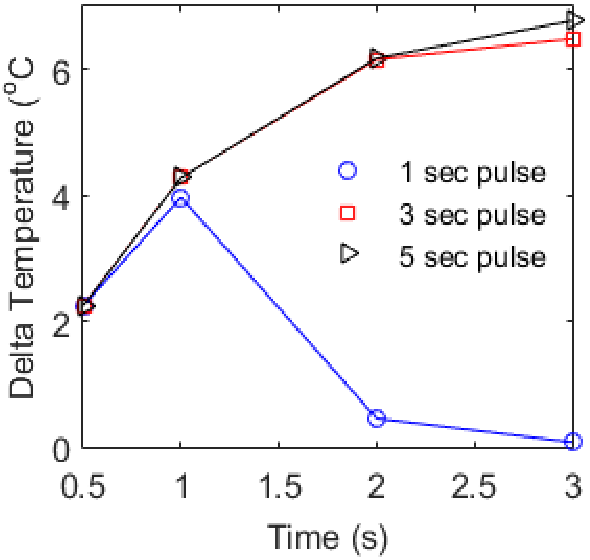


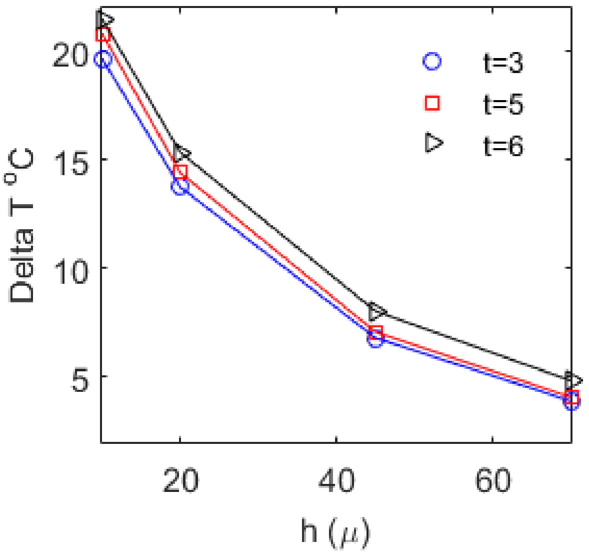
Diagram of static TPRE test-bed



Effect of H_2 concentration



Effect of pulse duration



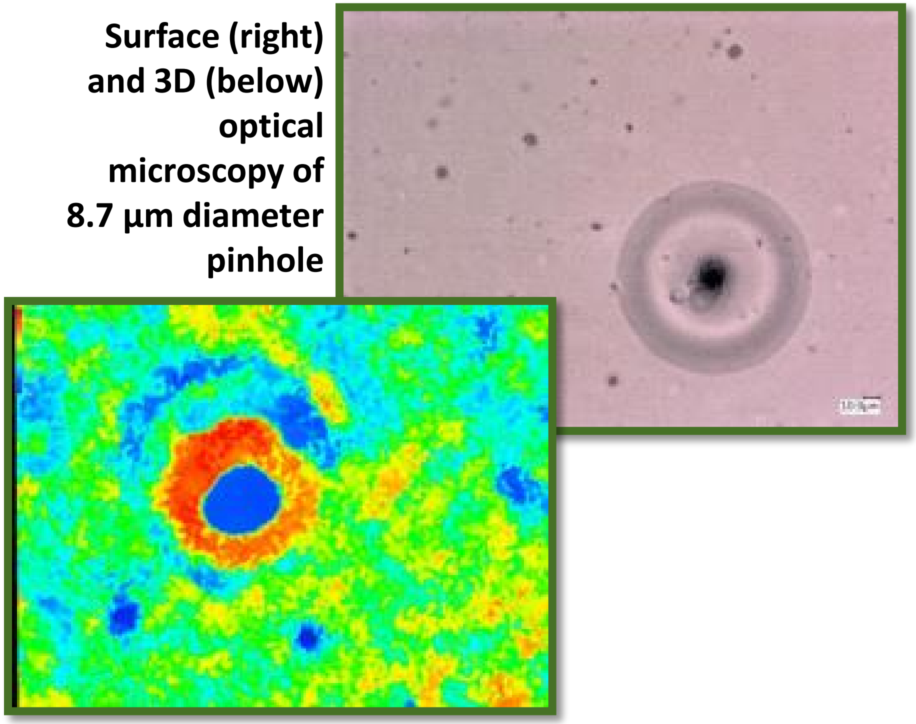
Effect of membrane thickness

Base case for all results: 500 sccm flow, 99% H_2 / 1% N_2, 5 second reactive gas pulse with N_2 purge flow, pinhole width of 120 µm

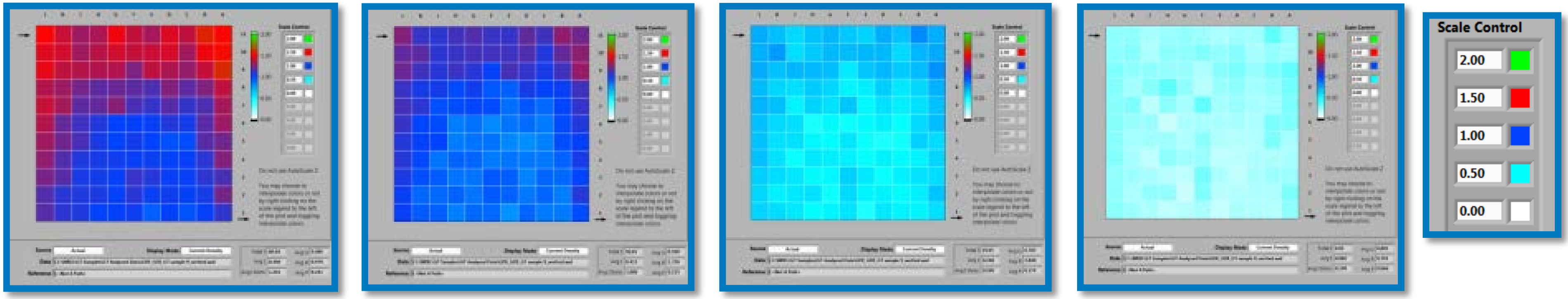
Technical Accomplishments

Spatial performance of membranes with EBL-drilled pinholes

- Georgia Tech used electron-beam lithography (EBL) to create very small (~10 µm) pinholes in 50 µm Nafion membrane
- NREL used these membranes to assemble cells with in-house sprayed GDEs
- No local or total cell initial performance impact observed
- Future studies will include lifetime testing and a range of pinhole sizes



Surface (right) and 3D (below) optical microscopy of 8.7 µm diameter pinhole



1.2 A/cm² **1.0 A/cm²** **0.6 A/cm²** **0.2 A/cm²**

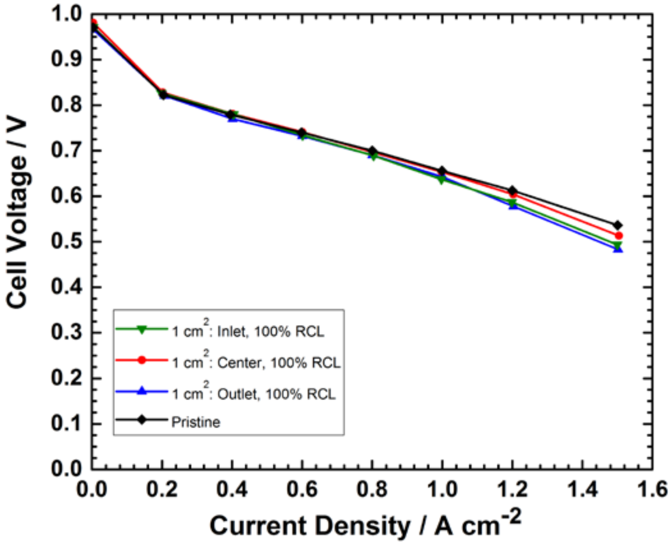
Spatial initial performance for pinhole at 100/50 %RH

Technical Accomplishments

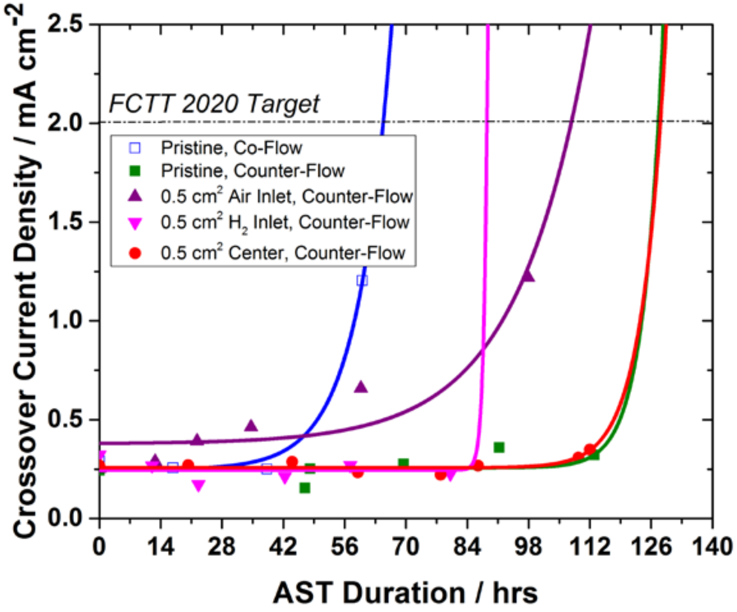
Continued in situ effects of defects studies: Example study

Effect of defect location on performance and lifetime

- Cathode bare spots at inlet, center, outlet
- Initial performance effects
    - Observed at high current density for 0.5 and 1.0 cm^2 irregularities
    - Greater impact observed when irregularities located at inlet or outlet
- Failure study
    - Pristine cells last ~2x longer in counter-flow compared to co-flow
    - Cells with irregularities at air and H_2 inlets fail sooner than cells with defects in the center
    - Defect at H_2 inlet appears to be worst case



Initial performance comparison for 1.0 cm^2 defect



Failure comparison

Technical Accomplishments

In situ testing details

- Initial Performance: Tcell = 80°C, 100/50, 32/32% RH, 150/150 kPa, 1.5/2 stoich. H2/Air
- Prolonged Performance: T_{cell} = 80°C, 100/100% RH, 150/150 kPa, 105/350 sccm H_2/Air
- Accelerated Stress Test: T_{cell} = 80°C, 80/80% RH, Ambient pressures, 500/500 sccm H_2/Air, 30/30 sec cycling
- Normalized voltage difference is calculated at a single total cell current
    - Take initial (cycle 0) VI curve
    - Every 72 cycles, take another VI curve
    - At each of these measured cycles X, the normalized voltage difference is calculated as the ratio of the voltage at cycle X to the voltage at cycle 0. That is why the normalized voltage at cycle 0 is 1 for all samples
    - Normalized voltage difference > 0 implies that the voltage at cycle X > voltage at cycle 0. This can be seen to exist in some cases (e.g., pristine at 72 cycles), but normally doesn't occur
    - Normalized voltage difference < 0 implies that the voltage at cycle X < voltage at cycle 0. This is what is expected as the drive cycle should cause a decrease in performance over time