NREL
Transforming ENERGY

International Meeting on Membrane Electrode Assembly Quality Control for Electrolysis and Fuel Cells: HFTO/NREL Update

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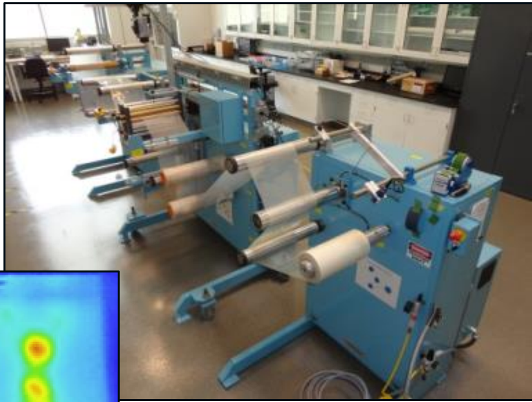
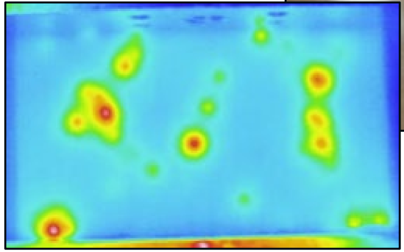
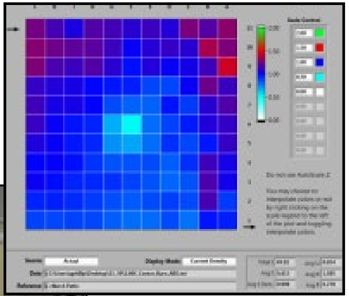
Challenges we try to Address

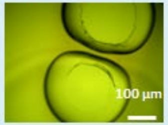
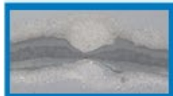
- How can we detect defects in MEA materials in ways that are amenable to the fabrication process?
- How do we understand how defects formed during fabrication and handling affect performance and lifetime?
- How do we understand how the parameters of the ink formulation and fabrication process affect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







Overview of QC Techniques

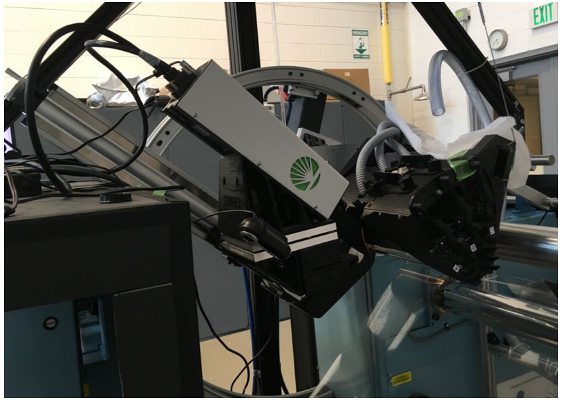
Material	Defects	Detection	Resolution (x-y)	Status
Membrane 	Pinholes, bubbles, scratches, agglomerates, etc.	Optical reflectance/transmission	micrometers	Demonstrated on web-line
	Thickness variation (mapping)	Optical absorption	micrometers	Demonstrated on motion prototype
		Optical reflectance (interference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

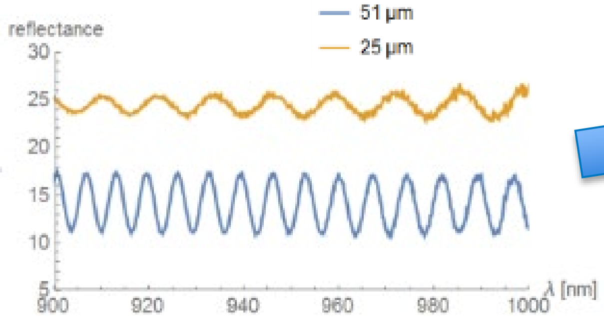
Updates on In-line QC Development Activities

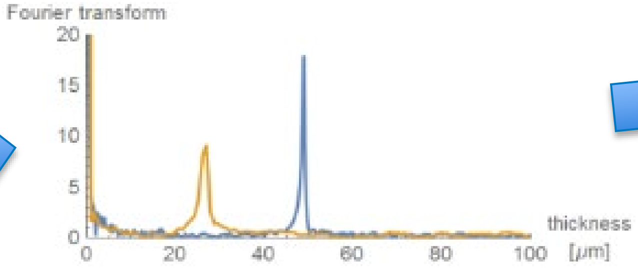
Membrane Thickness Imaging

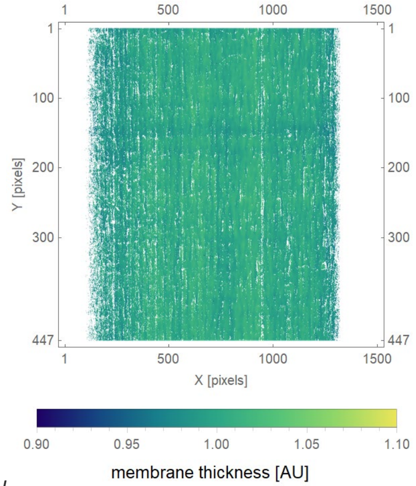
Overview

- Concept:
  - Hyperspectral imager
  - Detect 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 backer/liner







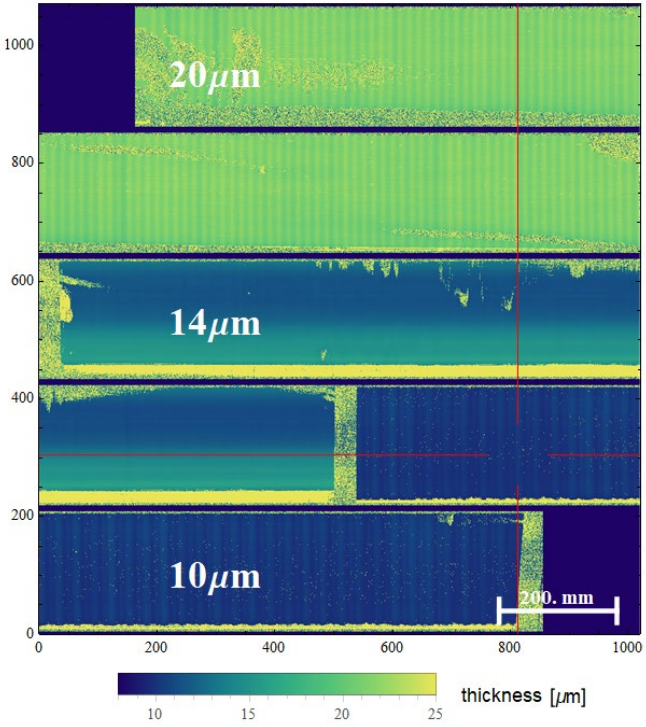


U.S. Patent 10,480,935 B2, "Thickness mapping using multispectral imaging," P. Rupnowski, M.J. Ulsh; November 19, 2019.

Membrane Thickness Imaging

In-line Demonstration

- Ran rolls of multiple commercial and experimental membranes, including state-of-the-art reinforced
  - Line speed from 1 to 30 fpm
- Hyperspectral imager ran at 100 Hz
  - Cross-web resolution was 80 µm using 6.5-inch FOV
  - Down-web resolution was linear with line speed, from 200 µm (at 4 fpm) to 1,500 µm (at 30 fpm)
  - Typical variation of thickness between repeats at the same location ± 0.2 µm
- Developed GPU-based data processing algorithms, toward real-time data processing

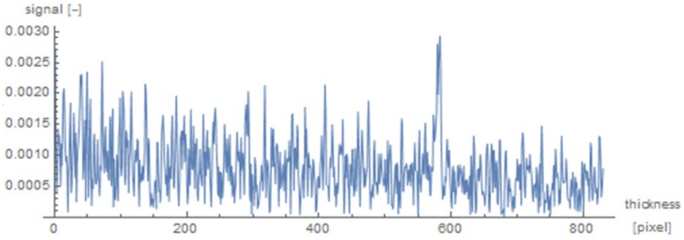


Imaging of experimental membranes at 1 fpm

Membrane Thickness Imaging

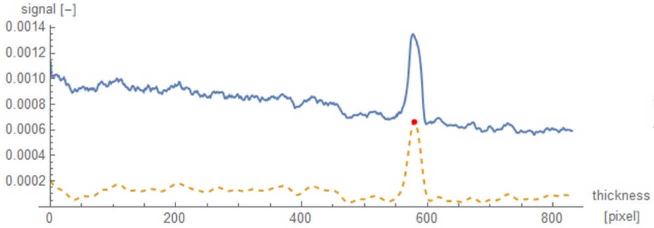
Methods for Thick Membranes

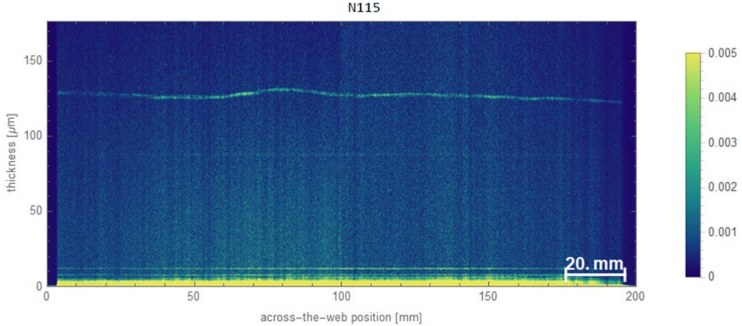
- Baseline algorithms don't work well for membranes > ~60 µm
- Detectors with increased wavelength resolution and/or higher wavelength measurement range can improve/enable thick membrane measurement → but these are high-cost options
- A low-cost option is to revise the processing algorithm to trade off physical resolution for wavelength resolution, thus lowering signal to noise
  - Reduced the cross-web resolution by a factor of 10
  - Added two filtering steps after Fourier transform
- Result:
  - Thickness signal extracted from the hyperspectral image for 75-125 µm membranes



Unmodified thickness signal after Fourier transform

Signal after Wiener (top) and Gaussian (bottom) filtering steps



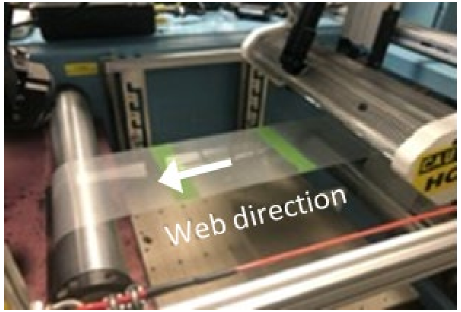


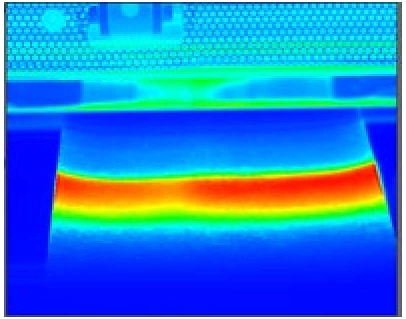
Processed hyperspectral image for N115 where green line is thickness (y-axis) as function of cross-web position (x-axis)

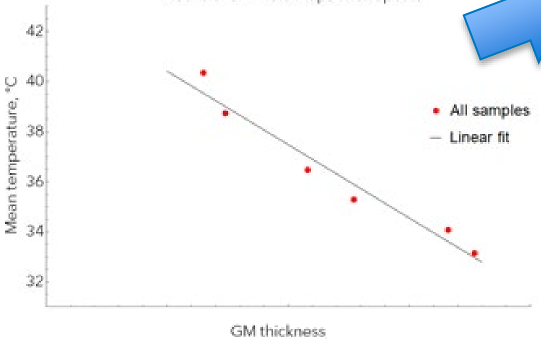
Active Thermal Scanning

Membrane Thickness in Half-MEA Roll Materials

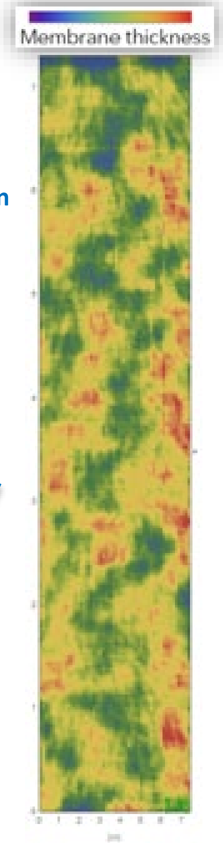
- Property measurement based on IR detection of thermal response to radiative input
- First web-line demonstration using half-MEA web materials fabricated by GM
- Linear response with membrane thickness
- Evaluating mapping mode







Thickness map of membrane in half-MEA



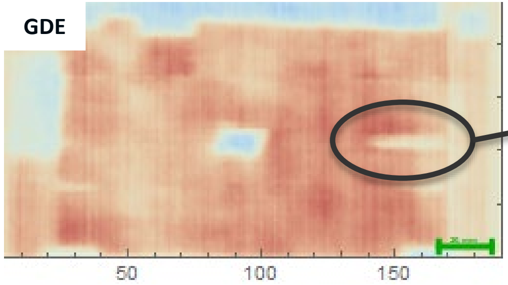
U.S. Patent 10,684,128 B2, "Batch and Continuous Methods for Evaluating the Physical and Thermal Properties of Thin Films." B. Sopori, et al.; June 16, 2020.

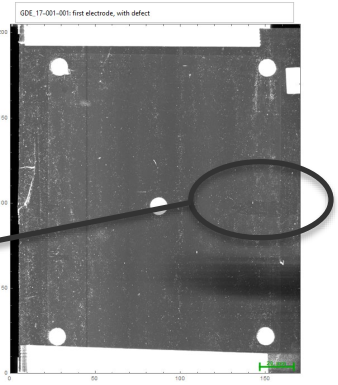
Optical and IR Imaging

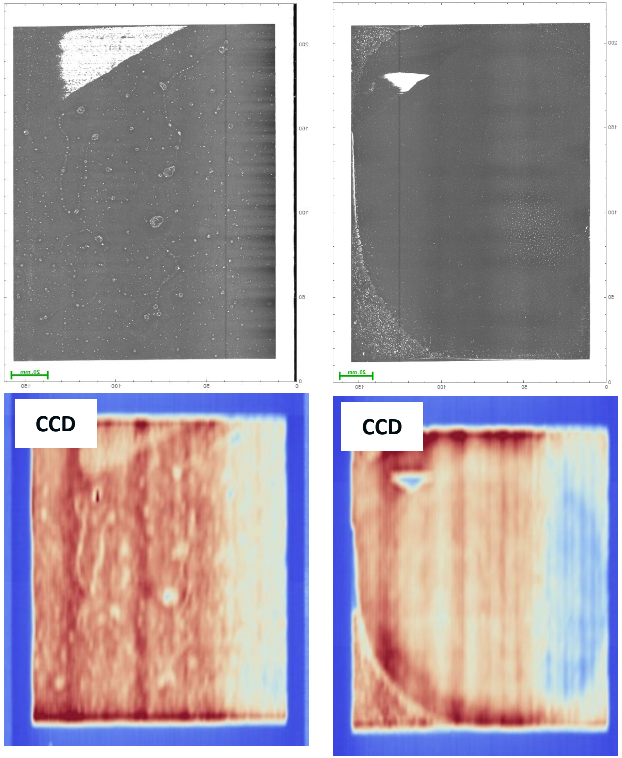
Collaboration with CEA-Liten to Evaluate Multi-modal QC

- Leveraged CEA collaboration to access different electrode manufacturing method (screen printing) for QC validation
  - Gas-diffusion electrodes (GDE) & catalyst-coated decals (CCD)
- Demonstrated in-line multi-modal imaging (simultaneous reactive impinging flow method and optical linescan)

Faintly visible change in grayscale in optical image, more visible as cooler (thus lower loading) location in IR image





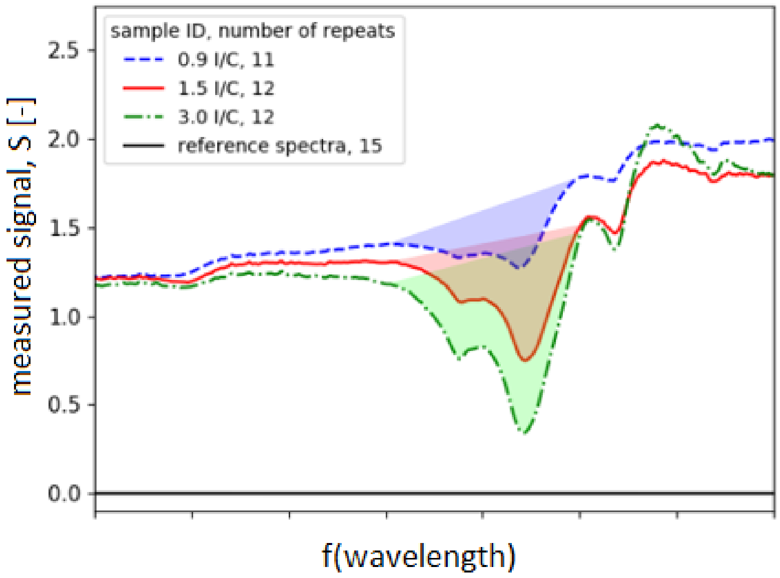


Examples of correspondence between optical (top) and IR (bottom) methods for process-created irregularities: circular features likely related to drying (left) and non-uniformity related to squeegee wiping (right)

Spectrometry-based Methods

Measurement of Nafion in Ink

- Motivation: in-line measurement of ionomer content in electrodes and inks has been identified as a quality inspection need
  - No current methods are known
- Explored multiple spectroscopy methods (UV-Vis, IR, ATR-FTIR, spectrofluorometry, capacitance spectroscopy)
- As an example, we identified a spectral region with signal proportional to ink ionomer loading
  - Similar result for a powdered catalyst layer
  - Exploring possible in-line configurations



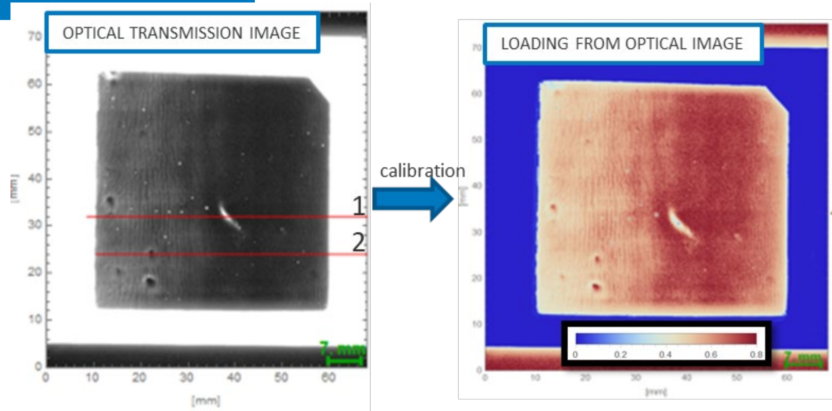
Measured spectra for inks with three ionomer:carbon ratios

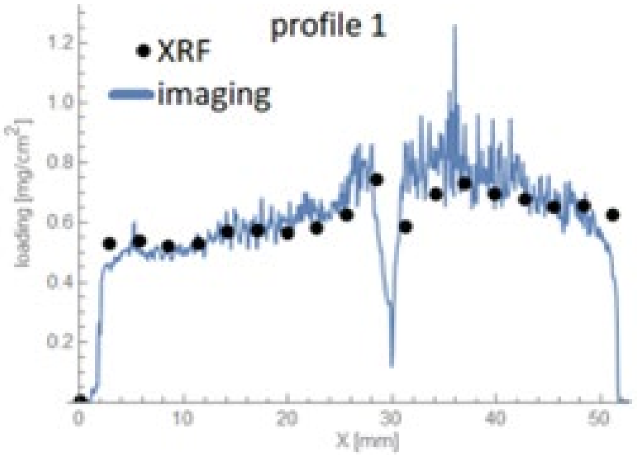
Method details have been minimized as a provisional patent is being pursued.

Optical Transmission Imaging

CCM Catalyst Loading, Defect Detection

- Performed fast optical scanning of experimental IrOx half-CCM
- Took XRF line scans through apparent irregularities in sample
- Good spatial correlation between loading from XRF and optical transmission





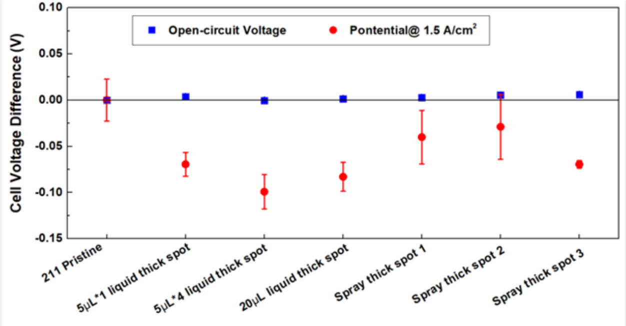
Correspondence of optical data along profile 1 in raw calibrated transmission image, and XRF line scan

Updates on In situ Defect Testing Activities

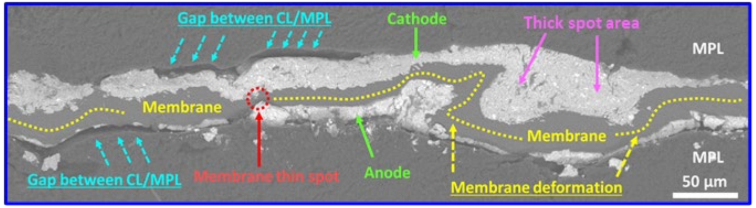
Effects of Electrode Thick Spots

Initial Performance

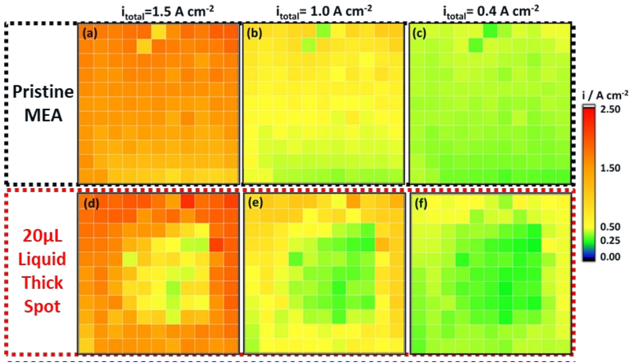
- Used drop-casting and spraying with mask to create thick spots
- SEM (after hot press but before testing) shows potential extensive morphology change due to thick spot
- Initial performance testing (on NRE211)
  - No impact on OCV
  - Significant impact (up to 100 mV) at 1.5 A/cm2
  - Spatial in situ testing shows large area of impact around the thick spot



Impact of thick spots on initial performance



SEM of hot pressed MEA of drop-cast '4x 5 µL' thick spot showing significant morphology impact (CSM)



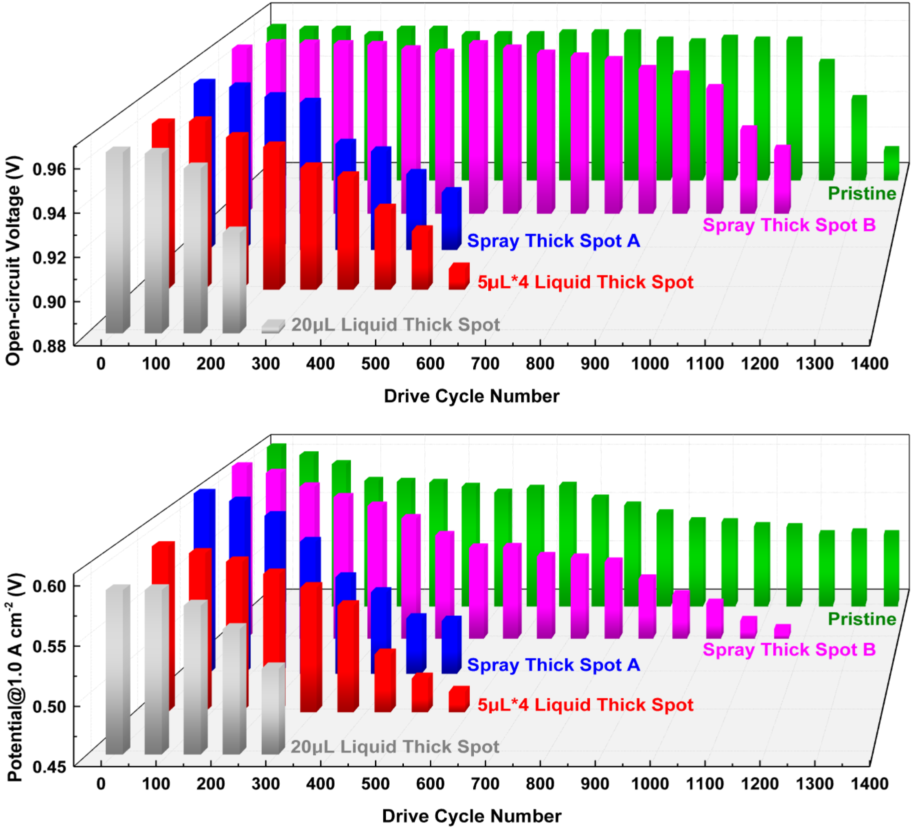
Segmented cell data at three current densities showing wide area of performance impact

ECS Transactions 2019, 92 (8), 351-359
J Power Sources 2020, 466, 228344

Effects of Electrode Thick Spots

Performance Degradation

- Drive cycle testing using 'New European Drive Cycle'
- Observe clear reduction of performance over time via both OCV and voltage measurements at 1 A/cm2

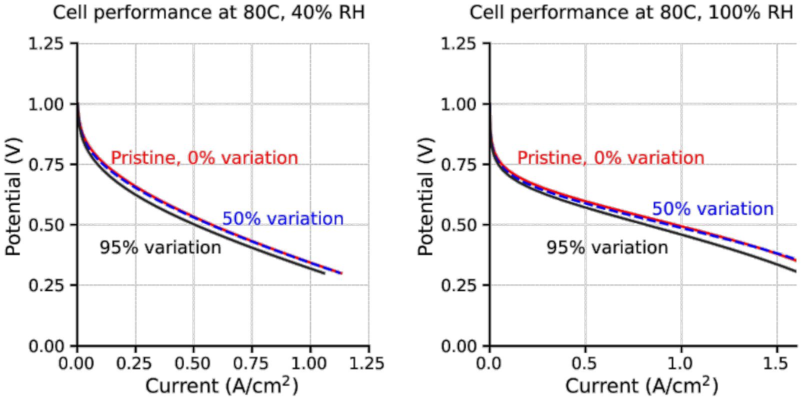


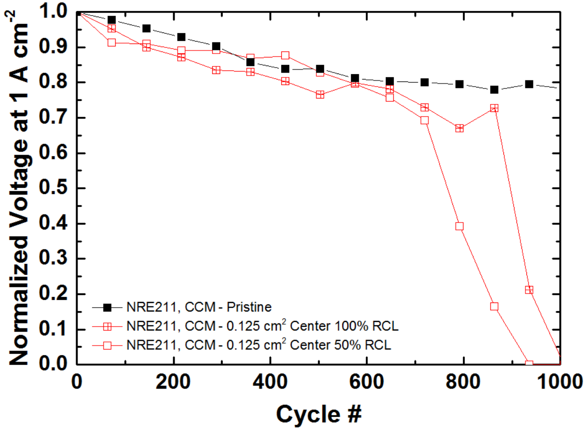
Drive cycle testing results vs. pristine for all thick spot cases (NRE 211 membrane): OCV (top), voltage at 1 A/cm2 (bottom)

Effects of Electrode Thin Spots

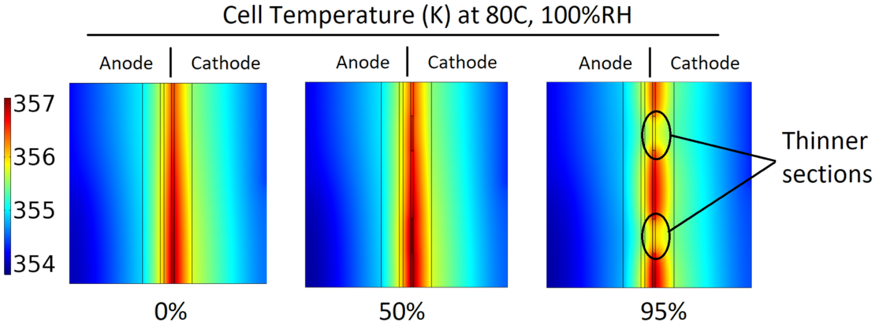
Performance Modeling by LBNL

- Steady-state model
  - Predicts small impact of thin spots on MEA performance, similar to previous NREL in situ measurements
  - However, thermal impact of thin spots could lead to faster failure, as observed in NREL drive cycle results





NREL drive cycle results with electrode thick spots on NRE211 CCMs

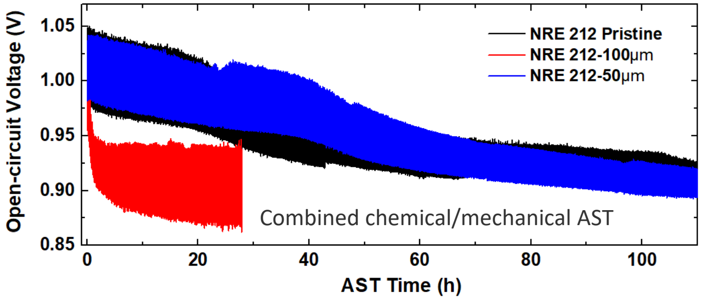


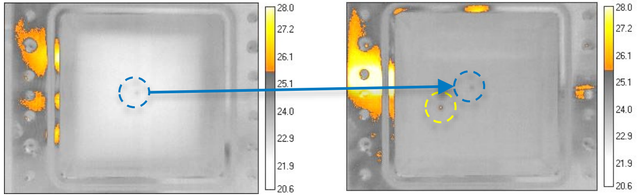
Performance impact (top) and thermal impact (bottom) of thin spots from steady-state model

Effects of Membrane Pinholes

Simulated Pinholes

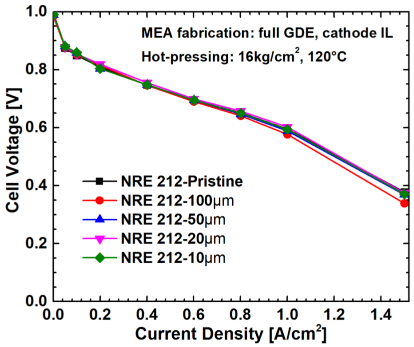
- Understand impact on performance and lifetime of pinhole size (using laser drilling): 10, 20, 50, and 100 µm
- NRE212 with pinholes
  - Minimal impact on initial performance for all but largest pinhole
  - Lifetime is severely shortened for 100 µm pinhole

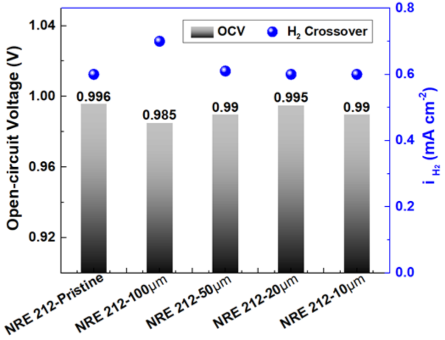




AST comparison (above) and EOT H2XO/IR showing development of separate failure point (below)

Initial performance impact as a function of pinhole diameter





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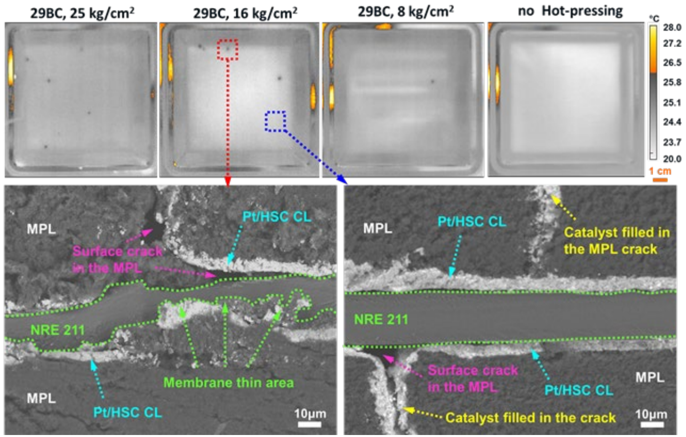
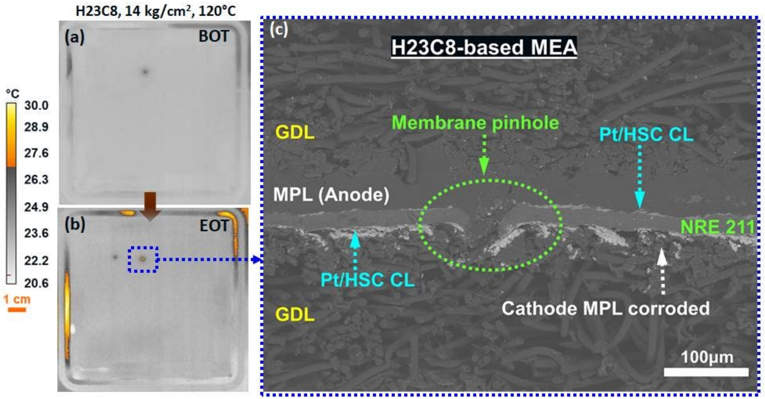
Process-induced Membrane Irregularities

Defects Induced by Hot-pressing

- Identified ‘intrinsic’ irregularities as a function of hot-pressing conditions (using GDE-based MEAs): “PIMs”
  - Points of locally increased hydrogen crossover using BOT infrared imaging (H2XO/IR)
  - Frequency is greatly impacted by hot-pressing pressure and temperature, and MPL roughness
- PIMs result in failure points in AST testing

H2XO/IR mapping and SEM (CSM) showing BOT irregularities, impact of hot-pressing conditions, and local morphology





BOT and EOT H2XO/IR mapping and SEM (CSM) showing that BOT warm spots can lead to failure points

Spectrometry-based Methods

Metrology for Multilayer Structures

- Performed IR spectroscopy of membranes and half-CCMs using benchtop device
  - NRE211, NRE212, N115 membranes
  - NRE211 membranes with 0.05, 0.1, and 0.15 mg Pt/cm2 electrode loadings
- Spectra from 3-7 µm very sensitive to membrane thickness and catalyst loading
- Exploring potential in-line method

IR spectra showing sensitivity to CCM catalyst loading (top) and membrane thickness (bottom)