MEA Manufacturing R&D

Advancing High-Throughput Hydrogen Component Manufacturing Through In-Line Quality Control and Defect Sensitivity Study

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National Renewable Energy Laboratory
WBS #10.1.0.501
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DOE Hydrogen Program
2024 Annual Merit Review and Peer Evaluation Meeting

Project ID: TA001

Photo from iStock-627281636

Project Goal

Our vision is to lead research, development and demonstration **of high throughput quality control methodology**, with the aim of facilitating the industry-wide scaling up of fuel cell and electrolyzer MEAs and stacks. This initiative operates synergistically with ongoing endeavors within the M2FCT, H2NEW and R2R consortia, ensuring a cohesive approach to advancing hydrogen and fuel cell technologies.

Project goals:

- Advance quality inspection techniques and delineate defect thresholds, with a specific emphasis on applications in heavy-duty fuel cells and low-temperature electrolysis.
- Improve, update and research new core capability platforms to continue to enable this unique knowledge development

If you can't measure it, you can't improve it. – Lord Kelvin (1824–1907)

If you can't measure it, you can't manage it. – Peter Drucker (1909-2005)

If you don't know what you want to manage, you're wasting your time measuring. – Alfons Staerk

Outcomes: transferring knowledge and methods to industry to expedite the process of commercialization

Overview

Timeline and Budget

- Project start date: July 2007
- Project continuation and direction determined annually by DOE
- The activity seamlessly transitions to operate within the framework of R2R Consortium

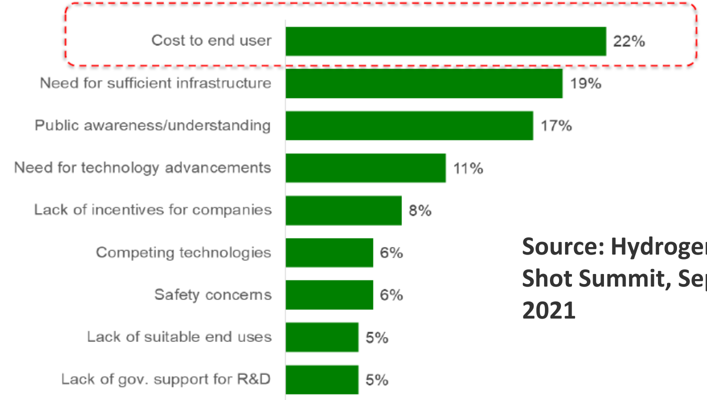
Barriers	Target*
E: Lack of Improved Methods of Final Inspection of MEAs	$20/kW (2025) at 100,000 stacks/yr
H: Low Levels of Quality Control	

*https://www.hydrogen.energy.gov/pdfs/20005-automotive-fuel-cell-targets-status.pdf

Budget and Funded Partners

Fiscal Year	NREL	LBNL
2023 (received)	$119,000	$0
2024 (planned)	$0	$0

Stakeholder Reported Barriers to Hydrogen Market Adoption



Source: Hydrogen Shot Summit, Sept 2021

Relevance and Potential Impact

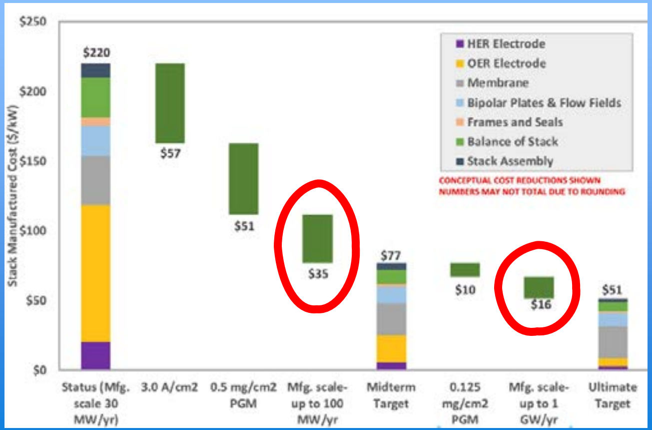
Hydrogen Energy Earthshot enablers addressed by this project:

- **Increased durability-lifetime**
- **Low-cost manufacturing processes**
- **Manufacturing at MW-scale**

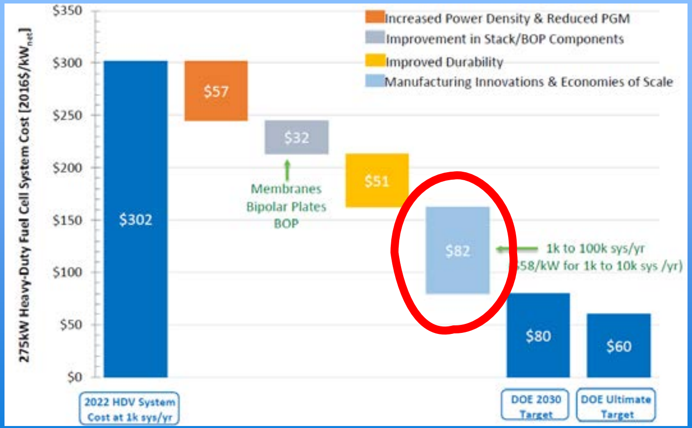
2020 DOE Hydrogen Program Plan: "…R&D efforts can help **achieve economies of scale** in manufacturing… key opportunities include: Technologies for **in-line diagnostics and quality control/quality assurance**; Sensors and other technologies to **reduce manufacturing defects** in high-throughput production…"

2022 DOE Fuel Cell Technologies Overview: "Substantial improvements needed in power density, durability, stack and BOP components, and **manufacturing**."

Pivovar, H2NEW, 2023 Hydrogen AMR



Papageorgopoulos, FC technology overview, 2023 AMR



Addressing DOE Goals: **Supporting manufacturing scale-up challenges, like quality control**, for fuel cell and electrolysis MEA and stack technologies **assists U.S. manufacturer competitiveness** and **job creation**, and contributes to the commercialization of technologies that will **lower pollutant emissions** and **enable clean energy power and fuel infrastructures** in the U.S.

Approach

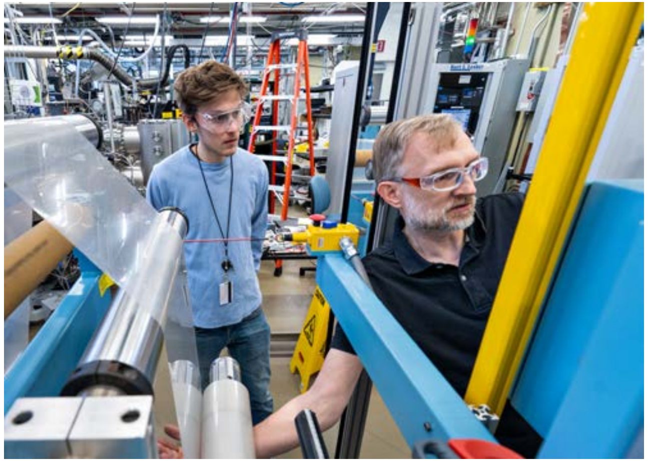
***Annual Milestone Criteria:**
- at least two material types
- samples with and without contamination
- engage with at least 3 radiograph vendors

Date [M/Y]	Milestone/Deliverable (status as of 3/4/24)	Complete
6/23	In-line mapping of loading/thickness/surface topography of opaque materials	100%
12/23	Interference fringe-based thickness mapping for transparent membranes	90%
3/24	Get broader LTE community feedback on the LTE MEA failure modes assessment	20%
3/24	Spatial LTE diagnostic study. Demonstrate functionality of segmented cell using reference cells and cells with electrode inhomogeneities	80%
6/24	Single-point, high-rate electrode coating thickness monitoring based on chromatic confocal probes.	50%
9/24	Radiography for inspection of MEAs, PTLs and GDLs*.	90%

Approach: Safety Planning and Culture

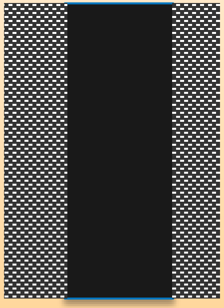
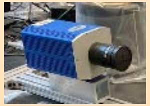
- This project was NOT required to submit a safety plan to the Hydrogen Safety Panel (HSP).
- Safety culture examples as applied to the project:
  - Installed light curtain on roll-to-roll web-line
    - allows for testing at high web-line velocity
  - Organized nano CT training to cover safety and operational aspects of the tool
    - the entire in-line QC team went through the training
    - lead by the tool producer
  - Upgraded safety aspects of handling Pt containing inks

Photos by Dennis Schroeder and Werner Slocum / NREL



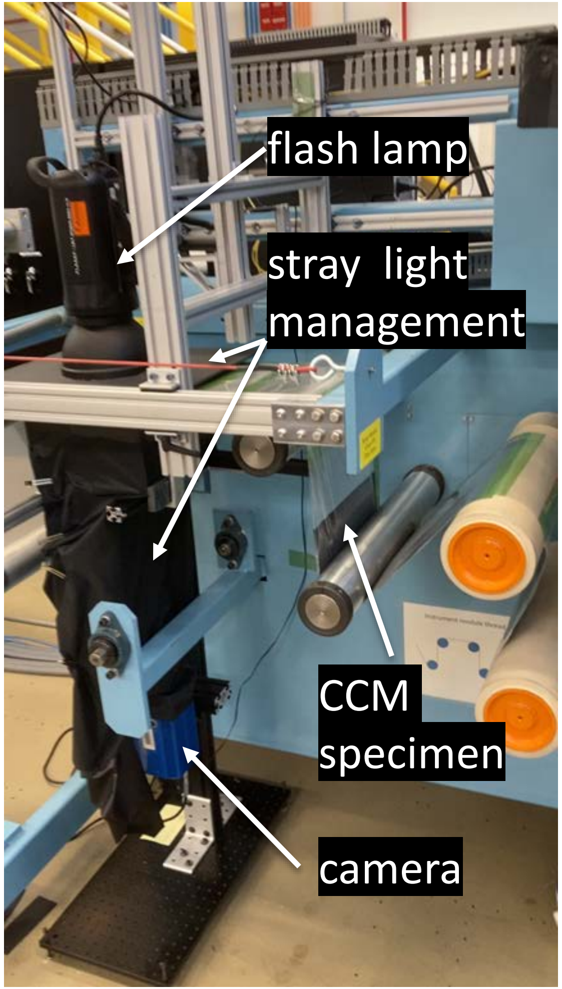
Accomplishments - Inspection of Opaque Multilayer Structures

Objective: Determine requirements needed to reliably acquire optical transmittance signal. If we find it feasible, the method can potentially be used for in-line monitoring of quality (uniformity, defects) of 3-layer CCMs for LTE

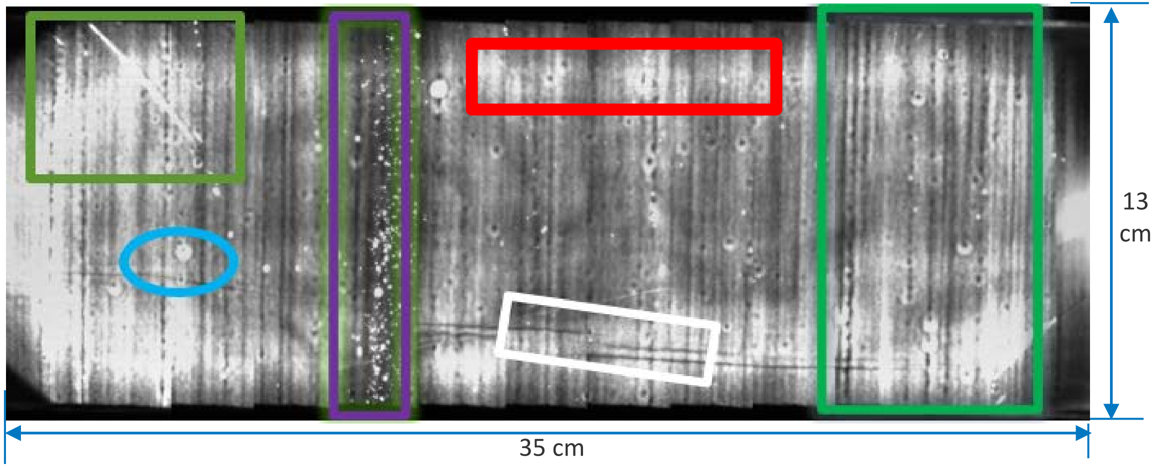
3 light sources		3-layer CCM	3 cameras			
					tested settings	fixed settings
LED		 electrolyzer CCM (two electrodes deposited on an opaque membrane with Pt-mitigation)		cooled Si 2D array (Coolsnap)	integration times: 10, 100 and 1000 ms	
class II red laser				standard line camera (P3)	line rates: 2.5, 13 and 23.5 klps	1x binning
tungsten-halogen bulb				Time Delay and Integration camera (HS)	binning: 1x, 2x, 4x and 8x	TDI=96, line rate =3.5 klps
Flash lamp						

- Added flash lamp as a new light source to this hardware configuration matrix.
- Observed that configuration with the lamp and the 2D array sensor yields images with good signal-to-noise ratio.
- The lamp delivers a powerful flash lasting ~1 ms, thereby freezing the motion of the material in in-line QC setup.

Accomplishments
Inspection of Opaque Multilayer Structures – R2R demonstration



Transmittance image of highly opaque CCM generated by stitching several individual 2D frames. Image features highlighted with green, blue, and purple frames likely result from **material variations**, while the red and white frames depict **effects introduced by the imaging system**.

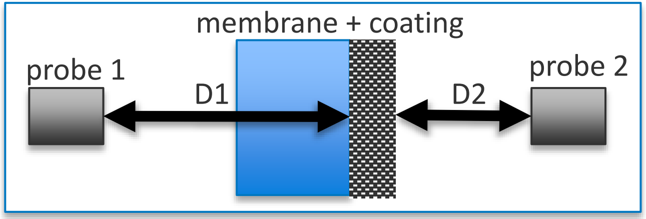


- NREL successfully developed and demonstrated the transmittance imaging method for 3-layer LTE CCMs.
- Next step should focus on proper white reference calibration and/or improving light uniformity.

Accomplishments
Electrode thickness monitoring

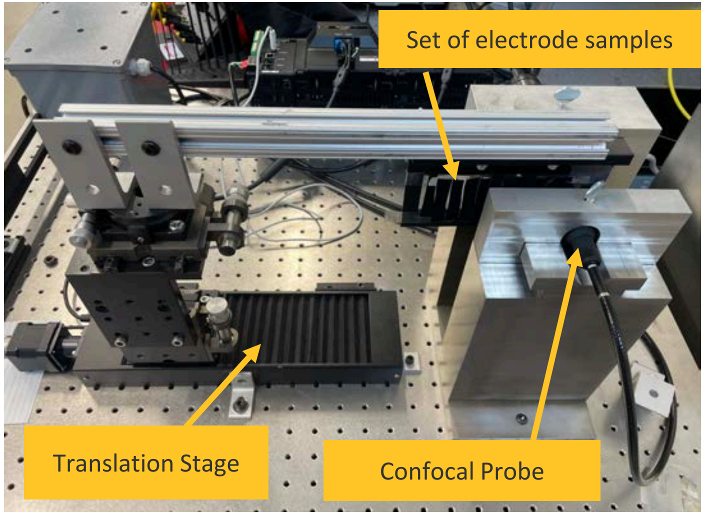
Technical objective: enable single-point, high-rate electrode coating thickness monitoring utilizing the chromatic confocal probes (thickness range 1-15µm)

- Potentially relevant for in-line monitoring of electrode thickness and porosity

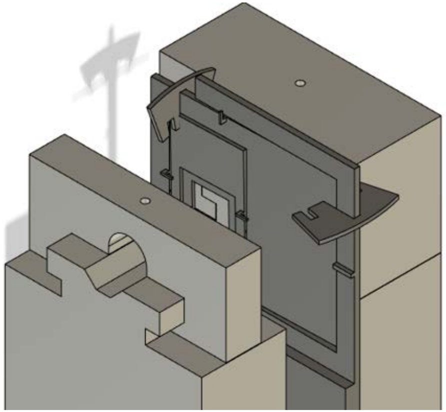


Double probe configuration.
Coating thickness = const – D1 – D2

- A new fixture holding the probes has been built and tested to mitigate the previously identified mechanical instability issues.
  - The confocal displacement sensors have been mounted on an Invar-36 mount to limit vibrations and thermal expansion related shifting over time.
- A motorized translation stage for thickness profiling, fast multi-sample set testing and to be able to find same location on the sample.
- An adapter was also designed and fabricated to verify coaxial alignment of the probes



Confocal displacement sensor setup

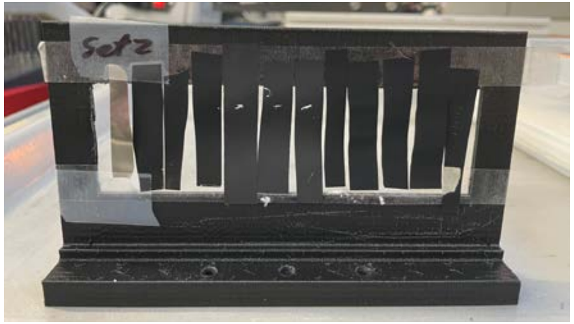


A design of an adapter for checking coaxial alignment of the displacement probes

Repeatability of the electrode thickness measurement

Sample Number	Pt Loading [$\frac{mg}{cm^2}$]	Exp 3 SD [µm]
1	N/A	1.1
2	0.115 Pt/HSC	1.3
3	0.099 Pt/HSC	0.9
4	0.3 Pt/HSC	0.4
5	0.3 Pt/Vulcan carbon	0.9
6	0.3 Pt/Vulcan carbon	0.4
7	0.2 Pt/Vulcan carbon	0.7
8	0.17 Pt/HSC	1.3
9	0.102 ± 0.018 Pt/HSC	0.8
10	0.14 ± 0.014 Pt/HSC	0.4
11	0.16 ± 0.013 Pt/HSC	1.8
12	0.061 ± 0.05 Pt/HSC	1.3
Average		**0.9**

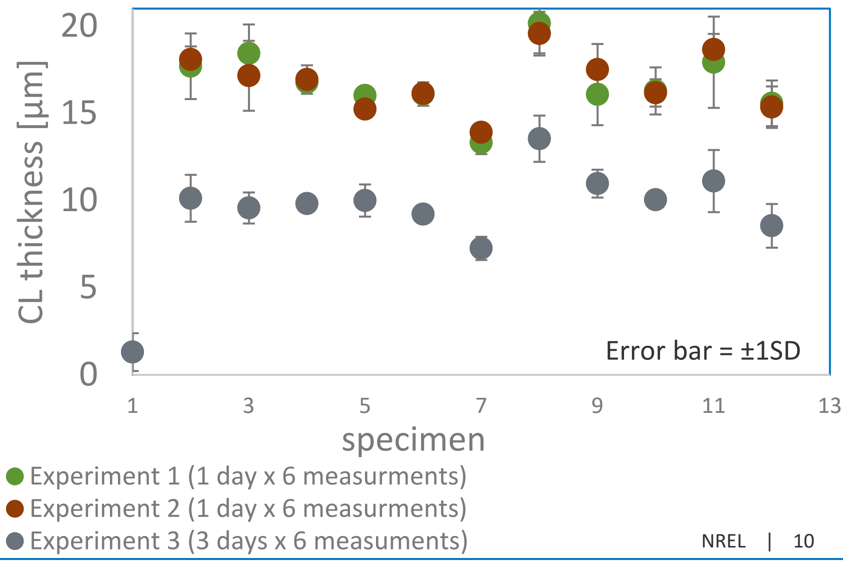
- 12 specimens, 3 experiments, 5 different days, **each sample was measured 30 times**
  - First two experiments did not include a proper thickness reference, and the values obtained were found to be shifted up about 7 µm
- Nevertheless, very similar relative sample to sample variations were observed in all 3 experiments.
- Based on the experiment nr 3
  - **repeatability** (average SD) was found to be **0.9 µm**. Before similar value was observed only within one day testing.
  - **good day to day stability of the setup**



Left: a frame containing 12 electrodes on membrane specimens employed in the study

Right-top: specimens' description

Right-bottom: thickness measurement results



Accomplishments – LTE Segmented Cell System

Technical objective: demonstrate functionality of segmented cell using reference cells and cells with electrode inhomogeneities, including EIS measurements and an experimental matrix for one defect type, such as a catalyst layer deformity.

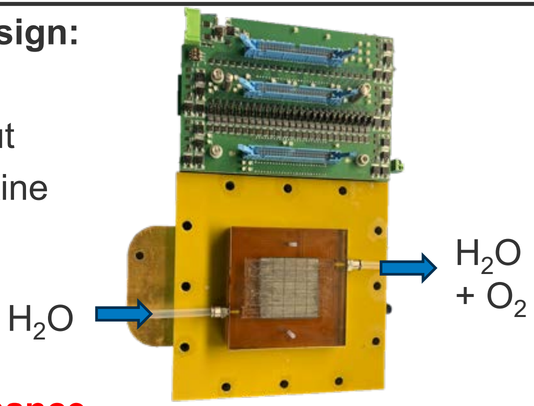
NREL LTE Segmented Cell Design:

Active Area: 25 cm^2

Segment Size: 1 cm^2, 5x5 layout

Flow Field: + 6 channel serpentine

+ *segmented anode*



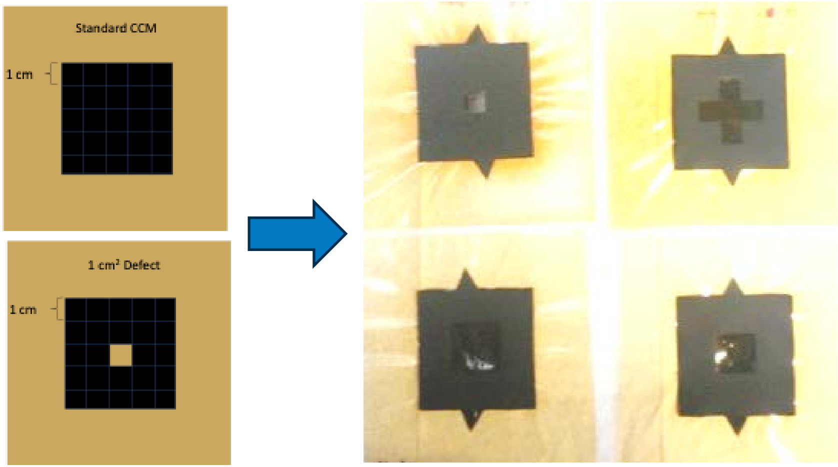
Cell Validation:

- Achieved acceptable contact resistance (30 mOhm-cm^2)
- Reached/maintained LTE conditions (e.g., 80ºC)
- Solved leakage by improving epoxy process
- Held flowing gas/liquids at relevant pressures (e.g., 2 barg)

Resolution of spatial performance allows the segmented cell platform to monitor key metrics for PEM LTE durability due to the presence of defects – determine how local defects (e.g., pinholes, catalyst layer aggregation) can spread and cause issues throughout the entire cell.

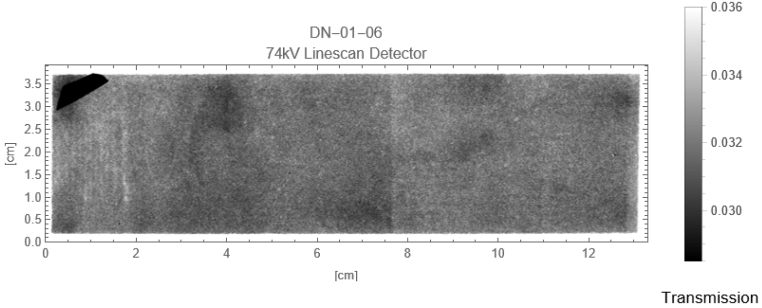
Fabricated CCMs with "Defects":

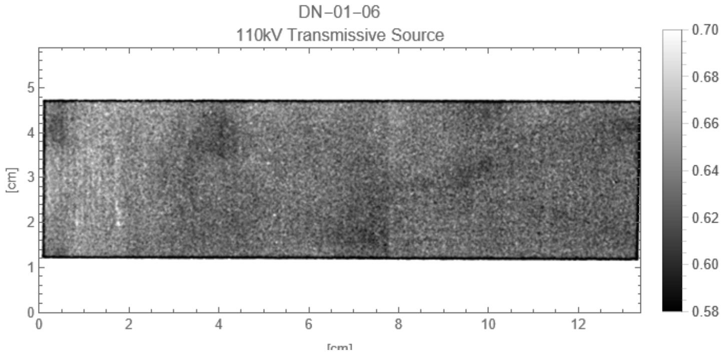
- Ultrasonic spray deposition
- 0.5, 1, 2, 3, and 5 cm^2 defects (voids) in anode

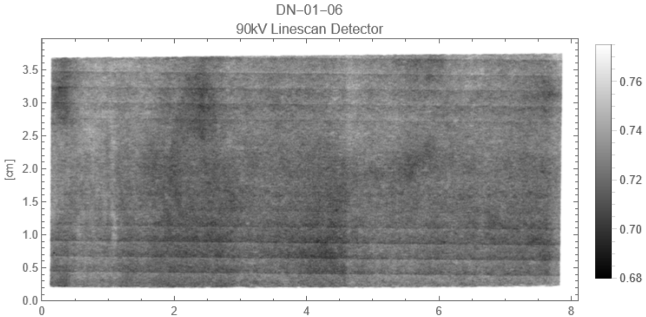


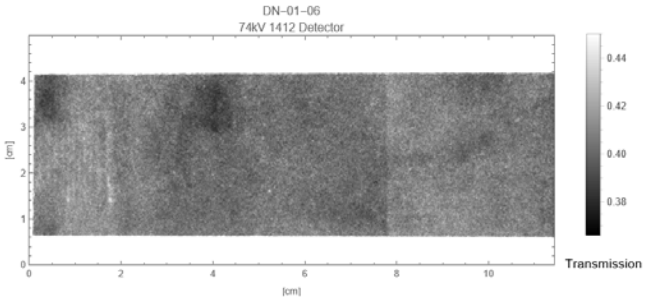
Accomplishments – Initial study of X Ray Transmission Technique

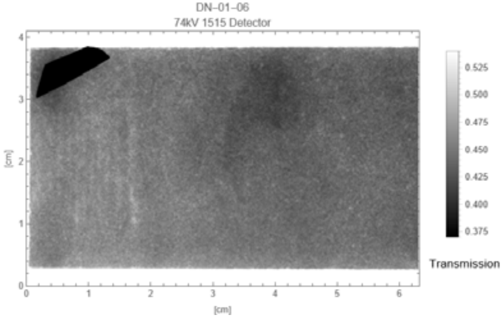
- Engaged with a few vendors, signed NDA with one to whom a set of PTL and MEA specimens was sent.
- Radiographs acquired using 5 different source/detector configurations were provided back to us.
  - PTL Image analysis identified features that are repeatable.
  - A correlation between x-ray transmission and areal density was established.
  - Areal density and porosity maps were generated.







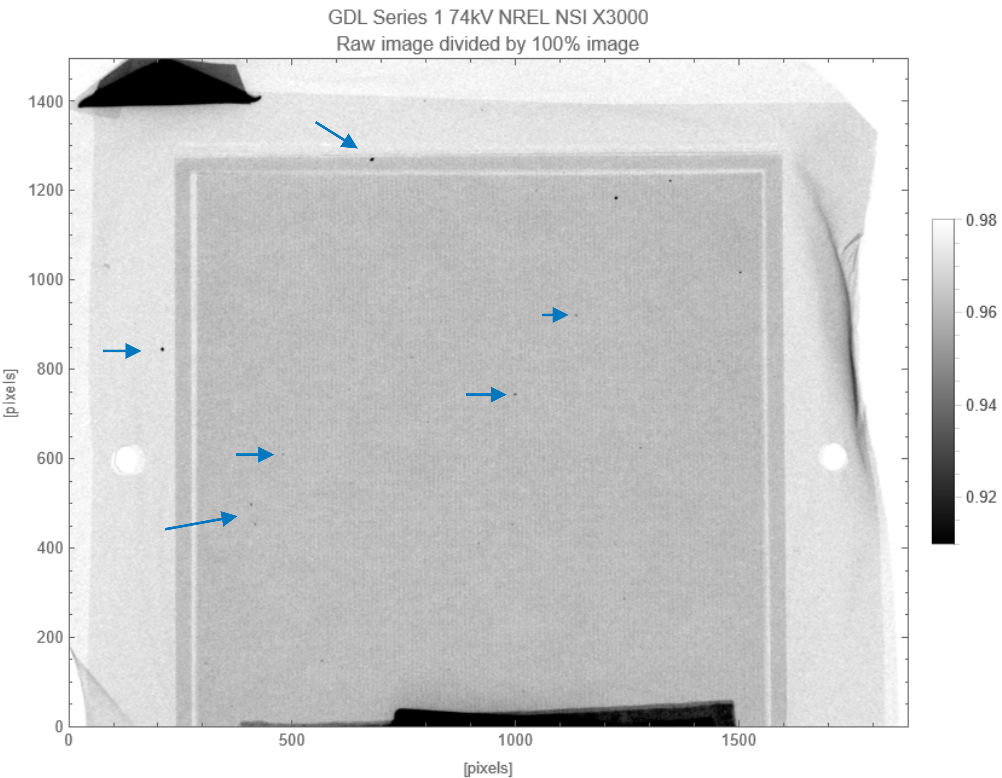




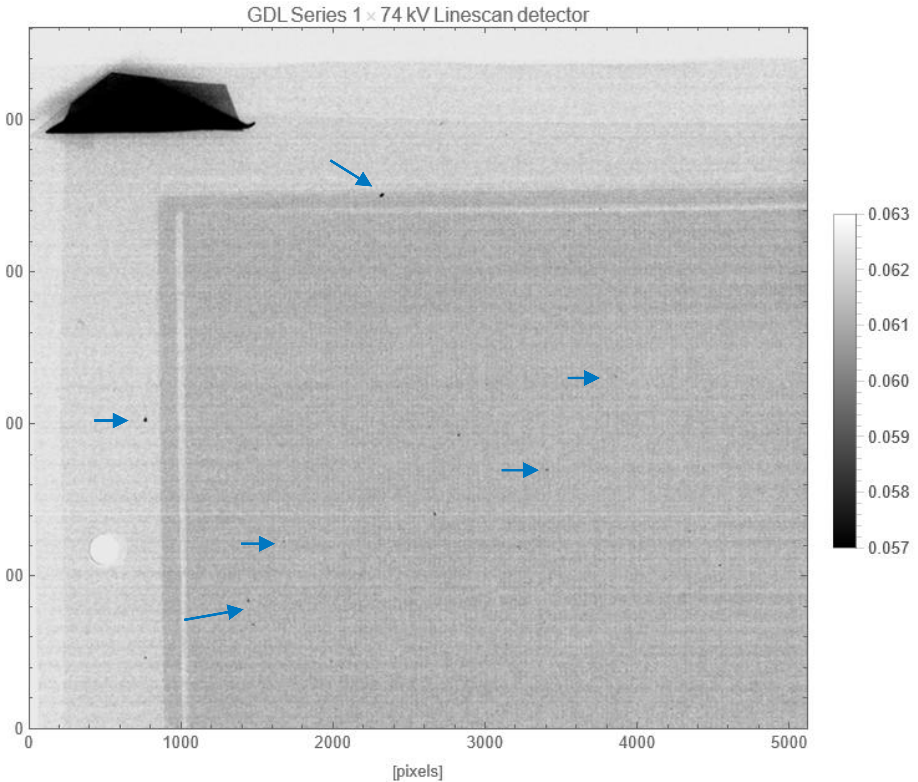
X-ray transmission of 5 layer FC MEAs

Radiographs were acquired by an outside vender and at NREL. In the latter case we utilzied nano CT device operating in basic transmission mode.

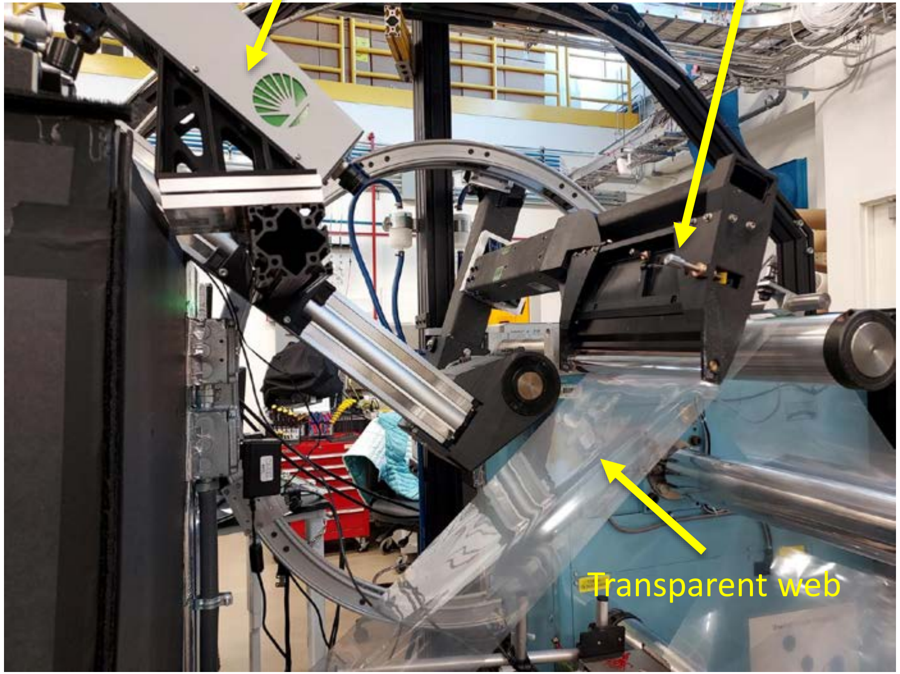
Radiograph from NREL's nano CT tool



Radiograph from external partner



Membrane thickness mapping

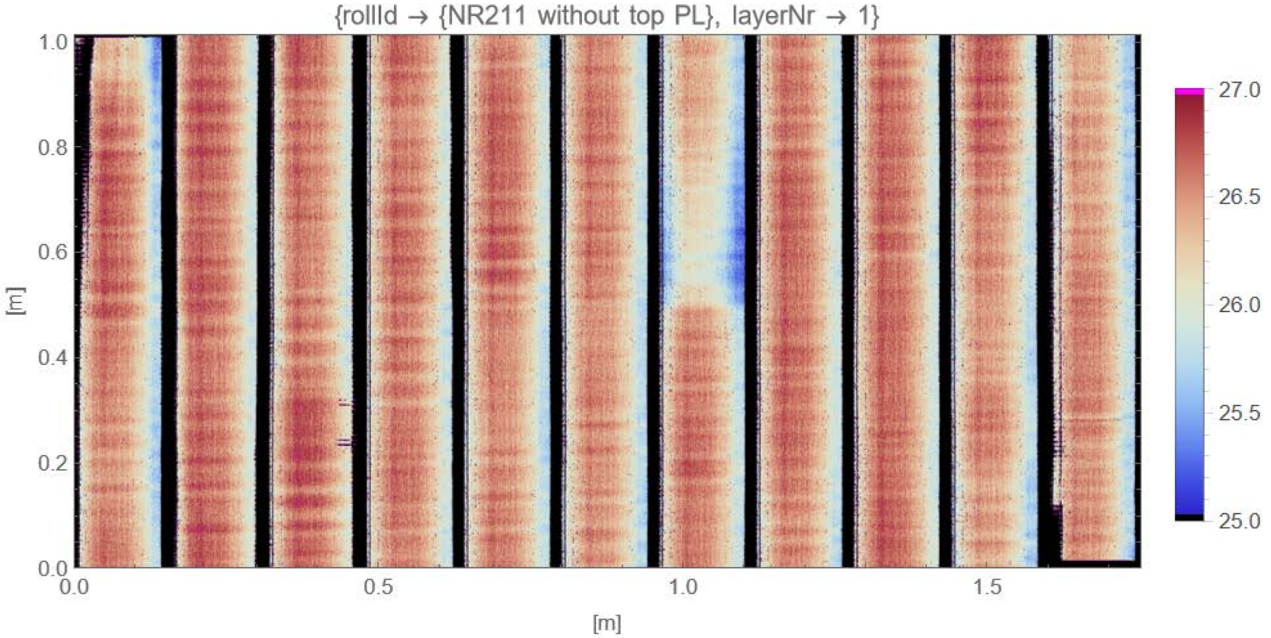


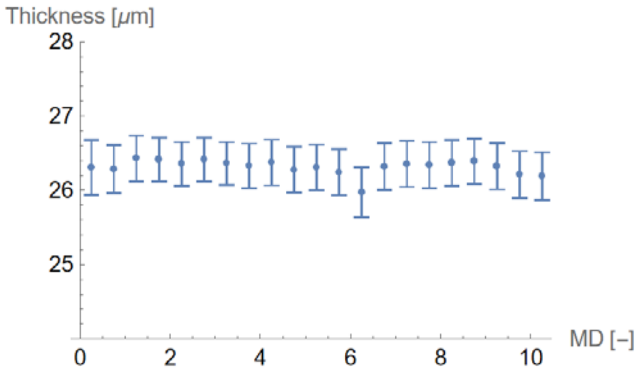
Experimental setup performing 200k thickness measurements per second

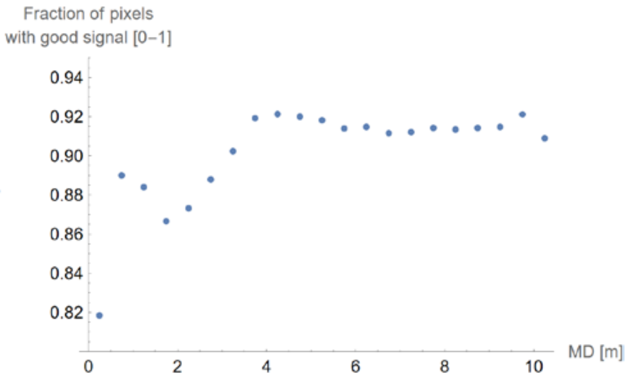
- Two cameras with Si (400-1000nm) and InGaAs (900-1700nm) detectors
- Membrane samples:
  - 10m long NR211, NR212 and N115
  - 6.5m long proprietary membrane
- Except N115 roll the membranes were scanned on a substrate
  - with and without additional top protective layer
- Mapping with (real-time) and without (off-line) simultaneous data processing
- Light source: halogen light (used <2% light intensity of an 150W Intralux-dc 1100)
- Frame rate: 100 Hz, web-line speed: 5 ft/min, pixel size MD=254 μm, CW=76 μm

NR211 results

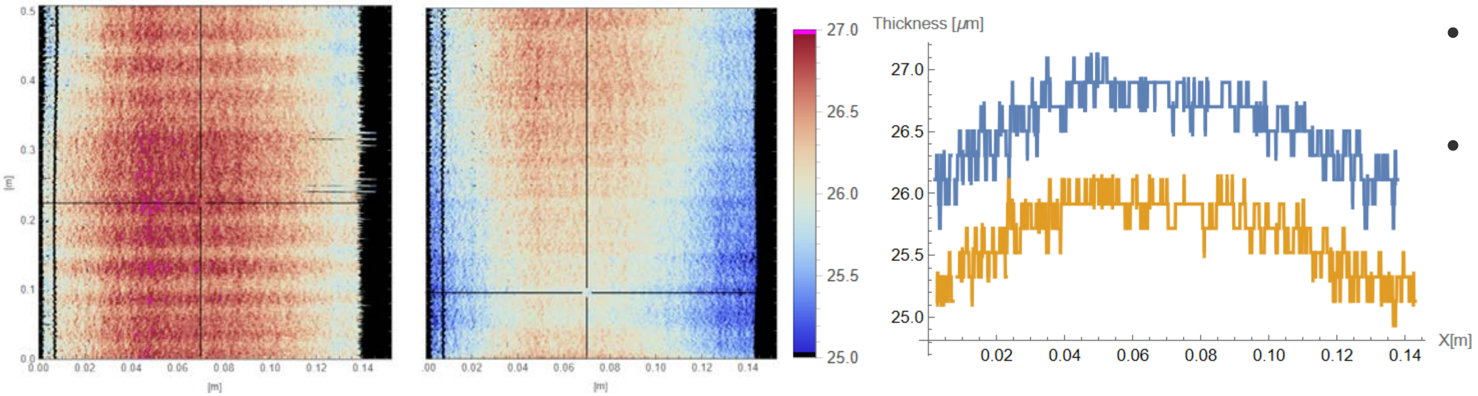
- The map shows thickness distribution for 10m long roll. It has been divided into 1m sections assembled horizontally for easier viewing.
- The contrast was boosted by setting 2µm thickness range.
- Good signal at 90% of pixels. It would be close to 100% if left and right edges are removed.
- Overall thickness 26.3±0.4µm (target 25.4)
- System is sensitive to detect both across-the-web and machine direction variations, though the variations are relatively small.



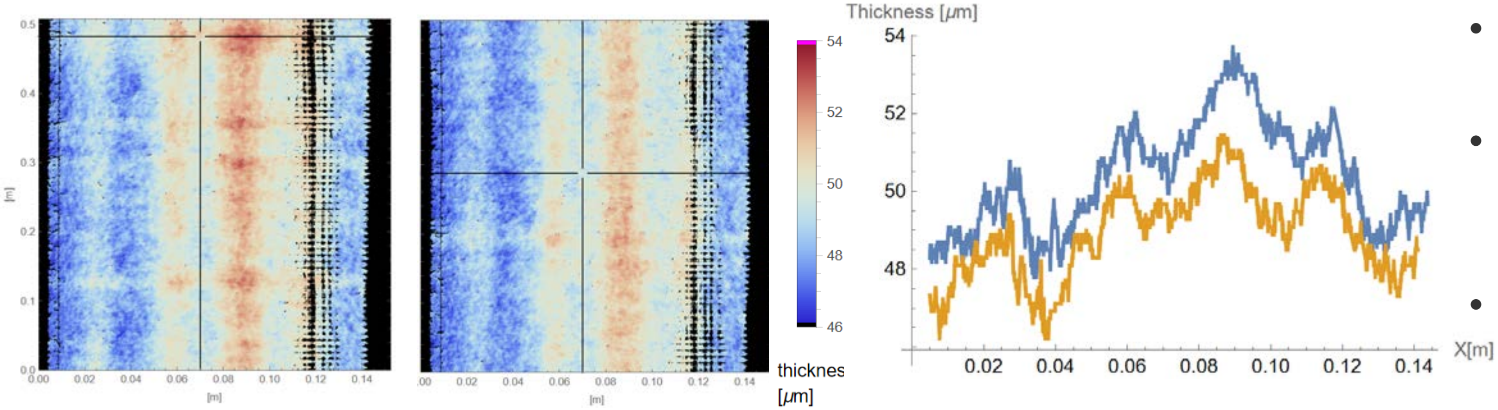




NR211 (top) and NR212 (bottom) results – selected sections



- Overall extremes: max 27.0, min 25.0µm
- Typically, 1µm variation within one section



- Overall extremes: max 54.0, min 46.0µm
- Typically, ~5µm variation along CW profile
- Uniform thickness in MD

Response to Previous Year Reviewers' Comments

Comments related camera selection, penetration depth of UV light and lack of physical model of the UV adsorption by Ce ions.

RESPONSE: While acknowledging the benefits of modern imagers, we have chosen the CoolSnap HQ2 CCD camera for its proven effectiveness in demanding applications and its availability in our lab. We have realized that **replacing the light source can solve the problem of low signal** and that substituting camera would be a less practical solution. Regarding UV penetration depth of PFSA, our study included the transmittance spectrum of pure Nafion samples, **demonstrating that the penetration depth is not small** in the wavelength range where we postulate to look for the signal attributed to Ce absorption. We fully concur that the physical model for UV adsorption by Ce ions would strengthen the findings from our experimental study.

Several comments on the scope of project, lack of deep immersion into industrial production requirements, and recommendation of putting more focus on predicting what changes to QC methodology are needed to improve cell response.

RESPONSE: Beside in-line quality control and impact of defects, in the past this project had focused also on process science, but this third scope of work was recently rolled under other HFTO consortia. **We agree that following this change the project title should be revised accordingly.** In our studies we have been focusing on the potentially most critical defects, e.g., thickness/loading variations, pinholes, surface protrusions, etc., we evaluate how often they are encountered in cell components, and we test or model their impact using in-situ diagnostics tools. This was the most reasonable approach we could take in the situation where there is no published roadmap defining specific QC needs and critical defect specifications that we could use as research objectives. Our effectiveness is the result of strong connection to industry - **just in the last year we applied our QC expertise to support 10 companies as shown in slide 11.**

Comment that determination of electrode thickness using chromatic confocal probes operating in single-point mode may not paint a full picture of CCM quality and would be improved if the scan area could be increased.

RESPONSE: If good Gauge R&R metric is obtained, we would like to propose thickness profiling or areal mapping utilizing high measurement rate of the confocal probes. Another direct method for electrode thickness measurement is **tedious destructive cross-sectioning**. However, the confocal probes solution seems to offer **many advantages over the traditional cross-sectioning**.

Collaboration and Coordination

Industry Collaborators

- We leverage separately funded activities with **Chemours, 3M, Nel Hydrogen, DeNora, GM** and **Fortescue Future Industries** to understand industry directions and challenges
  - partners provide materials, manufacturing QC requirement and needs,
  - we continue to get detailed input on prioritization of diagnostic development, feedback on technique capabilities, and pursue tech transfer
- SBIR project with **Lookin** to evaluate effectiveness of Terahertz imaging methods
- SBIR project with **Resonon (UCLA)** to commercialize membrane thickness mapping technique
- SBIR project with **Membrion**
- **Advent Technologies** loaned NREL's XRF system for in-line monitoring of Pt loading
- We are teaming with numerous commercial entities to pursue a diverse set of funding opportunities for future work

Labs and Academia

- **UMass Amherst:** Collaboration on in-line metrology and AI/ML; hosting interns

Proposed Future Work

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

Barriers and Needs

- We actively engage with partners to understand their needs, based on their specific processes, materials and MEA constructions to support them in fabrication scale up in the area of quality control.
- Provide QC technical support to help answer fundamental QC questions: what, when and how critical material parameters needs to be measured on a high-thruput production floor.

Future Focus

- Work under the umbrella of R2R Consortium and coordinate the development activities with M2FCT and H2NEW consortia
- Continue to work with and gather current information on challenges from as many industry partners as possible in the fuel cell and electrolysis space
  - Seek opportunities to implement diagnostics in industry
  - Transfer knowledge and demonstrate quality control methods of the highest potential value for the hydrogen industry
  - Commercialize novel in-line QC techniques that have been developed specifically for FC and LTE materials
- Evaluate new non-X-ray-based methods such as THz and ultrasonic absorption testing and continue study of X-ray and optical methods for MEA materials and structures.
- Study the effects of relevant defects and layer irregularities on cell performance and lifetime
- Continue to develop and apply predictive models to assist in the understanding of impacts of defects

Summary

- Relevance
  - Quality Control methodology, uniformity/defect specifications for MEA and stack components needs to be developed to derisk high volume production.
  - Scale up will be crucial to reduce hydrogen technology cost and to meet Hydrogen EarthShot and BIL goals
- Approach and Collaborations
  - Continued detailed partnership, collaboration, and information exchange with industry partners and H2NEW and M2FCT consortia on QC priorities. (Over last year we have been actively working on QC projects with 10 companies.)
- Accomplishments
  - Successfully developed and demonstrated a method which images uniformity of multilayer electrolyzer CCMs with mitigated membranes.
  - Have shown that our new a mechanically stabilized fixture for chromatic confocal probes is effective and allows for measurement of electrode thickness with ± 0.9 µm repeatability.
  - We are almost ready to demonstrate a functional 25 cm^2 segmented cell for PEM LTE.
  - Demonstrated that utilizing X-ray radiography it is possible to observe PTL density nonuniformities and point type irregularities in 5-layer MEAs
- Tech Transfer
  - Leveraging HFTO investments for many industry-focused projects including one new CRADA mod

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Hunter Simonson
Robin Rice

Thank You

www.nrel.gov

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NREL Transforming ENERGY

Technical Backup and Additional Information

DEIA/Community Benefits Plans and Activities

- This project has neither Diversity, Equity, Inclusion, and Accessibility (DEIA) plan nor Community Benefits Plan (CBP)

Technology Transfer Activities

Technology transfer

- New CRADA mod with GM to continue development of a quality control method. This may lead to licensing of one of NREL patents.
- SBIR I project with Resonon to commercialize NREL's patent and software record.
- SBIR IIb project with Membrion to develop a quality control solution based on one of NREL patents.
- Presented two new records of invention to Resonon, Nel Hydrogen and DeNora

Current industry support projects

- HFTO Electrolysis Manufacturing FOA projects with 3M and Nel Hydrogen
- SBIR I project with Lookin

Other collaboration activates:

- Loaning NREL's XRF system for in-line monitoring of Pt loading to Advent Technologies

Special Recognitions and Awards

- PI received Key Contributor Award, 12/2023, NREL
- PI received Employee of the Month Award, 9/2024, NREL

Publications and Presentations

- Presentations:

1. R2R USA Conference, October 2-5, 2023, Milwaukee, WI, “In-line, R2R compatible, quality monitoring methods for fuel cell and electrolyzer materials” P. Rupnowski (presentation itself was funded by the R2R Consortium)
2. 2024 APS March Meeting, March 3 - 8, 2024, Minneapolis & Virtual , “In-line, High-throughput Quality Monitoring for Fuel Cell and Electrolyzer Components based on Transmission and Reflection Imaging”, W. Dang, P. Rupnowski

- Publications: none in the last year