Hydrogen from Next-generation Electrolyzers of Water

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H2NEW: Hydrogen (H2) from Next-generation Electrolyzers of Water

H2NEW LTE: Manufacturing, Scale-Up, and Integration

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WBS 12.1.0.519

Project ID # P196C

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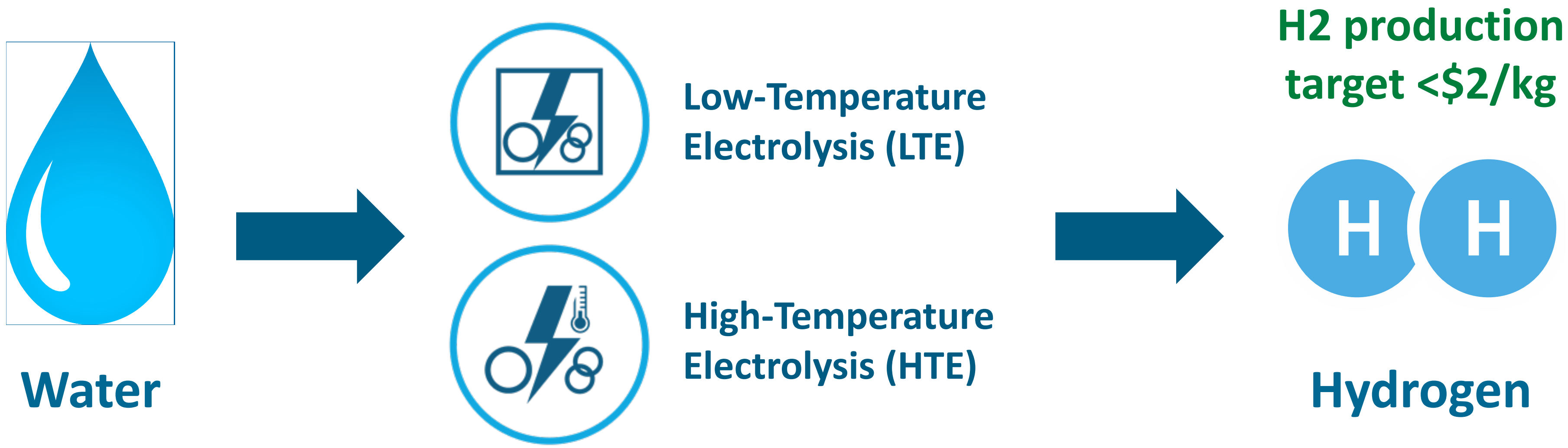
DOE Hydrogen Program

2022 Annual Merit Review and Peer Evaluation Meeting

Project Goals

<u>Goal</u>: H2NEW will address components, materials integration, and manufacturing R&D to enable manufacturable electrolyzers that meet required cost, durability, and performance targets, simultaneously, in order to enable $2/kg hydrogen.



H2NEW has a clear target of establishing and utilizing experimental, analytical, and modeling tools needed to provide the scientific understanding of electrolysis cell performance, cost, and durability tradeoffs of electrolysis systems under predicted future operating modes

H2NEW Task 3a,b: Manufacturing, Scale-Up, and Integration Overview

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Timeline and Budget

- Start date (launch): October 1, 2020
- Awarded through September 30, 2025
- FY23 DOE funding: **$2.3M**
- Annual budget adjustments anticipated

Barriers

- **Durability**
- **Cost**

Consortium Task Team

NREL NATIONAL RENEWABLE ENERGY LABORATORY
BERKELEY LAB
Argonne NATIONAL LABORATORY
OAK RIDGE National Laboratory

Deputy Director:
Rangachary Mukundan(LBNL)

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Jacob Spendelow (LANL)
Siddharth Komini Babu (LANL)
Svitlana Pylypenko (Mines)
Shawn Litster (CMU)

Relevance and Impact

Electrolyzer Stack Goals by 2025		
	LTE PEM	**HTE**
Capital Cost	**$100/kW**	**$100/kW**
Electrical Efficiency (LHV)	**70% at 3 A/cm^2**	**98% at 1.5 A/cm^2**
Lifetime	**80,000 hr**	**60,000 hr**

- Task 3 specifically focuses on manufacturing cost reductions through enabling high throughput fabrication techniques:
  - Understanding inks
  - Catalyst layer optimization and fabrication
  - Porous Transport Layer (PTL) design and optimization
- MEAs, PTLs and other components developed within Task 3 crosscut with Tasks 2 and 3

Approach: Task 3 Work Breakdown

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Task 3a: MEA fabrication, Interface engineering

i. Inks
- Constituent interactions ink, formulation and preparation of the ink predefine the micro- and macro-scale behaviors
- Ink morphology: particle size/agglomeration, stability, level of adsorption of ionomer, supported and unsupported catalysts

ii. Electrodes
- Coatability: rheology, wettability, drying, particle size, coating method
- Electrode morphology: porosity, distribution of ionomer, thickness homogeneity

iii. Cell Integration, Interfaces, and Defects
- Engineered cell interfaces: PTL surface modifications (laser ablation, protective coatings)
- Impact of cell defects: modifications to PTL surface (abrasion, protective coating variations) and membrane pinholes

Task 3b: Components

i. Porous Transport Layers
- Develop understanding of structure and function, design of new structures (bilayers, MPLs)
- Porous transport electrodes

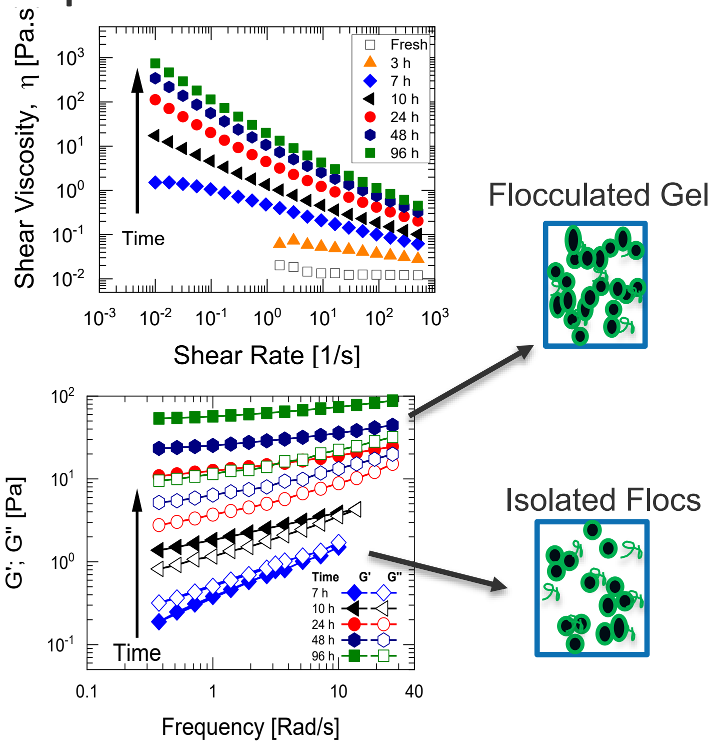
ii. Recombination Layer Membranes
- Model impact, develop understanding of structure and function, aid in design of new structures

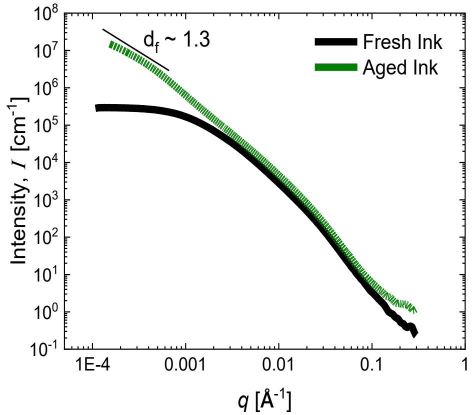
Approach: Year 3 Milestones

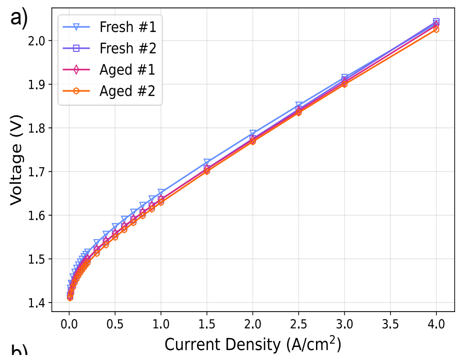
Milestone Name/Description	Due Date	Type	Status
Quantifying impact on degradation of high throughput scaled up processes. Determine impact of anode casting method and parameters, as compared to the baseline spray-coated anode, on performance degradation rates using proposed catalyst ASTs (e.g., triangle cycling from 1.45 to 2 V and 0 to 2 V (1 min duration)), targeting a degradation rate similar to the baseline anode.	6/30/2022	QPM/ GPRA	Completed (Slide 10)
Prepare and test performance of at least 5 variations of PTLs with discrete surface modifications; complete voltage breakdown analysis and investigate mechanism of performance change. Deliver PTL sample set to Task 2 partners for characterization.	12/30/2022	QPM	Completed (Slide 15)
Synthesize at least 5 novel GRC containing membranes with controlled catalyst content and distribution to pursue in cell testing and model validation efforts.	3/31/2023	QPM	Completed (see slide 29)
Probe gas recombination layer properties, performance and durability using model systems fabricated using two different methods at three different loadings and ionomer contents, provide data for modeling efforts.	6/30/2023	QPM	In progress

Accomplishments and Progress: Further Understanding of Ink Thickening

- IrO_2 catalyst inks are challenging to handle and process due to low viscosity and high sedimentation
- In FY22, we found that water-rich inks leads to a gelation with aging
- FY23 work focus on understanding mechanism and determining impact on MEA performance





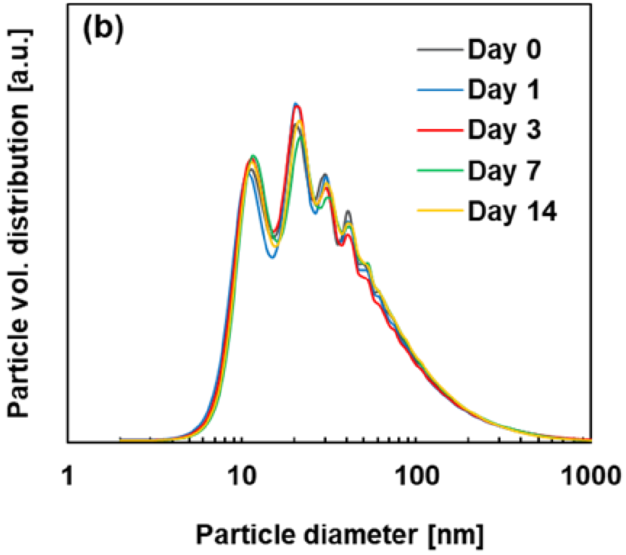


- **Demonstrated that ink age/viscosity not showing impact on performance**
- **Experiments show thickening is caused by ionomer, likely due to bridging**
- **Thickening not dependent on catalyst type or dispersing process**

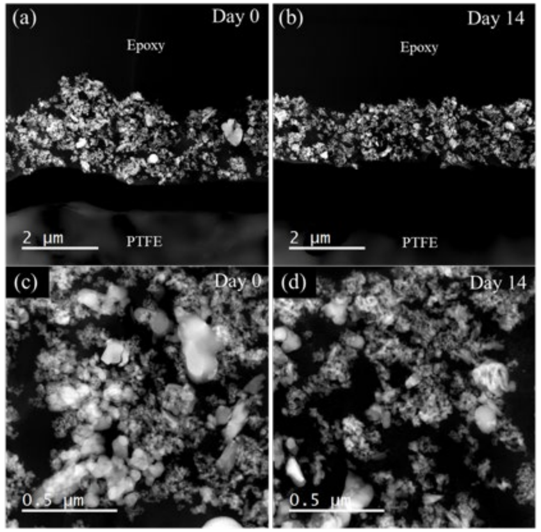
Accomplishments Progress: Understanding shelf-life stability of IrO_2 inks

- There is a critical need to understand catalyst particle and ink stability over time relative to use and storage in an industrial setting
- Catalyst, ink, and electrodes were studied over two weeks to investigate if changes occur

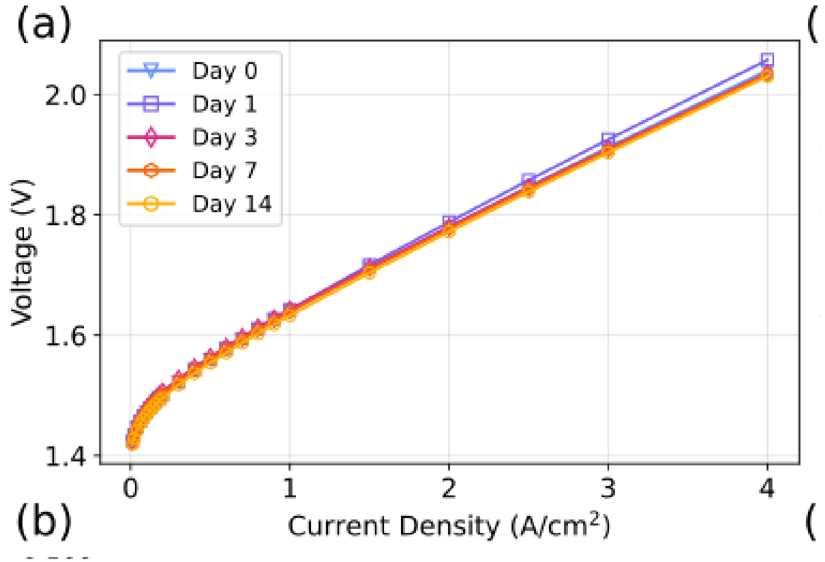
USAXS of Catalyst Inks



Catalyst Layer TEM



MEA IV Performance



- **Measurements of ink and catalyst layers do not show significant differences in properties**
- **Age of ink does not impact MEA performance indicating good shelf stability of inks**

Accomplishments and Progress: In situ measurements of Ink Mixing Methods on Particle Size Distribution

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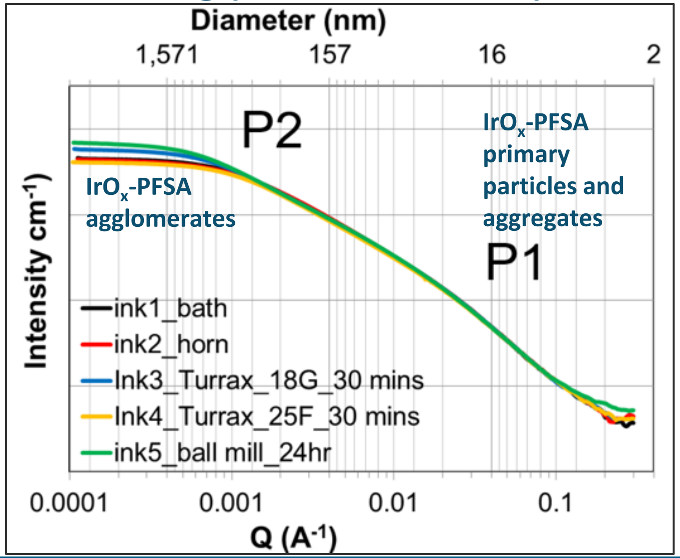
Quantified catalyst ink particle size distribution through in situ and ex situ x-ray scattering measurements ink mixed with different methods

Alfa Aesar IrO_x/D2020 (I:C=0.2)/Water-nPA (1:1) Ink
Mixing Methods:

- Bath sonication (Ink 1)
- Horn sonication (Ink 2)
- High shear mixing Turrax18G (Ink 3)
- High shear mixing Turrax 25F (Ink 4)
- Ball Milling (Ink 5)

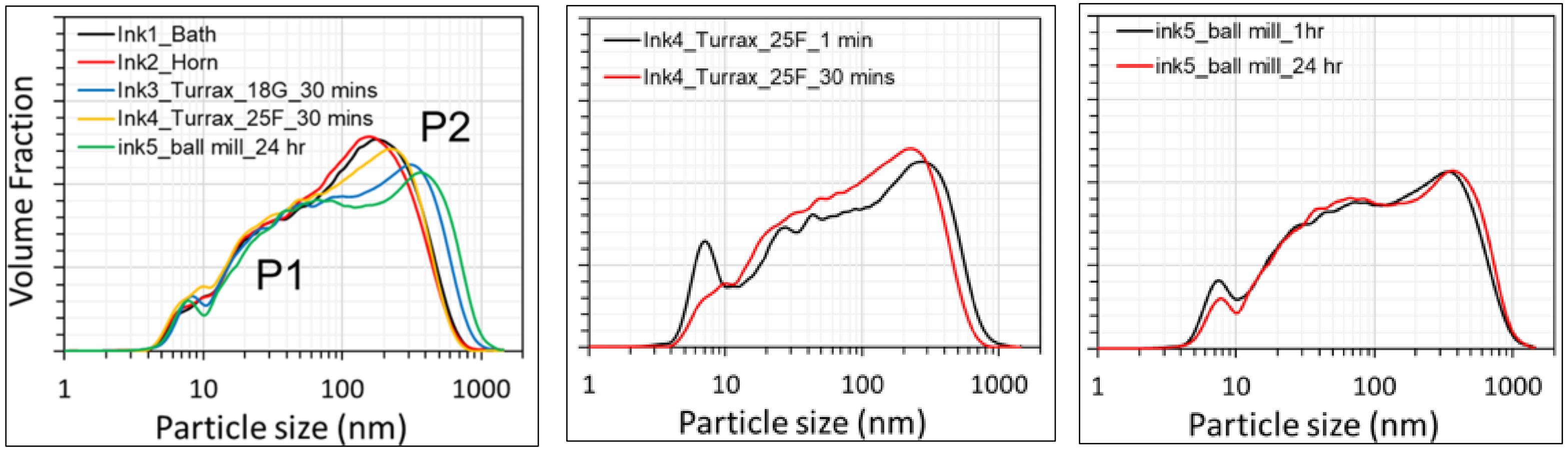
Ultra-small angle X-ray and small-angle scattering (USAXS and SAXS) of inks



Aggregate and Agglomerate Size Distributions from SAXS/USAXS

Fitting range: Q= 0.09 to 0.00012 Å^{-1}

Mixing Methods | High-Shear Mixing Time | Ball Milling Time



Aggregate size (P1):

- **Similar for all processing methods**

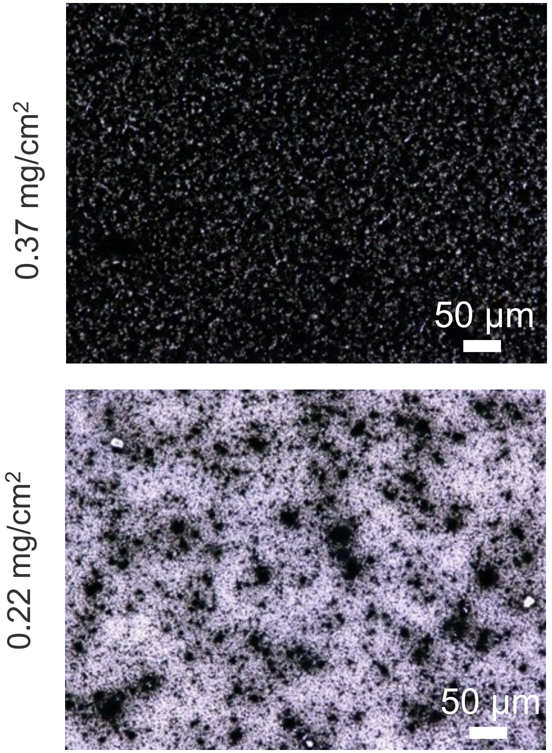
Agglomerate size (P2):

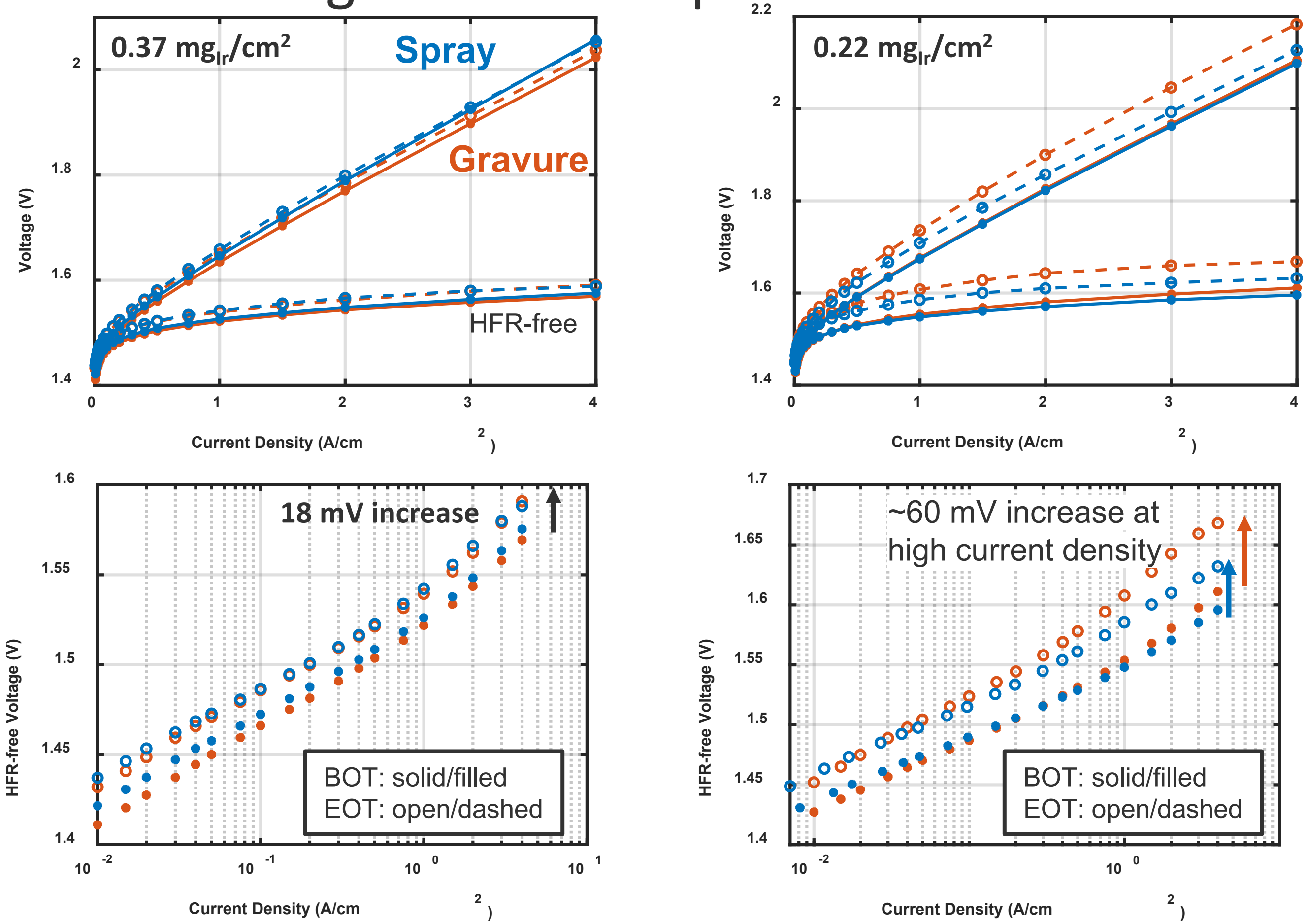
- **Horn < Bath < Turrax 25F < Turrax 18G < Ball mill**

Accomplishments and Progress: Determining Impacts of Coating Method Durability

Conducted testing to understand impacts of coating methods on performance and durability

Gravure-coated electrodes





Bekaert 2GDL10-0.25 commercially coated | MGL 280
N115 Membrane
0.1 mg_{Pt}/cm^2 cathode (Pt/HSC)

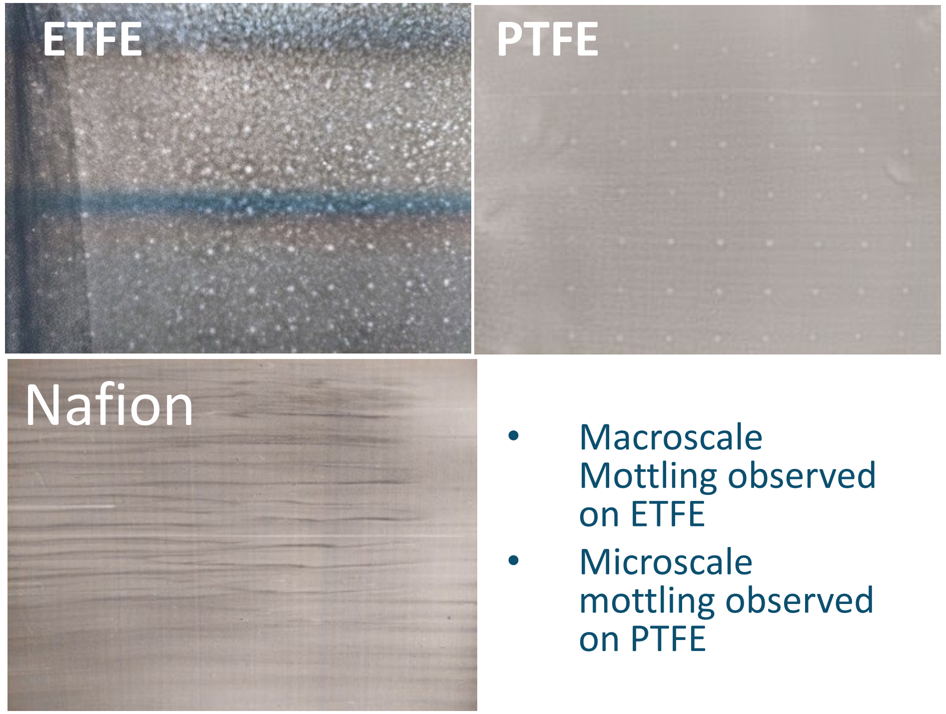
AST protocol: 30,000 cycles square wave (1.4 V – 2.0 V), 1 minute per cycle (500 hr total)

- **CL coating method and homogeneity do not impact IV performance**
- **Higher CL heterogeneity not coating method accelerates degradation**

Accomplishments and Progress: Addressing challenges of ultra-low loaded anodes

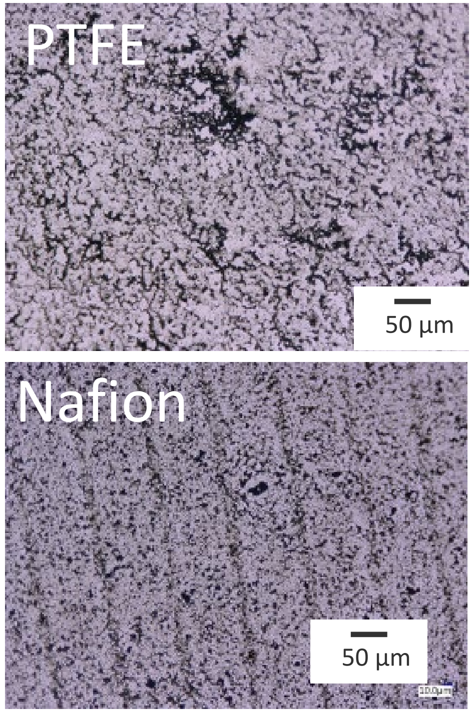
- DOE 2030 Goal – 0.125 mg_{PGM}/cm^2
- Conducted work towards developing inks and scalable coating processes to produce catalyst layers with target loading and performance
- Investigating impacts of ink formulation, ink-substrate interactions, drying on catalyst layer uniformity

Macroscale Defects

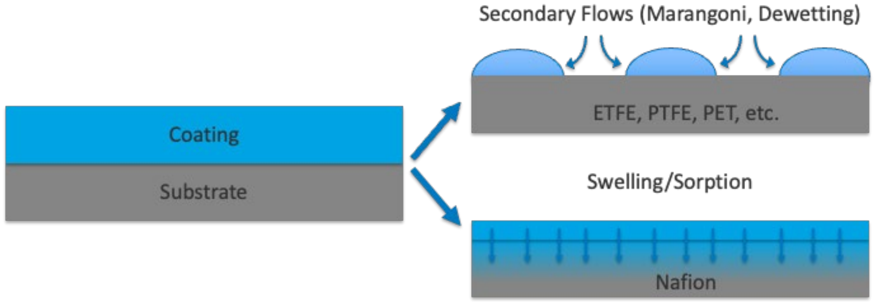


- Macroscale Mottling observed on ETFE
- Microscale mottling observed on PTFE

Microscale Defects



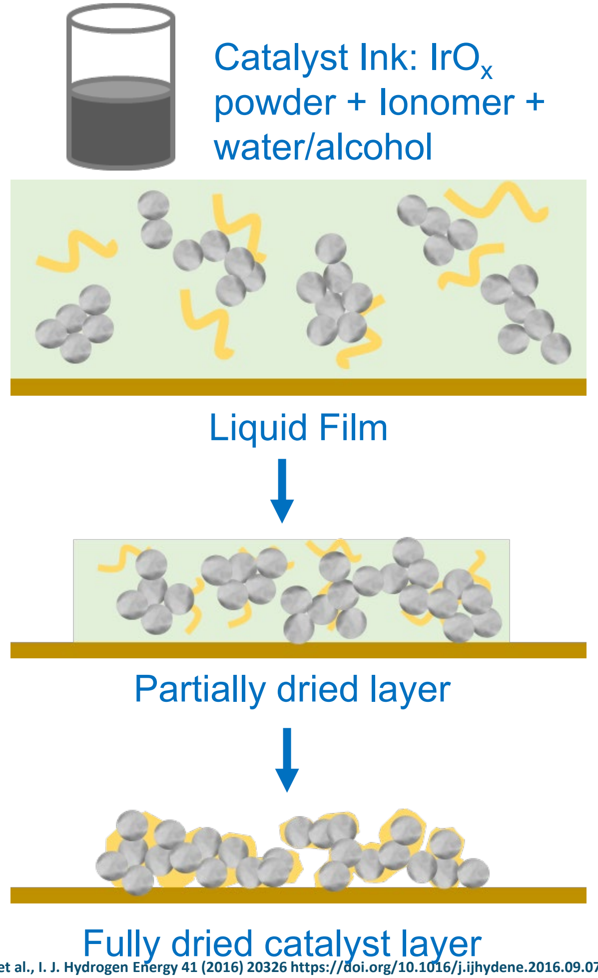
Mechanism



- **Improved homogeneity with moderate ink loadings, permeable substrates**
- **Particle size limits uniformity for <0.2 mg/cm^2**

Accomplishments and Progress: Quantifying Impact of Drying Rates on Anode Structure

Utilized X-ray scattering to quantify aggregate and agglomerate structure of catalyst layers dried under difference conditions

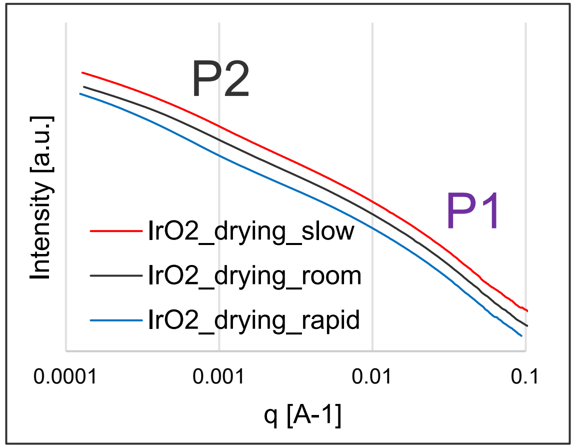


T. Suzuki et al., I. J. Hydrogen Energy 41 (2016) 20326 https://doi.org/10.1016/j.ijhydene.2016.09.078

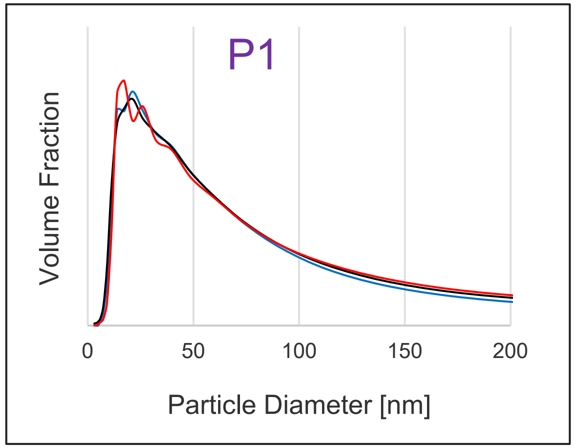
3 different ink drying conditions:

- Slow solvent removal: solvent removal in presence of solvent vapor
- Room temp: solvent removal at room temp
- Rapid: solvent removal at 100° C

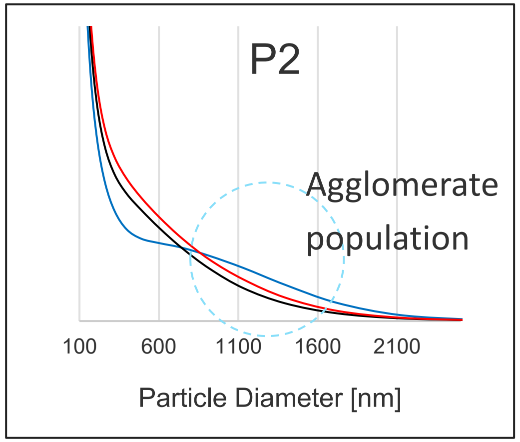
USAXS/SAXS



Aggregate Size Distribution from SAXS Fitting



Agglomerate Size Distribution from USAXS Fitting



- **Rapid drying results in larger IrO_x agglomerates**
- **Drying rate can be used control electrode structure**

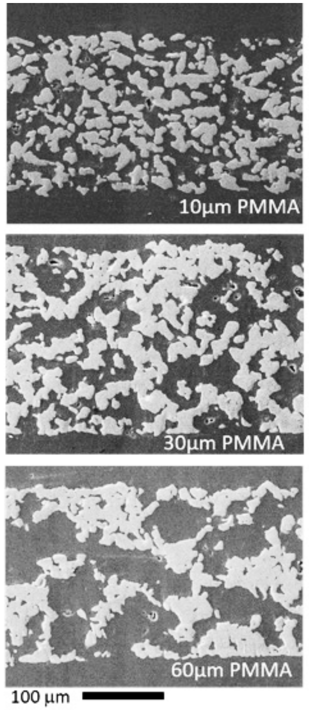
Accomplishments and Progress: Development of PTL with improved performance

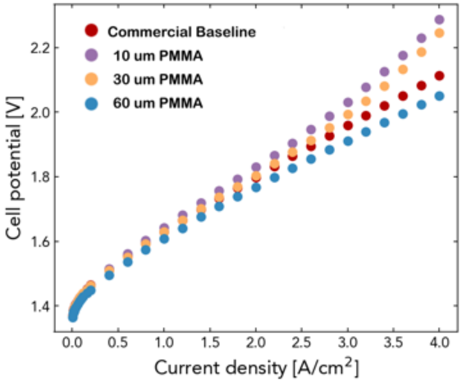
Objectives:

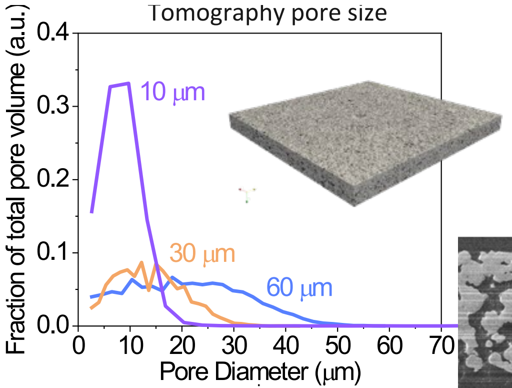
- Develop PTLs with optimized structure using scalable processing methods
- Improve understanding of critical structural parameters (pore size, pore shape, pore volume, graded porosity)
- PTL/MPL structures

- **Accomplishments**
  - **Demonstrated good control of structure via tape casting**
  - **Surpassed performance of baseline commercial PTL**

Control of Pore Size with PMMA Porogen

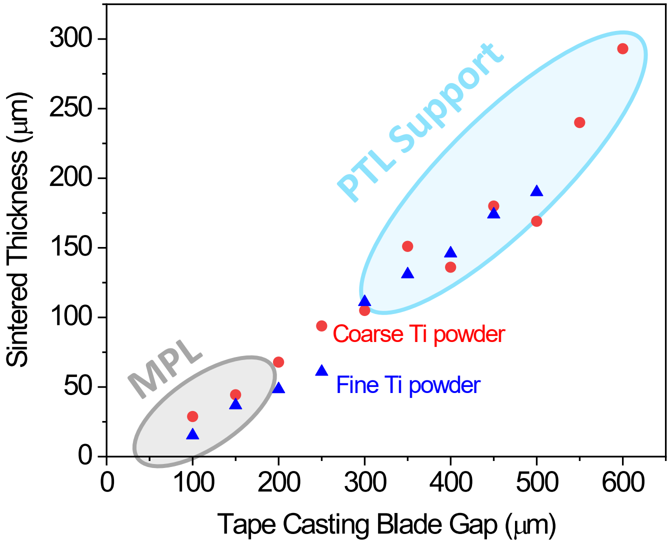




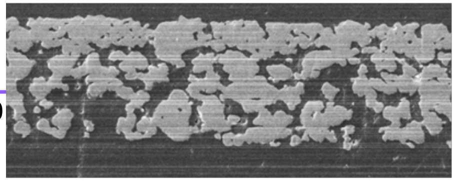


Support/MPL Bilayers

Control of layer thickness



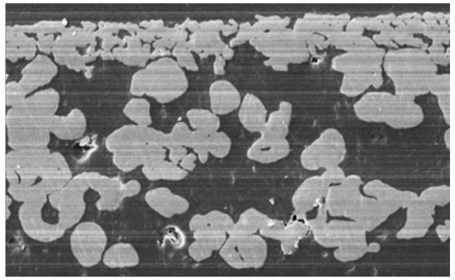
Fine MPL



Fine support

100µm

Fine MPL



Coarse support

Free-standing MPL

Accomplishments and Progress: Improving CL/PTL Interface via Laser Ablation

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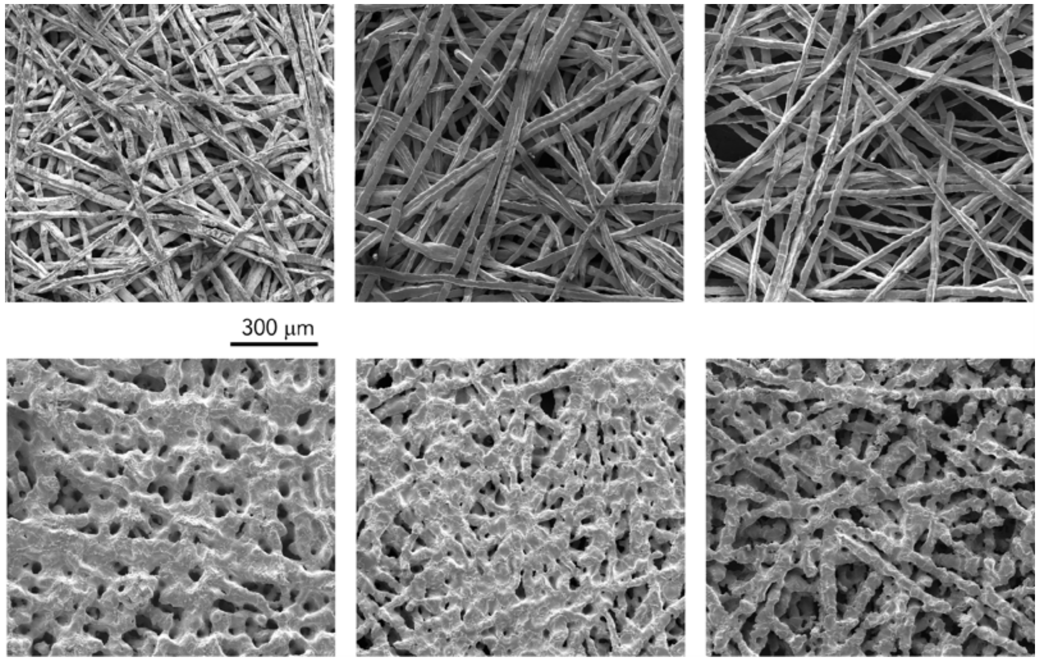
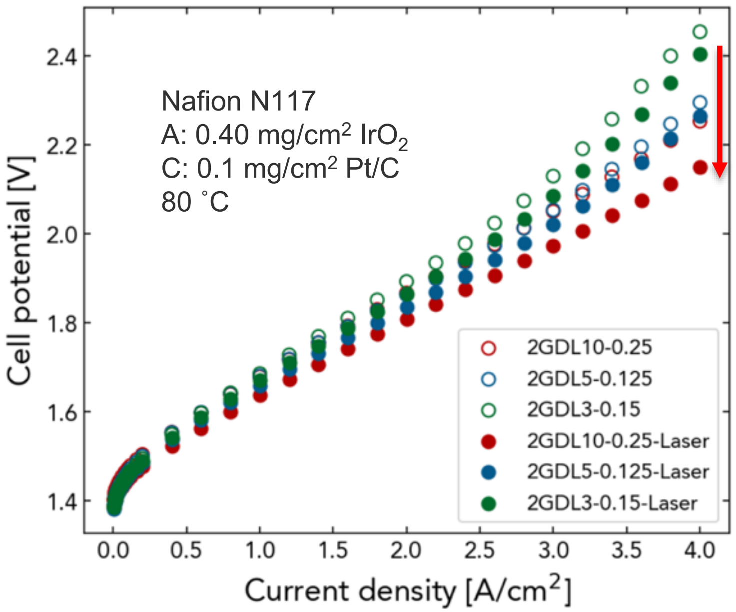
2GDL10-0.25 | 2GDL5-0.125 | 2GDL3-0.15

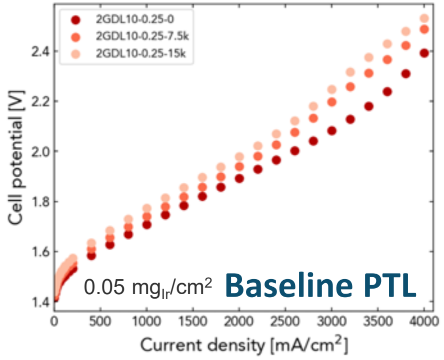
As-received / Laser Ablated

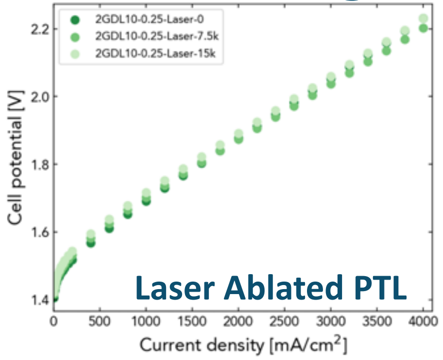


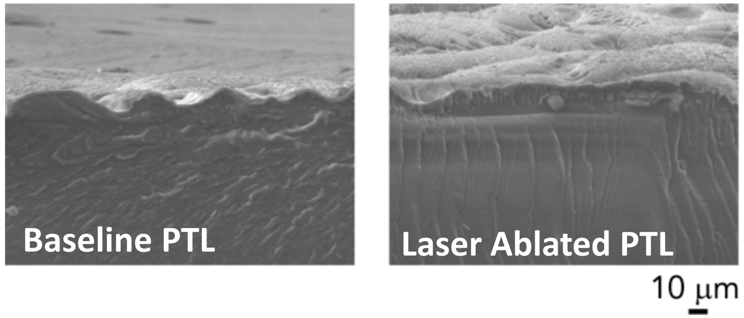
IV Performance



Accelerated Stress Testing







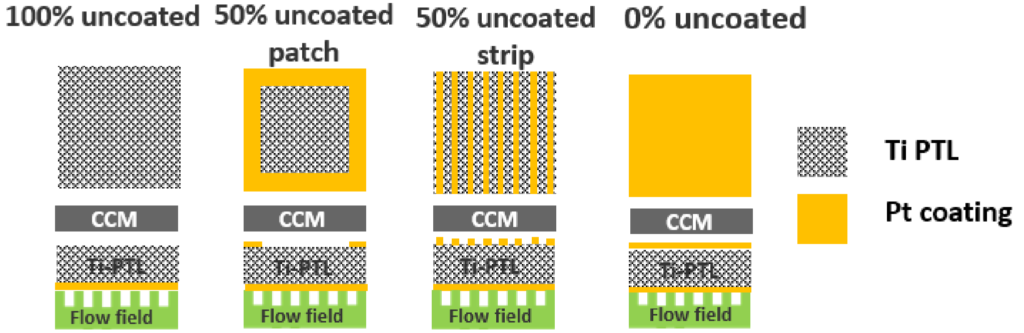
- Investigated use of laser ablation to improve CL/PTL interface and impacts on performance and durability
- Laser ablated PTLs show increase in the measured double layer capacitance, indicating larger ECSA.
- Observed less indentation to the CL/Membrane seed with laser ablated PTLs after AST
- **Demonstrated that laser ablation improves MEA IV performance and durability**

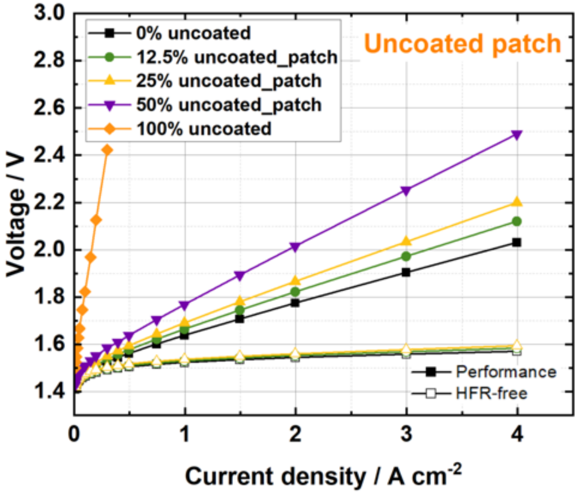
Accomplishments and Progress: Effect of CL/PTL Interface on Performance

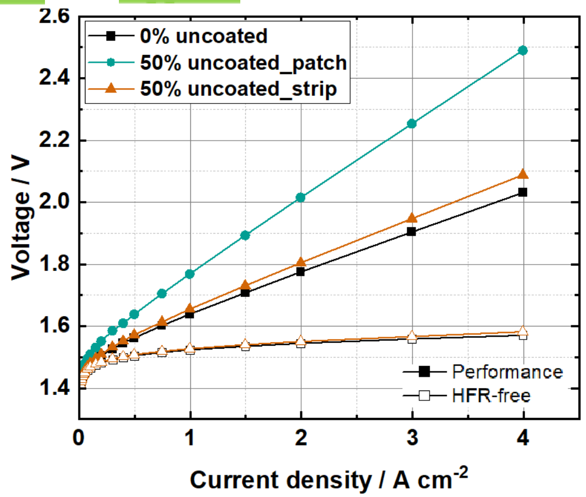
Performance Effects of PTL Pt-coating quality

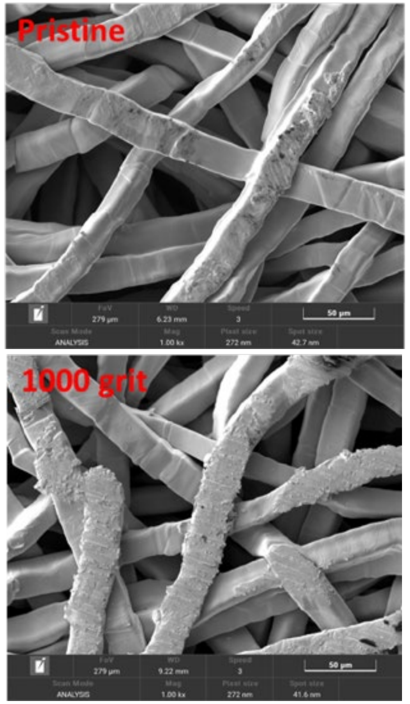
- Uncoated strip patterns = scratches or local delamination
  ⇒ Low impact
- Uncoated patches = global delamination or poor coating
  ⇒ High impact

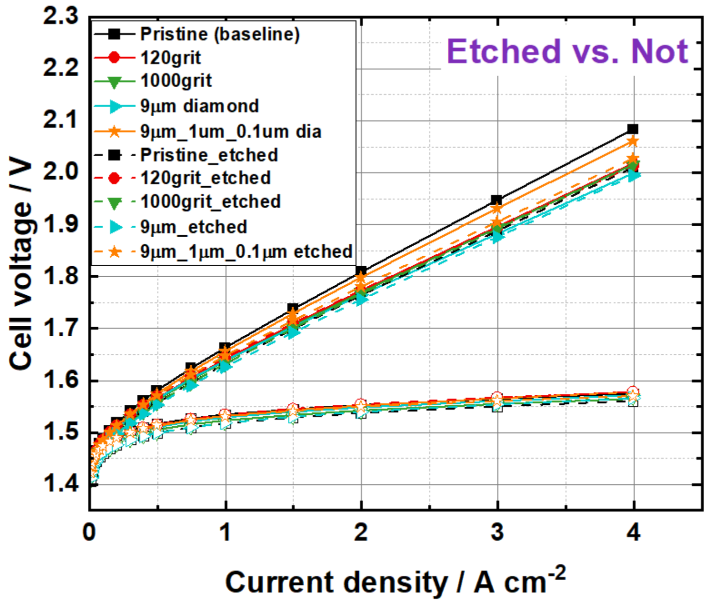
⇒ **Continuous defect size/shape matters**







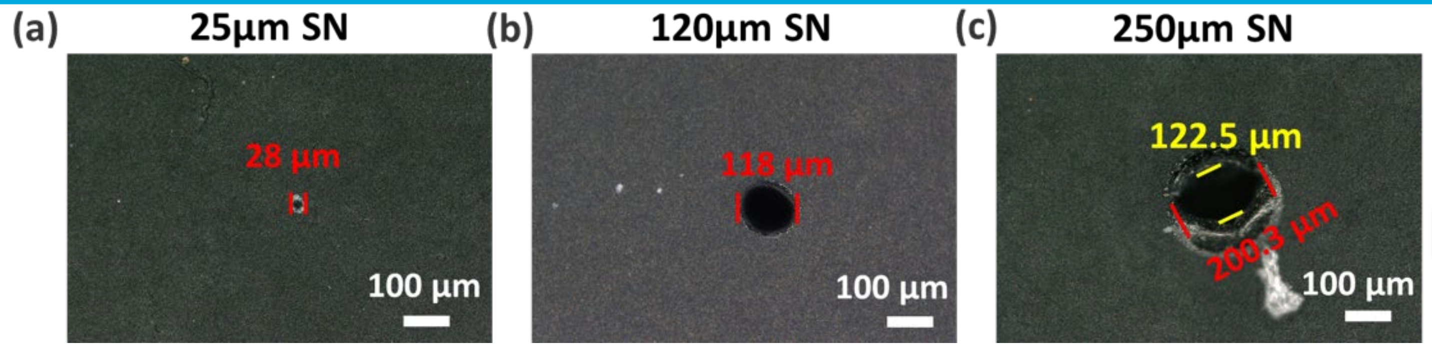


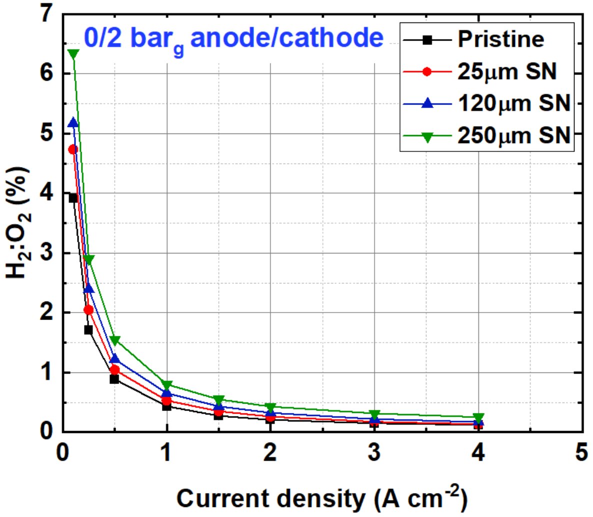


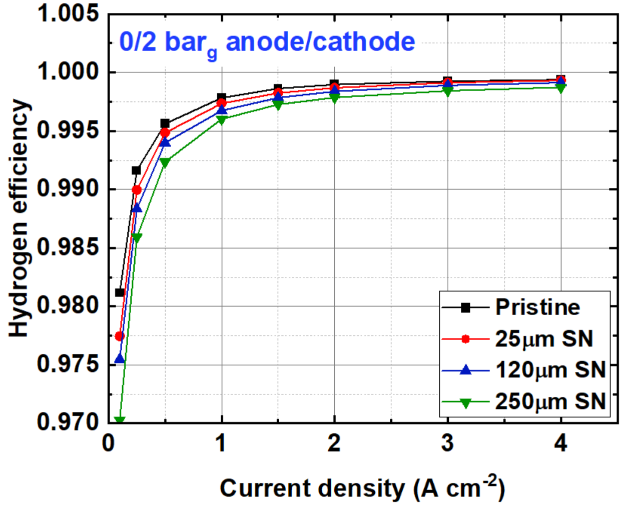
Performance Effects of PTL abrasions

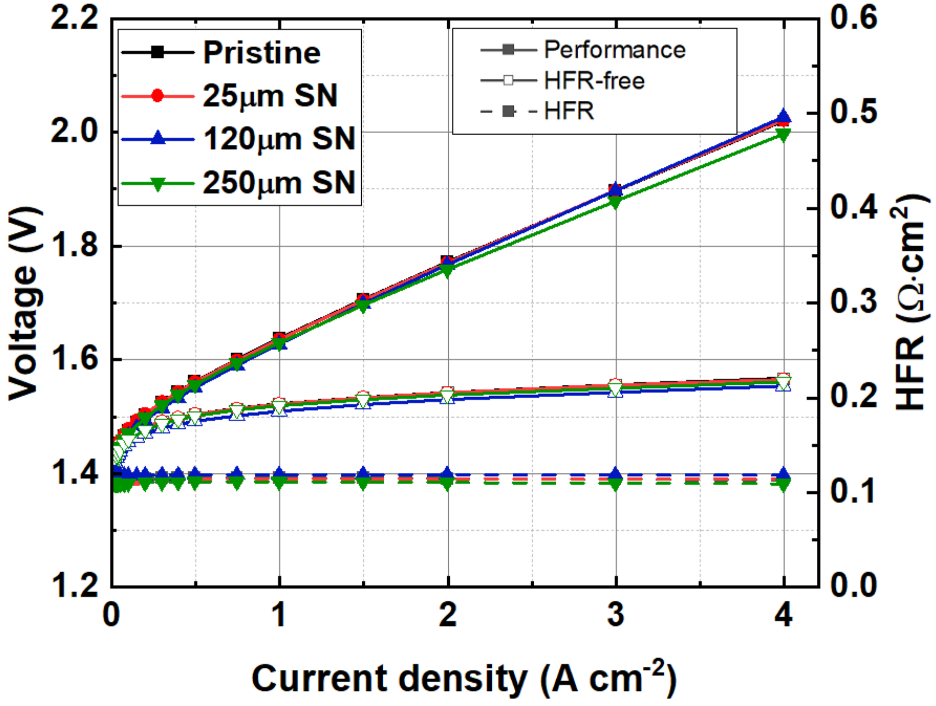
- Improvement up to ~80 mV at 4 A cm^{-2}.
- Possible causes:
  - Removing or reducing the TiO_x layer
  - Increasing the PTL surface roughness and improving contact area at interface
  - Flattening top surface for more contact

Accomplishments and Progress: Performance and Efficiency Effects of Pinholes









- Tear- and open-shaped pinholes intentionally added to CCMs
- Pinholes have minimal (beneficial) impact on VI-performance of cell
- Tear-shaped pinholes may close or obstruct H_2 permeation to some extent
- **Pinholes significantly impact H_2 crossover, specifically during differential pressure operation**
- **The bigger and the more open the pinhole, the higher the $H_2:O_2$ ratio and the lower H_2 efficiency**

Accomplishments and Progress: Leveraging unique capabilities of discretionary projects to study catalysts and catalyst layers

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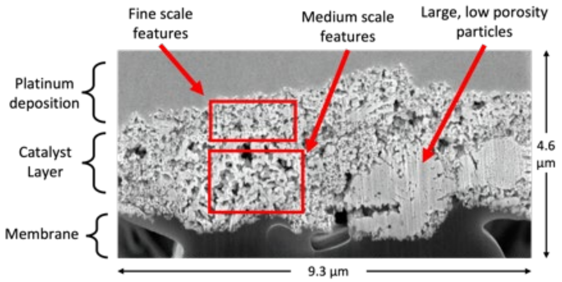
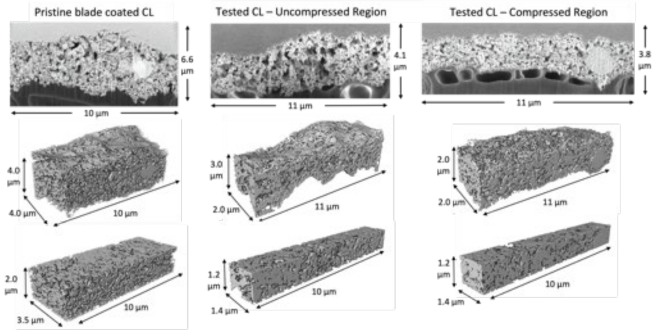
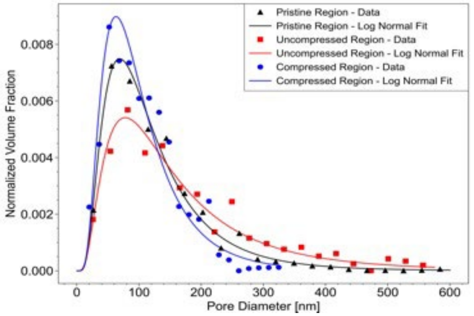
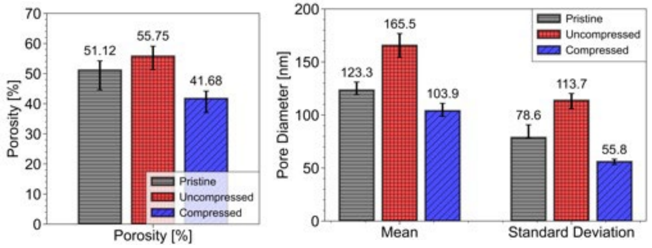
Electrode Porosity and Pore Size Distribution Comparison (pFIB-SEM) – Carnegie Mellon

Objective: Investigate differences in pore morphology between regions of heterogeneity within an IrO_2 electrode







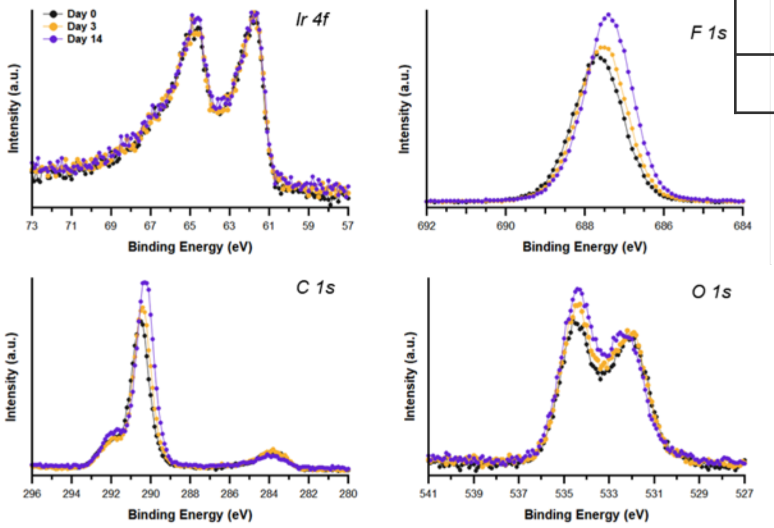


Locally compressed region had significantly lower porosity and mean pore size than locally uncompressed region

Catalyst and Electrode Composition (XPS) Colorado School of Mines

Objective: Investigate potential changes in catalyst chemistry and electrode composition as function of ink age

Area ratios	F/Ir	CF_x/Ir
Day 0	51.8	5.4
Day 3	57.5	6.2
Day 14	61.1	6.6



- **No changes in iridium states**
- **Increased ionomer at top surface with ink age**

Responses to Previous (2021) Year Reviewers' Comments

- The project is focused on standard technologies and material sets. It would be great to see some investigation into promising alternatives that have the potential to leapfrog over the existing state of the art. The recommendation is not necessarily for an in-depth study but rather for some assessment of the potentials and problems with these promising alternatives
  - *Work in FY22 and FY23 has included work on the development of new PTL structures and next-generation catalyst materials (supported, unsupported, alloy)*
- There should be even more emphasis on facilitating scale-up of electrolyzer production. The benefits of economies of scale are a huge assumption behind estimates of future low-cost electrolyzers. Manufacturability should be a key lens for the entire consortium
  - *The research activities addressing ink stability, coating methods, and low-loading challenges for R2R coating are directly addressing the manufacturability of electrolyzers.*

Collaboration and Coordination

NREL Team Members: Carlos Baez-Cotto, Sunil Khandavalli, Scott Mauger, Chance Parrish, Jason Pfeilsticker, Elliot Padgett, Chang Liu, Guido Bender, Michael Ulsh, Jake Wrubel, Robin Rice [Ink characterization and studies, Electrode coating, In situ testing, MPL studies, Recombination Layer Fabrication]

LBNL Team Members: Grace Lau, Jason Lee, Michael Tucker, Adam Weber, Ahmet Kusoglu, Elizabeth Greenberg, Ashley Bird, Xiong Peng, Rangachary Mukundan[Fundamental material interactions and interfaces studies, Electrode coating, PTL fabrication and surface modification, In situ studies]

ANL Team Members: C. Firat Cetinbas, Nancy Kariuki, Debbie Myers, Jaehyung Park [X-ray characterization studies for inks and electrodes]

ORNL Team Members: Xiang Lyu, Alexey Serov, Dave Cullen, Haoran Yu, David Arregui-Mena [Ink characterization and studies, Electrode coating, Electron microscopy]

LANL: Tanvir Arman, Sergio Diaz-Abad, Kaustubh Khedekar, Siddharth Komini Babu, Kui Li, Jacob Spendelow, Mahlon Wilson, Abdurrahman Yilmaz [Recombination layer fabrication and testing, PTL and MPL fabrication]

University Collaborators: Svitlana Pylypenko, Jayson Foster (CSM) [Electron microscopy and XPS]; Shawn Litster, Kara Ferner, Fausto Pasmay (CMU) [Tomography]

Remaining Challenges and Barriers

- Improve anode ink stability for new IrO_2 catalysts
- Understand and predict ink interactions
- Improve coating uniformity of low-loaded R2R electrodes
- Optimize MEA interfaces, especially catalyst layer-PTL
- Understand MPL coating and target properties/design
- Validate benefit of new concepts
  - Laser ablation/structuring of PTL
  - Multilayer coatings
- Advanced membranes for reduced/mitigated crossover

Overall Goal: Understand component integration and scaling while maintaining or improving durability

Proposed Future Work

Task 3a: MEA fabrication, Interface engineering

i. Inks
   - Better understanding of ink thickening mechanism to control this behavior
   - Develop inks for next-generation commercial materials (supported and unsupported)

ii. Electrodes
   - Fabrication of catalyst layers with next-generation commercial materials
   - Improve homogeneity for R2R-coated catalyst layer with loadings < $0.2 mg_{Ir}/cm^2$

iii. Cell Integration and Interfaces
   - Effects of local membrane thinning and pinholes on cell performance and durability
   - Studying the effect of TiO_x and PTL coating defects on the performance and durability
   - Nanostructure fabrication of PTL surface with laser ablation

Task 3b: Components

i. Porous Transport Layers
   i. Optimize bi-layer, phase inversion, and freeze tape cast structures
   ii. Porous transport electrode (PTE) fabrication and testing using commercial and H2NEW-made materials

ii. Recombination Layers
   - Model impact; develop understanding of structure and function, aid in design of new structures

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

Summary—Task 3

- The task 3 effort focuses on cell integration and scale-up aspects of the overall H2NEW goals
  - Efforts are highly integrated with Task 1 durability and Task 2 performance efforts
- Task 3 work areas include inks, electrodes, integration and interfaces, PTLs, and MPLs
  - Completed foundational studies of the impacts of and interactions between ink constituents
  - Completed studies to understand the efficacy of scalable coating methods compared to the spray-coated baseline fabrication
  - Coordinated across labs on ink and anode coating baselining
  - Explored laser modification of PTL surfaces and control of PTL properties via processing routes
- **Key findings to date include:**
  - Interactions between ink constituents as well as levels of agglomeration are highly dependent on formulation
  - Anode ink stability is a practical processing issue – formulation thickening can improve stability and processability
  - R2R coatings can perform comparably to spray-coated baseline at FuGeMEA loading of 0.4 mg_{Ir}/cm2, but further work required to achieve uniform coatings at lower loading
  - Laser ablation or mechanical abrasion of the PTL surface can improve performance and mass transport
  - Pinholes have minor VI-performance impacts but potentially large safety implications
  - Engineering PTL porosity can result in performance improvements