Energy Materials Network
U.S. Department of Energy

HydroGEN
Advanced Water Splitting Materials

High Efficiency PEM Water Electrolysis Enabled by Advanced Catalysts, Membranes and Processes

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Nel Hydrogen
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Project ID # P155

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NREL | BERKELEY LAB | Sandia National Laboratories | INL Idaho National Laboratory | Lawrence Livermore National Laboratory | SRNL

Project Overview

High Efficiency PEM Water Electrolysis

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Iryna Zenyuk, University of California, Irvine

Karren More, ORNL

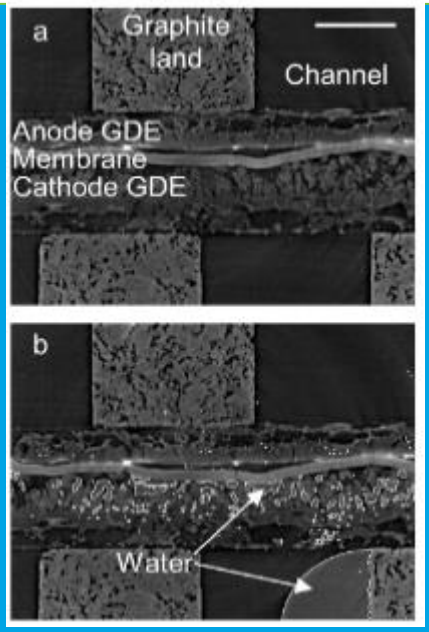
Award #	EE0008081
Start Date Project End Date	9/1/2017 8/31/2020
Total DOE Share Current BP Share Total Cost Share	$1.0M $387K $0.25M

Project Vision

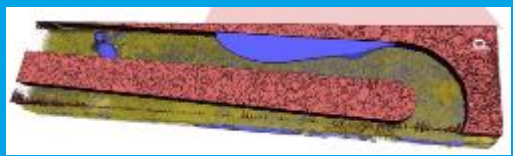
We are solving the cost barriers for PEM electrolysis by integrating advanced cell designs and materials supported by fundamental characterization

Project Impact

The anticipated impact of incorporating all elements of the advanced membrane, catalyst, electrode fabrication techniques, and cell modeling is to realize a reliable MEA configuration with efficiency meeting the 43 kWh/kg targets



Example of tomography and colored liquid water image



Approach- Summary

Project history

Thinner membranes and alternate catalysts have shown promise for stable operation of PEM electrolyzers at improved efficiency. This project advances material performance and integrates components together, while leveraging fundamental characterization to understand and push design limits.

Proposed targets

Metric	State of the Art	Proposed
Membrane thickness	*175 microns*	*50 microns*
Operating temperature	*58°C*	*80-90°C*
Cell Efficiency	*53 kWh/kg*	*43 kWh/kg*

Barriers

- Long term durability: understand degradation through accelerated tests and fundamental characterization
- Higher defect sensitivity with adv. materials and operation: refine cell design and characterize in situ

Partnerships

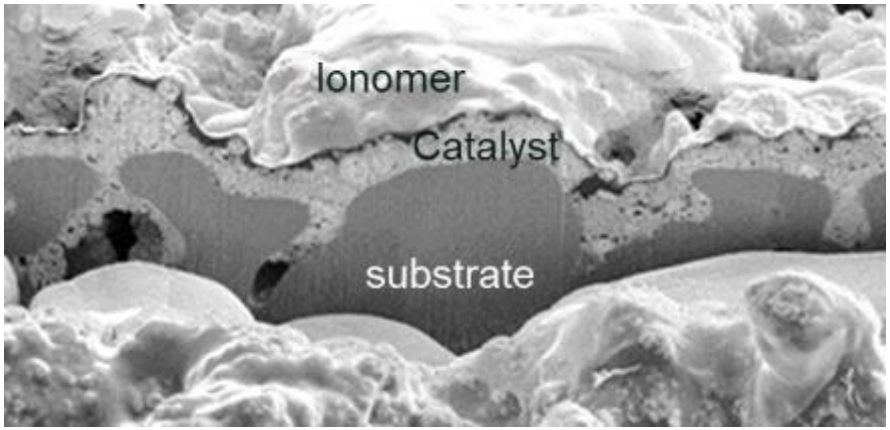
Iryna Zenyuk, UCI: In situ tomography to characterize CLs, PTLs, and water distribution

David Cullen, ORNL: TEM of platinum group metal migration

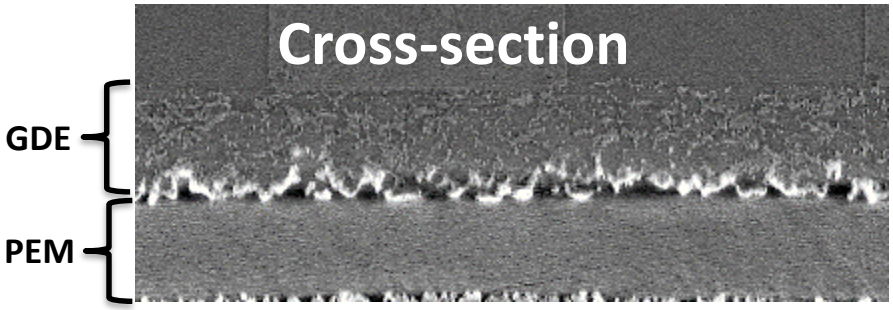
Approach- Innovation

- PEM electrolysis has the potential for significant efficiency improvement – challenge is integrating and extending what we know, where complex interactions exist
- Holistic view of problem including interaction with EMN nodes
  - Understanding of catalyst dissolution and membrane hydration to support formulations and methods of manufacture
  - Porous substrates: understanding and improving uneven distribution, coatings
  - Impact of deposition methods, synthesis conditions, binders etc. on cell performance and reliability

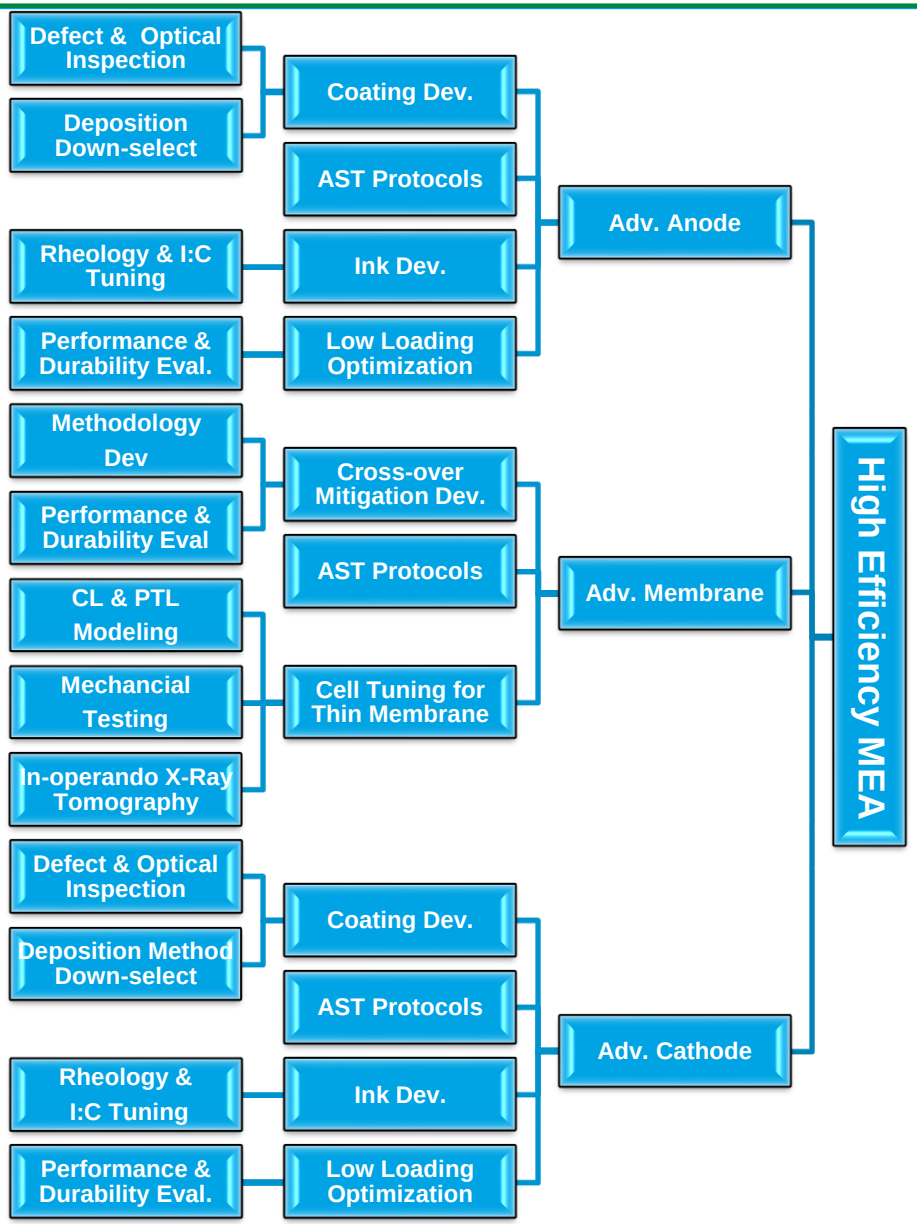
Approach - Innovation



Cross-section of GDE



In-situ imaging shows catalyst as highlighted features



Relevance & Impact

- PEM water electrolysis has significant development opportunities for increased electrical efficiency, without sacrifice in durability through:
  - Integration of membranes ≤ 50 µm thick, capable of 80-90 ^{o}C operation, while controlling mechanical creep and gas crossover
  - Reducing the catalyst loading by at least 1/10th on both electrodes, while controlling water distribution and the PTL/CL electrochemical interface
  - Synthesis of higher activity OER catalysts and refinement of electrode fabrication process
  - Integration of these characteristics into a full MEA
- Supporting National Labs and subcontractors will assist in characterizing materials and process modification
  - Accomplished through material characterization, in-operando analysis, and advanced modeling of membrane and PTL interactions
- Final deliverable of the project will be an advanced electrolysis stack producing H_2 at 43 kWh/kg and at costs of \$2/kg H_2

Accomplishments: Budget Period 2 Quarterly Milestones

BP 2 (12 months) Milestones	Quarter	BP	Completion
Demonstrate 500 hr durability using steady state or AST of target advanced MEA at > 80 ^{o}C compared to baseline	8 * (go/no go)	2	100%
Downselect crossover mitigation using operational data and TEM characterization. H2 recombination effectiveness should be >75%	9	3	100%
Ex-situ and in-operando data are fed into deterministic contact mechanics model. The results are delivered to LBNL for cell performance modeling	10	3	100%
Provide Hydrogen with advanced MEA for validation based on 500-h durability downselect, as discussed above. Total electrode PGM content will be 0.9 mg/cm2 with final down-selected hydrogen cross-over mitigation included	11	3	50%
Demonstrate activity and 500 hr durability of advanced MEA in 3-cell 86 cm^2 electrolysis stack that meets all the project specific targets	12	3	25%

*** Q8 milestone was successful and approval given for BP3 extension.**

Accomplishments to Date

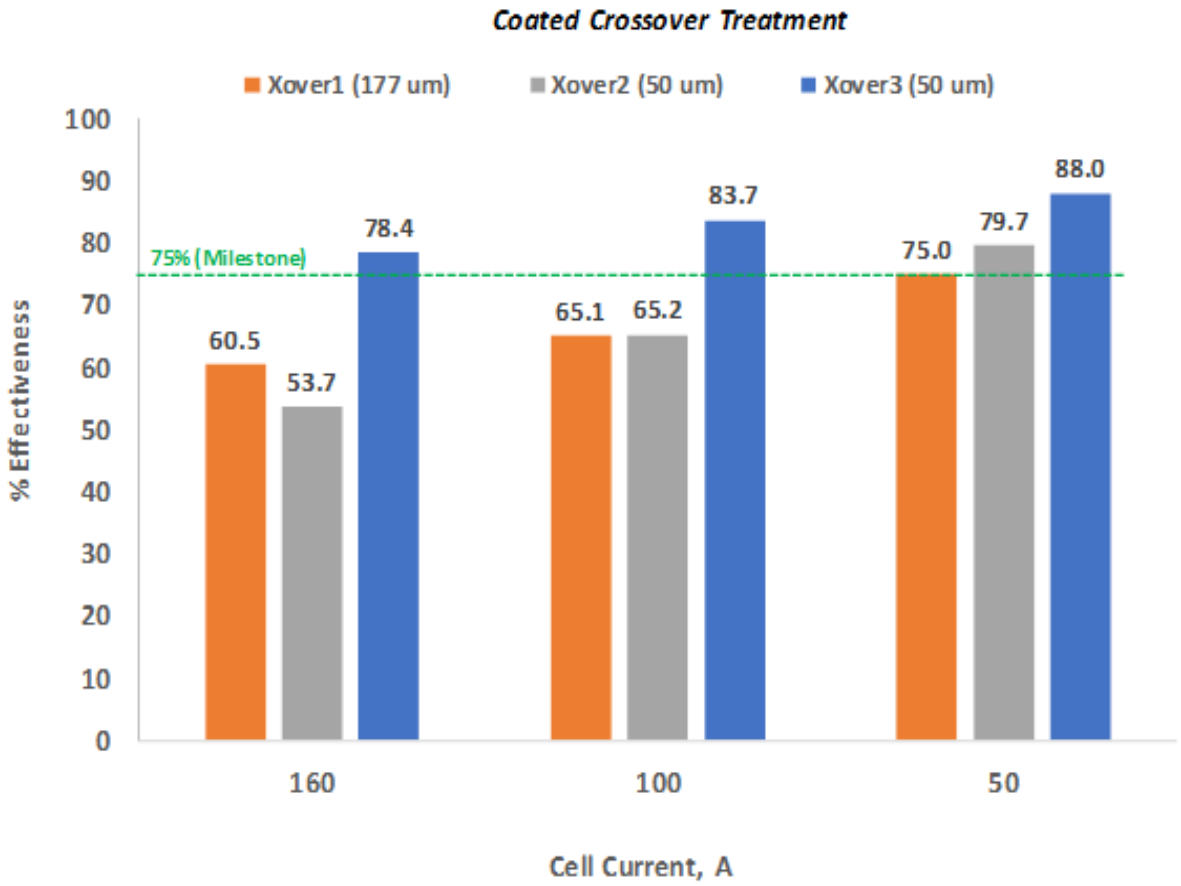
- Ex-situ characterization of catalysts by NREL: RDE/ICP for changes in activity resulting from dissolution of OER catalysts
  - Commercially sourced OER catalysts screened
  - Various blends of pure IrOx and IrRuOx tested for stability
    - Down-selected source of pure IrOx from U.S. supplier
    - Showed good stability and improved performance over baseline
- PTL development on-going at NREL
  - Ink and deposition improvements made to address lack of MPL on PTL
    - Early wetting issue being addressed
- X-ray tomography conducted during electrolysis operation
  - Sintered particle and fiber PTLs assessed
  - Loadings varied between low (33% of baseline), medium (66% of baseline), and high (baseline)
  - Catalyst coated membrane (CCM) versus gas diffusion electrode (GDE)
  - Assessments made on which configuration provided highest utilization

Accomplishments to Date

- 2D model electrolysis model created and validated through operational data
- Mechanical testing of membrane samples hydrated at various temperatures in progress
  - Stress/strain curves generated to look at changes in creep characteristics
  - Assessment made of ex-situ and in-situ hydrated membranes
  - Varied thickness, chemistries, and hydration temperature explored
- ~1400 hours achieved with advanced OER catalysts and higher efficiency membrane
  - Voltage shown stable at ~1.7V(~72% LHV efficiency), 80°C and 1.8 A/cm^2
  - Voltage shown stable at ~1.75V(~70% LHV efficiency), 80°C and 2.3 A/cm^2

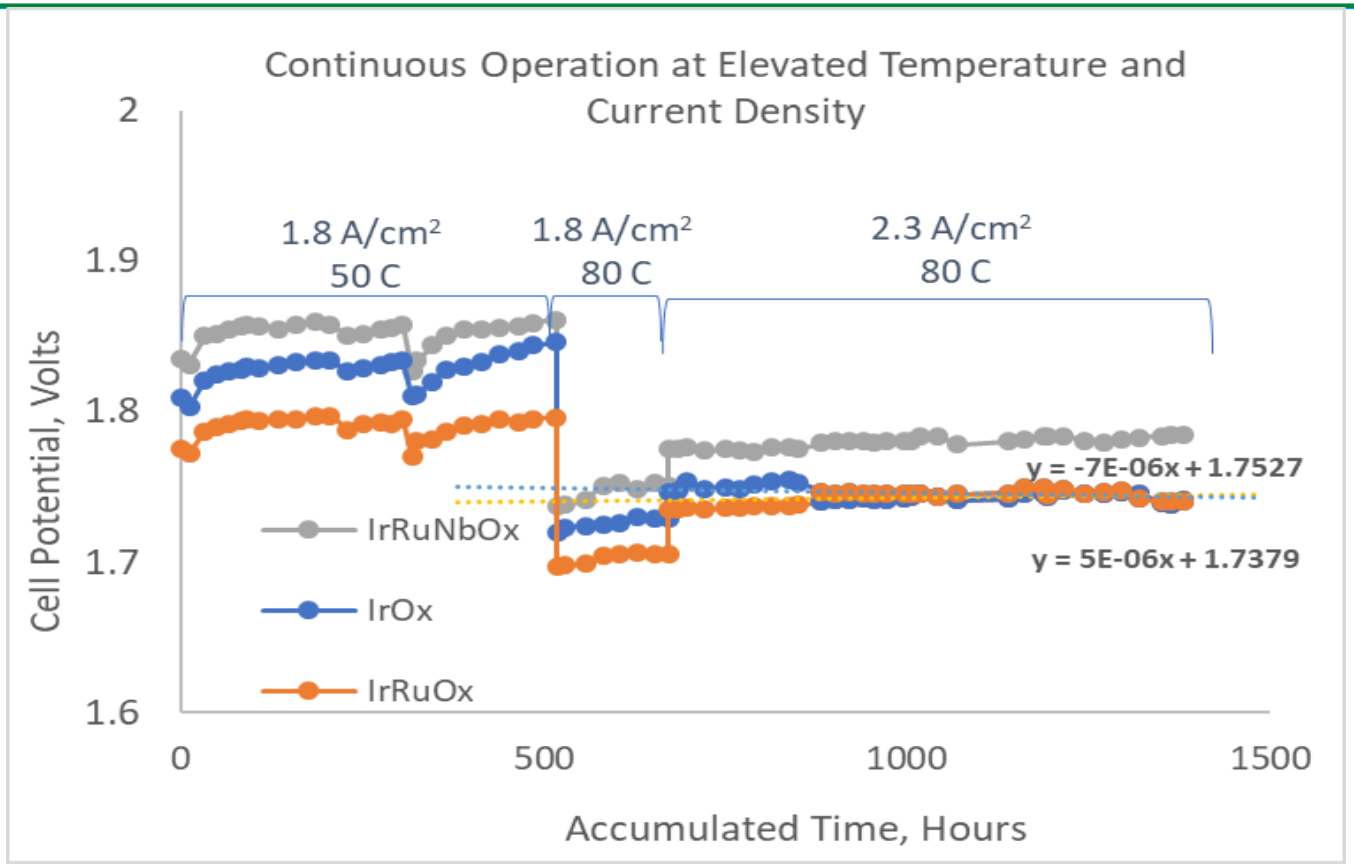
Accomplishments: Where we are today – Crossover

- Several different methods of hydrogen mitigation have been assessed
- Initial testing looked at effectiveness on baseline N117
- Once process established, transitioned to 50 micron (~2 mil)
- Optimization of treatment has resulted in a >78% effectiveness at full hydrogen production
- 88% effect during turndown testing



Test	Membrane	Cross-over Layer
Xover1	7-mil	Baseline
Xover2	50µm	Baseline
Xover3	50µm	4x loading

Accomplishments: Where we are today - Testing



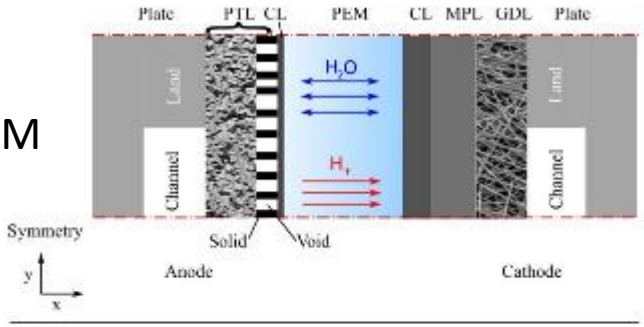
- **Operational tests using the down-selected OER catalysts and transition to supported HER catalysts have translated into significant efficiency improvements**
  - **Results also capture use of 50 micron membrane**
  - **HER loading was reduced by 75% versus baseline**
- **>70% LHV achieved at baseline current density of 1.8 A/cm^2 and 50C**
- **70% LHV efficiency maintained with increase of 25% in current density to 2.3 A/cm^2 and 80C**
  - **Keeps high efficiency, while allowing for further CapEx reductions**

Collaboration—Electrolyzer Modeling

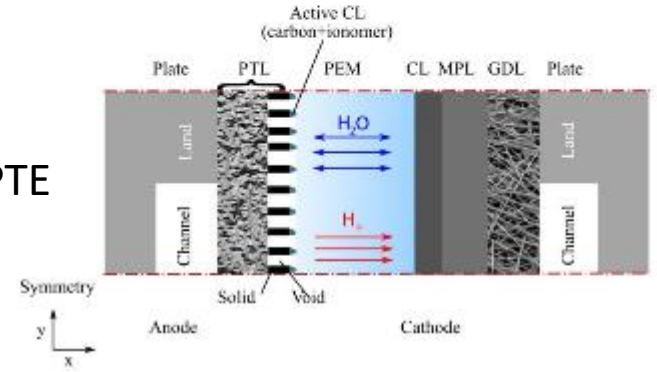
2-D MEA cross-section model

- Hybrid layer approach to simulate contact of solid PTL with catalyst
- Uniform catalyst film in CCM
- Discreet particles on top of PTL in PTE
- Macro-homogeneous, multi-physics model

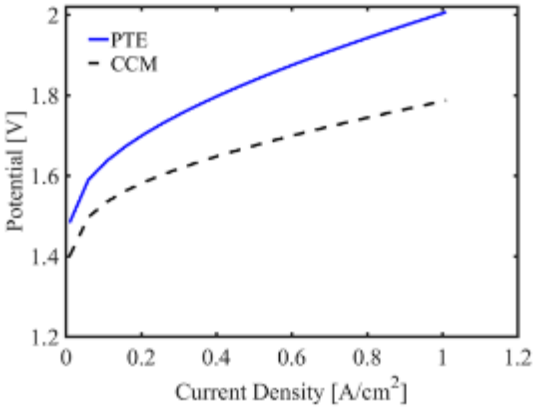
CCM

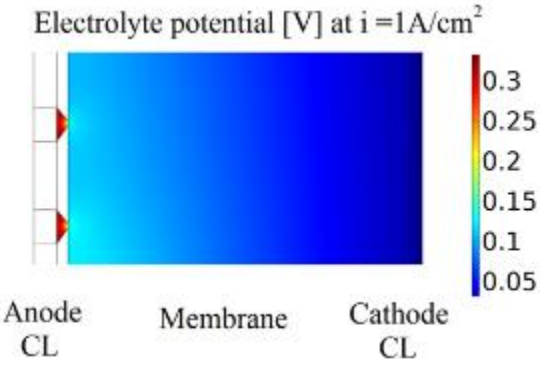


PTE



- Model shows accurate performance similar to the experimental results for this cell configuration
- CCM has better performance due to better connected ionic pathways
- PTE has catalyst deposited on Ti PTL -> Few electrolyte contacts
- Entire proton flux must be tunneled through few contact points
- Significant ionic potential loss occurs at the choke points

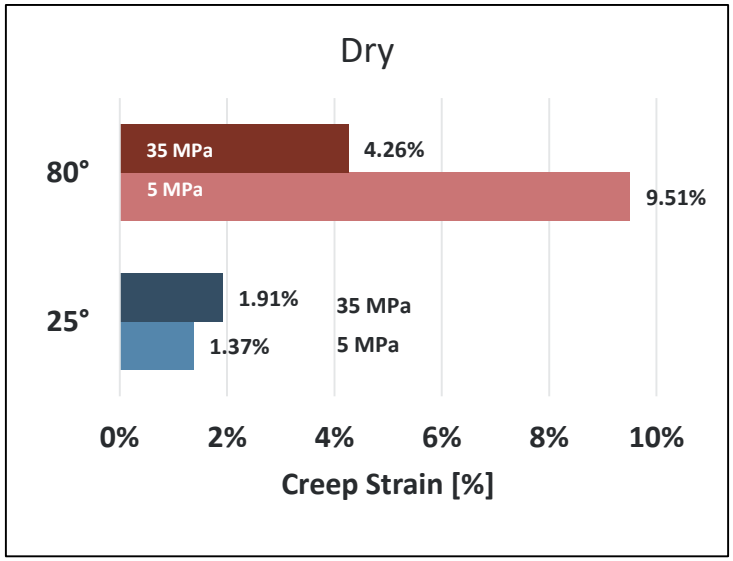


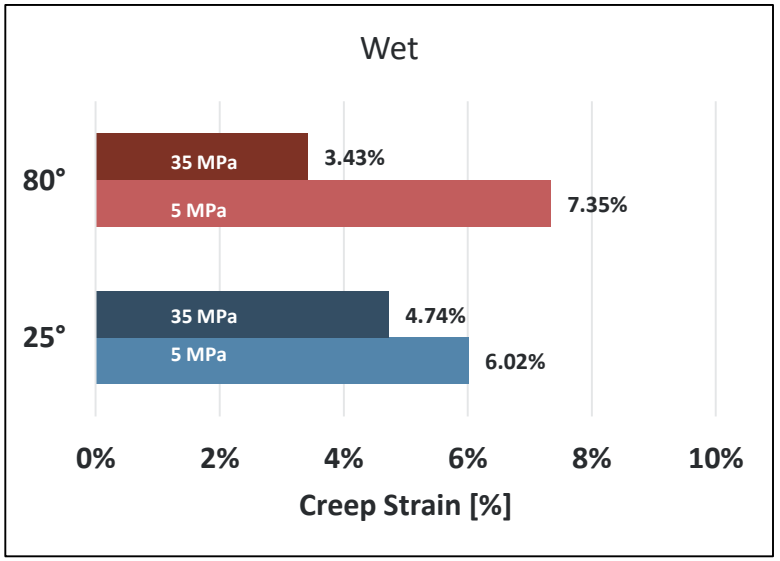


Collaboration– Membrane: Effect of Temperature on Creep

- **Elevated temperature increases creep in dry state**
- **Elevated temperature affects creep in wet state, depending on compression**
  - Higher creep at high temperature; but rate is lower at higher compression
  - At high temperature, compression levels suppress the creep response
  - Hydration increases creep response at 25° but is negligible at elevated temperature

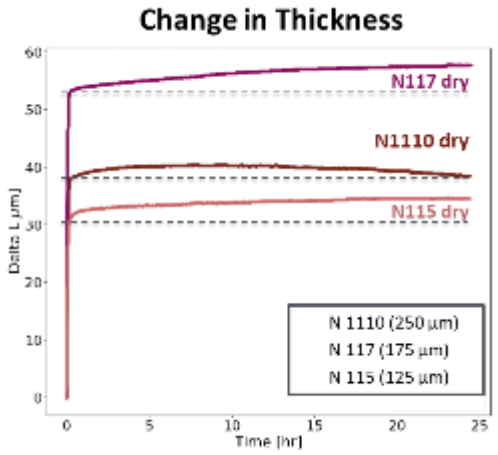
			ε_i	ε_f	ε_{creep}	Creep rate [/hr]	ε_f-ε_i
Dry	25°	5 MPa	16.3%	17.4%	1.4%	**0.343E-02**	1.15%
		35 MPa	29.2%	30.5%	1.9%	**0.478E-02**	1.36%
	80°	5 MPa	7.5%	16.3%	9.5%	**2.38E-02**	8.79%
		35 MPa	13.4%	17.1%	4.3%	**1.06E-02**	3.68%
Wet	25°	5 MPa	14.6%	19.8%	6.0%	**1.51E-02**	5.14%
		35 MPa	44.0%	46.7%	4.7%	**1.18E-02**	2.65%
	80°	5 MPa	25.3%	30.8%	7.3%	**1.84E-02**	5.49%
		35 MPa	38.4%	40.5%	3.4%	**0.858E-02**	2.11%

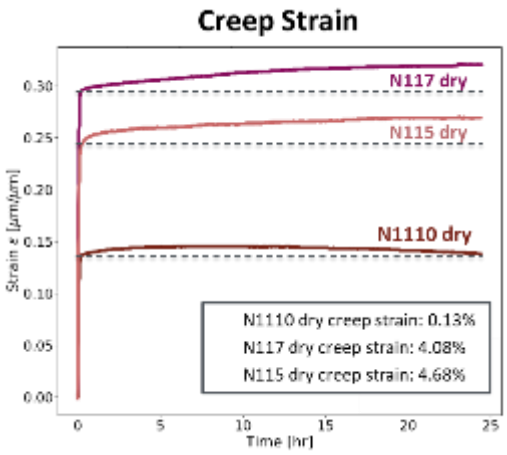




Collaboration–
Membrane: Effect of Thickness on Creep

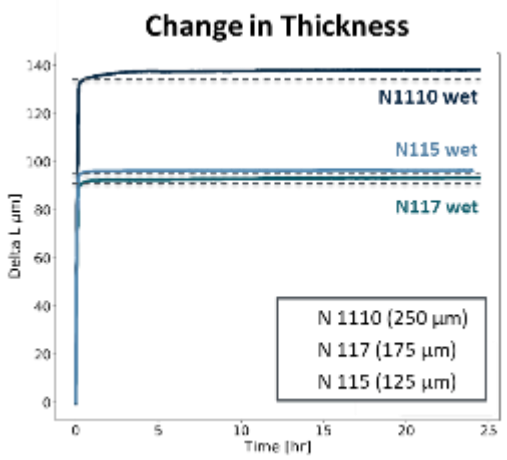
Experiment A: Creep Compression with 35 MPa stress held for 24 hours at 25˚C (Dry)

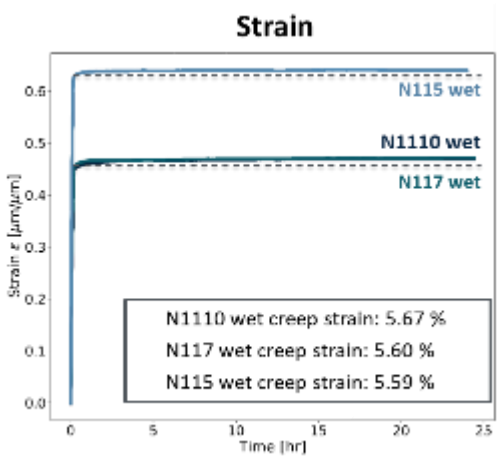




- **Thinner membranes creep more in dry state**

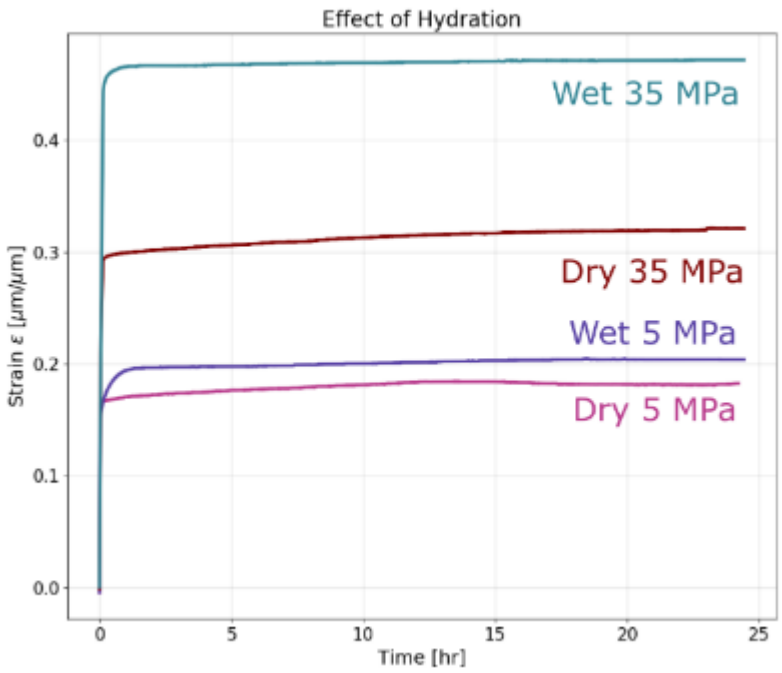
Experiment B: Creep Compression with 35 MPa stress held for 24 hours at 25˚C (Wet)





- **Thinner membranes creep less in water**

Collaboration—
Compression creep of Nafion: Dry vs. Wet

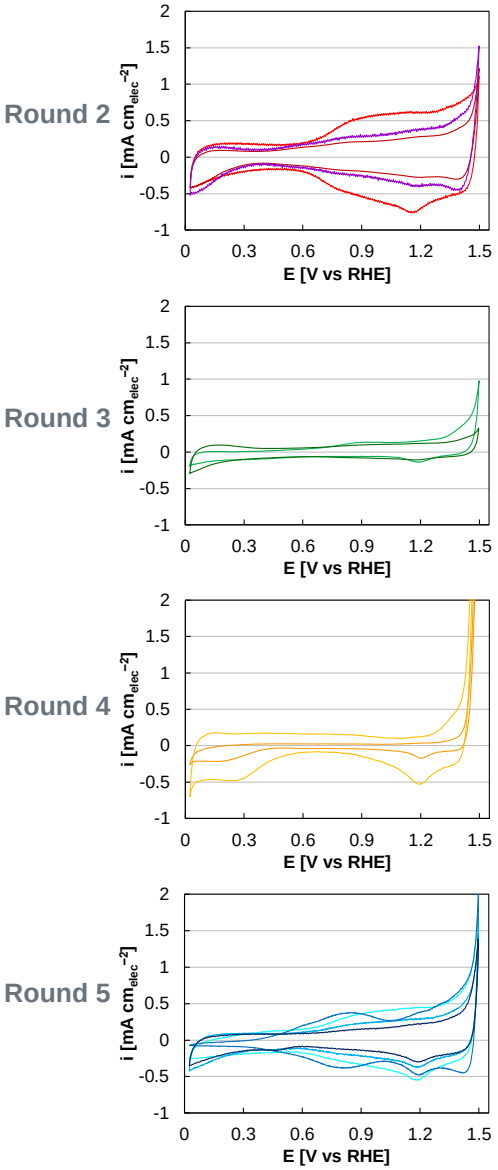


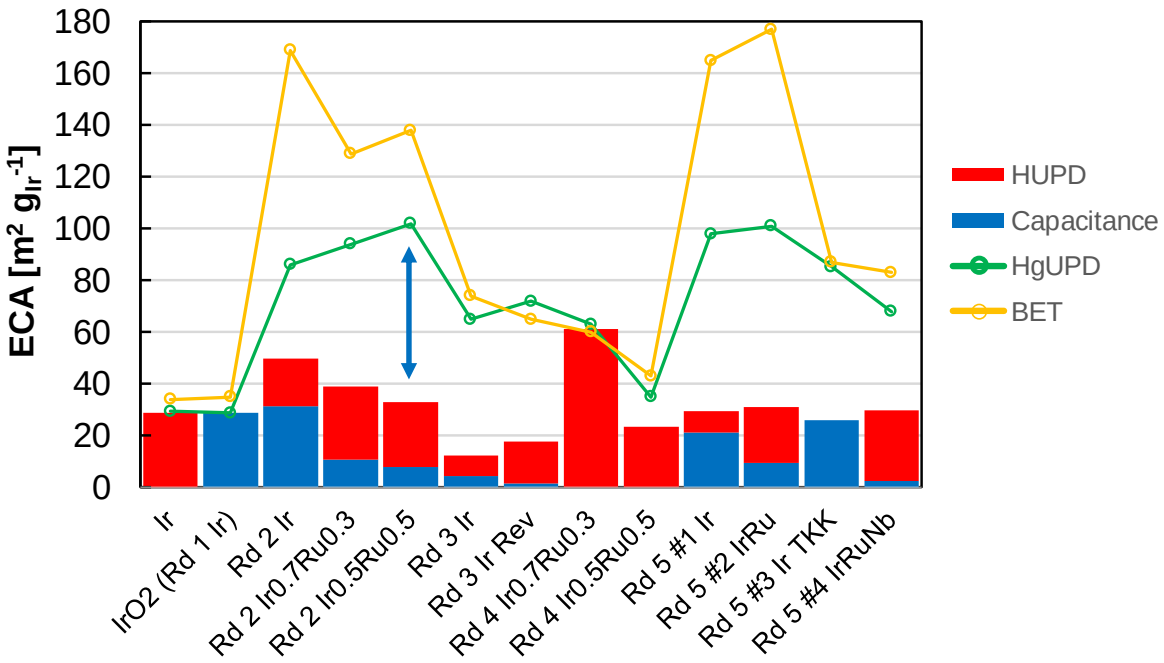
- Nafion 117 Pretreated membranes
  - Dry state vs. Wet State at 25°C
- Hold pressure:
  - 5 MPa (725 psi) for 24 hours
  - 35 MPa (5000 psi) for 24 hours
- Nafion is more resistant to creep in water. Creep strain:
  - Wet: 0.0132 µm/µm
  - Dry: 0.0718 µm/µm
- In water, Nafion exhibits a stronger dependence on stress (compression) level, which results in a bigger change in thickness reduction (due to creep)

Collaboration

- **Catalyst: Evaluating factors of surface area, composition, oxide content, morphology, and crystallinity**
  - Understand differences between catalysts
  - Provide explanation for how these differences effect activity/durability
  - Develop understanding of how RDE activity translates to MEA performance, when incorporating Ru and mixed surfaces
- **PTL: Directly coat an iridium oxide ink-based catalyst layer onto a highly porous, sintered titanium substrate**
  - Reduce production steps compared to a transfer liner technique
  - Decrease ohmic losses due to low contact quality between PTL and catalyst layer
  - Avoid direct coating of membrane which requires swelling mitigation (difficult in roll to roll manufacturing)

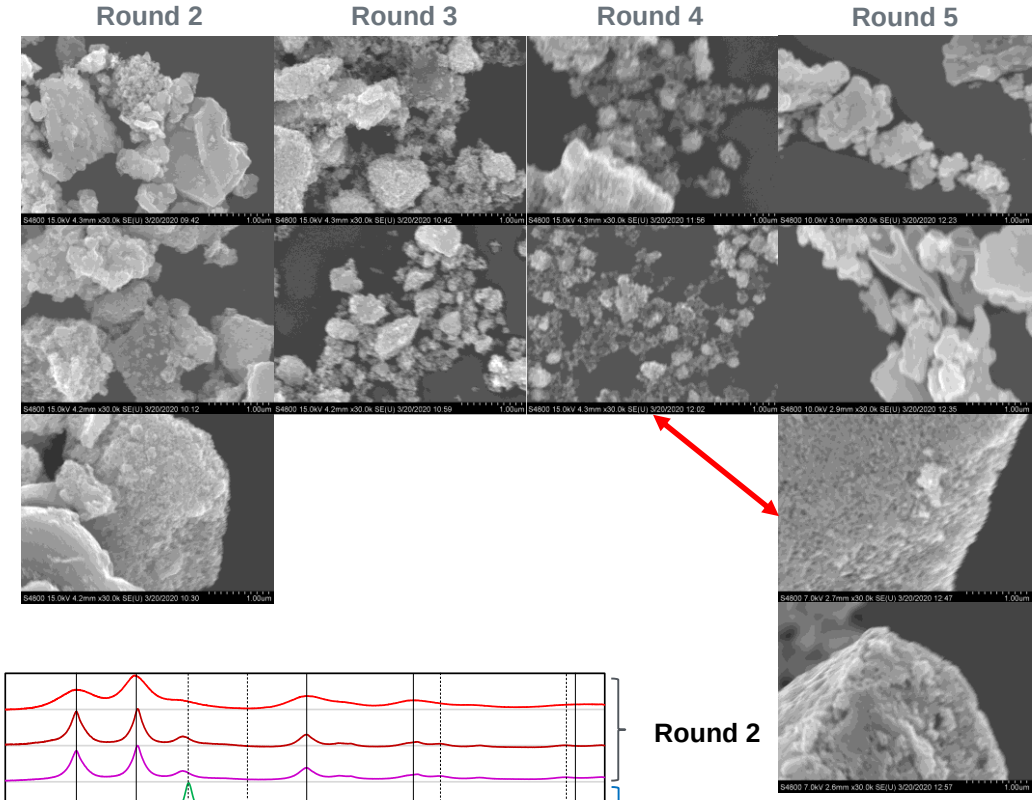
Collaboration—Catalyst: Surface Area, Metal/Oxide Near-Surface

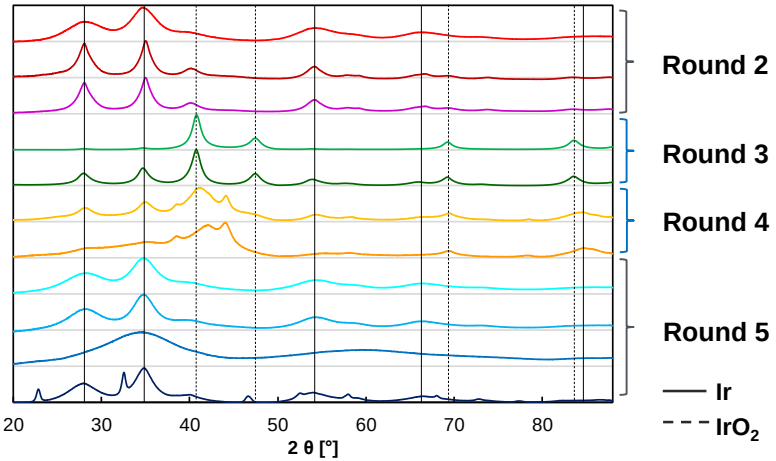




- Differences in HUPD, capacitance across material sets. Used to qualitatively separate sources of surface area.
- Difference to HgUPD due to mixed oxides; neither HUPD/capacitance are reflective of total composition.
- Notable separation in HgUPD/BET observed, particularly with multicomponents and high surface area. May require Ru/Nb considerations and lower loading.

Collaboration—Catalyst: Morphology, Crystallinity





- Material differences in relative surface roughness, aggregate size
- For catalysts with high porosity, large aggregates, may be difference between electrolyte/gas site access
- Catalysts relatively crystalline, indicate mixture of metal/rutile in bulk
- Translation of surface composition to the bulk. Example: Rd 3 and 4 primarily participate in HUPD, metal reflections.

Collaboration—PTL Development

- A series of ink solvent system experiments were performed to test wettability on the PTL substrate and to determine the best system for a uniform coating
- An ink based on a 1:20 nPA:glycerol mixture was rod coated and successfully produced uniform coatings
  - Three 1:20 nPA:glycerol based ink rod coated samples were sent to Nel for performance testing
- The project goal was achieved in that catalyst layers were successfully coated directly onto PTL substrates. Unfortunately, their performance was not as good as the catalyst coated membrane architecture.

Wetting comparison. Left to right: 1:1, 1:3, 1:10, 1:30 (nPA: glycerol)

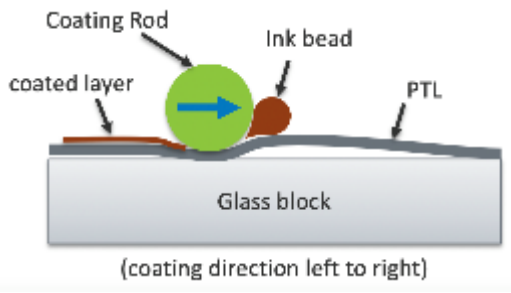
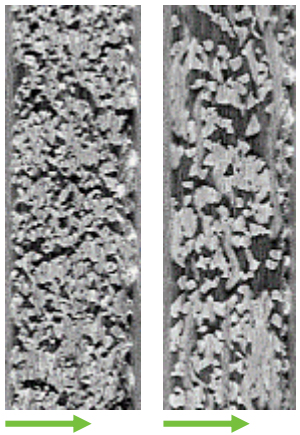
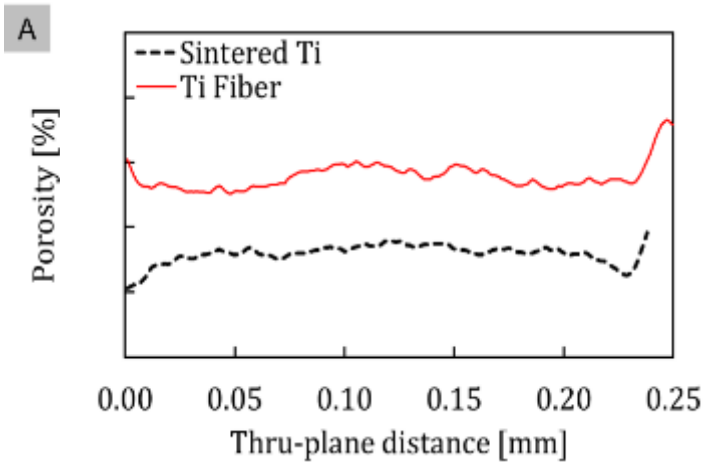


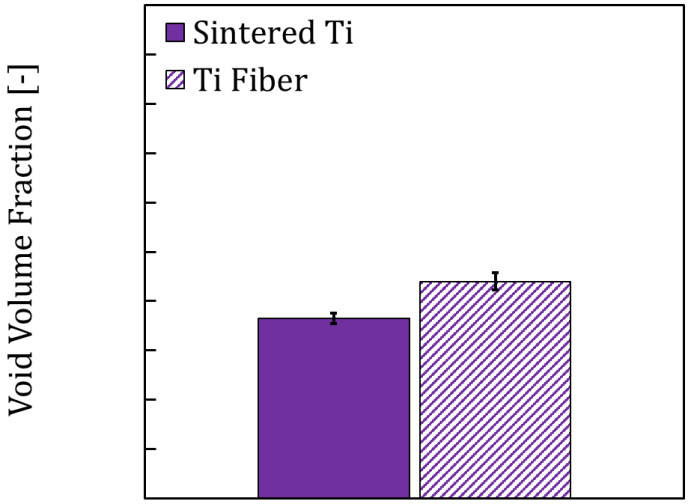
Diagram of Rod coating

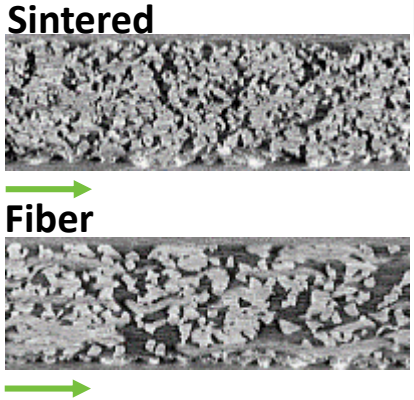
Final test samples sent to Nel for performance testing

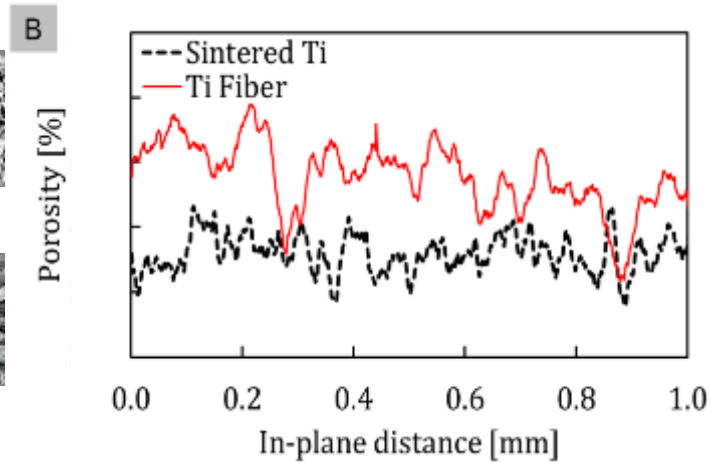
Collaboration–
Ex-situ Morphology: PTL Sintered vs. Fiber Porosity

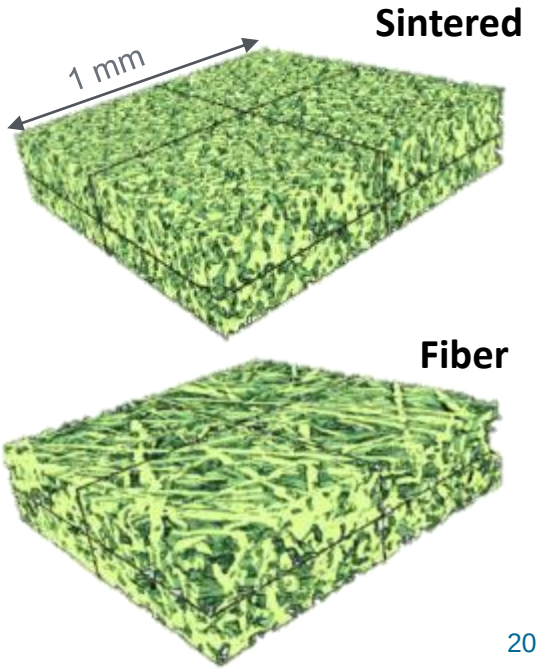








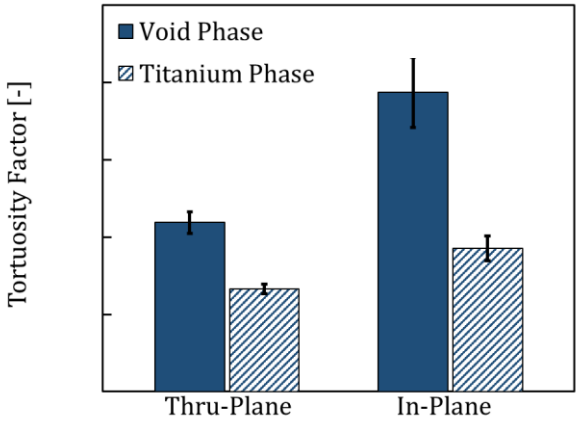


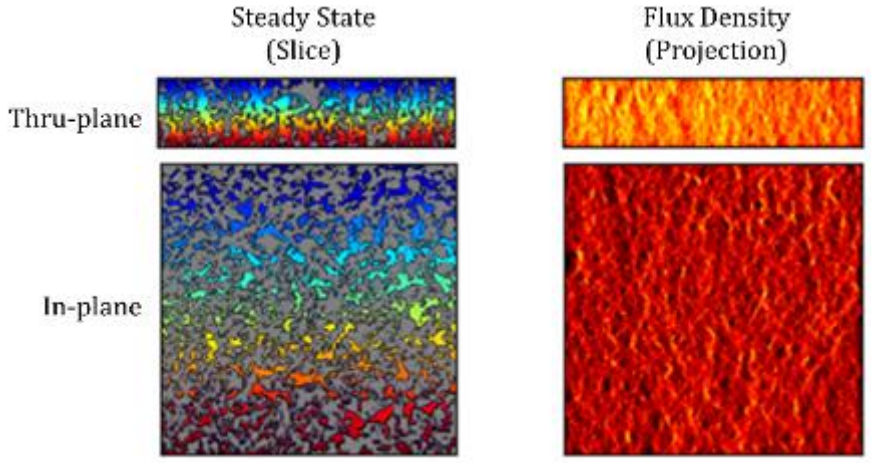


- In-depth characterization of morphology of sintered and fiber PTLs:
- Sintered Ti has more uniform in-plane porosity but lower than Ti fiber
- Ti fiber has a greater porosity compared to the sintered part

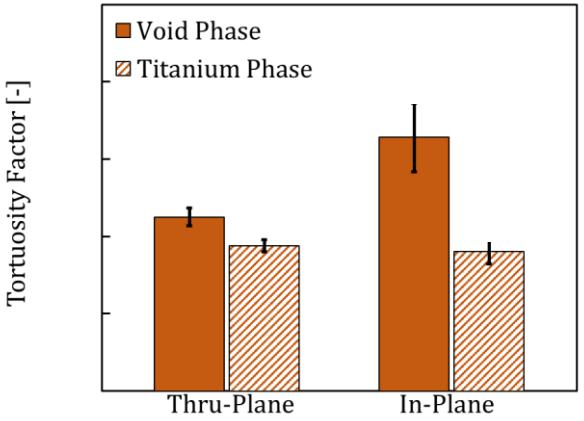
Collaboration–
Ex-situ Morphology: PTL Sintered vs. Fiber Porosity

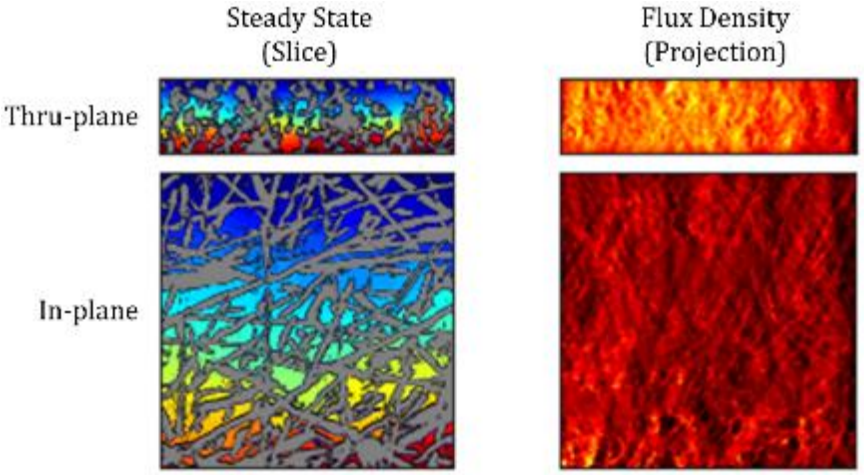
Sintered





Fiber

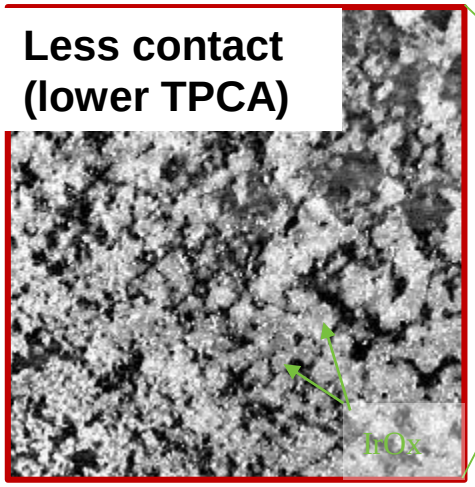


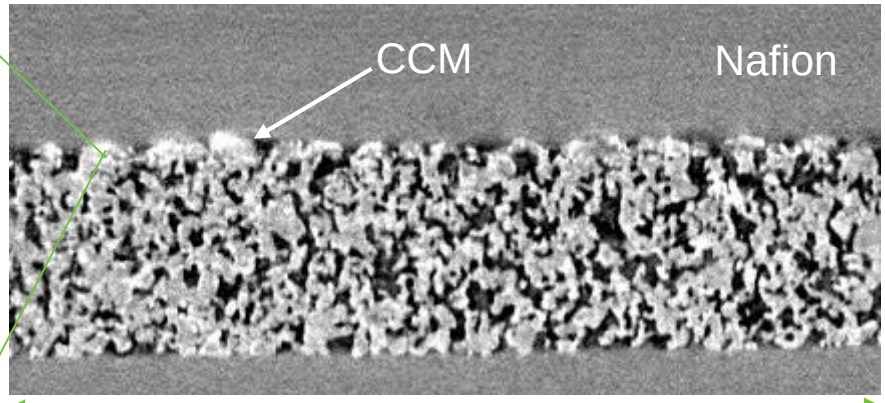


- **X-ray tomography of PTLs enables tortuosity calculation, which is critical to quantify ability of PTL to remove oxygen:**
- **For both layers tortuosity for both phases is higher in-plane vs through-plane**
- **Transport is better through-plane vs in-plane (opposite for fuel cell GDLs)**
- **Sintered Ti has higher in-plane void phase vs. Fiber Ti**

Collaboration–
Operando X-ray CT of Sinter vs Fiber PTL | CCM Interfaces

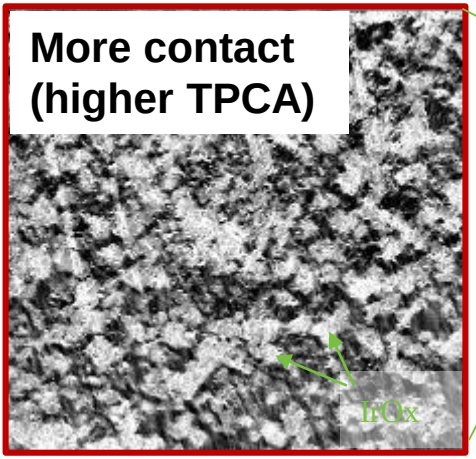
Less contact (lower TPCA)

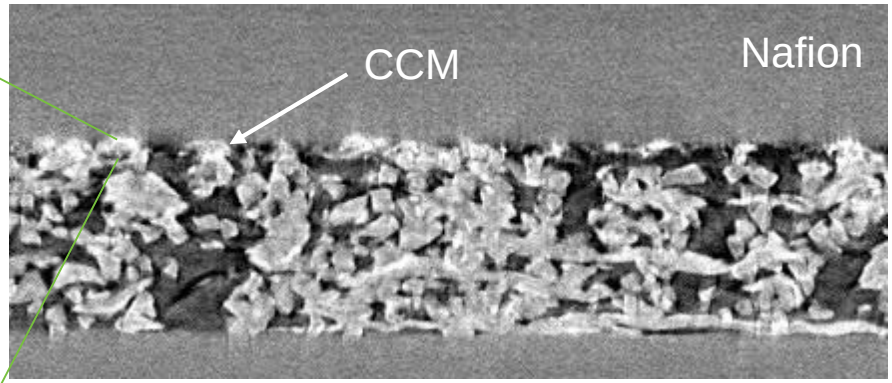


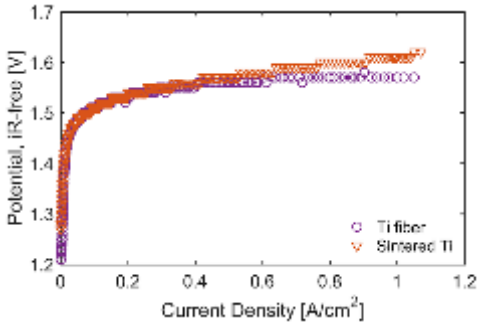


1.1 mm

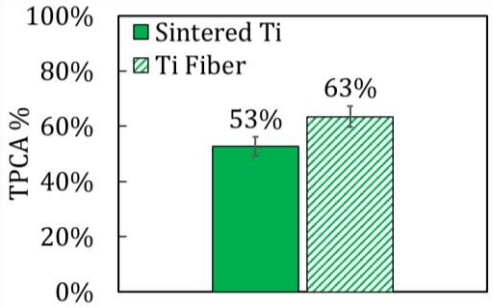
More contact (higher TPCA)







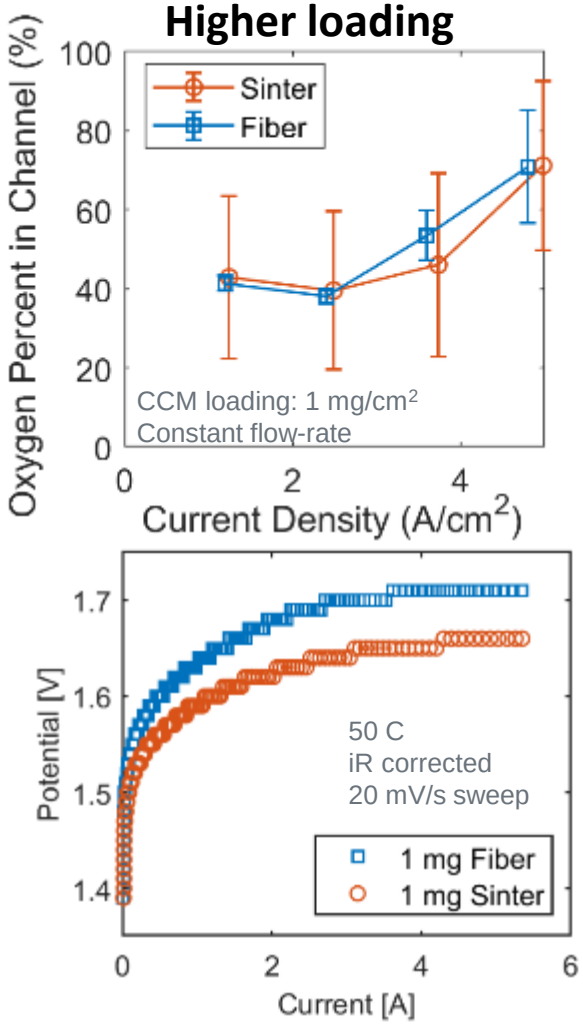
Catalyst|membrane contact area



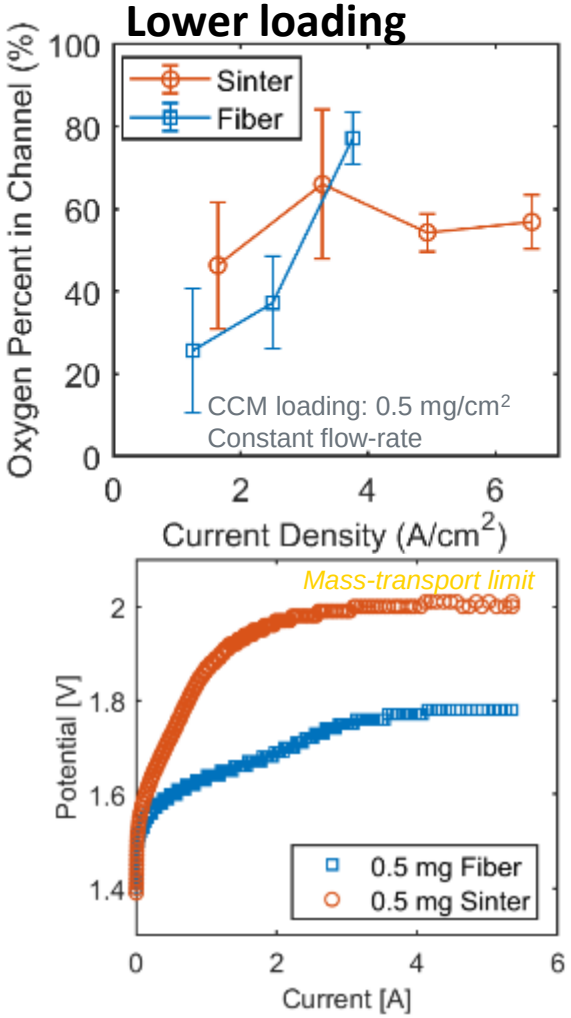
- X-ray tomography of PTLs quantifies interface and percentage of catalyst in contact with PEM and PTL:
  - Ti Fiber has higher amount of catalyst contacting both membrane and fibers
  - This translates into 50 mV potential gain at 1 A/cm²

Collaboration–
Operando Radiography for Sintered vs Fiber CCMs

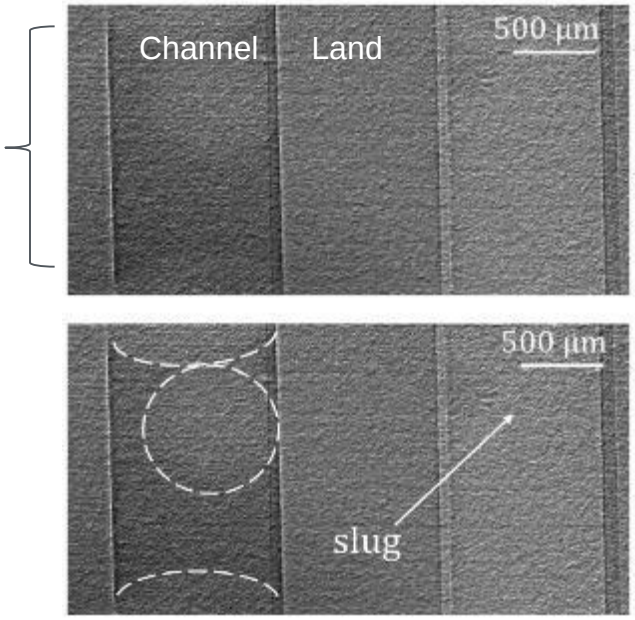
Higher loading



Lower loading



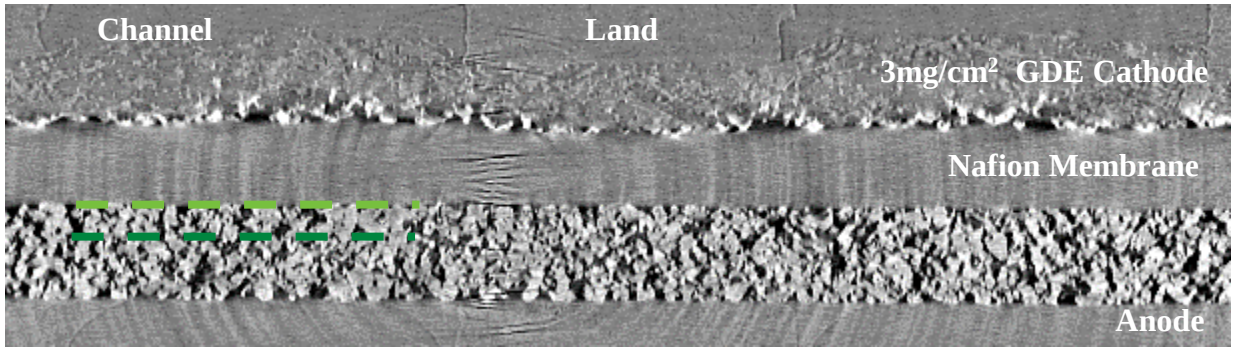
Radiography



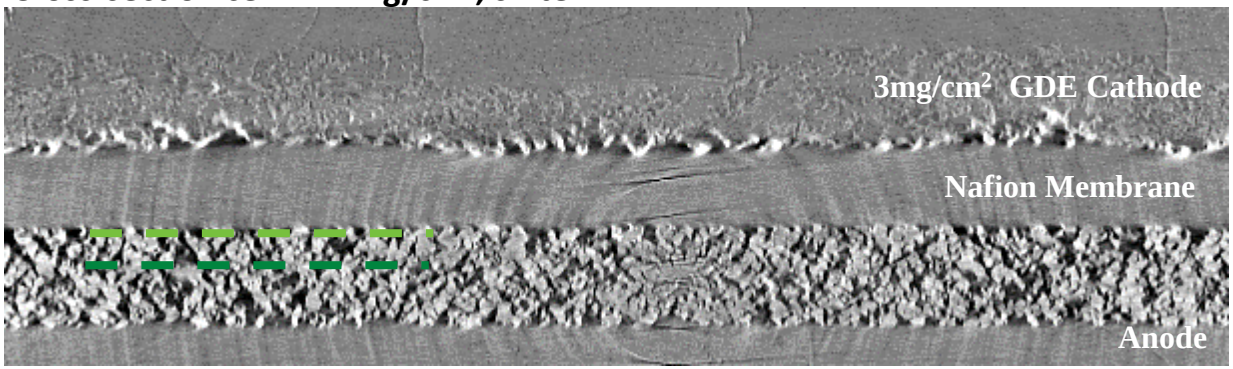
- **At higher loading of ≥ 1 mg/cm² sinter and fiber PTLs show similar performance and oxygen content in the channel**
- **At lower loading ≤ 0.5 mg/cm² fiber PTL shows better performance and ability to remove oxygen from CCM (higher oxygen content in channel means lower content within the PTL).**

Collaboration–
Operando Tomography for PTE Loading Study

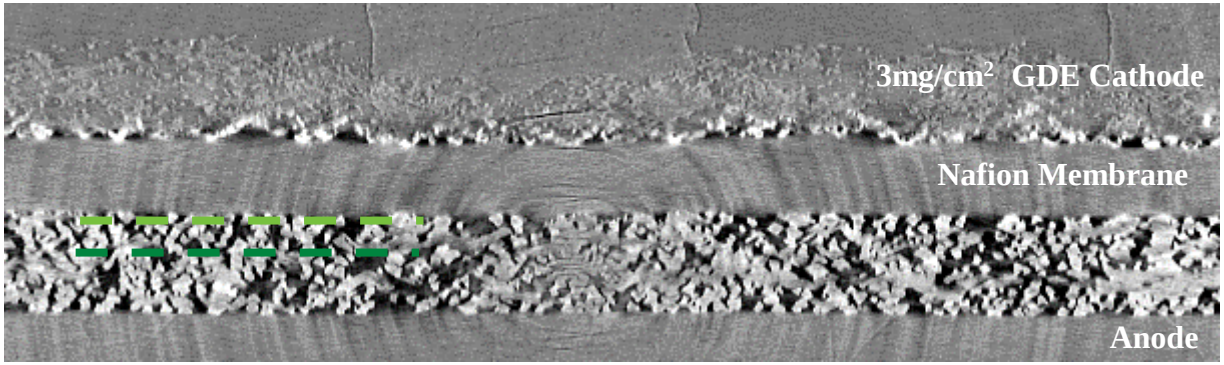
Cross-section cell: 0.65 mg/cm², sinter PTE



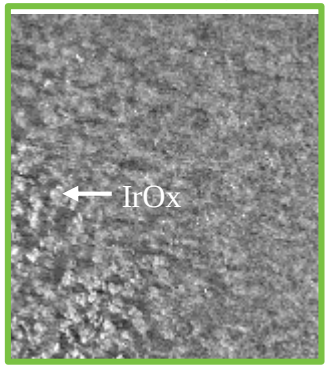
Cross-section cell: 1.1 mg/cm², sinter PTE



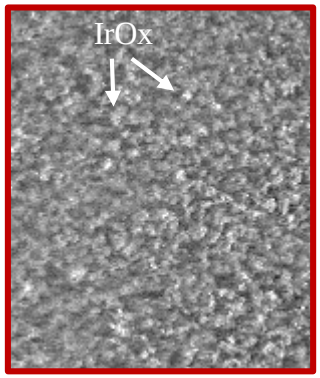
Cross-section cell: 1.1 mg/cm², fiber PTE

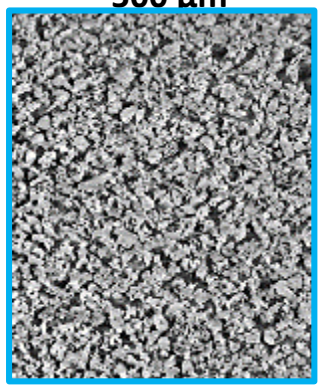


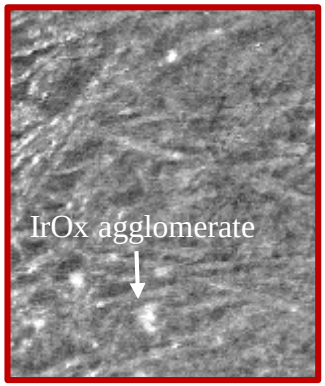
Near catalyst | **In bulk of PTE**



500 µm







Collaboration: Effectiveness

- Active engagement between contract partners and nodes has been consistent
  - Information routinely exchanged between team members has shaped test plans
  - Targeted at industry requirement for cost reductions resulting from CapEx and OpEx improvements
  - Efficiency improvements realized from fundamental characterization
- Output from internal testing and inputs from nodes has resulted in an optimized MEA configuration

Proposed Future Work

LBL: Continuation of Creep (long-term strain hold)

- Evaluation of membrane response as a function of applied compressive force and hydration conditions
- 2 different supplier chemistries to be assessed
- Continue refining model, based on operational inputs from Nel and image analysis from UCI

NREL: Complete OER catalyst characterization

- Oxide state and pore size
- Additional work will focus on characterizing cross-over mitigation strategy of process and parts developed at Nel

UCI: Assess the PTL configuration for sintered and particle components

- Imaging will continue to resolve differences in catalyst utilization
- Effect of different deposition techniques will be explored, as well as varying loadings
- Bubble formation and removal as a function of PTL configuration, flow rates, current density

ORNL: Complete analysis of operated samples to look for catalyst migration within electrodes and membrane

Nel: Assemble long-term durability test in 100 cm^2 cell to evaluate full MEA with all improvements incorporated

Project Summary

- Progress continues in the evaluation of oxide catalysts and how activity and dissolution translate to in-cell performance
  - ICP measurements have shown dissolution rates lining up with changes in activity
- X-Ray tomography studies have shown interactions between PTEs and CCM and catalyst utilization
  - Clear differences in interface between sintered and fiber PTLs
  - Bubble formation and removal rates continue to be characterized for flow field optimization
  - Results are being shared with LBL for improved model convergence
- Additional creep studies planned and will provide input for cell design and material management over life of system
- Steady-state testing conducted with stable operation of an optimized configuration, achieving 1400hrs before test halted
  - 1.7V achieved at 1.8 A/cm^2, 400 psi, and 80°C

Publications & Presentations

- *K. E. Ayers, W. L. Gellett, and C. B. Capuano, "*Electrochemical Generation of Fuels: Matching Research and Application for Advanced Water Splitting and Other Technologies", Spring ECS 2018
- K. Ayers and C. Capuano, "High Efficiency PEM Water Electrolysis Enabled by Advanced Catalysts, Membranes and Processes", DOE AMR 2018
- K. Ayers and C. Capuano, "High Efficiency PEM Water Electrolysis Enabled by Advanced Catalysts, Membranes and Processes", ECS Fall 2018
- K. Ayers and C. Capuano, "High Efficiency PEM Water Electrolysis Enabled by Advanced Catalysts, Membranes and Processes", DOE AMR 2019
- K. Ayers and C. Capuano, "High Efficiency PEM Water Electrolysis Enabled by Advanced Catalysts, Membranes and Processes", ECS Fall 2019