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High Performance Platinum Group Metal Free Membrane Electrode Assemblies Through Control of Interfacial Processes

P. I./Presenter: Kathy Ayers

Organization: Proton OnSite

Date: June 7th,2017

Project ID: PD123

DE-EE0006958

Overview

Timeline

- Project Start: 1 May 2015
- Project End: 30 April 2017
- Percent complete: 100%

Budget

- Total project funding
  - DOE share: $1,000,000
  - Cost-share: $250,000
- Funding for FY16
  - DOE share: $546,765

Barriers

- Barriers addressed

  F: Capital Cost

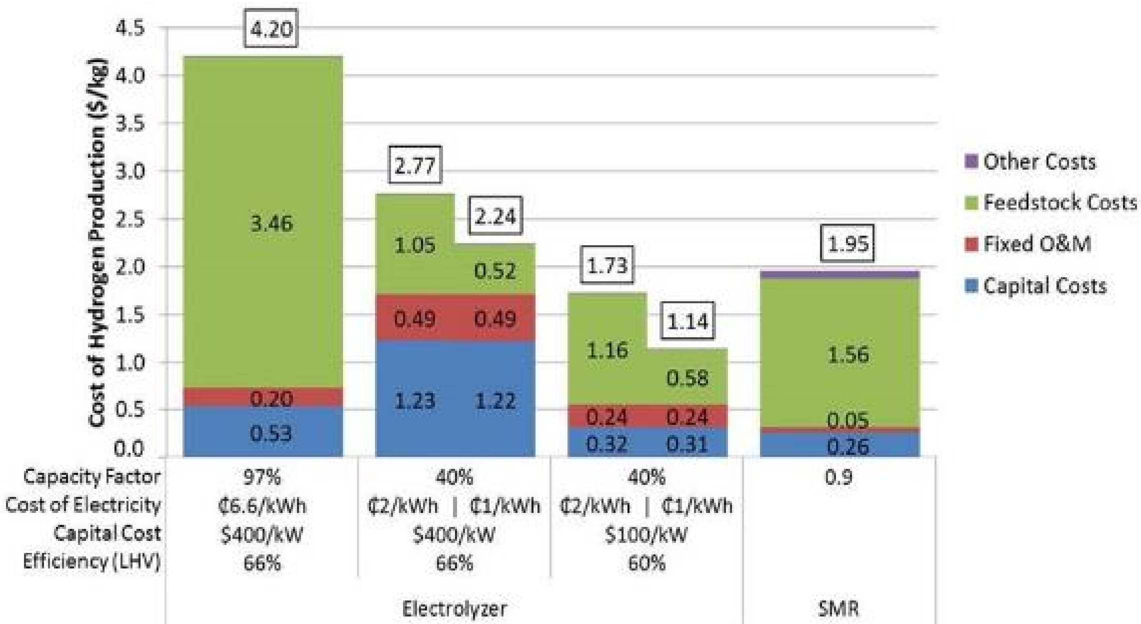
Table 3.1.4 Technical Targets: Distributed Forecourt Water Electrolysis Hydrogen Protoduction [a, b, c]				
Characteristics	Units	2011 Status	2015 Target	2020 Target
Hydrogen Levelized Cost [d] (Production Only)	$/kg	4.2 [d]	3.9 [d]	2.3 [d]
Electrolyzer System Capital Cost	$/kg $/kW	0.70 430 [e, f]	0.50 300 [f]	0.50 300 [f]
System Energy Efficiency [g]	%(LHV)	67	72	75
	kWh/kg	50	46	44
Stack Energy Efficiency [h]	% (LHV)	74	76	77
	kWh/kg	45	44	43

Partners

- Northeastern University
- Pennsylvania State University
- University of New Mexico

Relevance: Problem and Barriers Addressed

- H_2 cost depends on capital and operating cost scenarios including use parameters
- AEM based electrolysis enables elimination of most expensive cell materials: PGM and valve metals



Project Goals:

- Develop ex-situ and in-situ comparisons to connect lab evaluation and device results
- Increase stability of PPO membranes through cation spacers
- Optimize water management through tuning of porosity and hydrophobic properties
- Advance understanding of non-PGM active sites and reaction mechanisms to improve stability

Approach: AEM Electrolysis

- **Catalyst**:
  - *Goal*: Show feasibility of non-PGM catalysts in AEM
    - Evaluate non-PGM OER and HER catalysts for AEM electrolysis
    - Conduct interfacial study on effect of carbonate and KOH on ionomer and catalyst electrode structure
- **Membrane and ionomer**:
  - *Goal: Enhance membrane and ionomer stability to achieve long term cell operation*
    - Control water uptake and conductivity for improved mechanical stability
- **Cell and System Design**:
  - *Goal: Demonstrate 500 hr of stable operation at <2V for fully integrated AEM cell at 500 mA/cm^2*
    - Optimize water management and balance of plant configuration

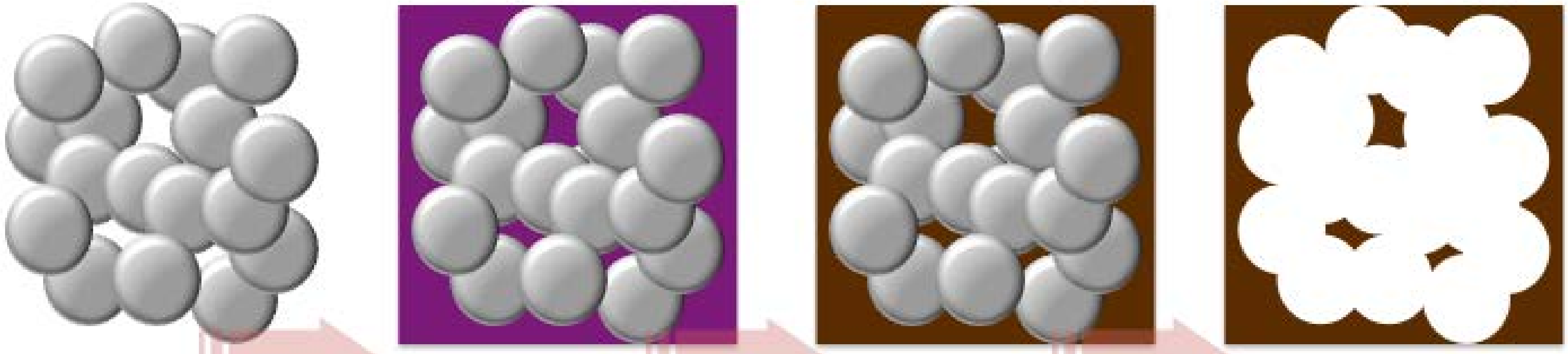
Approach: Task Breakdown

- Task 1.0 Synthesis of HER & OER Catalysts
  - 1.1 Catalyst Component Identification
  - 1.2 Refinement of Composition & Micro-structure
  - 1.3 Synthesis of Single Oxides
  - 1.4 Synthesis of Spinel Materials
  - 1.5 Scale-up of SSM Materials
- Task 2.0 Membrane/Ionomer Synthesis
  - 2.1 Scale-up Benzyl Side Chain AEMs
  - 2.2 Synthesis Optimization & Scale-up
- Task 3.0 Characterization of Catalyst Materials
  - 3.1 3-Electrode Testing
  - 3.2 2-Electrode Testing
  - 3.3 Structural Characterization
- Task 4.0 Characterization of Interfacial Effects
- Task 5.0 Cell Engineering
- Task 6.0 Prototype System & Demonstration

Approach - Milestones

Milestone Summary Table			
Recipient Name:	**Proton OnSite**		
Project Title:	**High Performance Platinum Group Metal Free Membrane Electrode Assemblies Through Control of Interfacial Processes**		
Task # /Title	**Milestone/ Go –No Go Description**	**Q**	**% Complete**
1: Catalyst Synthesis	**NUCRET**: Synthesize baseline Ni-Mo and Ni-Fe materials	Q1	100%
1: Catalyst Synthesis	**UNM**: achieve single oxide material with equivalent half cell properties to IrO2	Q2	100%
1: Catalyst Synthesis	**NUCRET:** Identify 3 promising Ni/MeOx cathodes; Identify 3 promising “MMO” (Ni-Fe-Mo/Co) anodes	Q3	100%
3: Catalyst Characterization	**NUCRET**: Demonstrate operation at 500 mA/cm2, $<$2 V with liquid fuel	Q4	100%
4: Electrode Fabrication and Characterization	**Proton:** Integrate non-PGM catalyst with novel AEM materials	Q5	100%
2: Membrane Synthesis and Characterization	**PSU**: Delivery of materials with PPO benzyl side chain architecture for electrode optimization and cell testing.	Q6	100%
1: Catalyst Synthesis	**UNM:** down select transition metal, precursor type; deliver material to Proton OnSite	Q7	100%
6: Prototype Demonstration	**Proton:** Demonstrate stable operation at 500 mA/cm2, $<$2 V with 2-electrode configuration	Q8	100%

Approach: Catalyst Development



Template: monodispersed amorphous silica

Fumed Silica: BET-SA ~400 m^2/g

infused with transition metal salt or salts

Decomposed on air

silica etched by KOH

Templated Self-supported OER Catalyst

Metals: Ni, Mo, Cu etc

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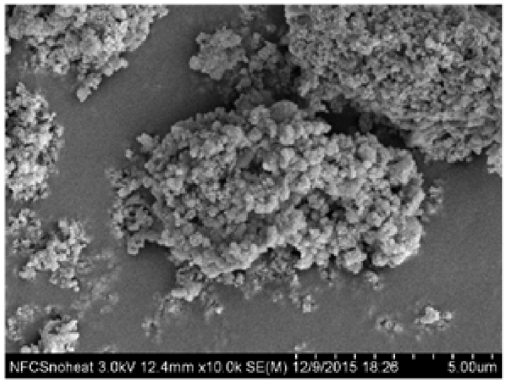
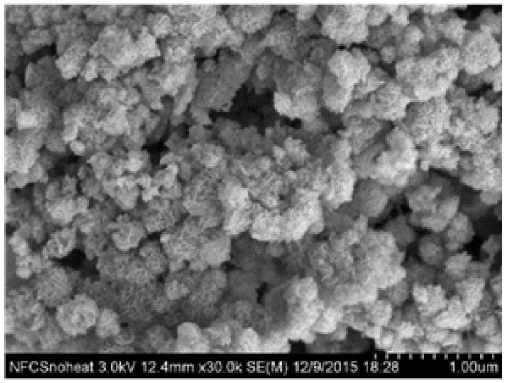
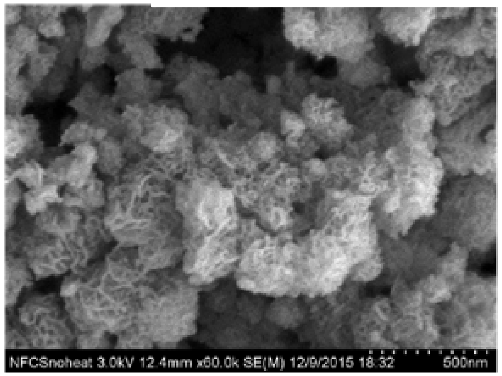
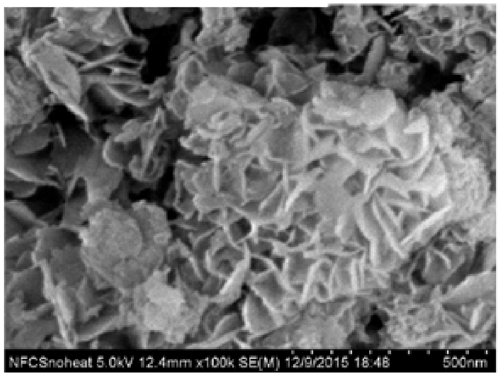
Approach: Catalyst Development







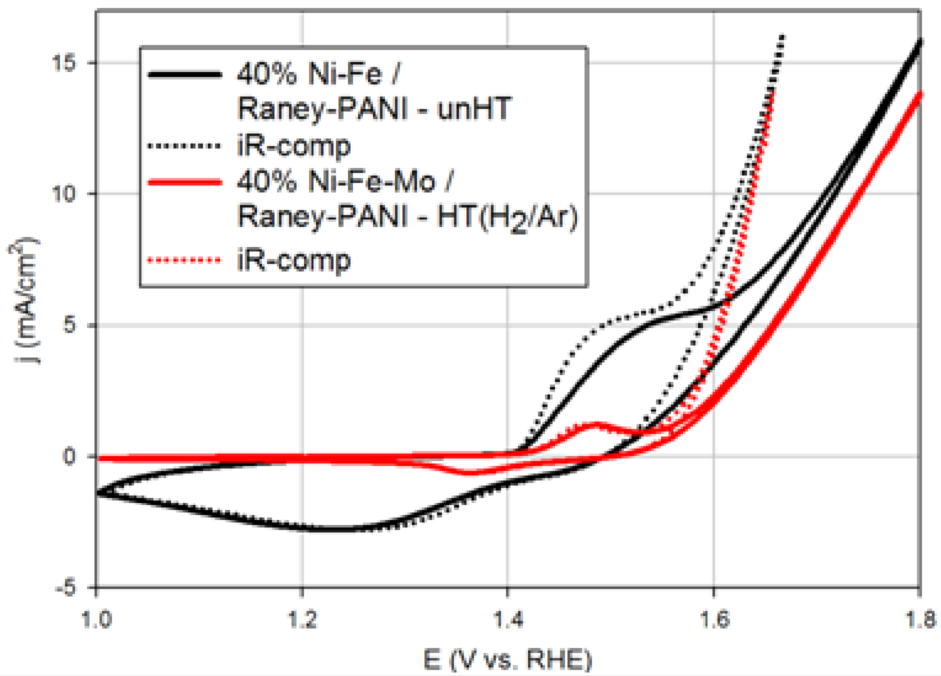


- Support synthesis through SSM method
- HER catalysts based on Ni-TM (TM=Cr, Mo) supported on Raney-Ni, C or SSM
- OER catalysts based on Ni-TM_1-TM_2 (TM=Fe, Mo, Co) oxides on Raney-PANI, or SSM

- Activity and stability optimization through tuning of composition, support of non-PGM catalysts
- Screening by 3-electrode solution testing by RDE and flooded gas diffusion electrodes
- Focus on reproducibility and uniformity of synthesized materials

Anode OER

250μg/cm² LD - 25C - 0.1M KOH (O_2-purged)



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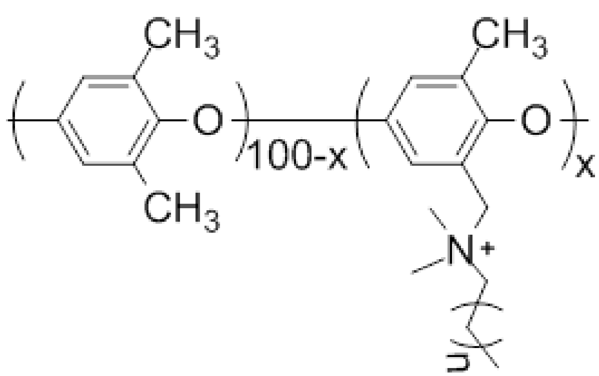
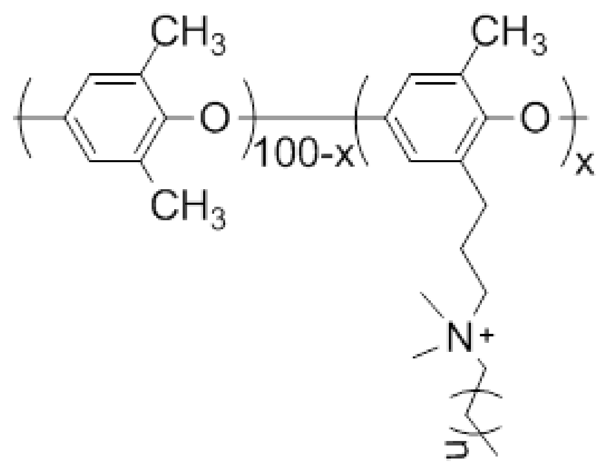
Approach: Membrane and Ionomer

- PPO is a highly stable backbone for AEMs
  - Absence of electron withdrawing groups in the main chain
  - Cation spacer polymers have 5-10X greater hydroxide stability than side chain benzyl-linked cation
  - Highly manufacturable and tunable for conductivity, water uptake, mechanical stability
  - Mechanical reinforcement added for increased strength

Side chain benzyl dimethylalkyl ammonium



Cation spacer dimethyldialkyl ammonium

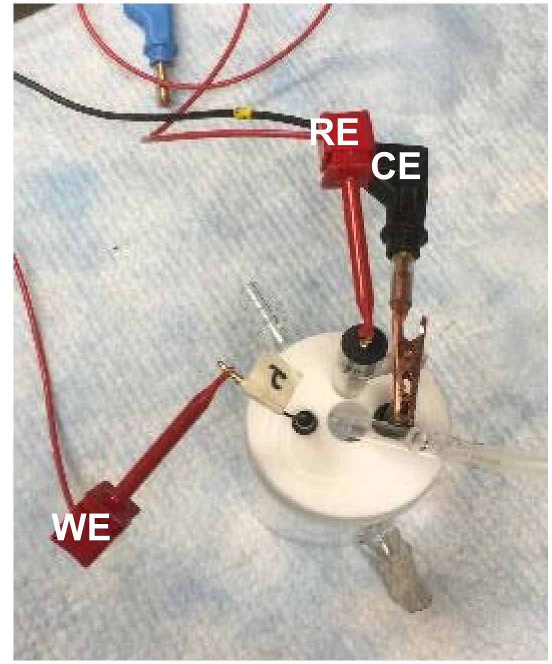


Approach: Interfacial Study

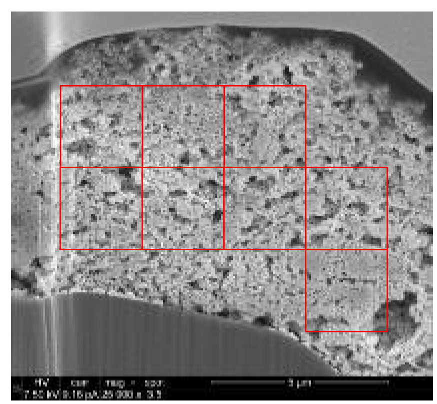
- CV and HER via microelectrodes

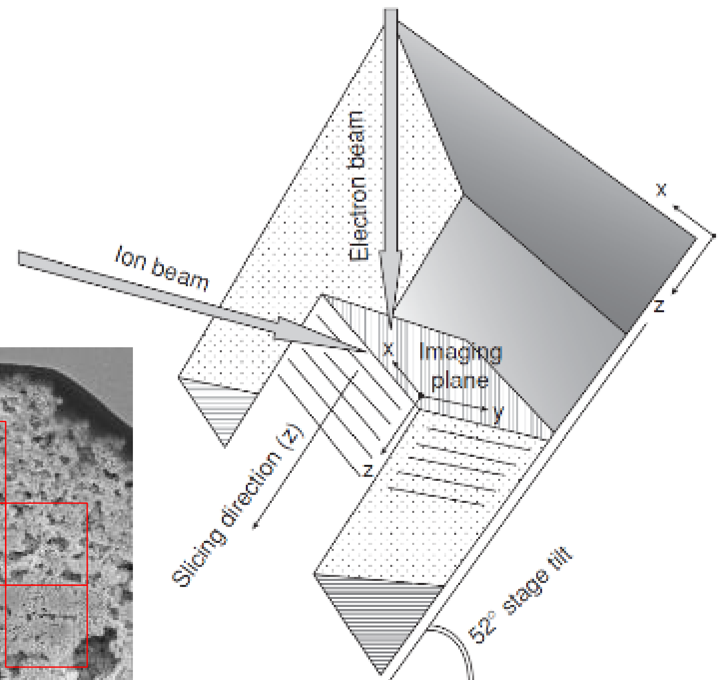
1% K_2CO_3 vs. 0.335% KOH (same conductivity), same pH, mixed solutions from high to low pH

  - WE: 50/100μm Pt,
  - CE: 1.6mm diameter Pt disc
  - RE: Hg/HgCl electrode



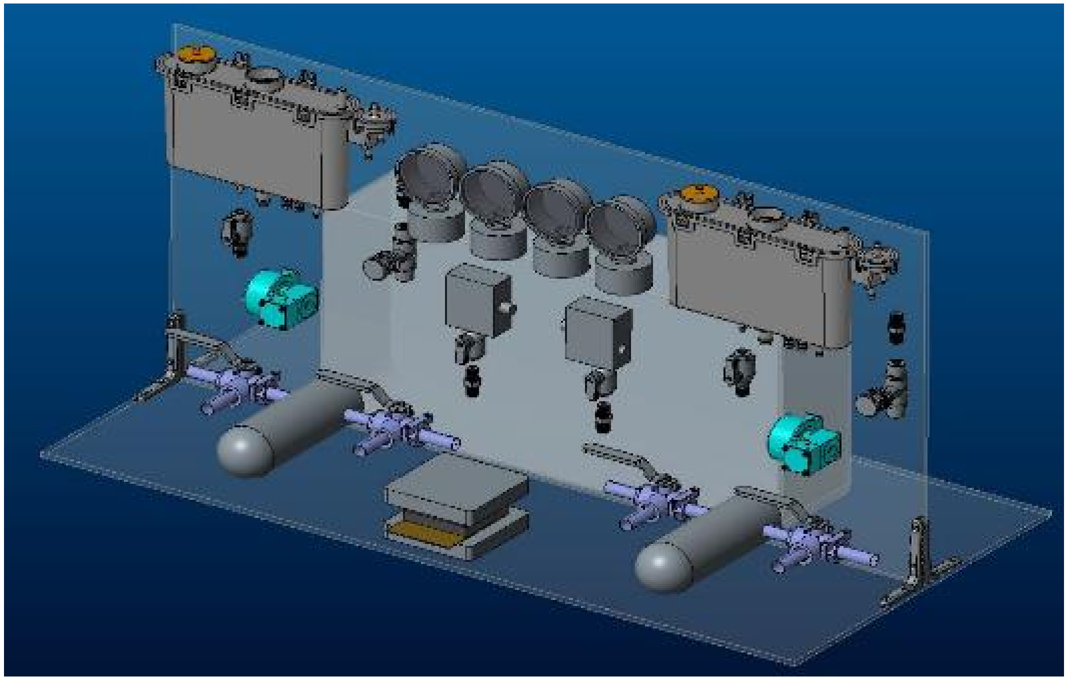
- Ion beam sectioning analysis on full electrodes
  - Use low energy methods for prep and analysis
  - Measure average solid and pore sizes, % porosity



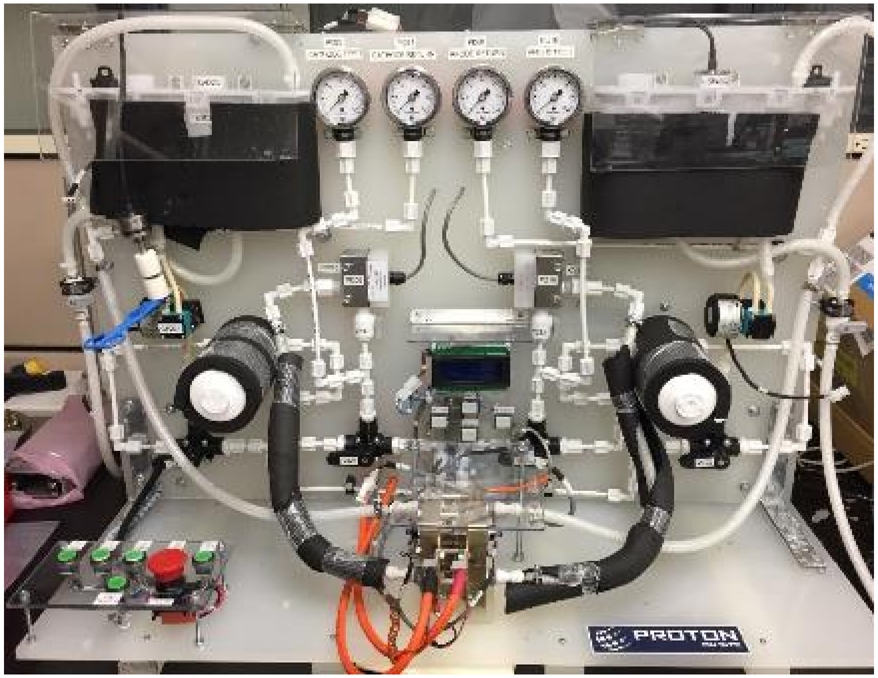


Approach: MEA Testing

- Gas diffusion electrodes fabricated with NEU/UNM catalysts
  - Test station was design and developed to evaluate optimal modes of operation



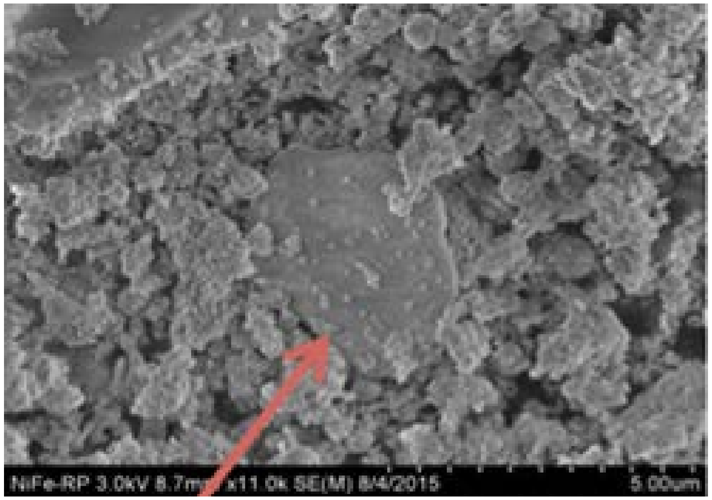
Test Stand Concept

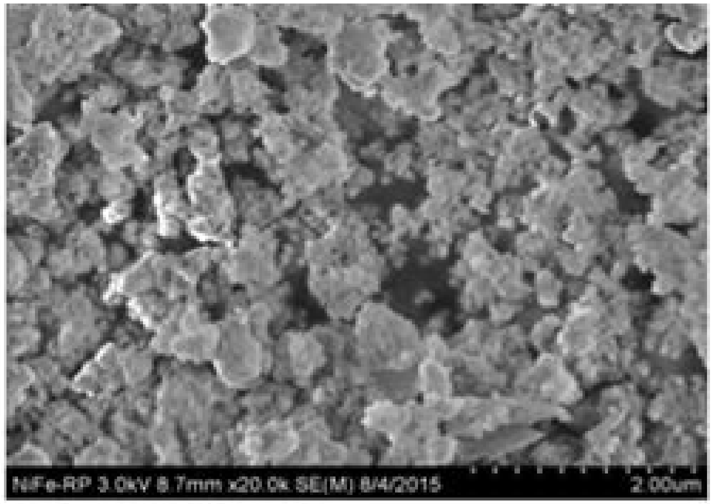


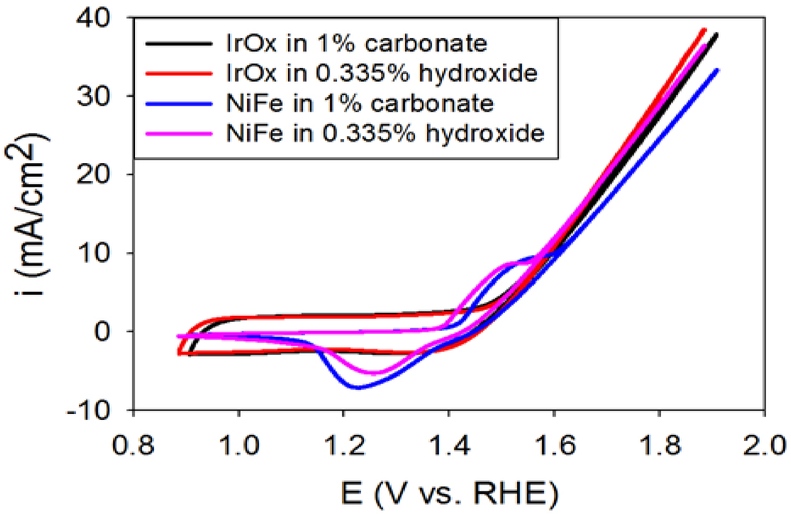
Test Stand As-Built

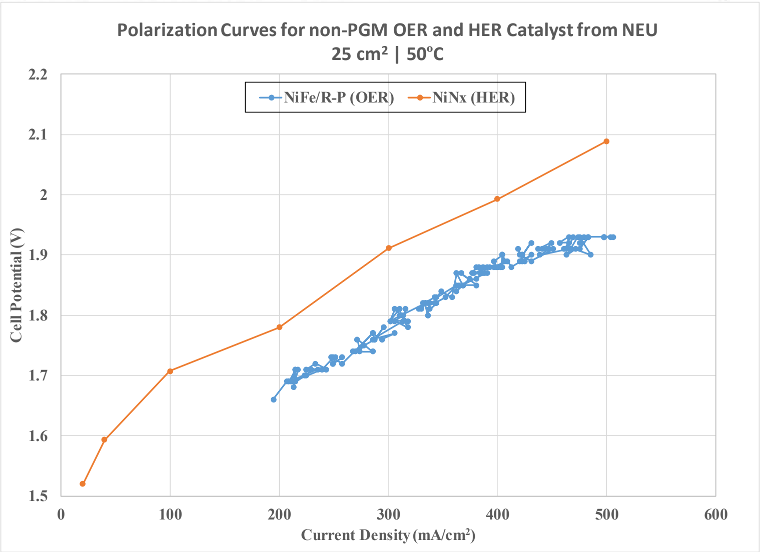
Technical Accomplishments: Catalyst

- Synthesized Ni-Mo & Ni-Fe composite ”MMO” materials
- Confirmed structure & composition via XRD & SEM

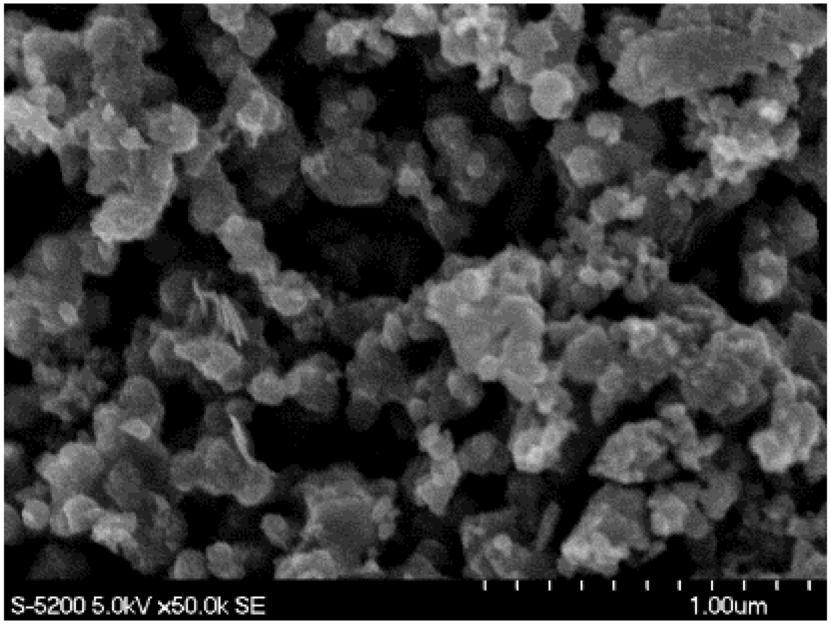


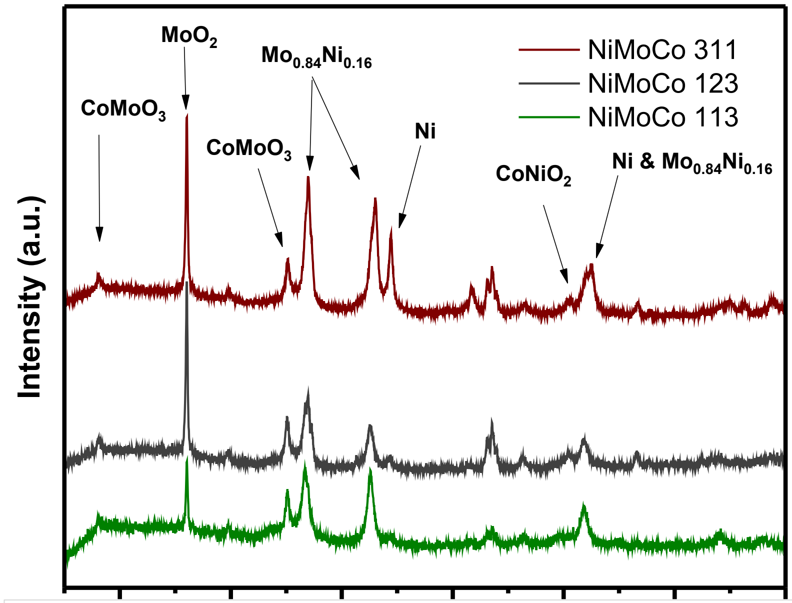


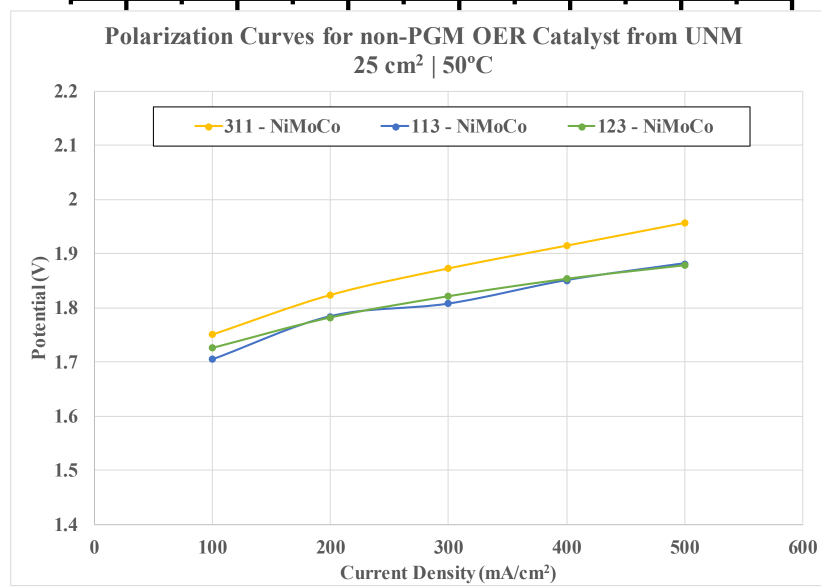




Technical Accomplishments: Catalyst



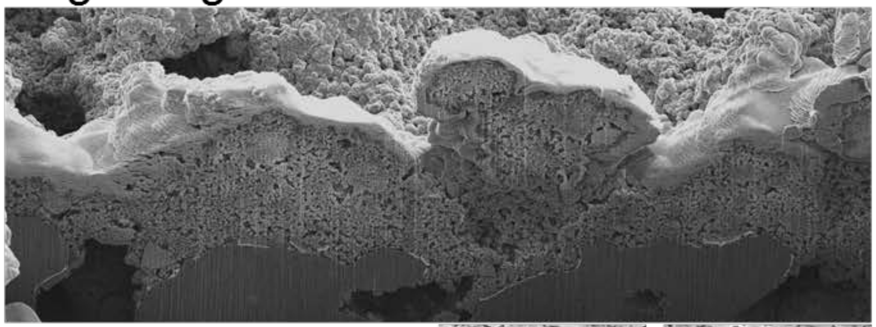


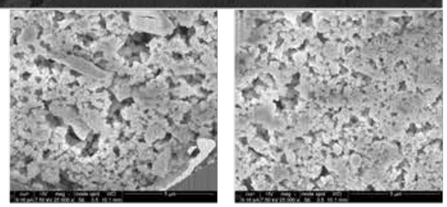


<u>NiMoCo materials</u>
<u>3D structure</u>
<u>Complex phase composition</u>

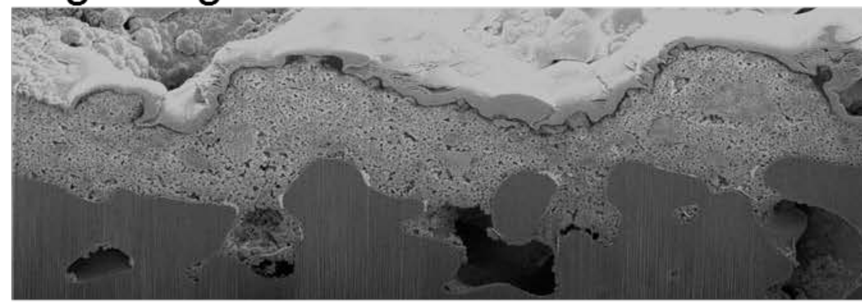
Technical Accomplishments: Interface Study

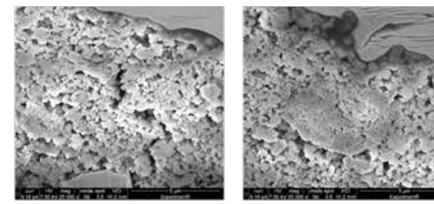
Beginning of Test AS4



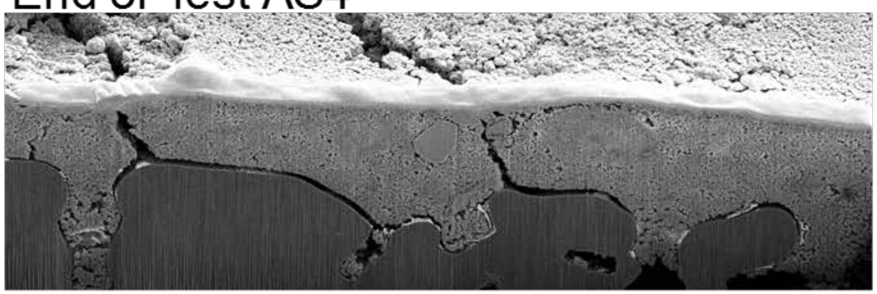


Beginning of Test Nafion

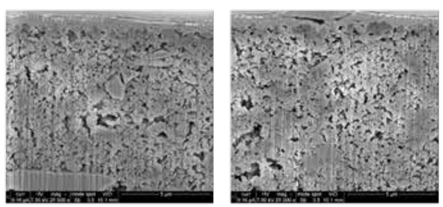




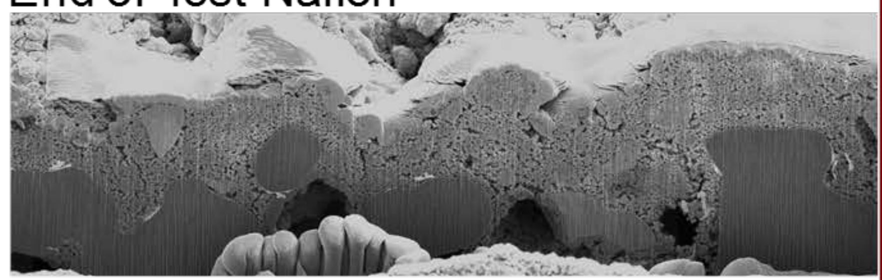
End of Test AS4



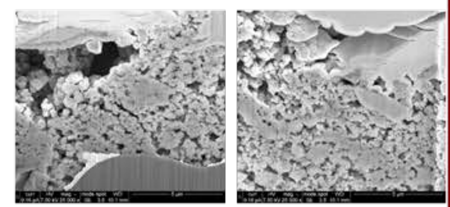
Collapse of pores is visible



End of Test Nafion

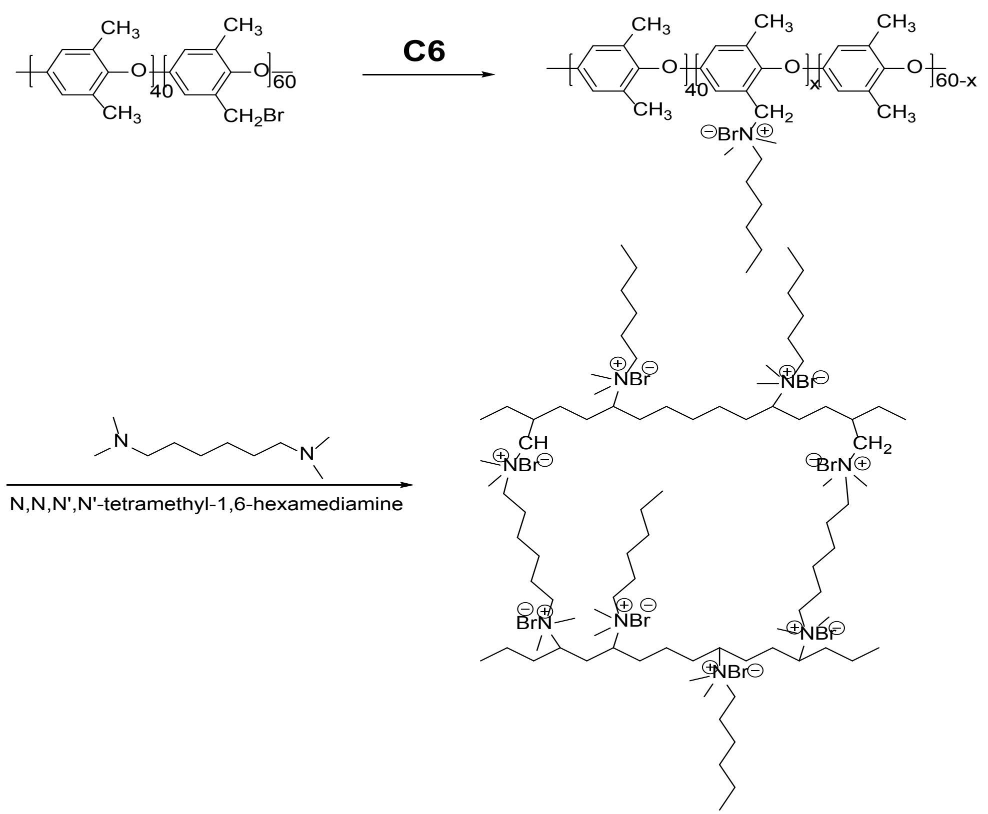


Opposite- growth of pores with some really large pores appearing after test

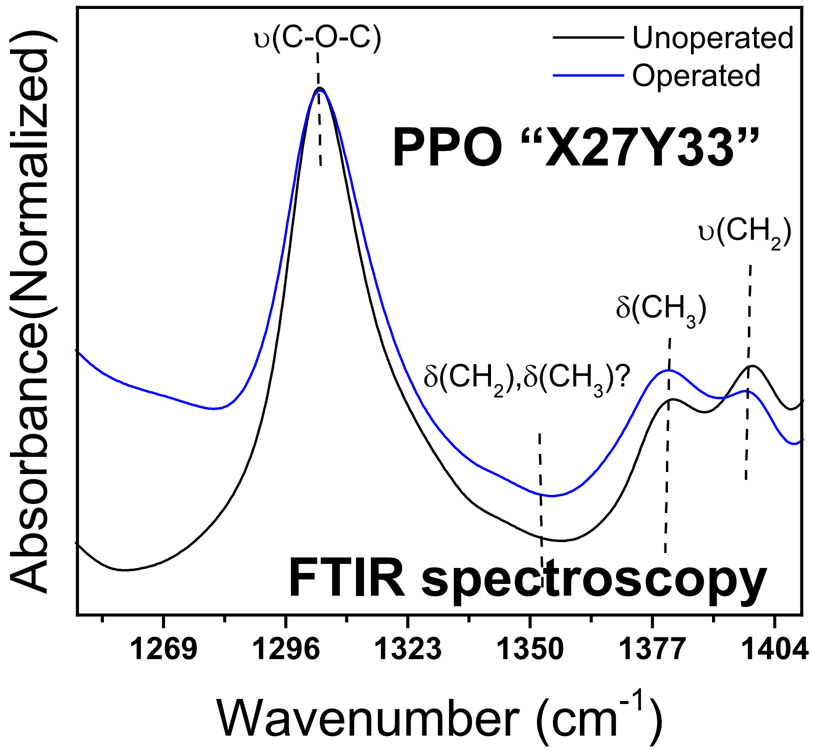


Technical Accomplishments: Membrane Synthesis

C6 x-link PPO "X27Y33"

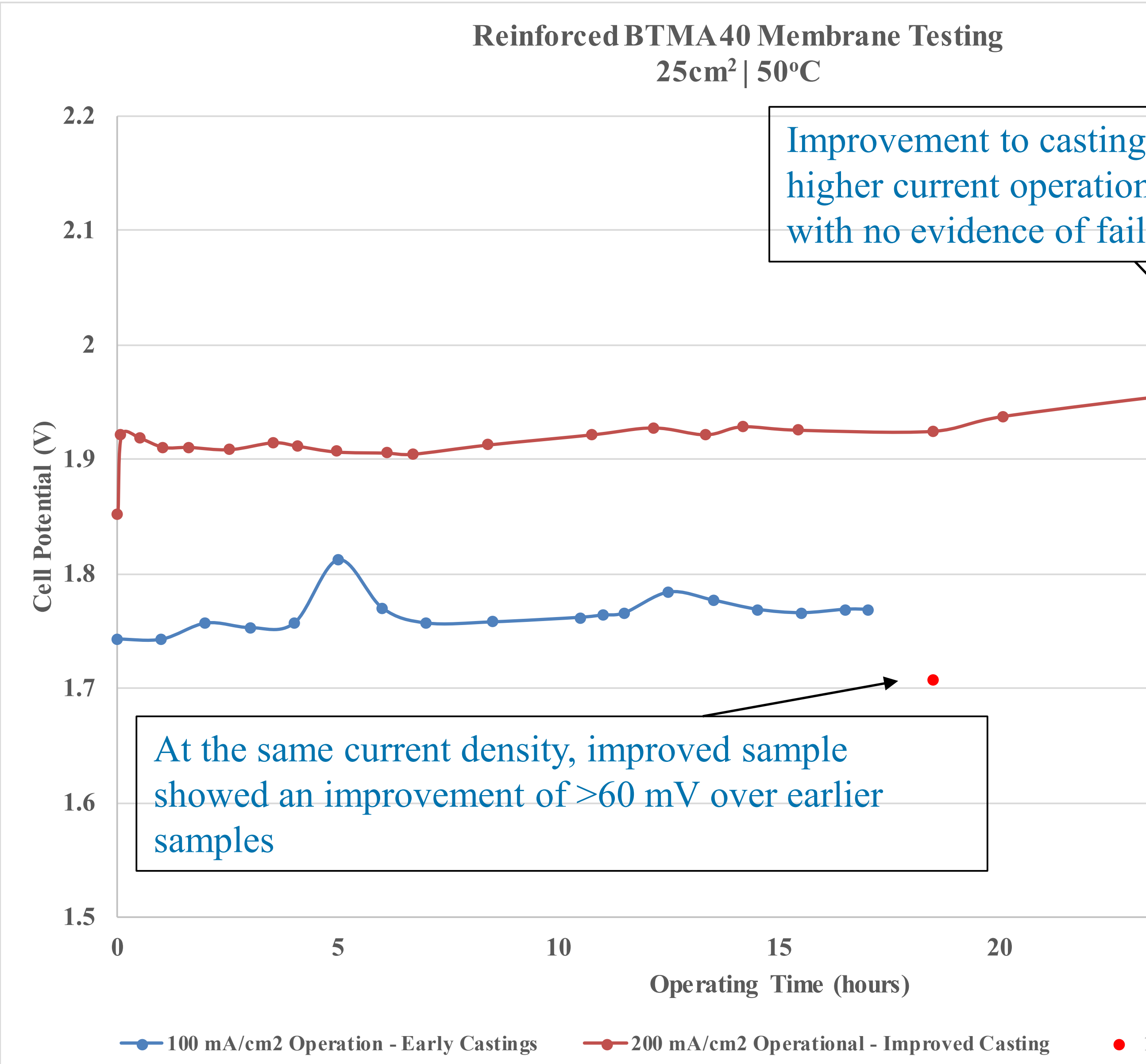


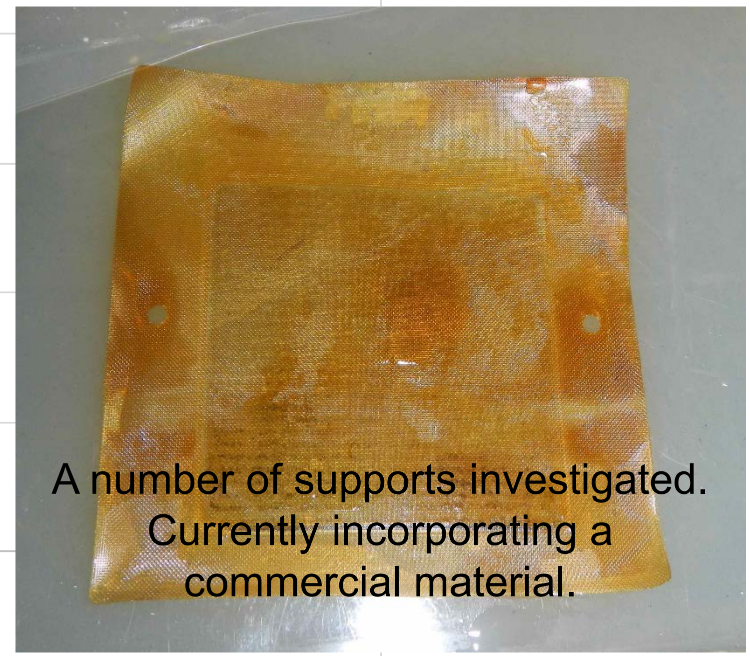
- CH_2 to CH_3 ratio decreases due to decrease in CH_2 groups in the polymer.
- Consistent with both Benzyl attack and Hoffman elimination.
- We used this ratio to give a qualitative estimate of degradation in the samples.



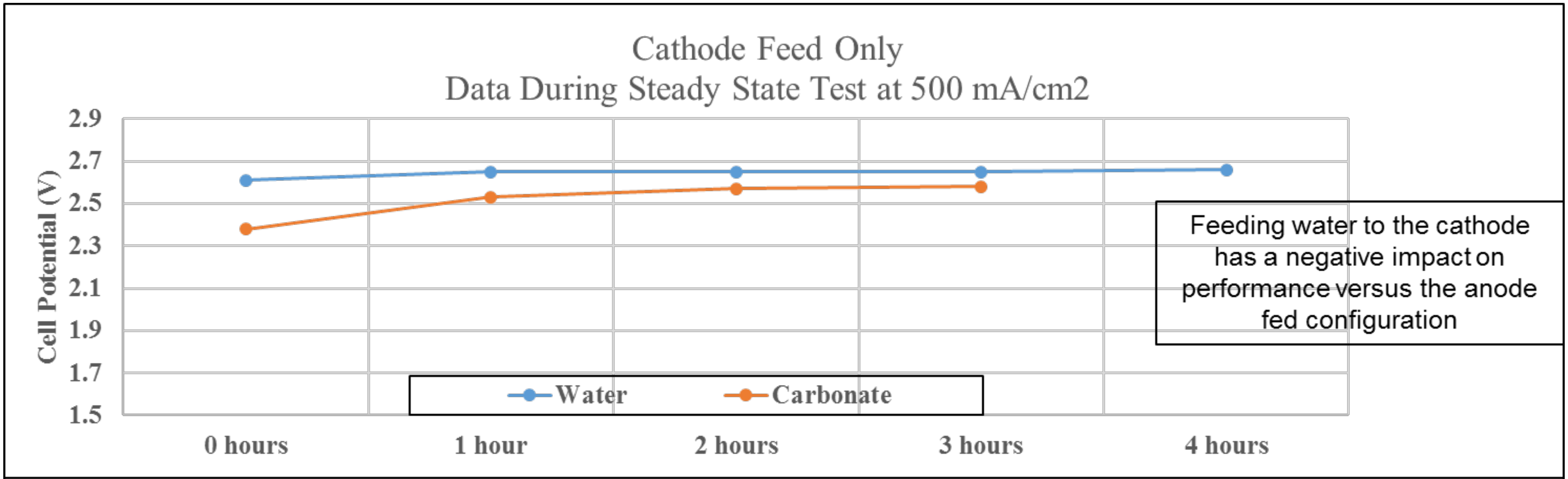
- Non-cross-linked samples showed poor processing performance
- Added cross-linking and reinforcement for stability
- Penn State has delivered over 30 7" x 7" samples to Proton for conducting cell testing in this project

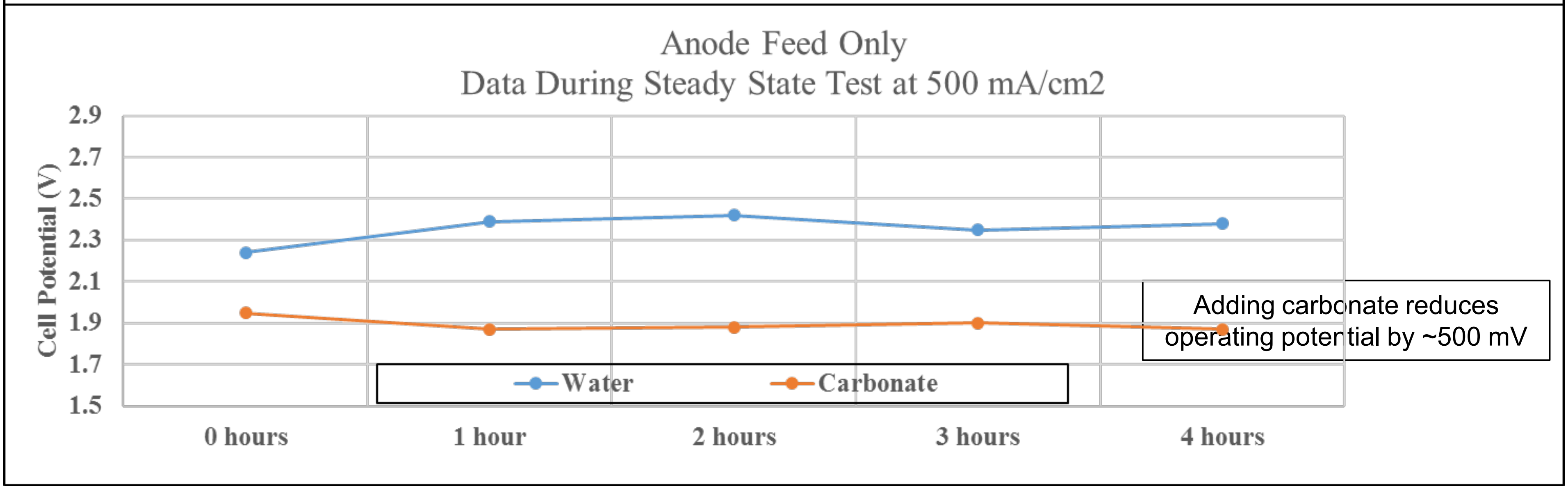
Technical Accomplishments: Membrane



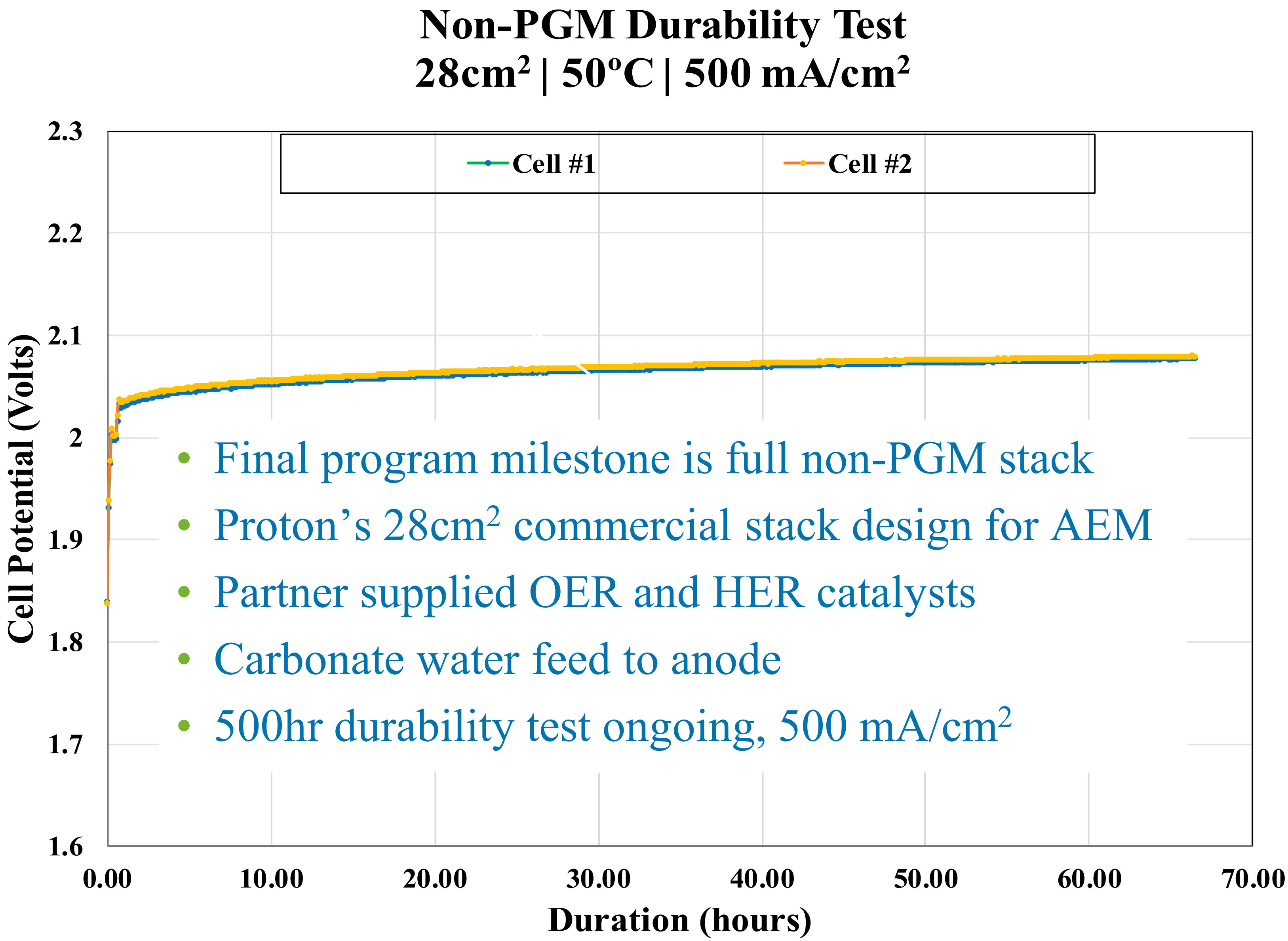


Technical Accomplishments: MEA





Technical Accomplishments: Durability



- Final program milestone is full non-PGM stack
- Proton's 28cm^2 commercial stack design for AEM
- Partner supplied OER and HER catalysts
- Carbonate water feed to anode
- 500hr durability test ongoing, 500 mA/cm^2

Collaborators

- Penn State (Subcontractor)
  - Synthesis and tuning of ionomer and membrane
  - Scale up batch sizes
- University of New Mexico (Subcontractor)
  - Sacrificial supports for pure oxides and spinel materials for OER
  - Optimize sacrificial support (SiO_2 vs MgO), metal precursor type, heat treatment parameters, and sacrificial support removal conditions
- Northeastern University (Subcontractor)
  - HER catalysts and effects of various post-synthesis heat-treatments.
  - Electrodeposited ternary Ni-Fe-X (X=Co,Mo,etc.) on GDEs
  - Wet synthesis of composite Ni-Fe-X materials with carbon nanotubes (CNTs) or other conductive nano-polymers (CNPs)

Summary

- **Relevance:** The goal of this effort is to produce a high-performance anion exchange membrane water electrolyzer (AEM-WE) completely free of PGMs
- **Approach:**
  - Optimization of electrocatalyst conductivity, dispersion, and utilization in the active MEA with focus on the understanding of catalyst-membrane-ionomer interfaces and how they differ from liquid electrolyte
  - Water management through GDL modification and system configuration
  - AEM material stability by incorporating of side chains, cross-linking, and mechanical reinforcement
  - Utilize cheaper materials of construction for cell stack and system design to further reduce total $/kg H_2
- **Collaborations:**
  - Pennsylvania State University: Development of a PPO based AEM and ionomer that is stable in alkaline operation and scalable to a batch process
  - University of New Mexico: Apply SSM (sacrificial support method) in the synthesis of catalyst materials with high surface area 3D structures
  - Northeastern University: Develop non-PGM HER and OER catalysts. Conduct characterization of interface between non-PGM catalysts and ionomer to study structure-activity relationships
- **Proposed Future Work:**
  - Continue synthesis and scale-up of highly active, PGM free HER and OER catalysts
  - Synthesize PPO based AEMs with added reinforcement and cross-linking for improved stability
  - Optimize cathode and anode GDEs to improve water management for operational stability
  - Evaluate operational mode with electrolysis system for stability (cathode vs anode feed)
  - Integrate all materials and operating modes into optimal cell and system configuration