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

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Organization: Proton OnSite

Date: June 8th, 2016

Project ID: PD123

DE-EE0006958

Overview

Timeline

- Project Start: 1 May 2015
- Project End: 30 April 2017
- Percent complete: 50%

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	0.70	0.50	0.50
	$/kW	430 [e, f]	300 [f]	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

Budget

- Total project funding
  - DOE share: $1,000,000
  - Cost-share: $250,000
- Total DOE funds spent*
  - DOE share: $474,984

*as of 3/31/16

Partners

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

Relevance: Hydrogen Value Proposition

Power Plants

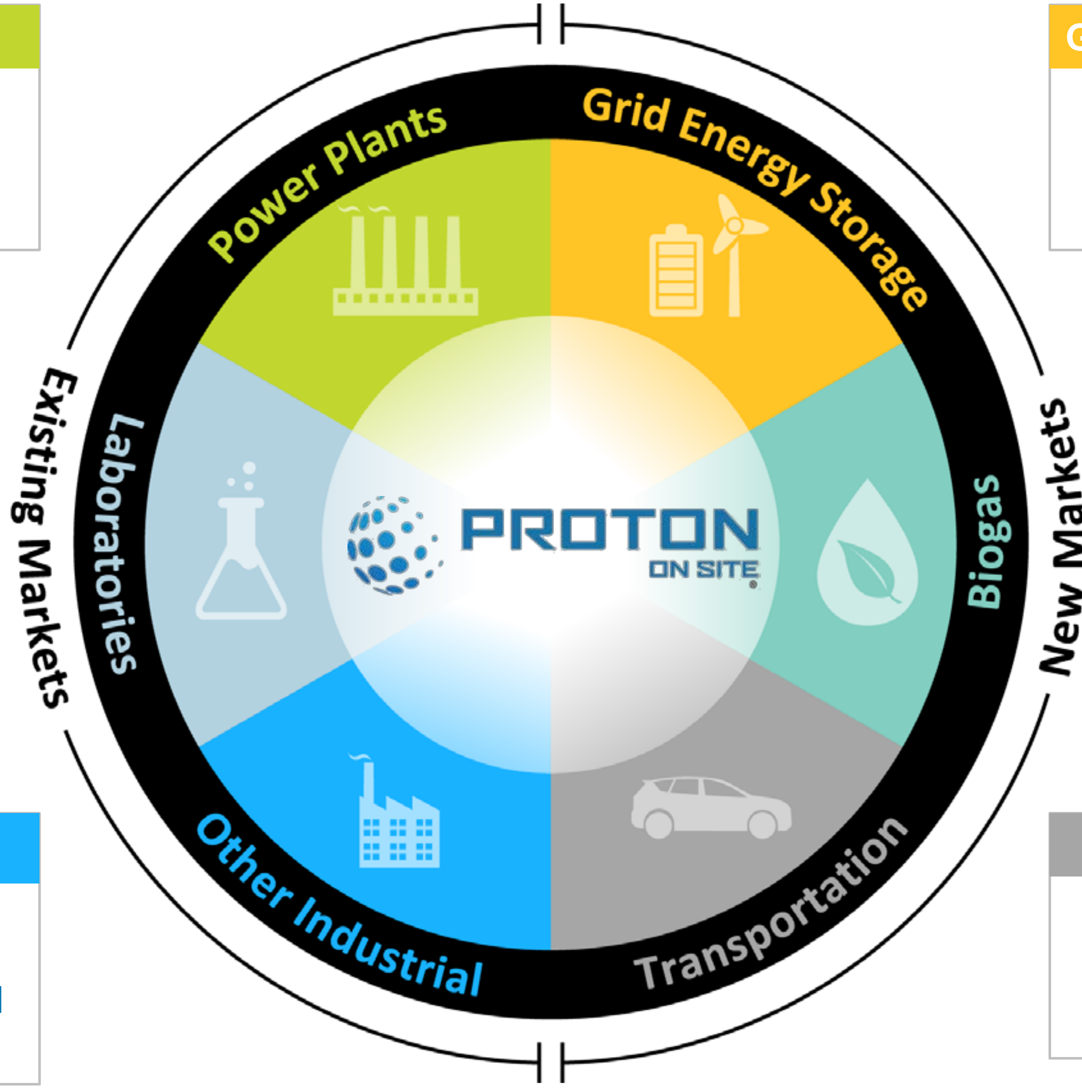
Cooling electric generators

Grid Energy Storage

Storing stranded excess renewable energy

Laboratories

Carrier gas for analytical instrumentation



Biogas

Turning waste CO_2 into methane

Other Industrial

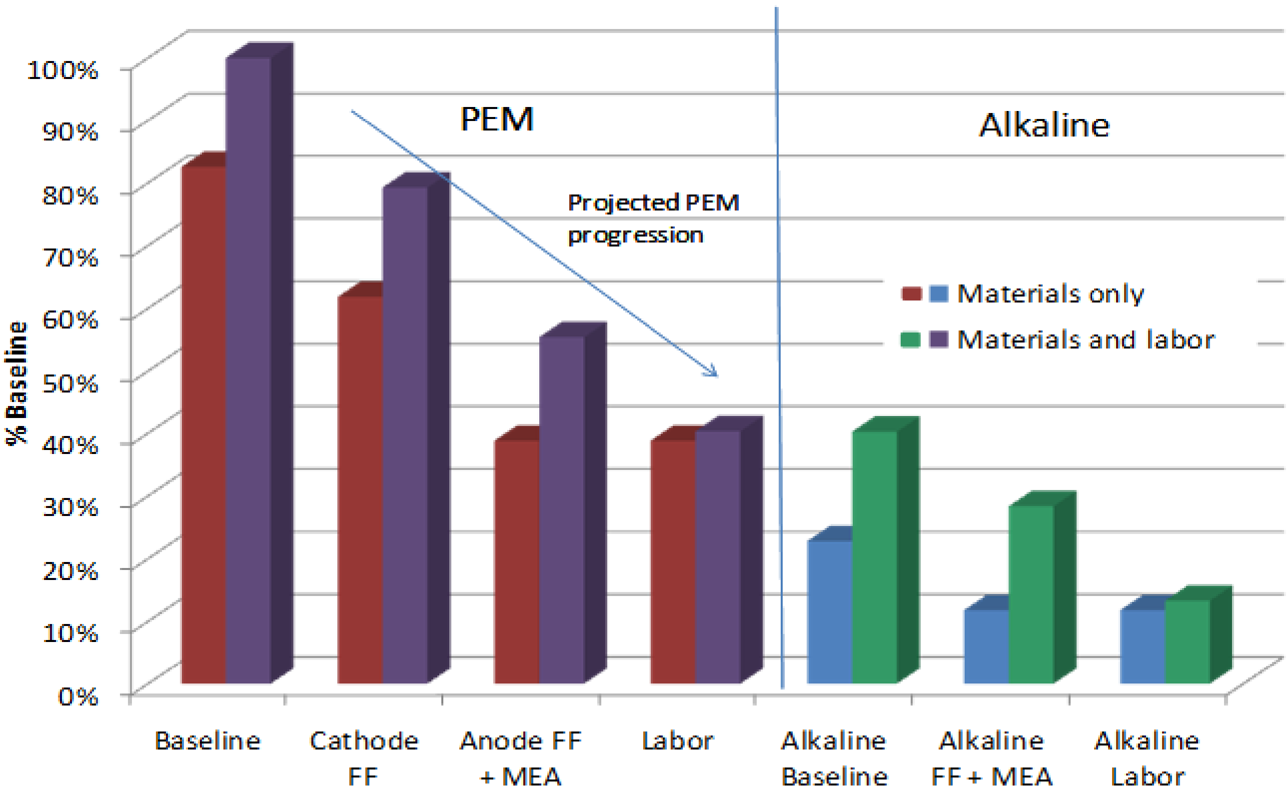
Process gas for semiconductors, heat treatment, and meteorology

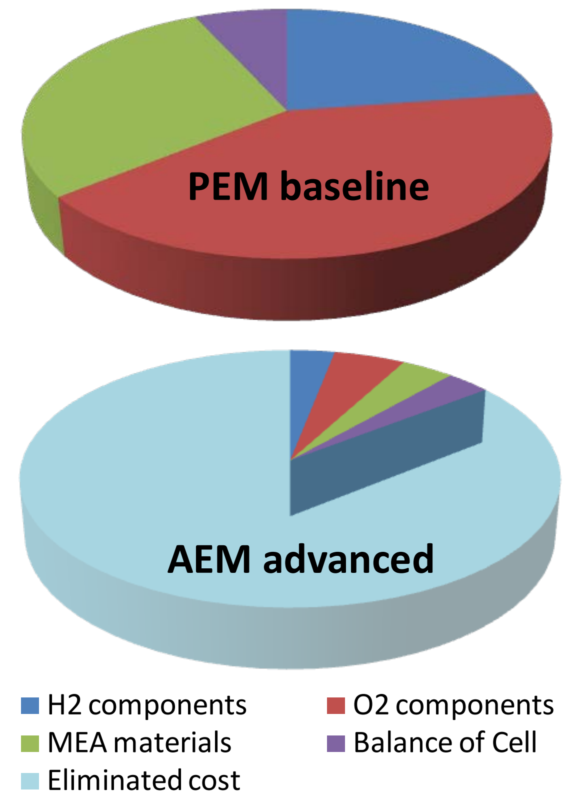
Transportation

Fueling fuel-cell vehicles

Relevance: Problem to be Addressed

- Electrolyzer capital cost and $/kg H_2
- AEM based electrolysis enables the elimination of most expensive cell materials: PGM and valve metals





Relevance: Specific Barriers Addressed

- Develop ex-situ and in-situ stability comparisons to connect ex-situ lab evaluation and in-situ device results
- Increase stability of PPO membranes through the use of cation spacers to decrease benzyl attack
- Optimize water management through tuning of GDL porosities and hydrophobic/hydrophilic properties
- Advance fundamental 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
    - HER overvoltage of less than 200 mV at 20 mA/cm^2
    - OER with overvoltage of less than 320 mV at 20 mA/cm^2
- **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

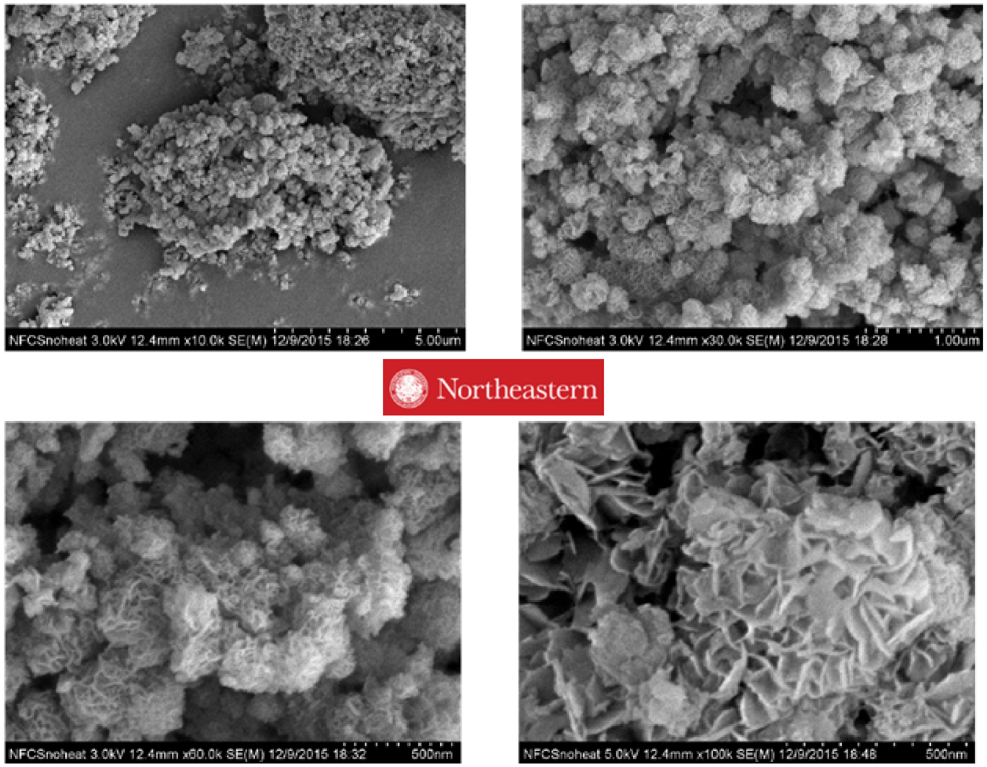
Approach
Task Breakdown

- Task 1.0 Synthesis of HER & OER Catalysts
  - Subtask 1.1 Catalyst Component Identification
  - Subtask 1.2 Refinement of Composition & Micro-structure
  - Subtask 1.3 Synthesis of Single Oxides
  - Subtask 1.4 Synthesis of Spinel Materials
  - Subtask 1.5 Scale-up of SSM Materials
- Task 2.0 Membrane/Ionomer Synthesis
  - Subtask 2.1 Scale-up Benzyl Side Chain AEMs
  - Subtask 2.2 Synthesis Optimization & Scale-up

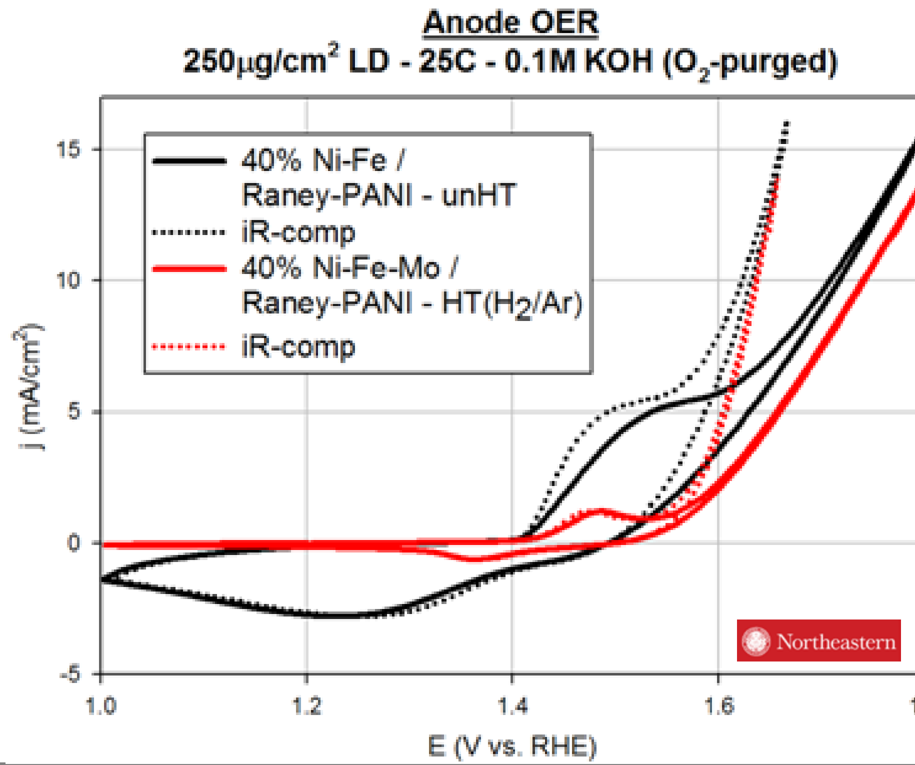
Approach
Task Breakdown

- Task 3.0 Characterization of Catalyst Materials
  - Subtask 3.1 3-Electrode Testing
  - Subtask 3.2 2-Electrode Testing
  - Subtask 3.3 Structural Characterization
- Task 4.0 Characterization of Interfacial Effects
- Task 5.0 Cell Engineering
- Task 6.0 Prototype System & Demonstration

Approach: Catalyst Development



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

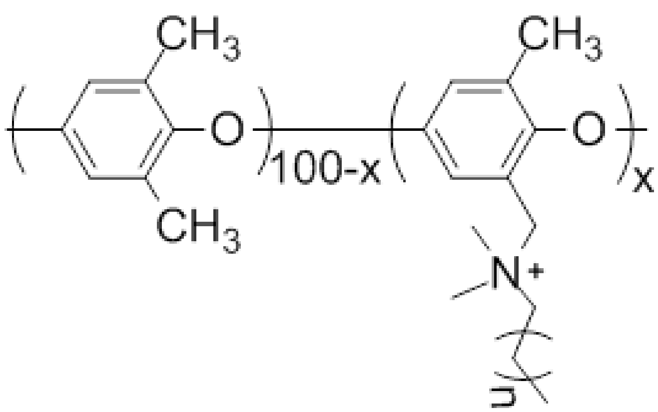


- Support synthesis through SSM method
- HER catalysts based on Ni-TM (TM=Cr, Mo) supported on Raney-Ni, C or SSM
- OER catalysts based on Ni-TM_1-TM_2 (TM=Fe, Mo, Co) oxides on Raney-PANI, or SSM

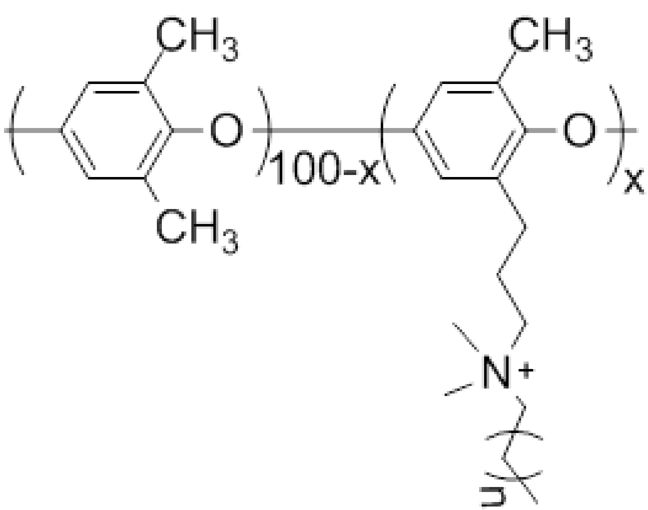
Approach: Membrane and Ionomer

- 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

Side chain benzyl dimethylalkyl ammonium

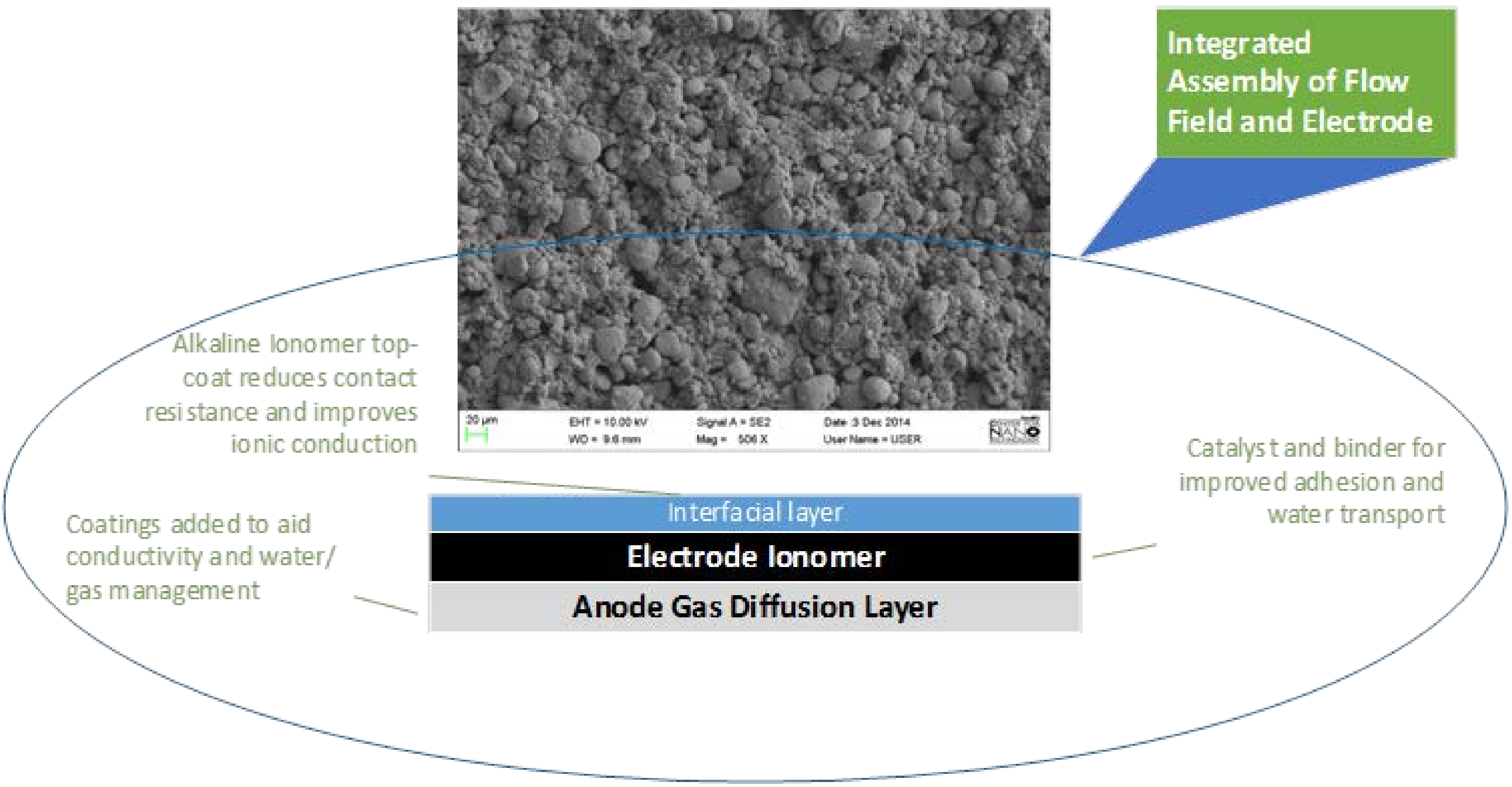


Cation spacer dimethyldialkyl ammonium



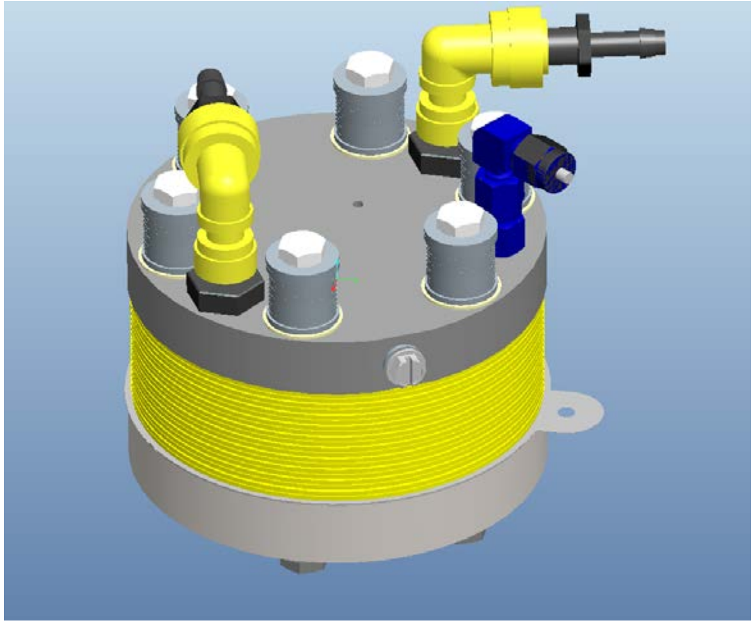
Approach: MEA testing

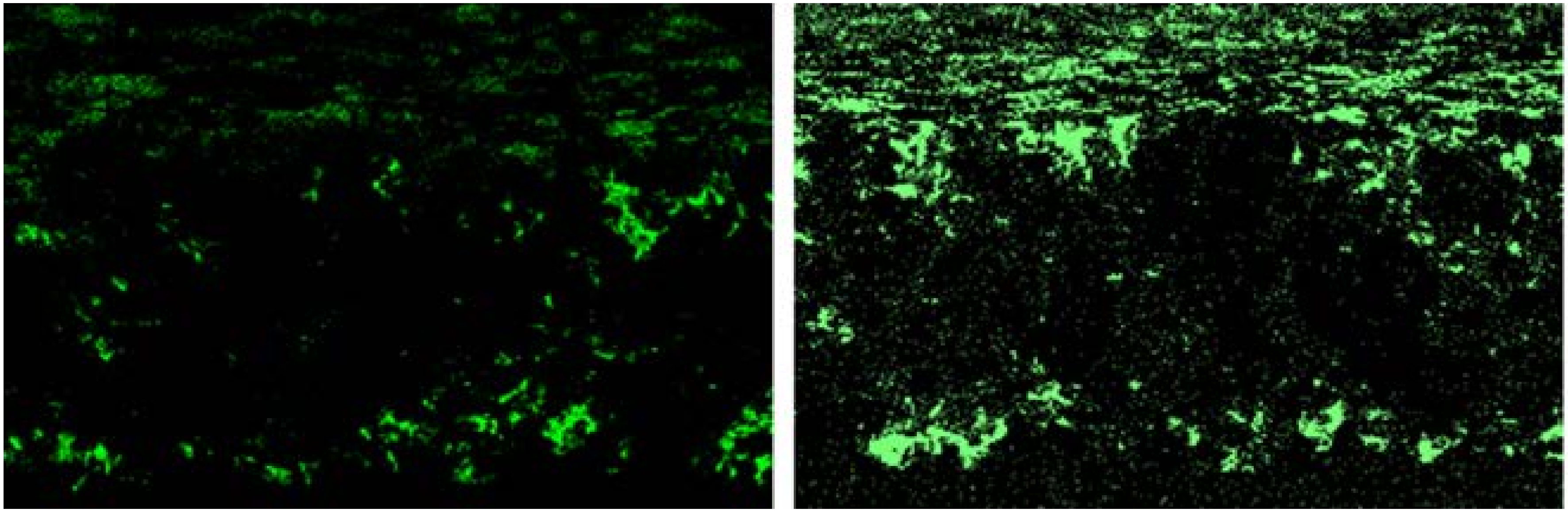
- Gas diffusion electrodes will be fabricated with Penn State ionomers and NEU/UNM catalysts
  - Water management through cell engineering



Approach: AEM Stack Design

- Stack design will incorporate cost-reduced materials compatible with AEM operation.
- Tuning of gas diffusion layers will be a primary objective for stable operation of the AEM-WE

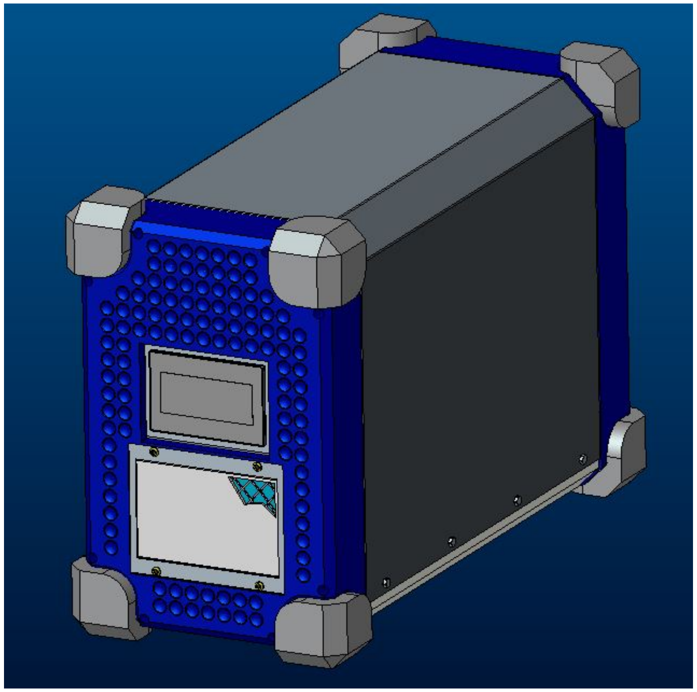




Varying treatment for water management

Approach: AEM System Design

- Water management within the system will be explored.
  - Durability and performance, as a function of water delivery.
  - Cathode versus anode feed of DI H_2O
- System will serve as test station for stack durability tests



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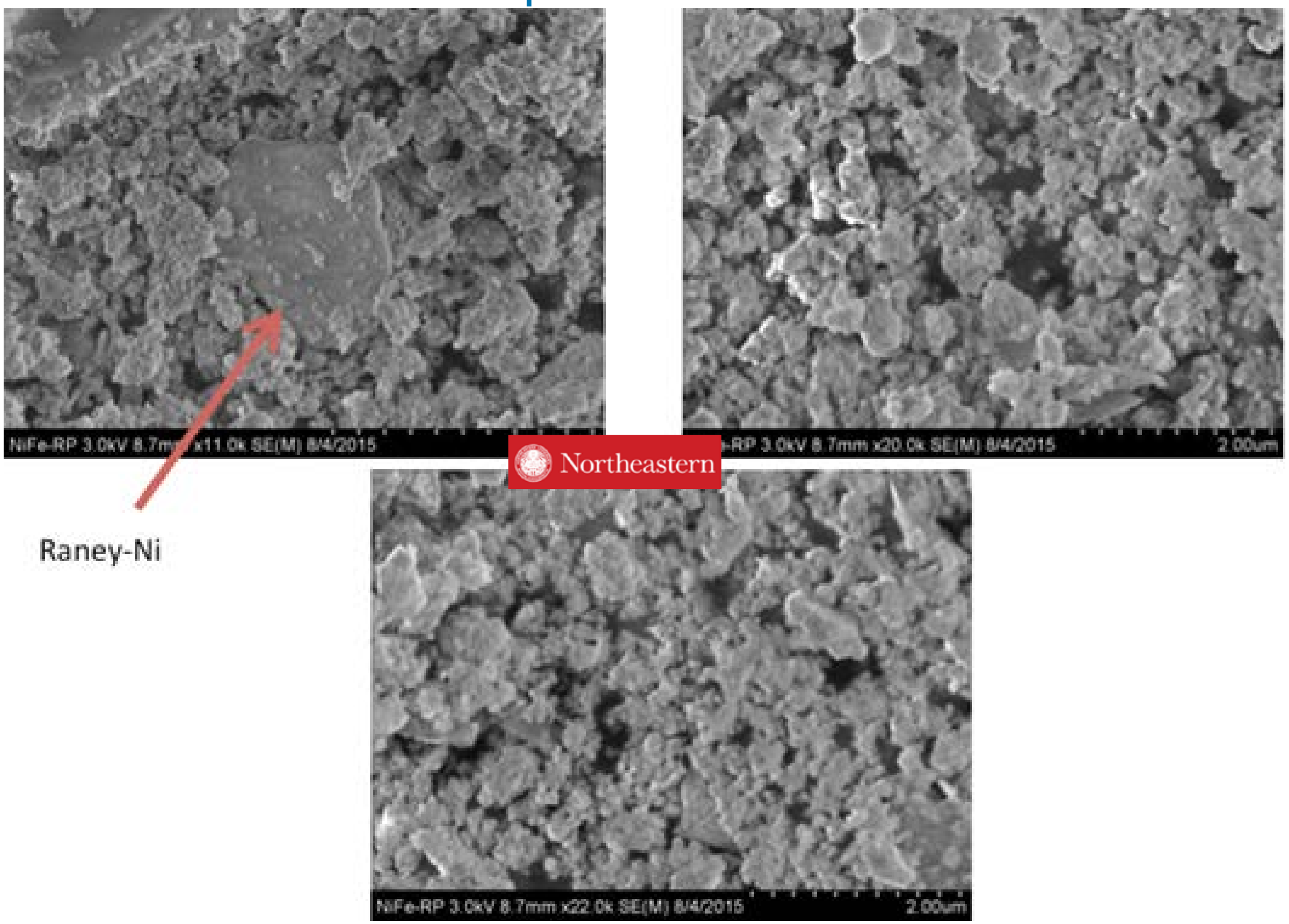
Northeastern

Technical Accomplishments - 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
1: Catalyst Synthesis	**NUCRET**: Synthesize baseline Ni-Mo and Ni-Fe materials	Q1
1: Catalyst Synthesis	**UNM**: achieve single oxide material with equivalent half cell properties to IrO_2	Q2
1: Catalyst Synthesis	**NUCRET:** Identify 3 promising Ni/MeOx cathodes; Identify 3 promising “MMO” (Ni-Fe-Mo/Co) anodes	Q3
3: Catalyst Characterization	**NUCRET**: Demonstrate operation at 500 mA/cm2, <2 V with liquid fuel	Q4
4: Electrode Fabrication and Characterization	**Proton:** Integrate non-PGM catalyst with novel AEM materials	Q5
2: Membrane Synthesis and Characterization	**PSU**: Delivery of materials with PPO benzyl side chain architecture for electrode optimization and cell testing.	Q6
1: Catalyst Synthesis	**UNM:** down select transition metal, precursor type; deliver material to Proton OnSite	Q7
6: Prototype Demonstration	**Proton:** Demonstrate stable operation at 500 mA/cm2, <2 V with 2-electrode configuration	Q8

Technical Accomplishments: OER Catalyst Synthesis - Milestone #1

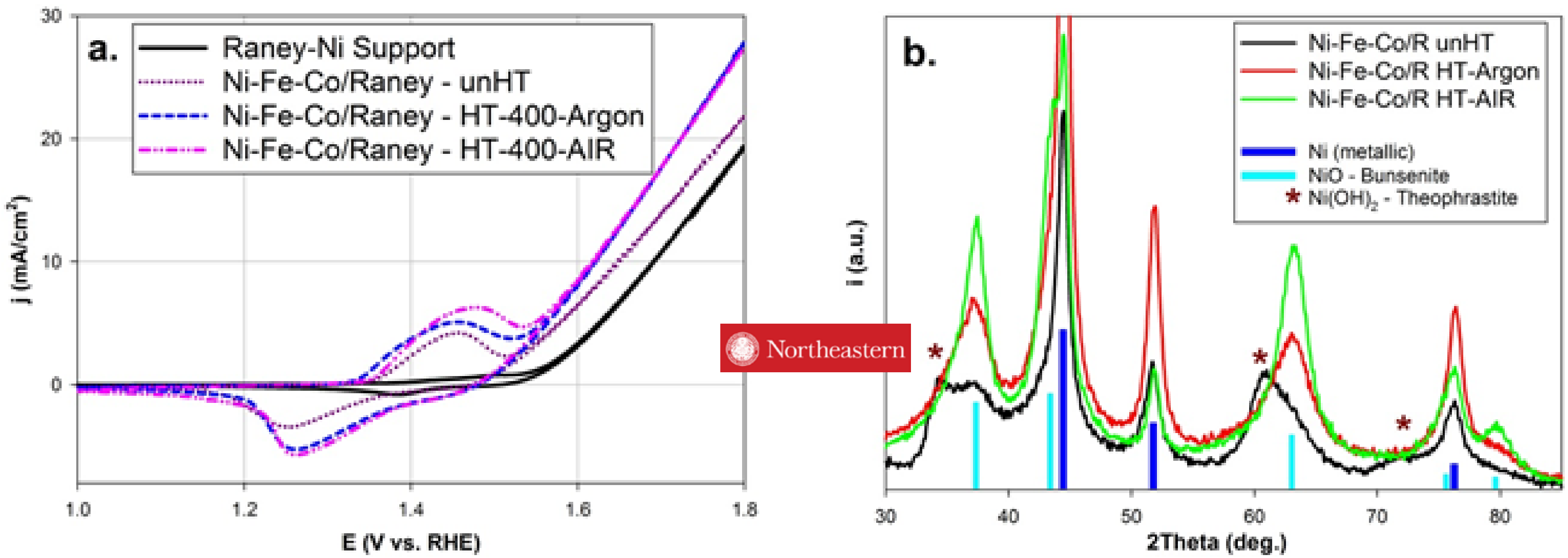
- Synthesized 0.5-1g Ni-Mo & Ni-Fe composite ”MMO” materials
- Confirmed structure & composition via XRD & SEM



SEM images of Ni-Fe/Raney-Ni-PANI

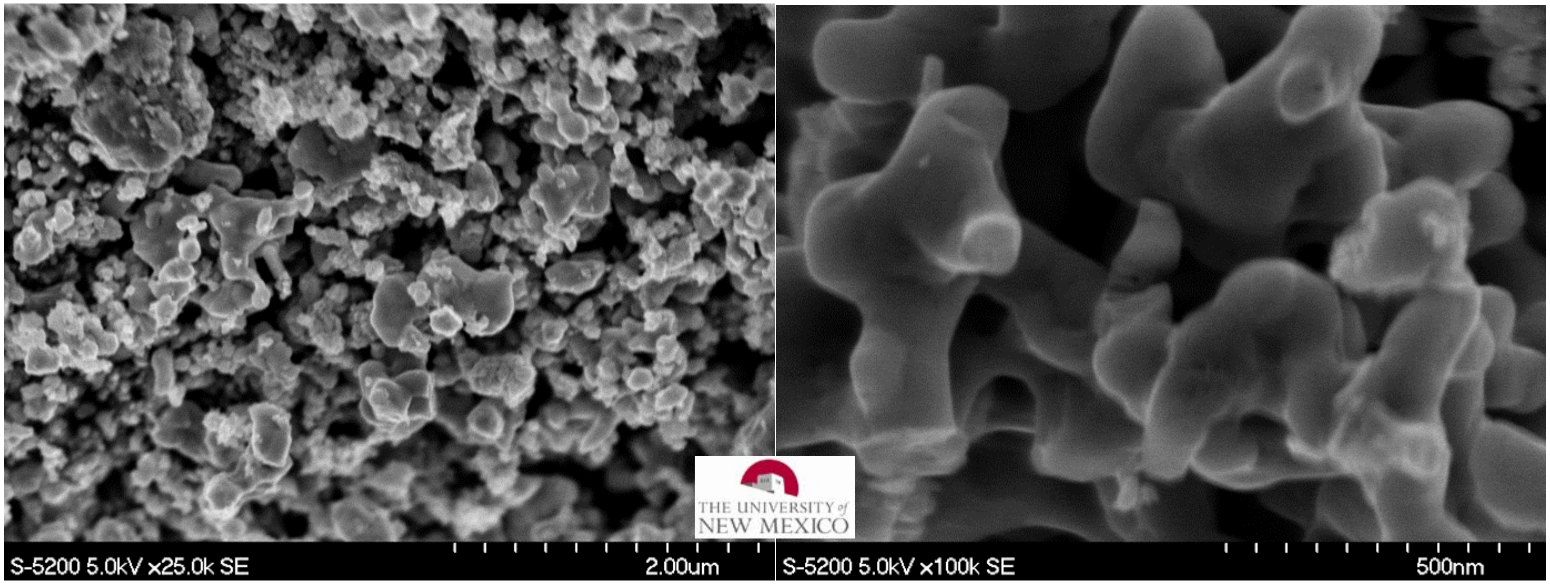
Technical Accomplishments: OER Catalyst Synthesis - Milestone #1

- Synthesis studies indicate annealing conditions affect OER activity in RDE testing in 0.1M KOH
- XRD confirms composition per milestone



Left) CV data showing HT-effects of Ni-Fe-Co on Raney-Ni support
Right) XRD data from Ni-Fe-Co/PANI-Raney

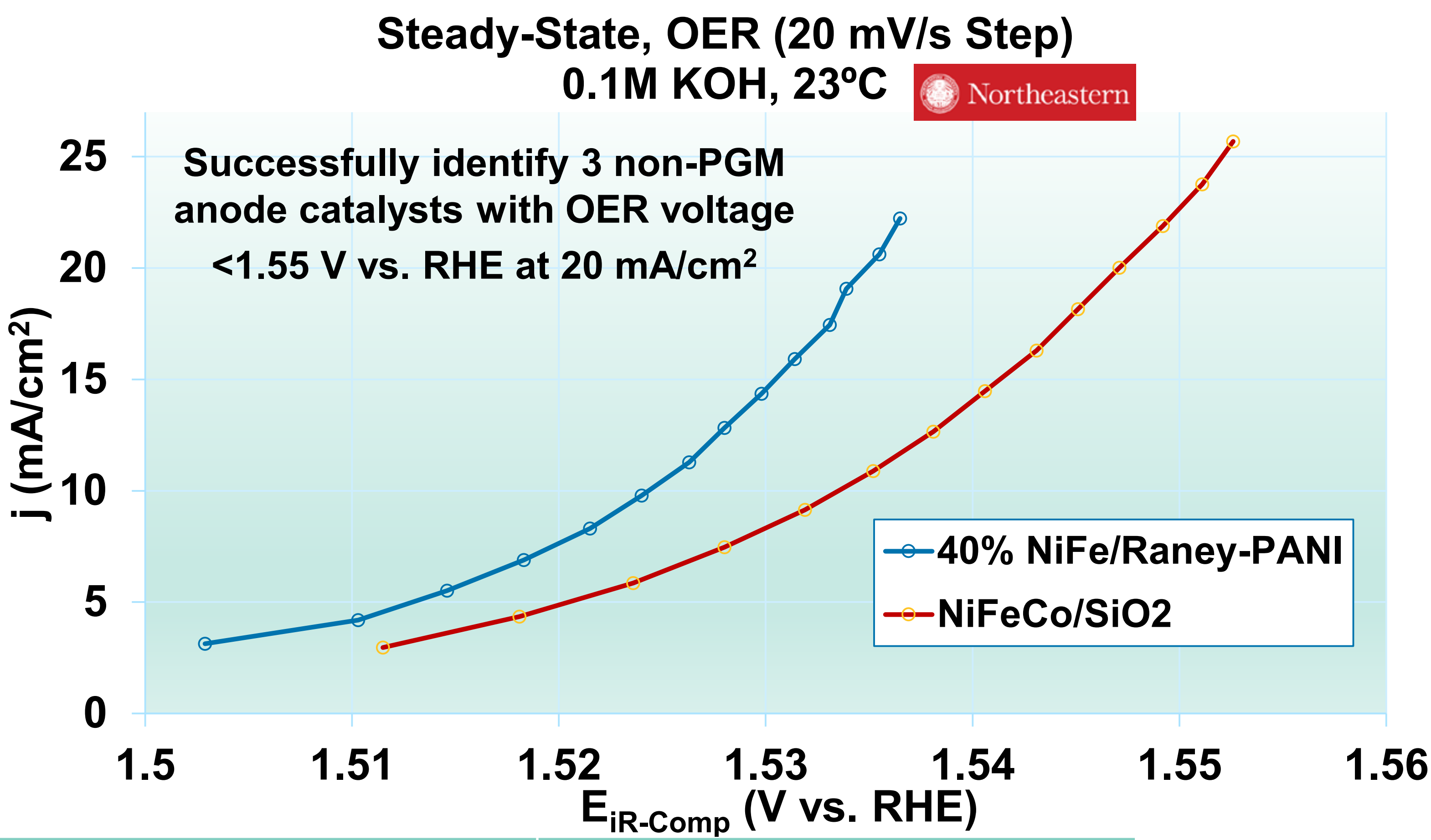
Technical Accomplishments: Support/Catalyst Synthesis - Milestone #2



BET analysis confirmed milestone target of >20 m^2/g

OER Catalyst	Conductivity [S/cm]	Onset Potential [V] vs RHE
NiO	0.00200	1.53
I-22 NiO SSM	0.00308	1.52
I-28 $NiCoO_3$ SSM	0.389	1.54
NiMoCu-II	4.47	1.51
IrOx reference	0.0102	1.43

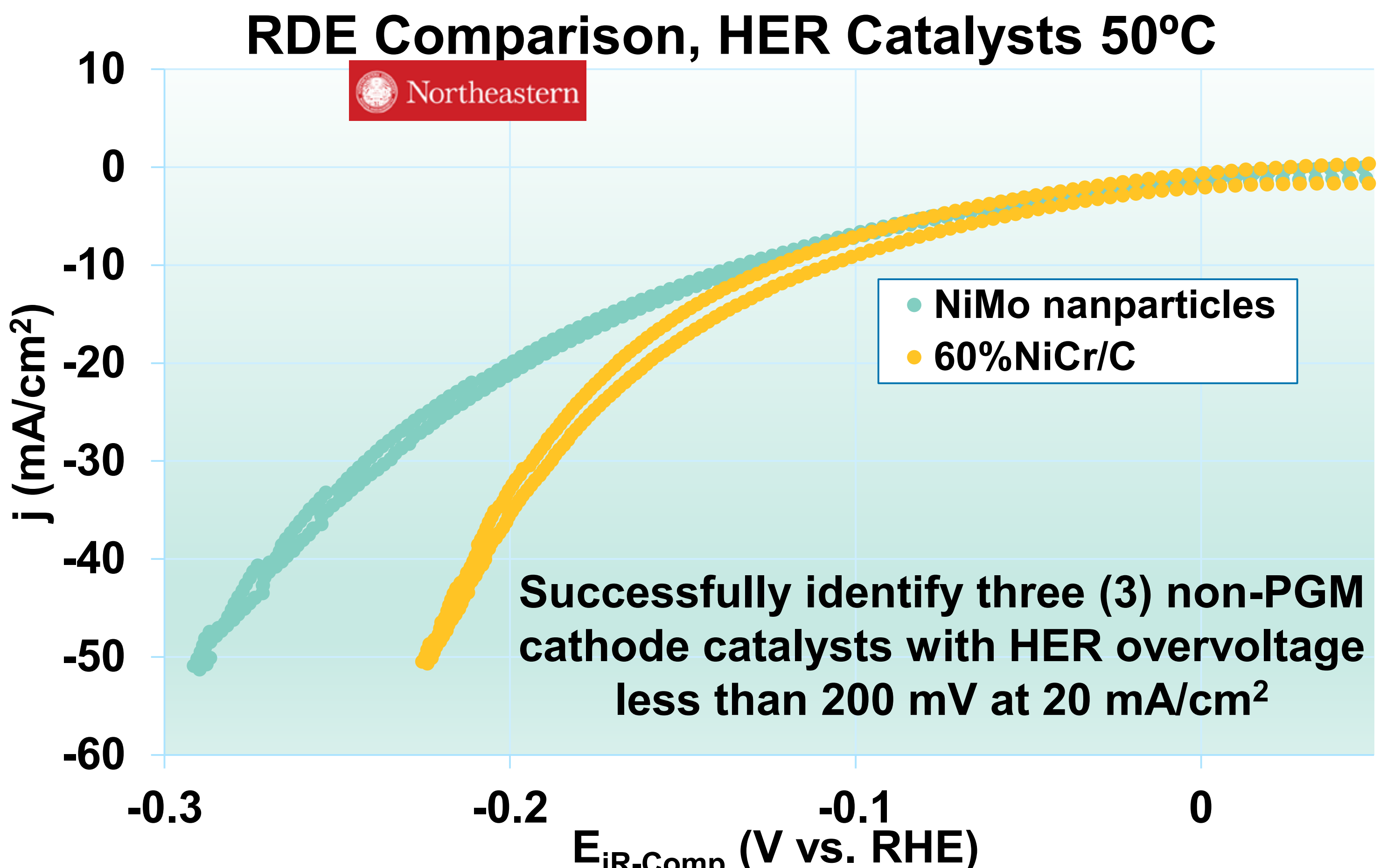
Technical Accomplishments:
OER Catalyst Synthesis - Milestone #3



OER Catalyst	Overvoltage at $20 mA/cm^2$
Ni-Fe-Co/SiO_2	1.546 V
40%Ni-Fe/Raney-PANI*	1.534 V
40%Ni-Fe-Co/Raney-PANI	1.547 V

* Sample selected for in-cell testing

Technical Accomplishments: HER Catalyst Synthesis - Milestone #3



HER Catalyst	Overvoltage at 20mA/cm^2
Ni-Mo	193.9 mV
60% Ni-Cr/Ketjen 600*	160.2 mV
20% Ni/50% Vox/C	199.8 mV

* Sample selected for in-cell testing

Technical Accomplishments: OER MEA testing

- Down-selection of OER catalysts
  - Based on 3-electrode testing and catalyst materials performance: BET surface area, conductivity, OER onset potentials

Down-selected in milestone

NiMoCo - unsupported

NiFeCo – unsupported

NiFe Raney PANI

→ **All three (3) samples promoted to MEA tests**

Technical Accomplishments: HER MEA testing

- Down-selection of HER catalysts
  - Based on 3-electrode testing and catalyst materials performance: BET surface area, conductivity, HER onset potentials

Down-selected in milestone

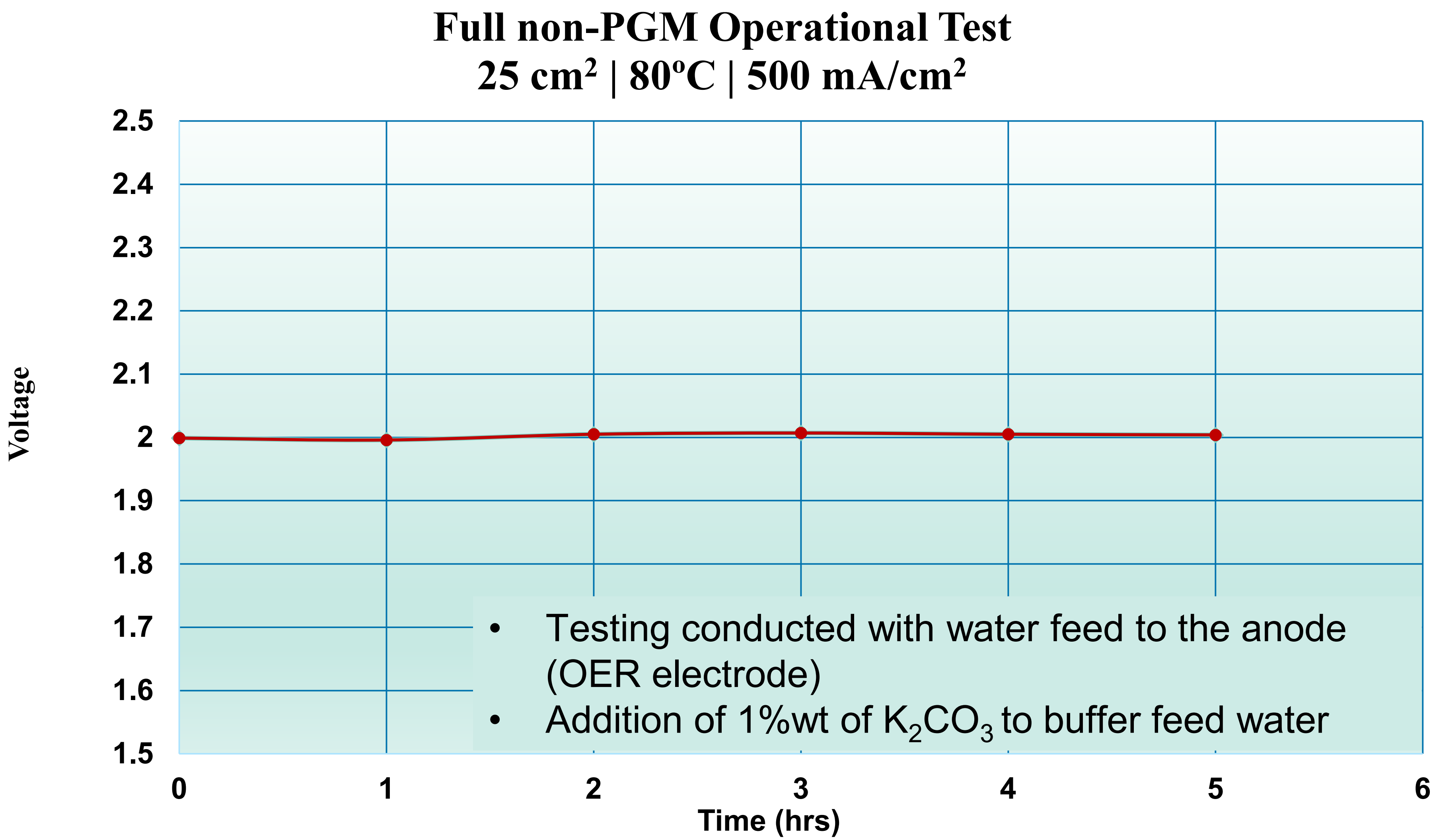
Ni-Mo
60% Ni-Cr/Ketjen 600
20% Ni/50% Vox/C

→

Operationally Tested In-Cell

60% Ni-Cr/Ketjen 600

Technical Accomplishments
Short Term Testing: Milestone #4



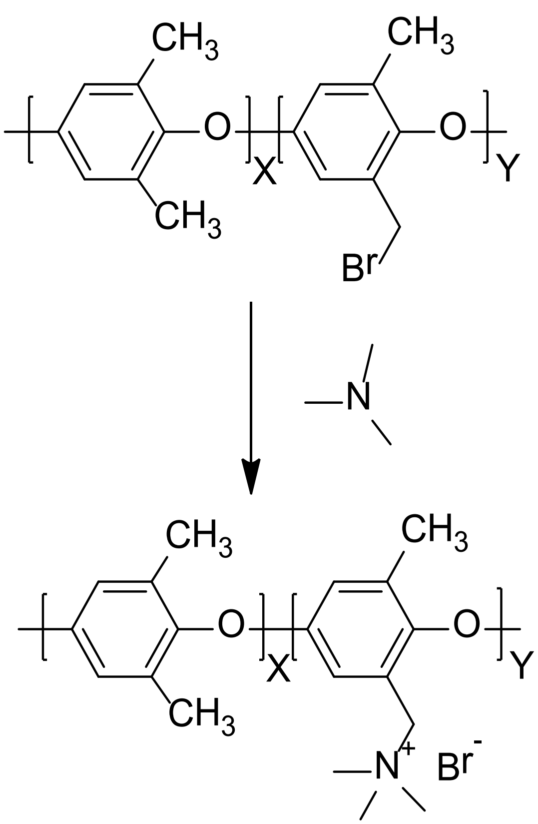
- Testing conducted with water feed to the anode (OER electrode)
- Addition of 1%wt of K_2CO_3 to buffer feed water

Technical Accomplishments: Membrane Synthesis

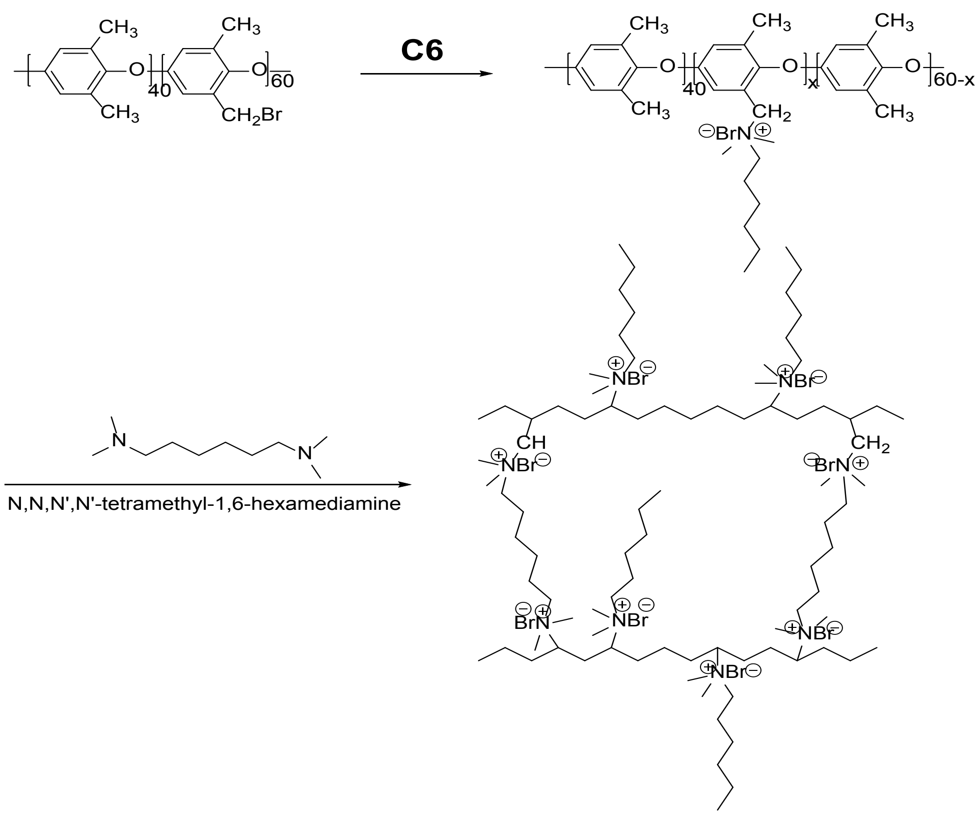
Gen 1: Non-cross-linked BTMA PPO AEMs show poor solvent resistance during processing at Proton.

Gen 2: New samples incorporate cross-linking to stabilize the PPO backbone structure.

BTMA PPO



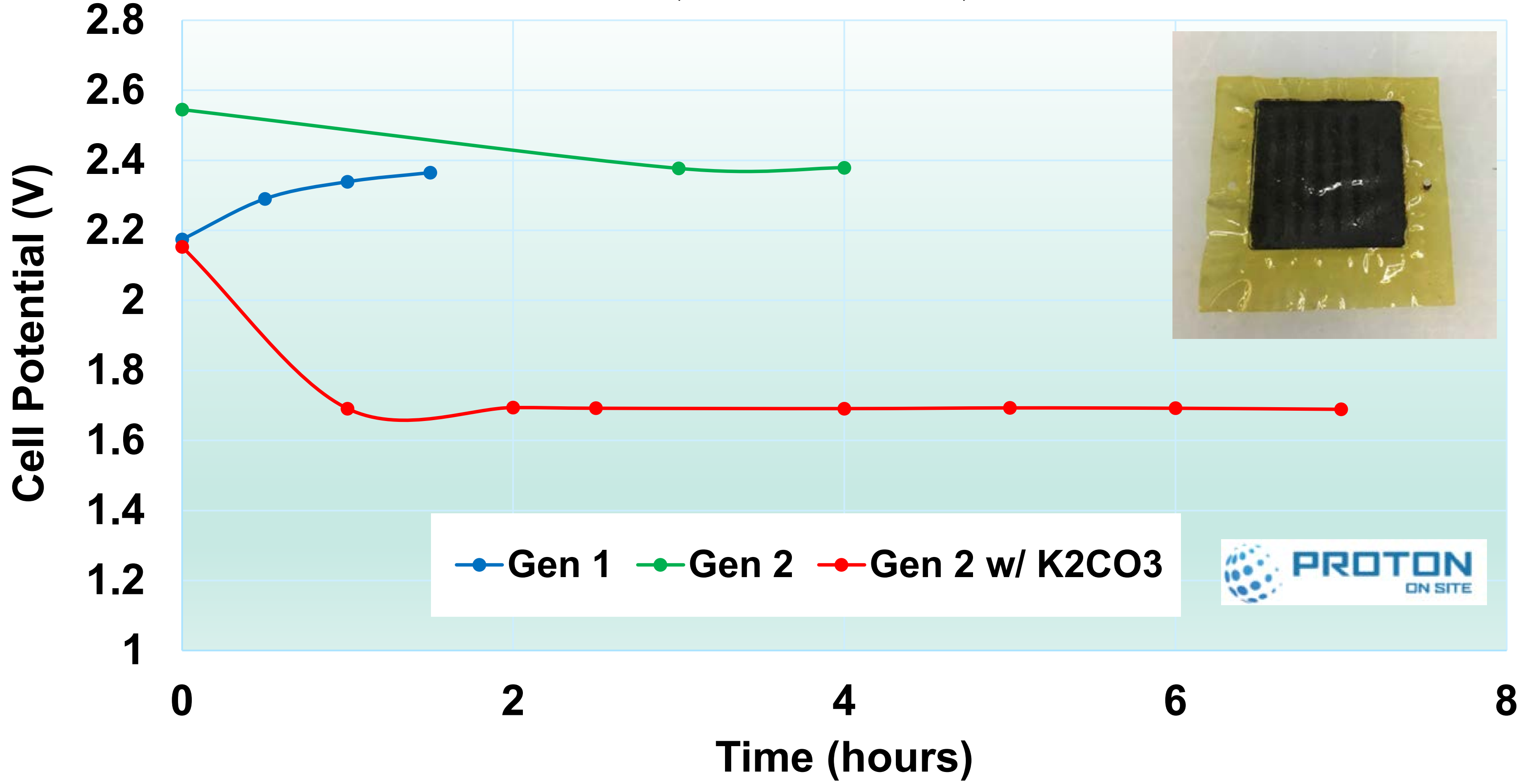
C6 x-link PPO



Technical Accomplishments: PPO membrane MEA testing

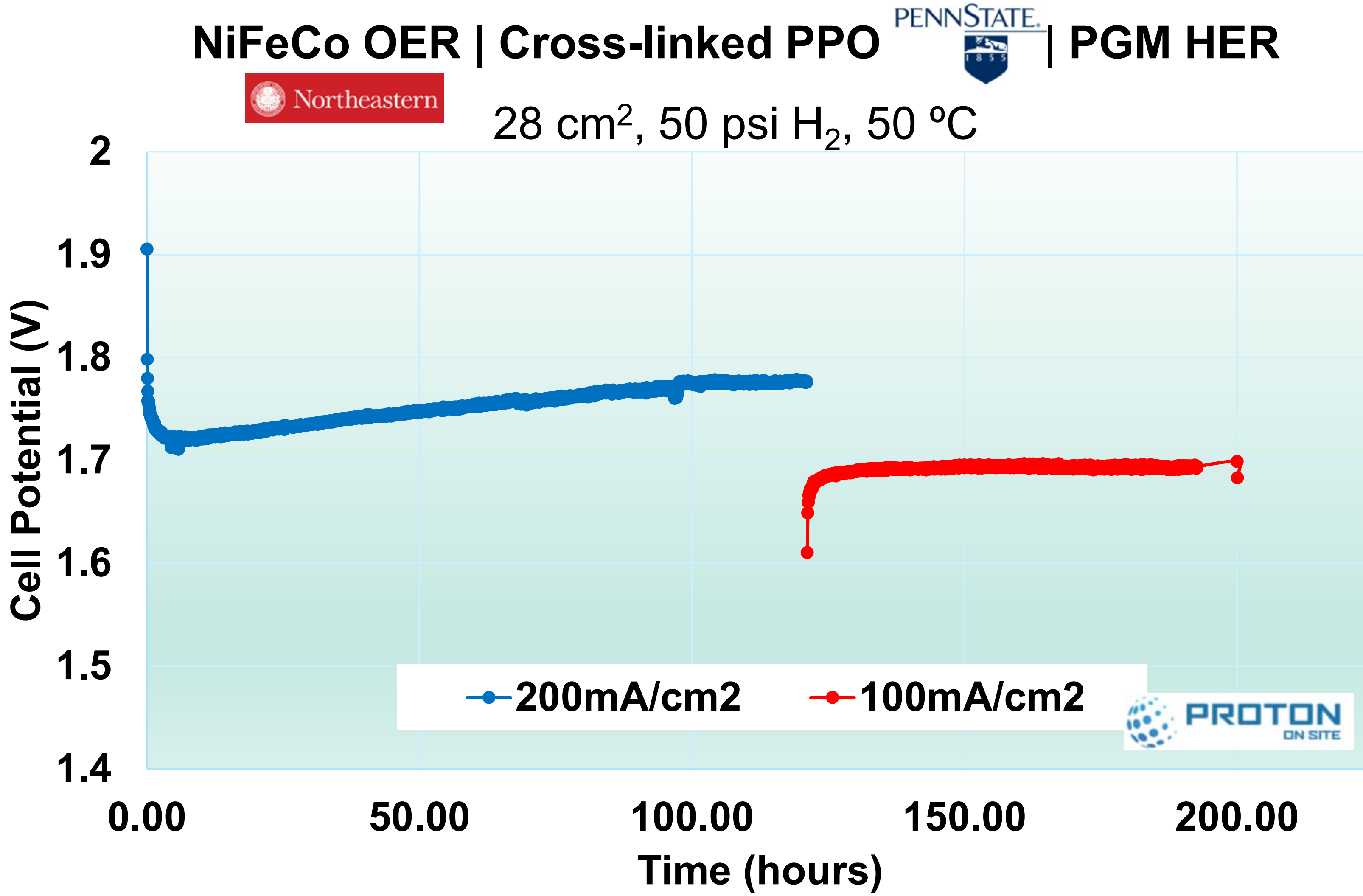
PGM OER | **PPO** | PGM HER

25 cm^2, 200 mA/cm^2, 50°C



Sample Gen 2 w/K_2CO_3 remained intact after disassembly

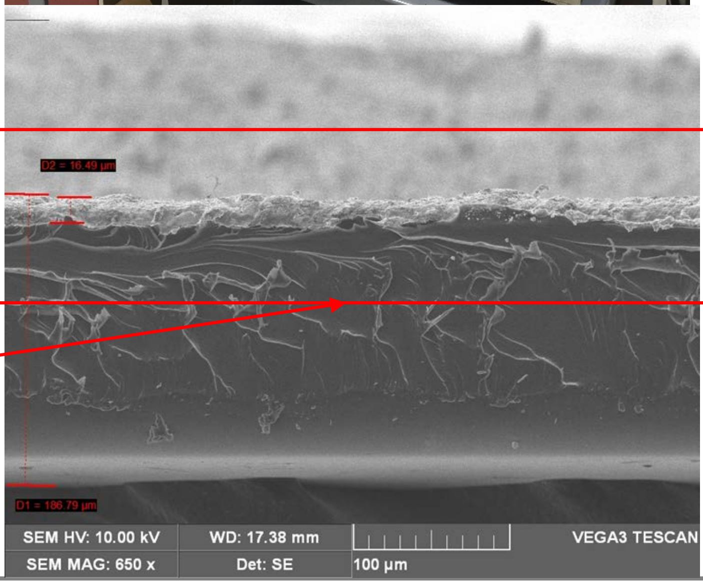
Technical Accomplishments: Non-PGM and PPO MEA Testing



Carbonate added to system to stabilize MEA degradation

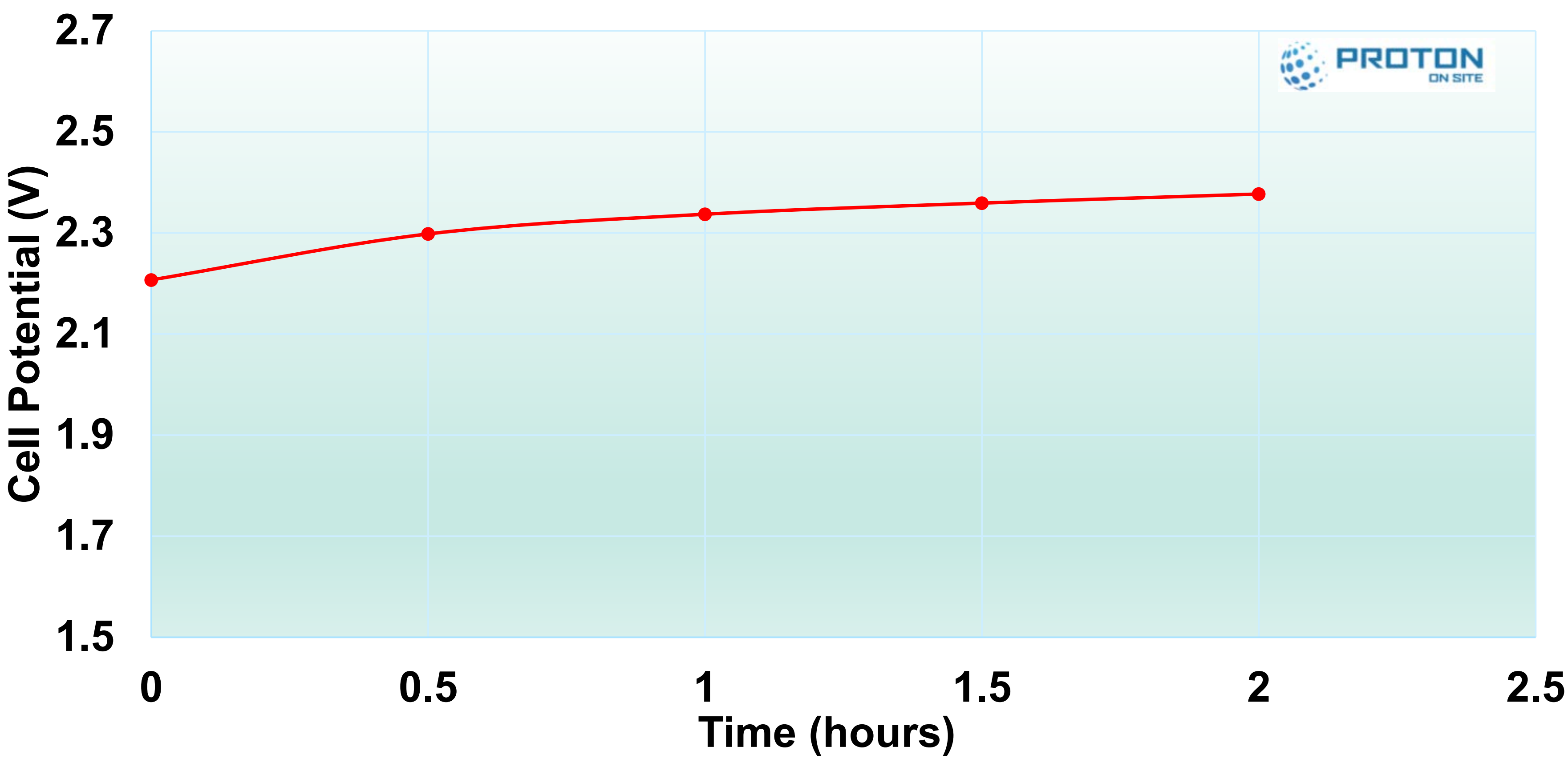
Technical Accomplishments: CCM Manufacture

- Direct deposition process for CCM fabrication initiated
  - Maintains low temperature process
  - No mechanical pressure for attachment
- Anode electrode feasibility demonstrated
  - Cross-section of intact layer shown at right



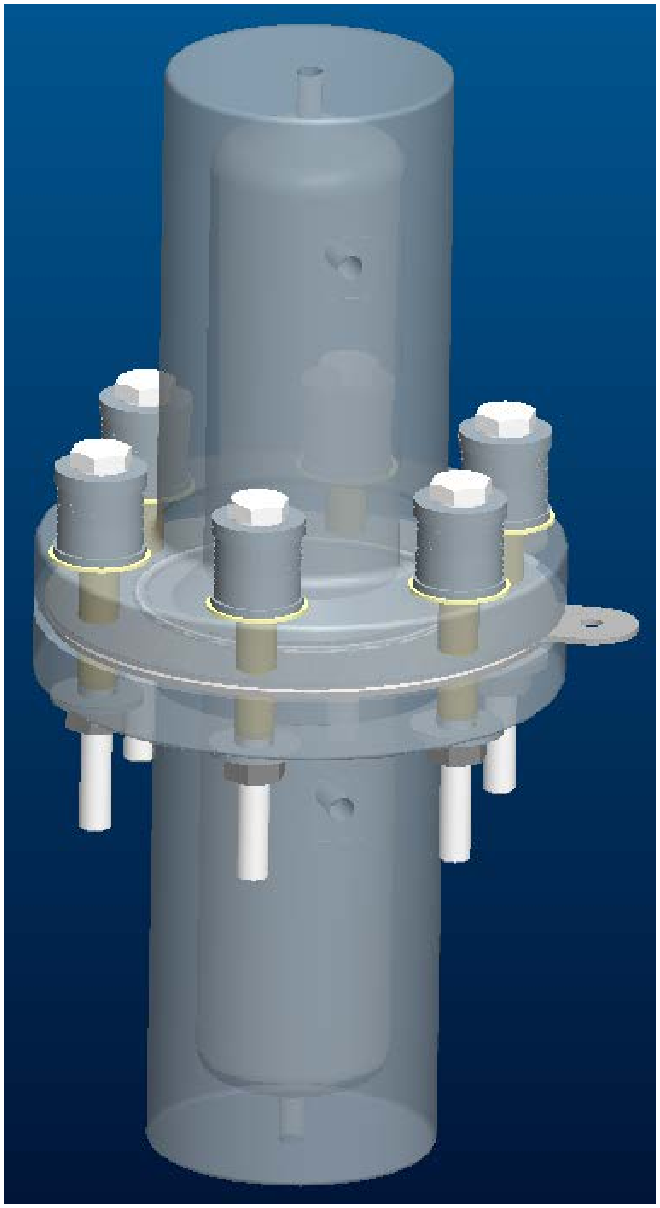
Technical Accomplishments: CCM Manufacture

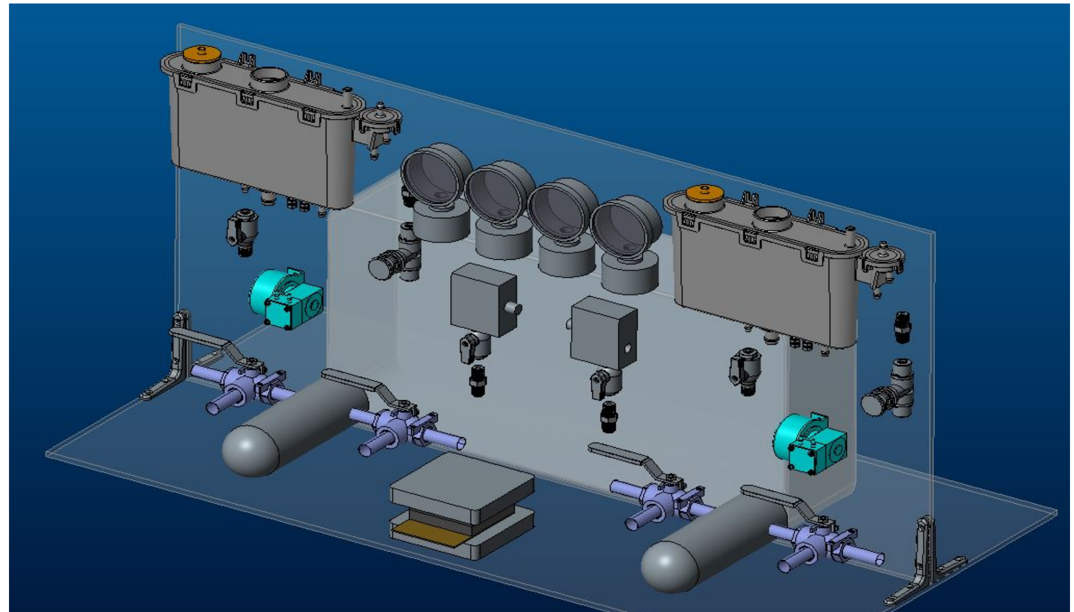
PGM HER | commercial membrane | **Direct Deposition PGM OER CCM**
25 cm^2, 500 mA/cm^2, 50 °C

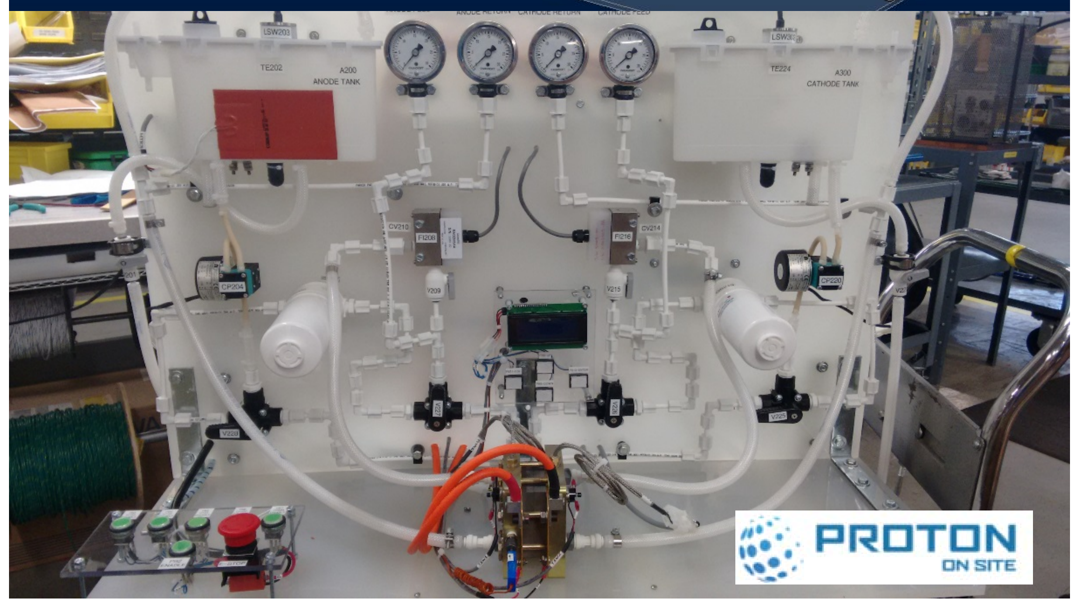


- Operation conducted at increased current density to test adhesion
- Stability improving at end of test and electrode intact after teardown

Technical Accomplishments: Water Transport and System Concept







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)

Future Work

- Catalyst
  - Use of sacrificial supports to synthesize un-supported mixed oxides or perovskite materials for OER
  - Demonstrate operation of non-PGM HER & OER catalysts at 500 mA/cm^2, < 2 V
  - Investigate catalyst – ionomer/solution interfaces
- Membrane and Ionomer
  - Synthesize membrane materials with PPO benzyl side chain architecture and OH- conductivity > 25 mS/cm
  - Incorporate mechanical reinforcement to improve durability
  - Investigate water transport rates vs. pressure
- Cell and System Design
  - Tune hydrophobicity, porosity, and geometry of GDLs
  - Investigate alternate modes of water feed
  - Demonstrate 500 hrs of operation at 500 mA/cm^2, <2 V

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