PROTON
THE LEADER IN ON SITE GAS GENERATION.

Economic Production of Hydrogen through the Development of Novel, High Efficiency Electrocatalysts for Alkaline Membrane Electrolysis

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Organization: Proton OnSite

Date: June 7th, 2017

Project ID: PD147

DE-SC0007574

Overview

Timeline

- Phase IIB Start: 11 April 2016
- Phase IIB End: 10 April 2018
- 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 $/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

Budget

- Current phase project funding
  - DOE share: $1,000,000
- Current funds spent*
  - DOE share: $432,969

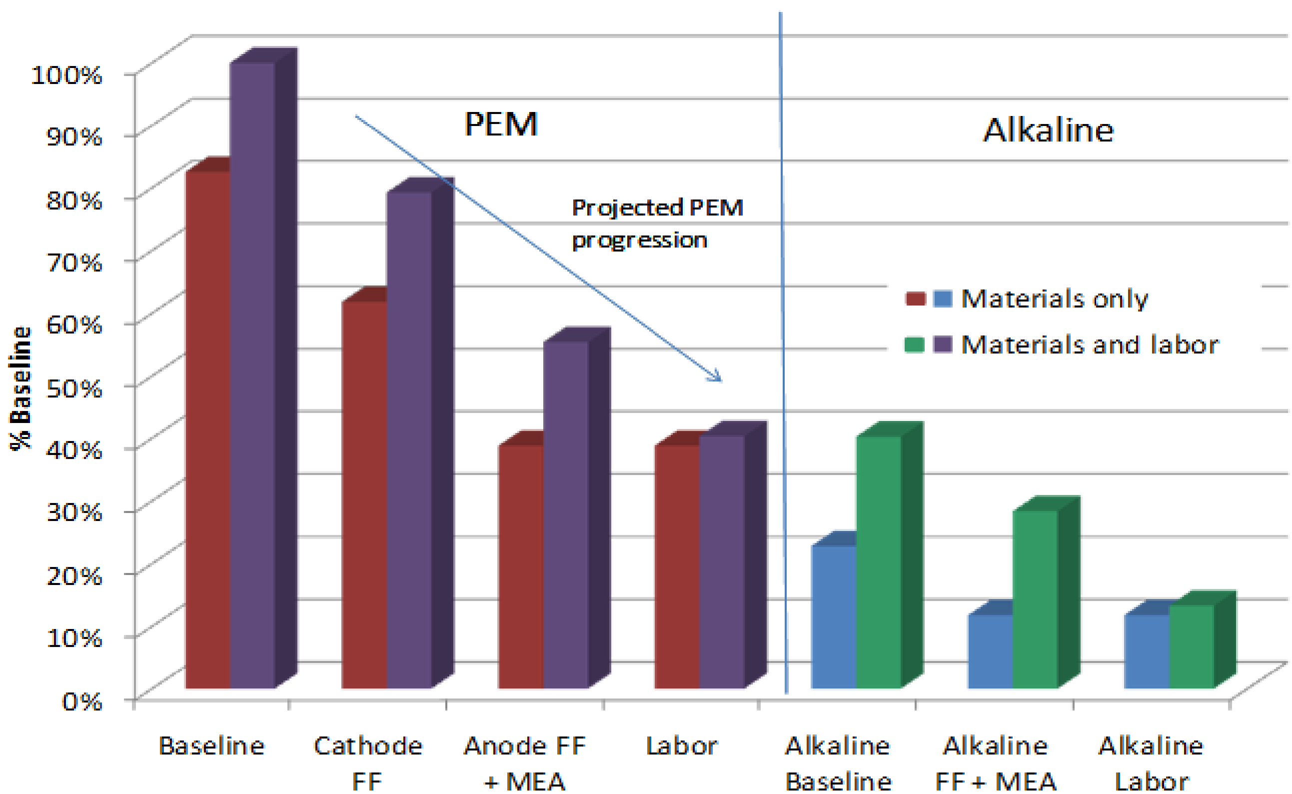
**as of 4/1/17*

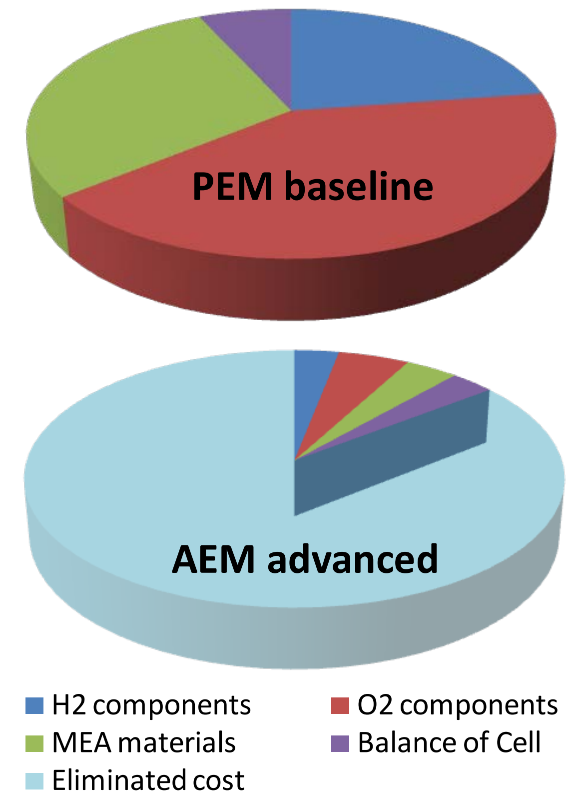
Partners

- Georgia Tech
- Pajarito Powder
- Washington University

Relevance: Problem to be Addressed

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





Relevance: Specific Barriers Addressed

Scale-up and Manufacture Anode Catalysts (**Pajarito Powder and Washington University**)

Develop Improved Stable Anode Ionomer Materials (**Georgia Tech and Washington University**)

Integrate Scaled-up Anode Catalysts and Down-Selected Ionomers into Gas Diffusion Electrodes (**Proton**)

Verify Laboratory Scale System and Stack, for Delivery of High Purity Hydrogen (**Proton**)

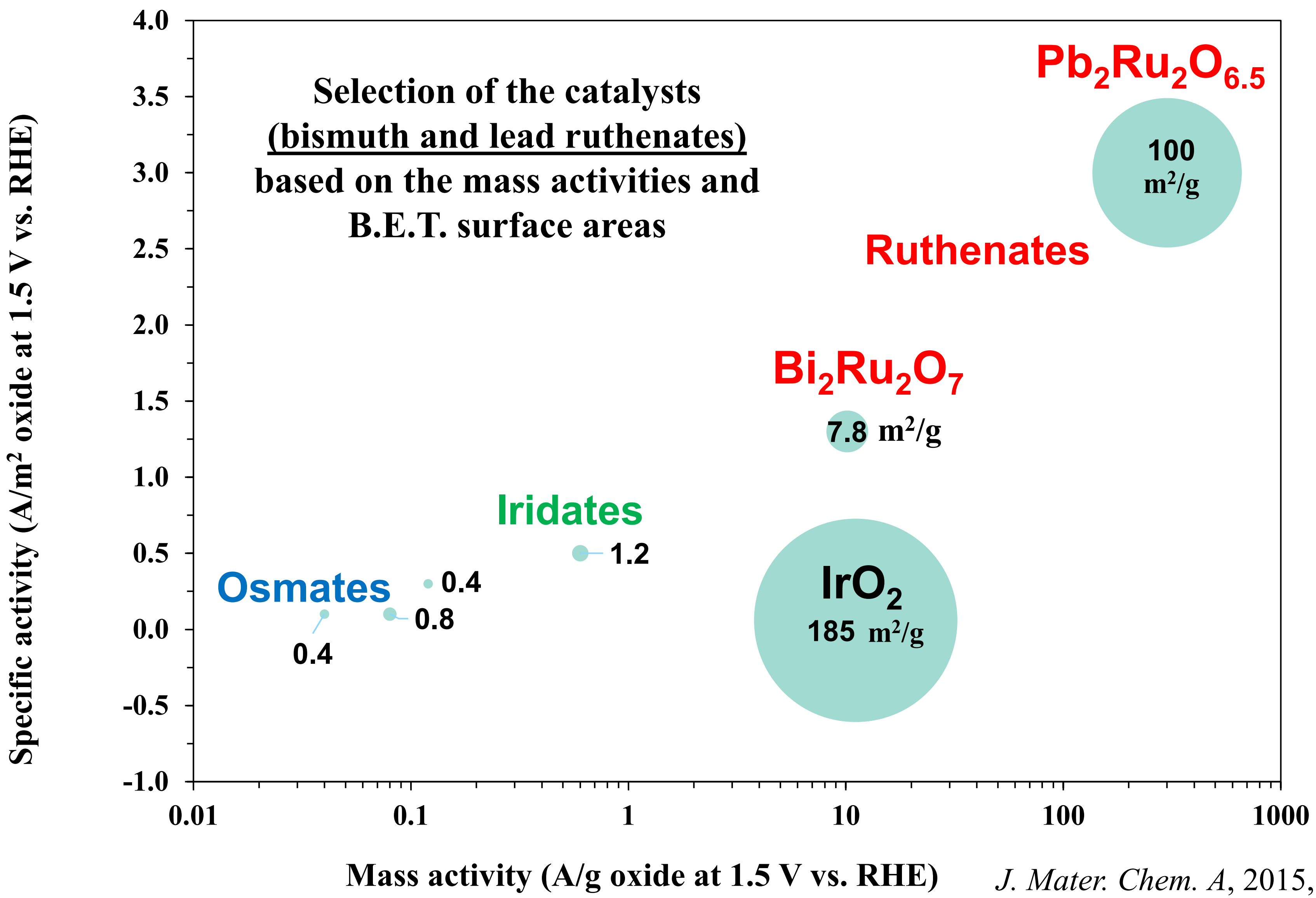
Approach: AEM Electrolysis

- **Catalyst**:
  - *Goal*: Refine lead ruthenate catalysts synthesis
    - *Achieve technology transfer to commercial facility*
    - *Scale-up to 100g batches and evaluate cost impact*
- **Ionomer Dispersion**:
  - *Goal: Baseline commercial materials and optimize ionomers in electrolysis mode*
    - *Improve stability through NMR analysis and bench operation*
- **Cell Stack and System Design**:
  - *Goal: Design and build 10-12 cell prototype system capable of AEM operation for lab markets*
    - *Integrate catalyst and ionomer into membrane electrode assembly*
    - *Design & build prototype system for 500 mA/cm^2 operation*

Approach
Task Breakdown

Task #	Task Description	Subtask	Subtask Description	Status
1.0	**Anode Catalyst Refinement and Commercialization**	*1.1*	Down-selection and Optimization of Anode Catalyst Synthesis	90%
		1.2	Anode Catalyst Refinement	75%
		1.3	Technology Transfer and Manufacturing Optimization	10%
		1.4	Batch Scale-up and Large Scale Manufacturing Study	0%
2.0	**Ionomer Integration and Down-select**	*2.1*	Ionomer Down-select	90%
		2.2	Ionomer-Catalyst Integration and Qualification	10%
3.0	**MEA Optimization and Characterization**	*3.1*	Component Degradation Characterizations	90%
		3.2	Accelerated Stress Testing	0%
		3.3	MEA Optimization	25%
4.0	**AEM Prototype Design and Verification**	*4.1*	12-14 Cell Stack Design and Verification	30%
		4.2	System Design	20%
		4.3	Prototype Demonstration	0%
5.0	**Product Release**			10%
6.0	**Cost Analysis and Program Management**			50%

Approach: Catalyst Selection



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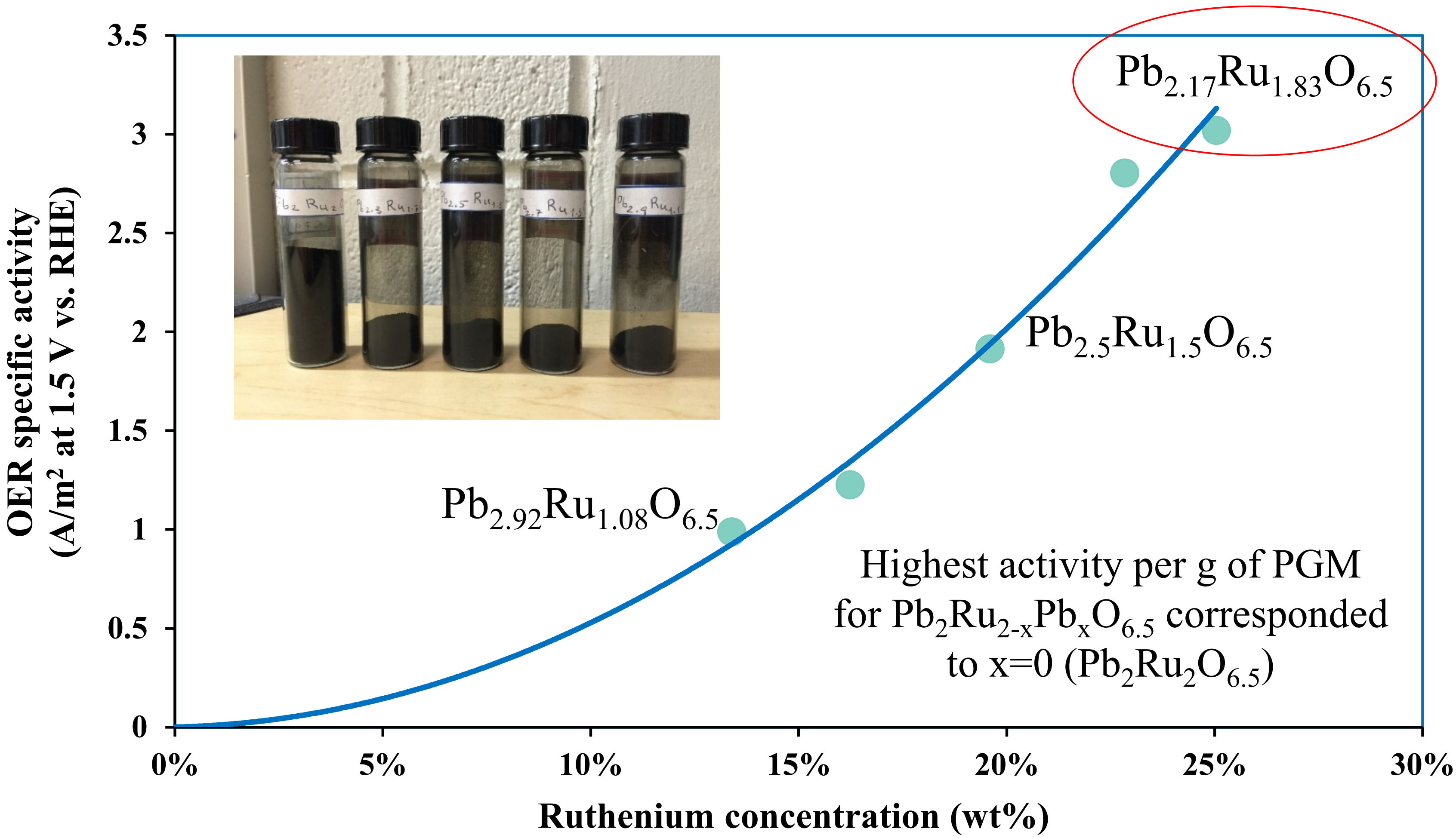
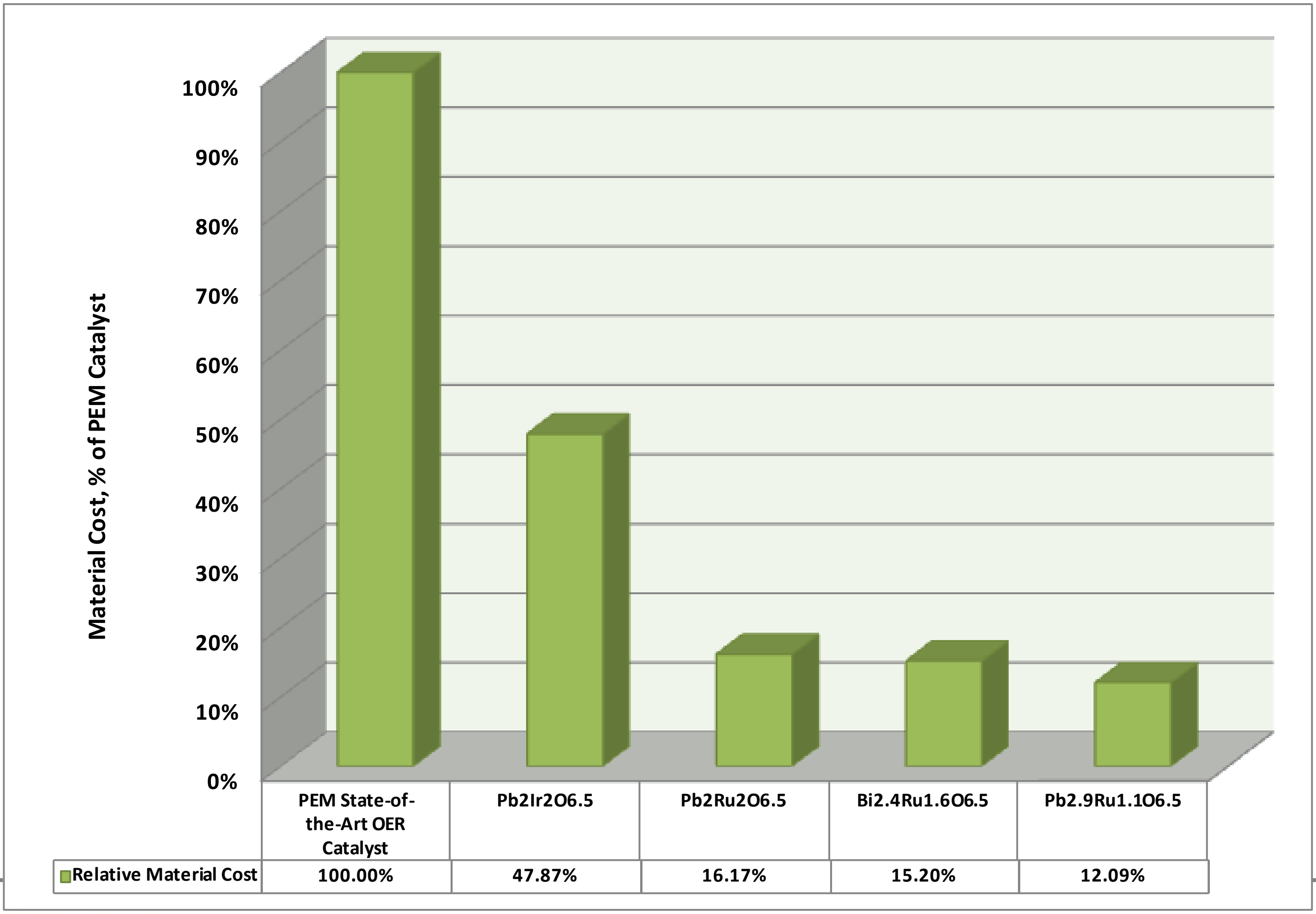
Approach: Catalyst Refinement



- Evaluate ratios of $A_2B_{2-x}A_xO_{7-y}$; A= Pb , B= Ru
- Refinement through PGM (Ru) manipulation
- Selection of highest activity per g of PGM for following stages of the project

Approach: Impact on Cost

- >80% material cost reduction over baseline OER catalyst
  - Optimum compositions of lead and bismuth ruthenates
  - Better utilization achieved with a more effective GDE structure
  - Cost reduced flow fields moving from Ti to stainless (>50% reduction)



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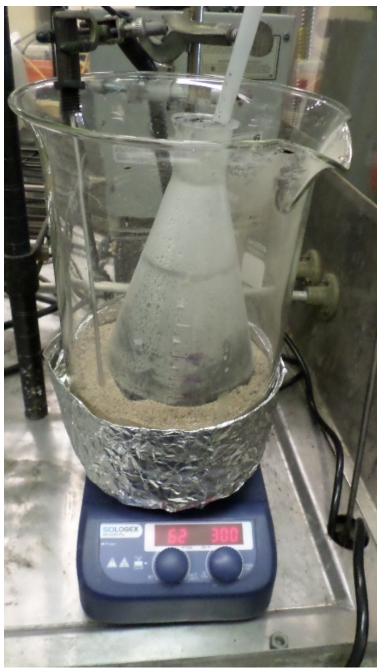
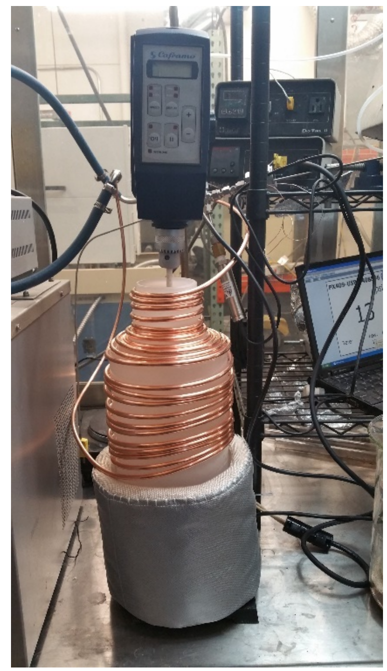
Approach: Catalyst Tech Transfer

- Pajarito Powder to work with Washington University on synthesis hand-off
- Verification of process transfer through instrumental analysis (XRD, BET, RDE)
- Operational testing at Proton
- On-site audits planned by Washington University
- Refinement of process will lead to 50 gram scaled up batch process
- Cost analysis and full-scale testing at Proton



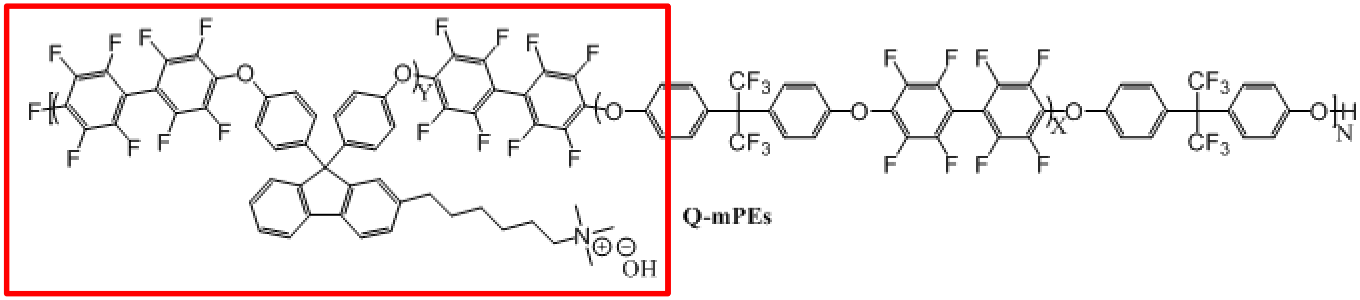
1L flask, ~5g
$Pb_2Ru_2O_{6.5}$



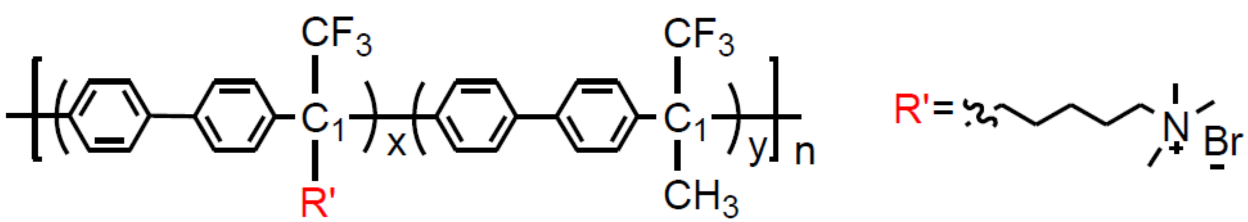
5L flask, ~25-30g
$Pb_2Ru_2O_{6.5}$

Approach: Ionomer

- Tokuyama AS-4 will be used as the baseline comparison
- Block copolymers explored in low molecular weight form



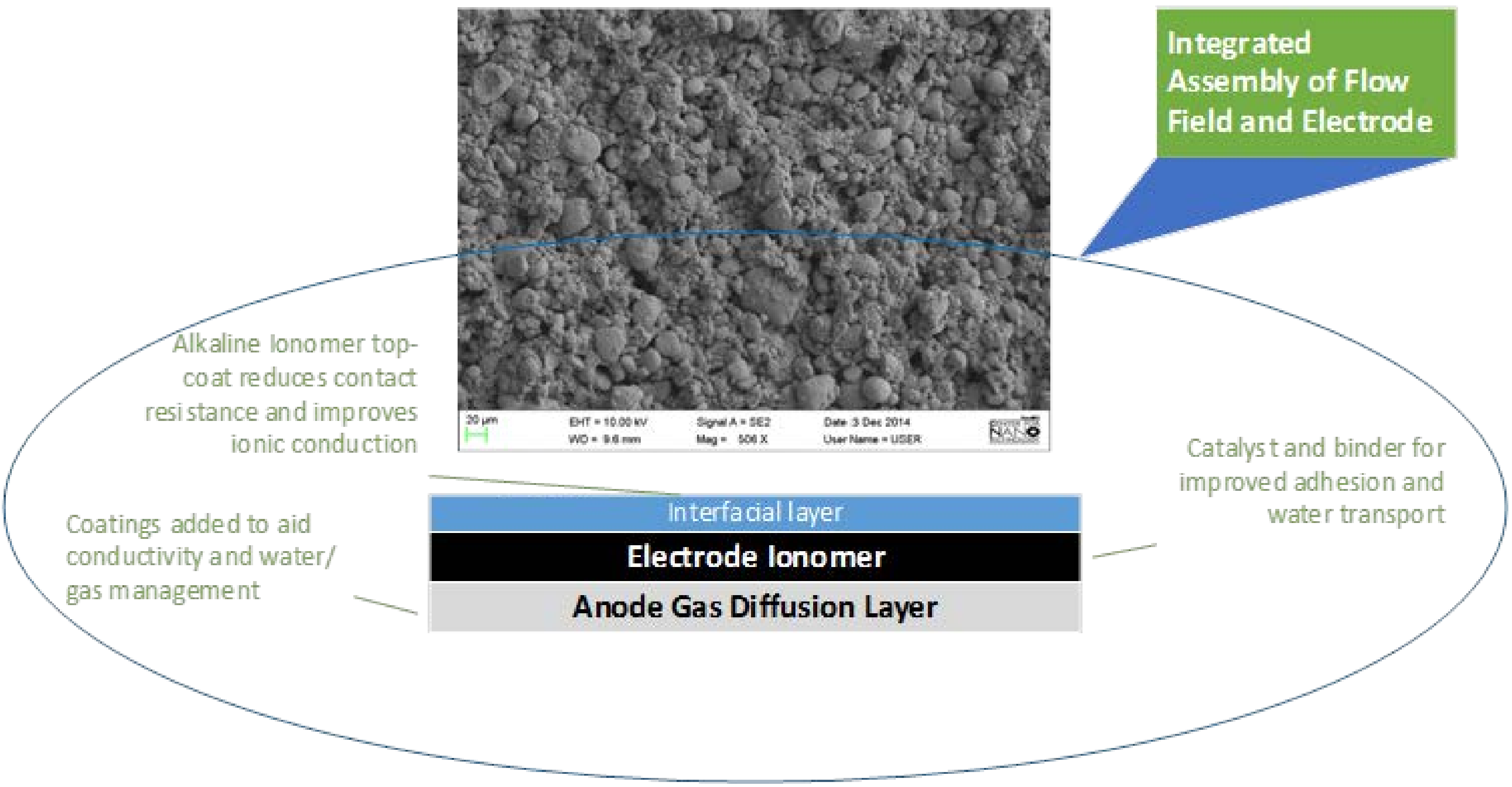
- Short blocks versions of the low MW ionomers used
  - Intended to create thin film on catalyst and retain efficient conduction
- Hydrophilic homopolymer evaluated
  - 2 different MW (3k/4k)
- Hydrocarbon copolymer (courtesy of Dr. Chulsung Bae, RPI)



Evaluate these materials as AEM electrolyzer anode ionomers

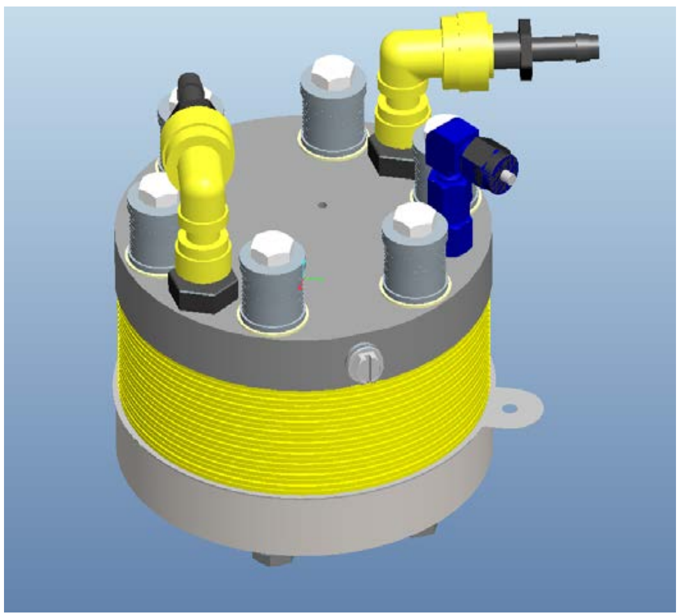
Approach: Ionomer/Catalyst Integration

- Gas diffusion electrodes will be fabricated with Georgia Tech ionomers and Pajarito catalysts
  - Water management through cell engineering

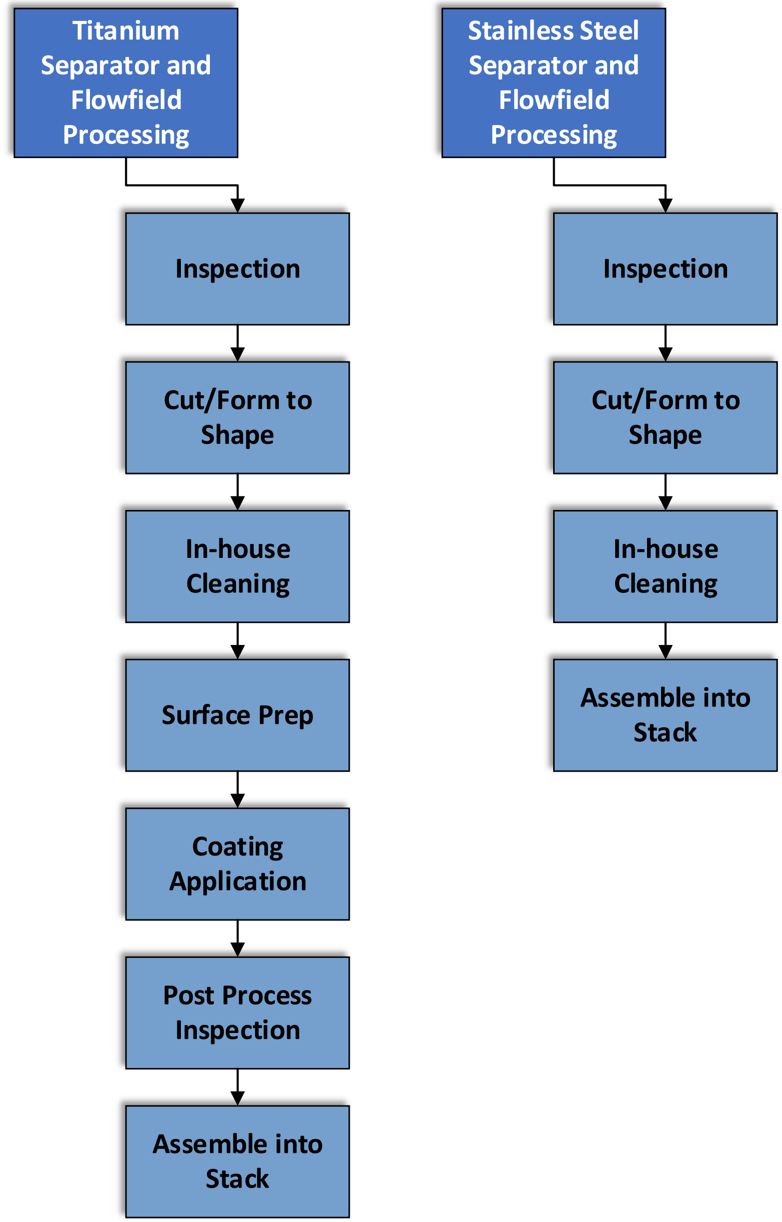


Approach: AEM Stack Design

- Incorporate cost-reduced materials compatible with AEM operation.
  - Raw material pricing of 316L SS roughly is ~1/6 of titanium
- Match size to max. current densities achieved at Phase II program end
  - Target is for 1L of H_2/min



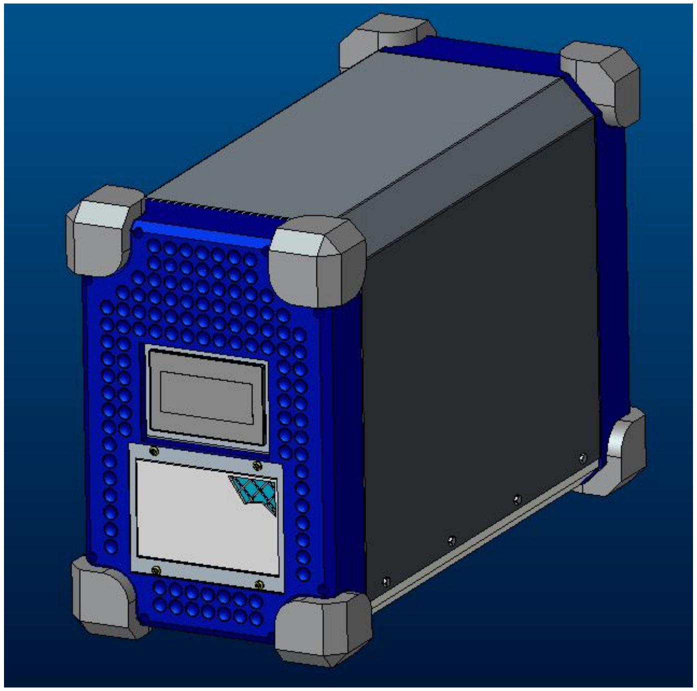
- 10-cell concept drawing



- Cost savings through process reduction

Approach: AEM System Design

- System design will evaluate concept required for 1L/min hydrogen output
- Leverage existing lab scale generator packaging
  - Thermal considerations, Manufacturability, Serviceability, and Lower Cost vs. PEM
- Swing bed dryer design explored for high purity

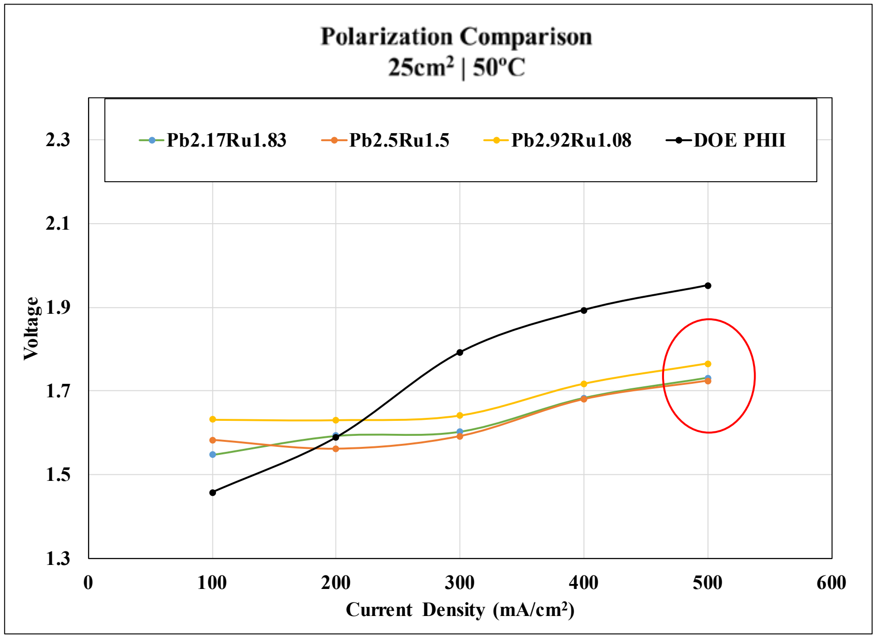


Technical Accomplishments - Milestones

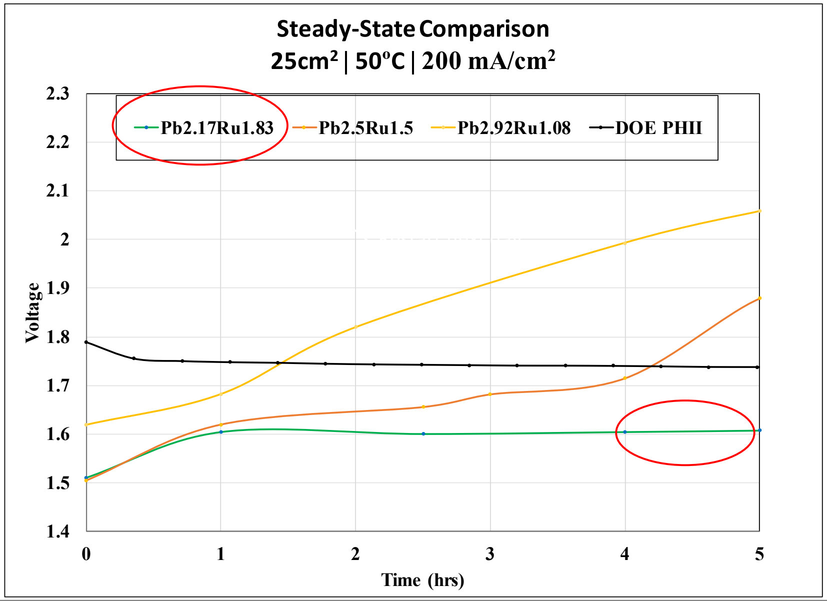
Task #	Milestone Description	Date/Status
1.1	Select up to 3 OER catalysts from synthesis optimization for cell testing based on surface area and RDE measurements.	7/10/2016 100%
1.1	Complete cell testing (constant current and polarization curves) of WU catalysts to provide feedback for Task 1.2	10/1/2016 100%
2.1	Establish kinetic parameters and estimate lifetime of three ionomers based on in-cell electrolyzer operation.	11/30/2016 100%
3.1	Characterize degradation methods for catalyst and ionomer based on post operational RDE and NMR to guide Task 3.2.	12/15/2016 75%
1.3	Reproduce WU synthesis process at Pajarito Powder and confirm results through physical and electrochemical characterization.	1/15/2017 100%
1.2	Complete refinement of OER composition and synthesis parameters. Polarization and steady-state data will be used to down-select the final composition.	2/10/2017 100%
3.2	Develop and conduct initial accelerated stress tests based on degradation mechanisms.	3/1/2017 10%
4.2	Hold concept system design review	5/1/2017 50%
1.3	Synthesize 25 gram batch of OER catalyst at Pajarito	7/15/2017 25%

Task #	Milestone Description	Date/Status
2.2	Down-select final ionomers through life-cycle testing at high current.	9/30/2017 50%
4.1	Verify sealing and active area loading for 12-14 cell 28 cm2 cell stack.	10/1/2017 100%
4.2	Complete fabrication of prototype system.	11/1/2017 10%
3.3	Develop ink composition for refined catalyst and ionomers and complete in cell testing.	12/1/2017 75%
4.3	Complete and pass pre-start-up safety review.	12/20/2017 0%
1.4	Deliver 50 grams of down-selected catalyst to Proton for multi-cell operational testing.	1/15/2018 0%
3.3	Conduct durability test with optimized materials in a single cell stack for up to 500 hrs.	2/15/2018 0%
1.4	Conduct economic analysis and evaluation of the catalyst scaled-up process and determine its potential and cost for commercialization.	3/15/2018 10%
6	Conduct cost-analysis on fully integrated stack and system.	3/31/2018 0%

Technical Accomplishments: Catalyst



- Operational testing was conducted to verify in-cell
- All samples showed similar behavior
- Comparison made against PHII result
- Improvements in synthesis procedure have translated to final product



- Steady-state testing conducted for stability
- Samples began to show separation
- Comparison made against PHII result
- Down-select for additional synthesis, tech transfer, and test identified

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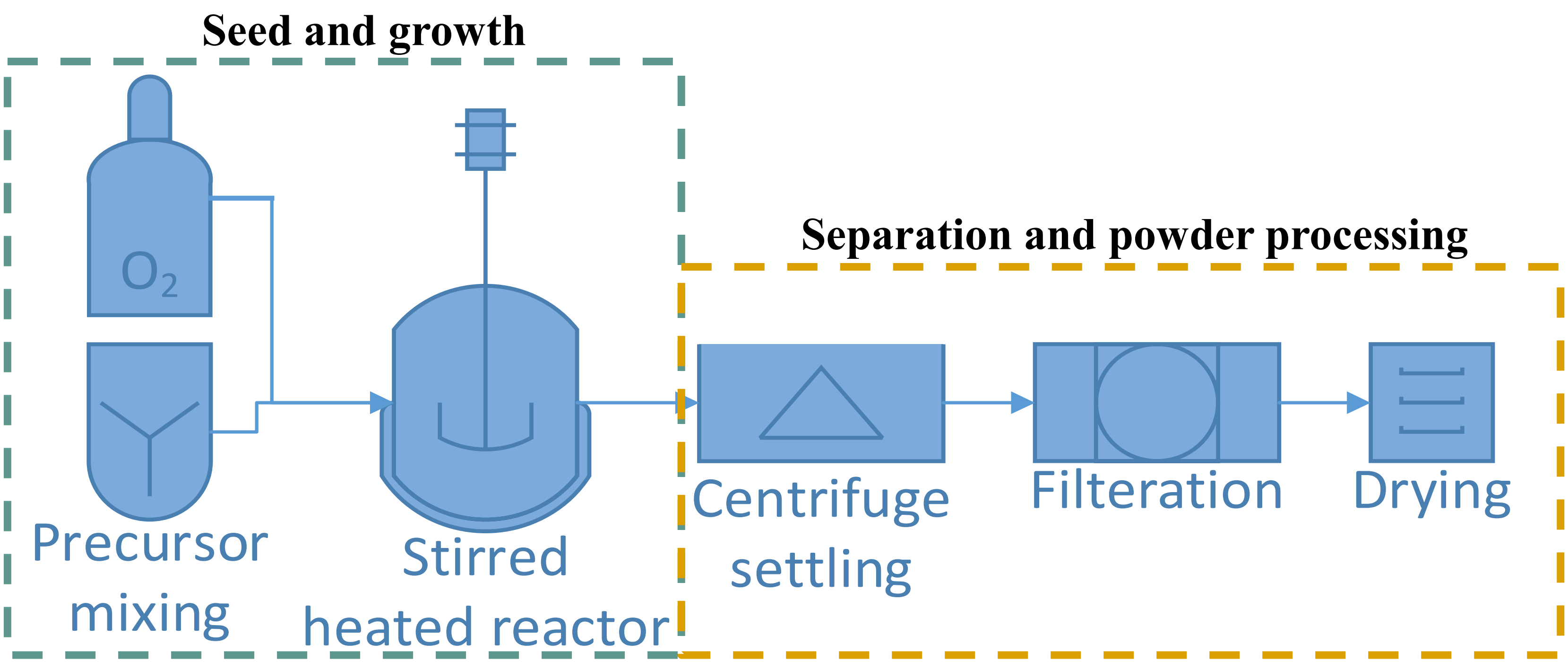
Technical Accomplishments: Tech Transfer

$Pb_2Ru_2O_{6.5}$ Synthesis Steps



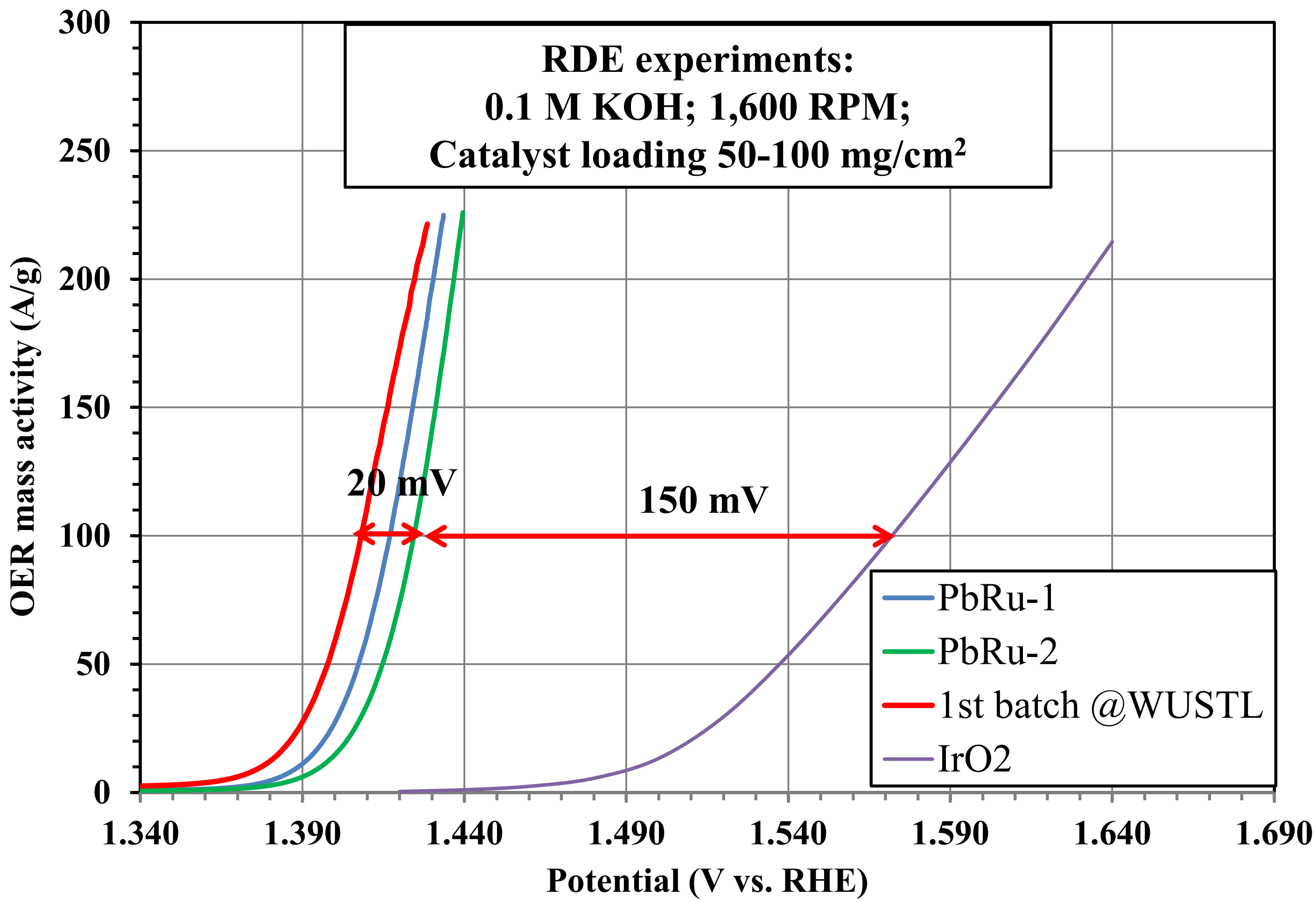
- Create dilute solution of precursors
- Heat and stir to seed and grow small crystallites
- Decant, filter/wash, and dry the solids

- Process has been implemented and conducted at Pajarito
- Several batches processed for RDE and operational testing
- Shipped to Proton and Washington U

Technical Accomplishments: Tech Transfer

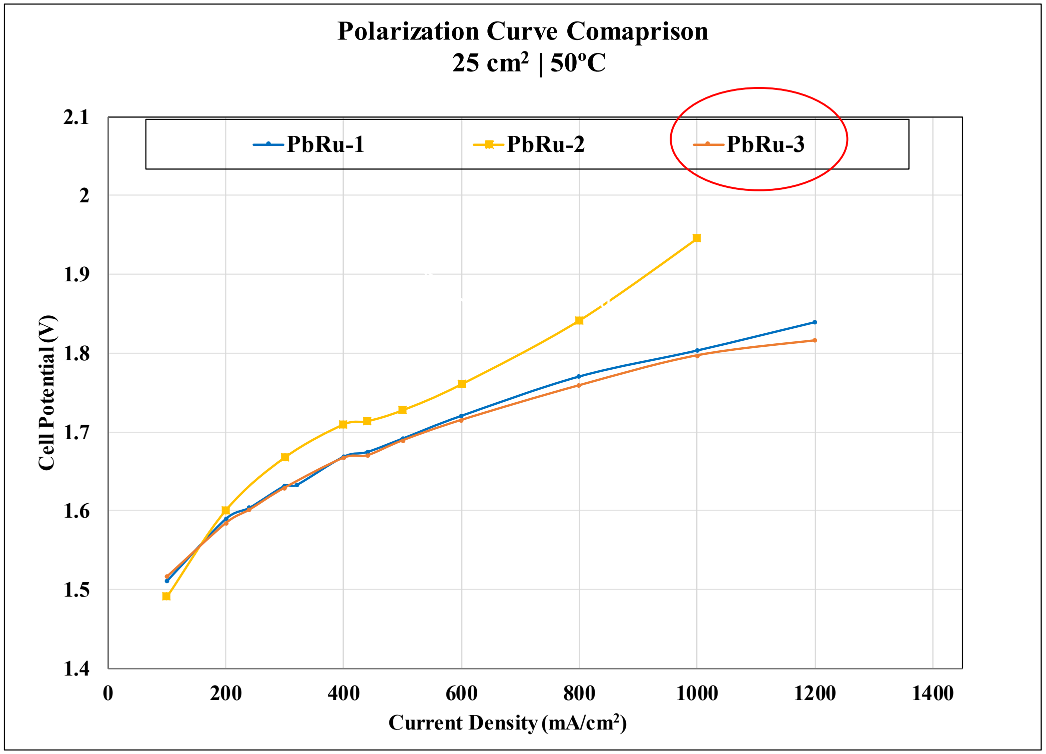
- **Differences in activity measured to be only 20mV max.**

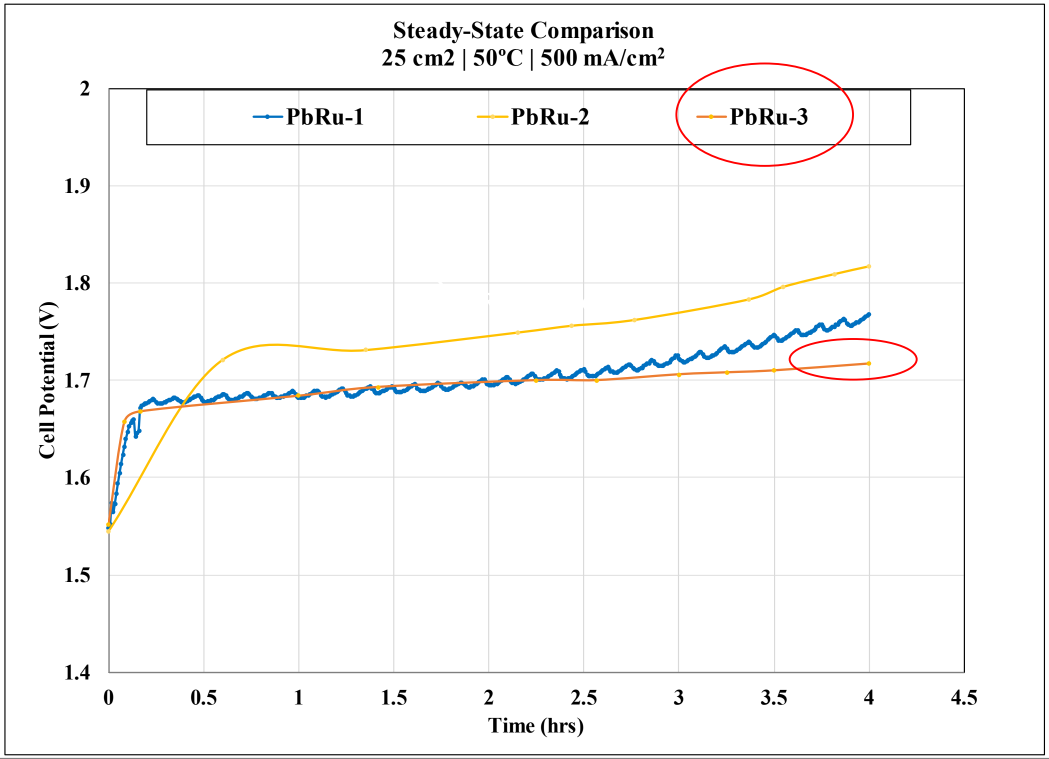
- Two batches synthesized by Pajarito Powder showed similar OER activity to batches synthesized at WUSTL
- Samples from each batch sent to Proton for operational bench-testing
- Third sample was also sent, but no RDE was available at the time of test
- Each sample reflected a modification to synthesis to improve throughput



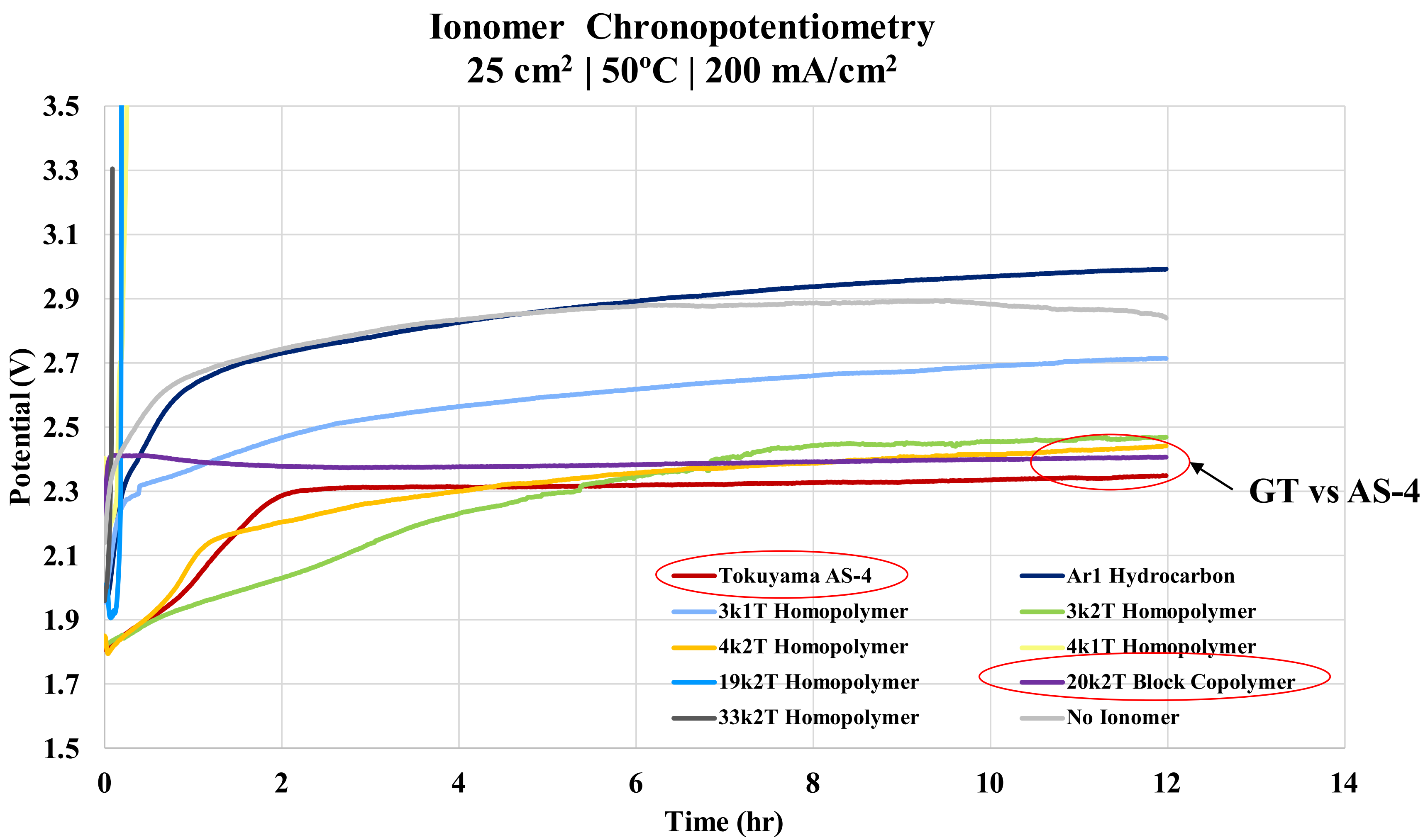
Technical Accomplishments: Tech Transfer

- Both polarization and steady-state trends follow RDE data for 2 samples tested
  - PbRu-1 outperformed PbRu-2
- The third sample PbRu-3, not tested in RDE, was similar to PbRu-1 in cell
  - Showed improved stability in steady-state operation
- PbRu-3 was selected for longer duration testing in future work





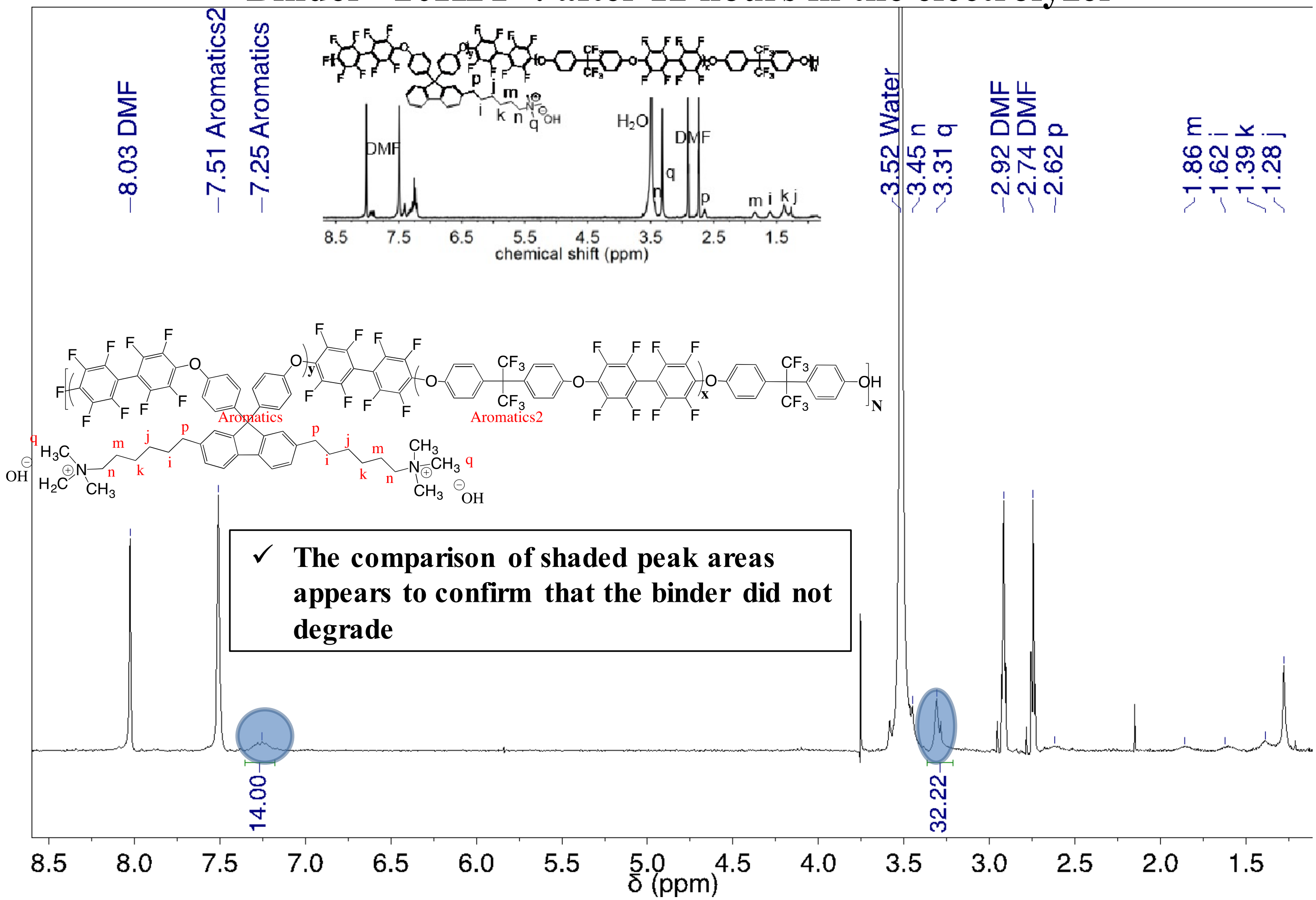
Technical Accomplishments: Ionomer



- Ionomer testing was conducted through steady-state operation at GT
- Variations in MW and conductivity were explored
- Compared to Tokuyama baseline for stability in pure water

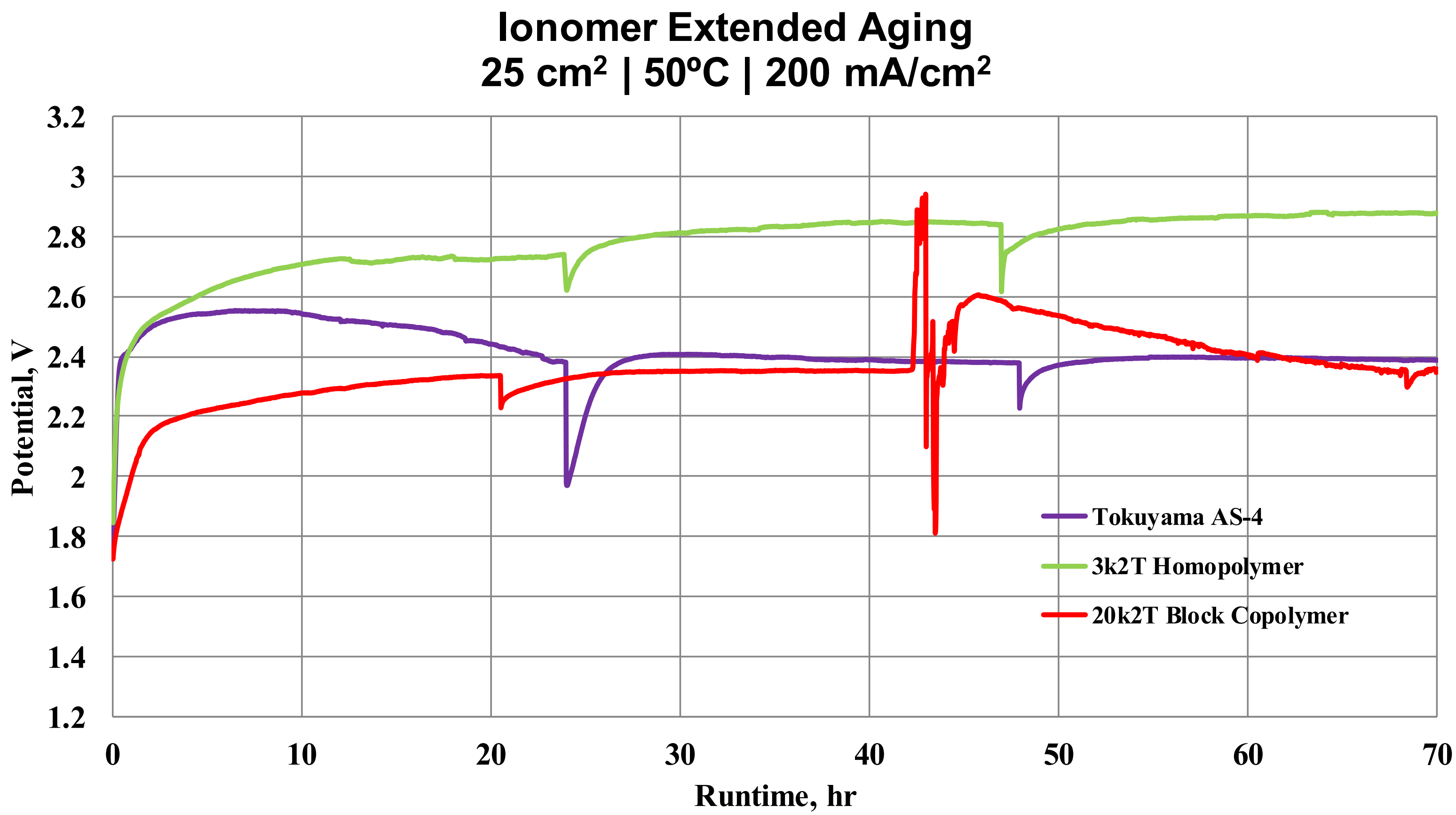
Technical Accomplishments: Ionomer

Binder "20K2T": after 12 hours in the electrolyzer



- Ionomer samples sent to Washington University
- NMR used to evaluate pristine versus operated samples for signs of degradation

Technical Accomplishments: Ionomer

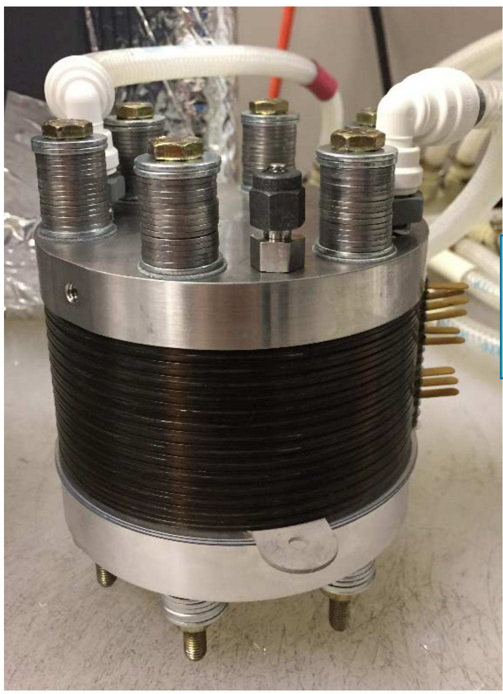


Note: 4k2T homopolymer sample is currently being tested. Will update with data once completed.

- **Down selection of ionomers based on initial 12 hour testing performance and NMR**
  - **3k2T Homopolymer, 4k2T Homopolymer, 20k2T Block Copolymer**
  - **Tokuyama AS-4 (for baseline comparison)**

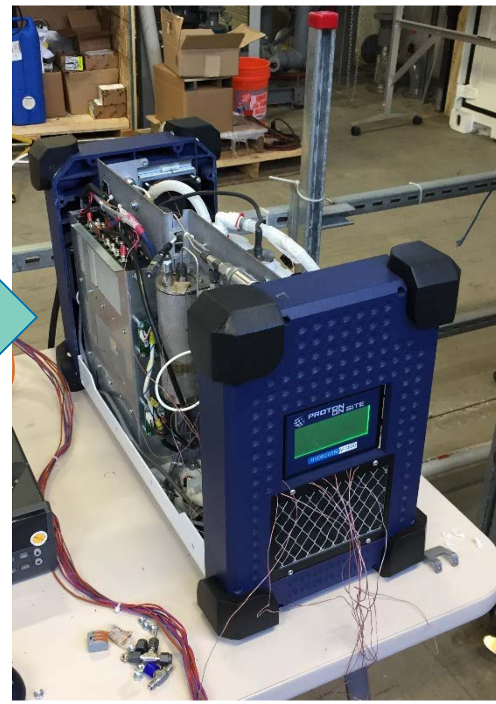
Technical Accomplishments: Stack and System Development

- Work initiated on stack and system concepts
- Test stack and system fabricated and moving towards verification testing
- Majority of effort in Year 2



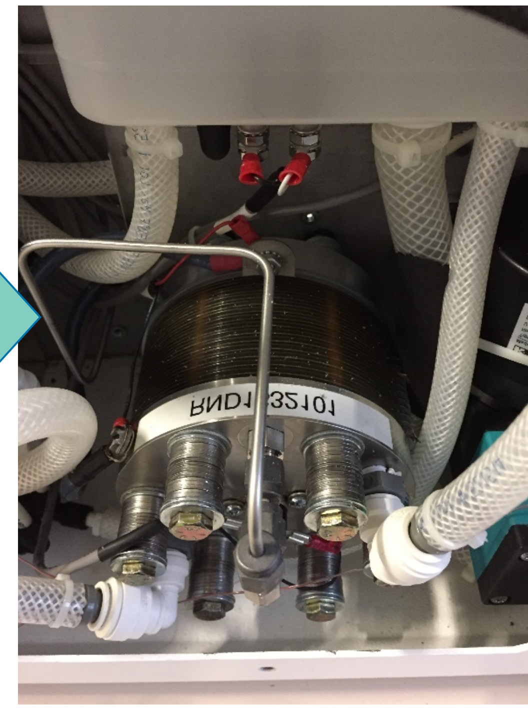
14-cell stack assembled against CAD models

Active Area & Sealing Loads Verified



Concept system functionally verified

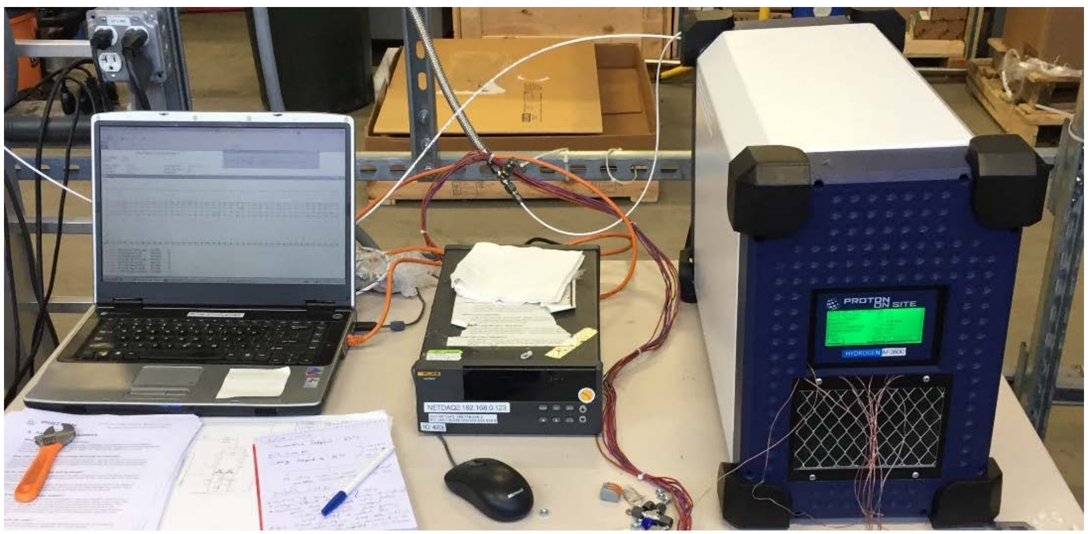
Stack Installed 1L/min

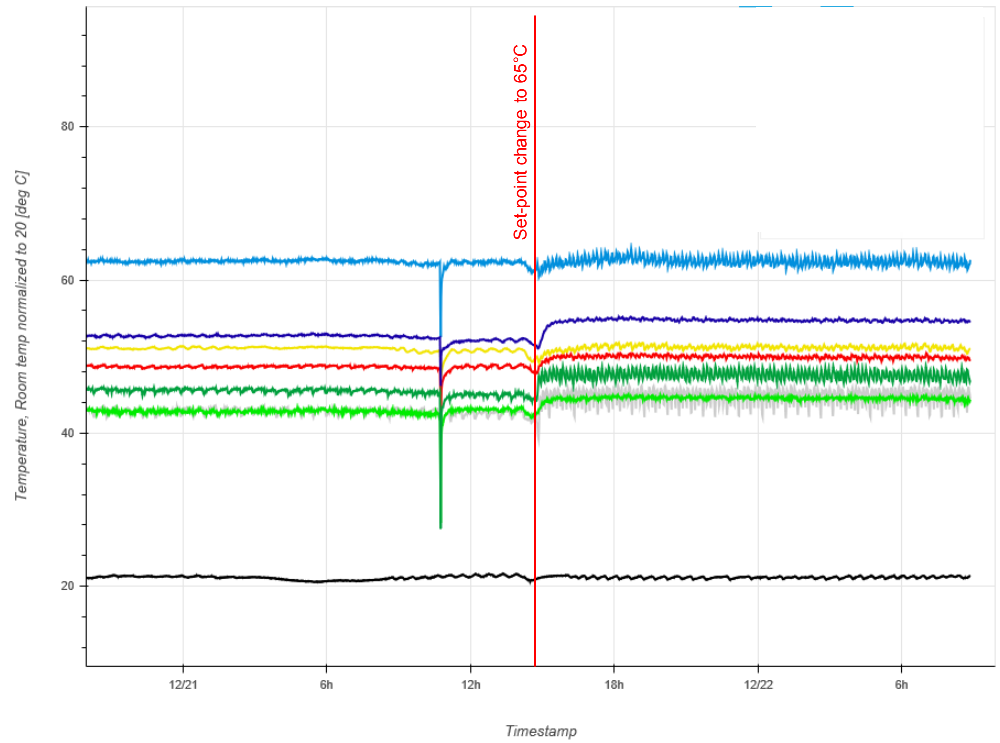


Operational testing at full output

Technical Accomplishments: Stack and System Development

- Gas purity verified through collection of dew point measurements
  - Evaluation of swing bed PSA dryer concept
- Product flow rates verified by mass flow meter measurements
- Thermal profile of system collected and used for iteration on cooling scheme and long-term stability

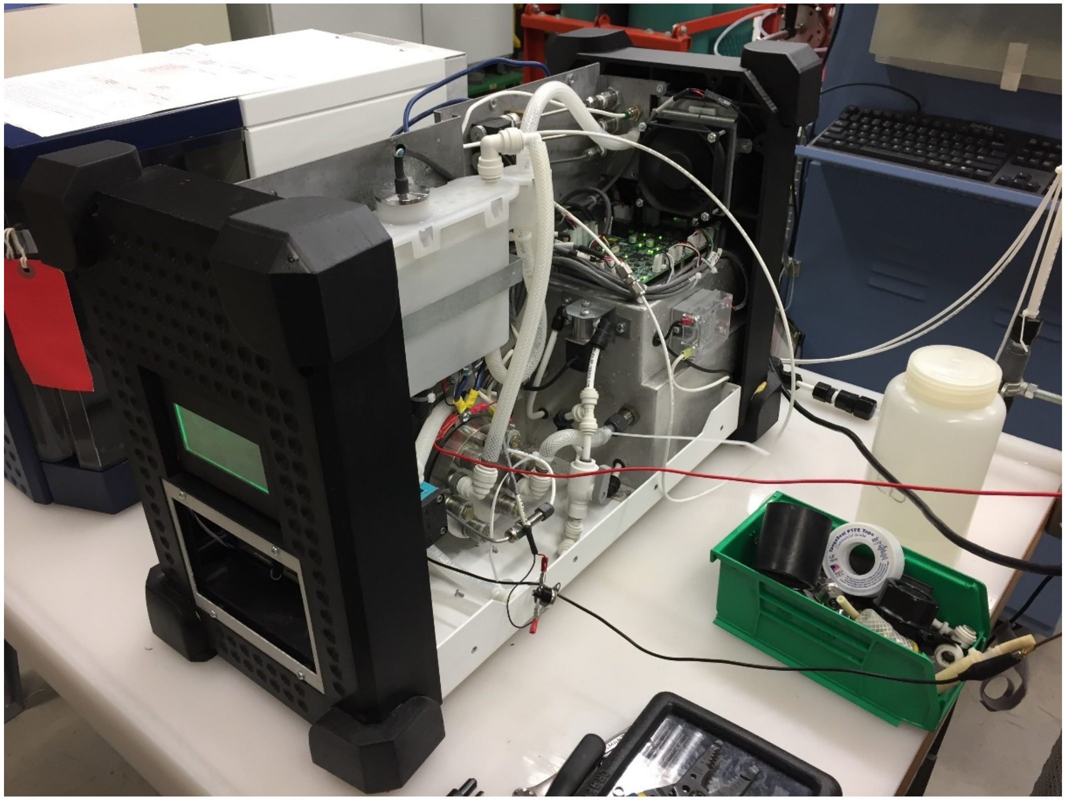


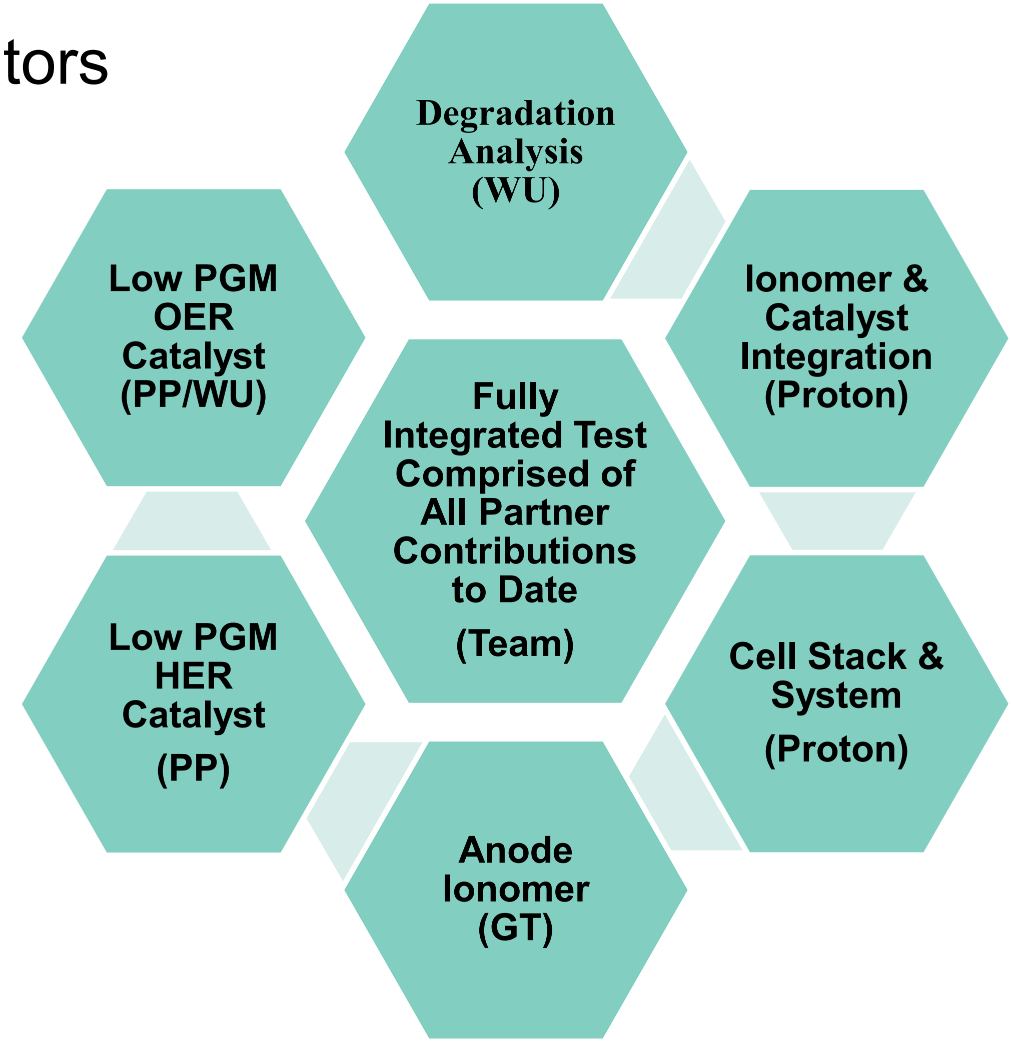


Example of thermal profile data set

Technical Accomplishments: Combined Operational Test

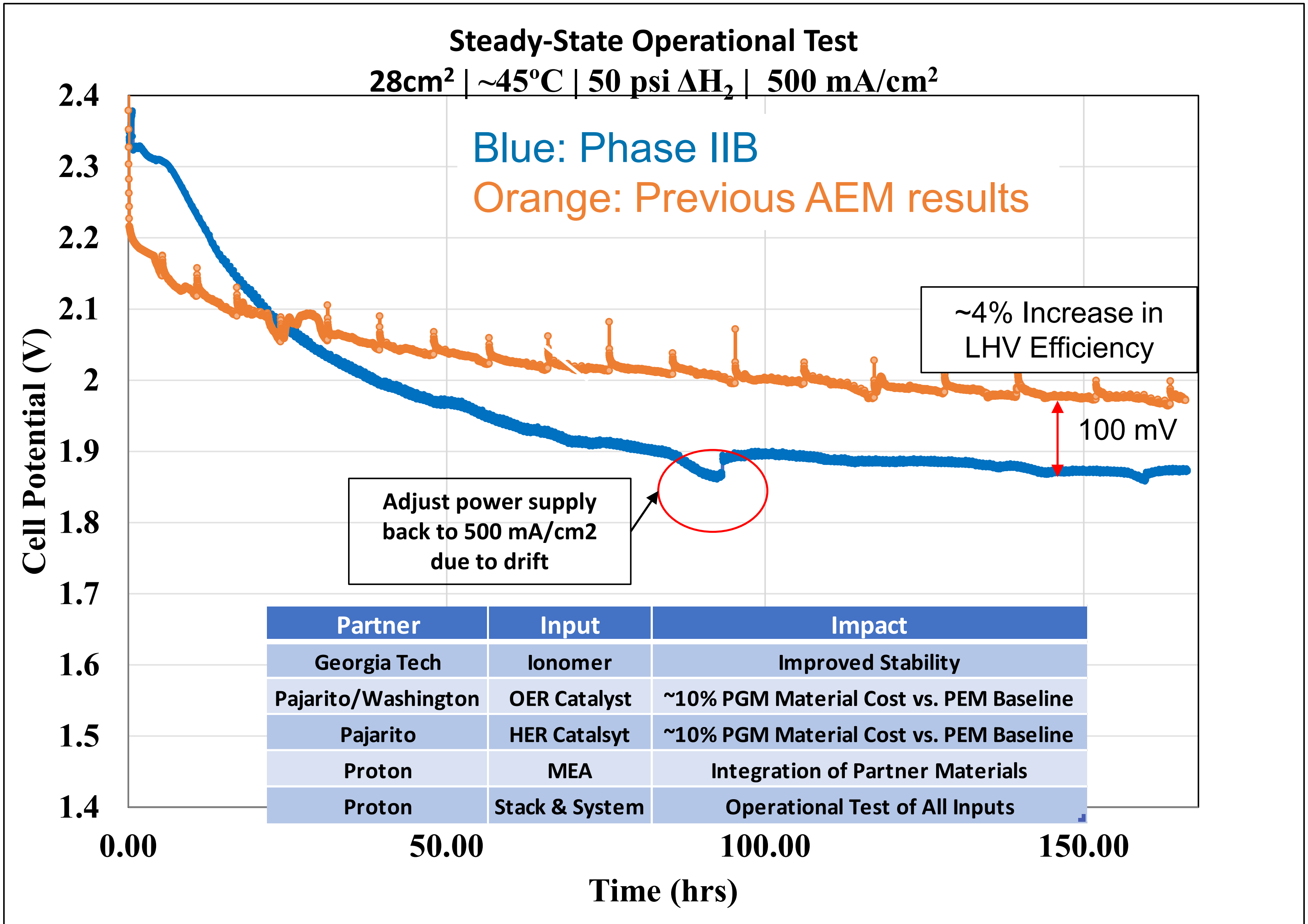
- 1-cell AEM stack was assembled
- Leveraged inputs from all collaborators





- Fully Integrated Durability Test

Technical Accomplishments: Combined Operational Test



Partner	Input	Impact
Georgia Tech	Ionomer	Improved Stability
Pajarito/Washington	OER Catalyst	~10% PGM Material Cost vs. PEM Baseline
Pajarito	HER Catalsyt	~10% PGM Material Cost vs. PEM Baseline
Proton	MEA	Integration of Partner Materials
Proton	Stack & System	Operational Test of All Inputs

Collaborators

- Georgia Tech (Subcontractor)
  - Synthesis and tuning of anode ionomer
  - Degradations studies and down-select for full-scale testing
- Washington University (Subcontractor)
  - Refine and down-select OER catalyst compositions
  - Support catalyst and ionomer degradation studies
  - Transfer the catalysts synthesis process to Pajarito Powder and assist with implementation at scale
- Pajarito Powder (Subcontractor)
  - Adopt the OER synthesis process and refine based on expertise
  - Identify methods for increased batch size and cost reduction through process refinement and leveraging economies of scale
  - Product 25-50g batches for delivery to Proton for full-scale testing

Future Work

- Catalyst
  - Continued refinement of synthesis process for increased yield and reduced cost
  - Verify structure and activity through XRD, RDE and in-cell testing
  - Cost estimates at production scale batch sizes (1kg)
- Ionomer
  - Test down-selected ionomers to high current and accelerated test protocols developed under PHII
  - Process materials for continued test availability in Year 2
  - Investigate water transport rates vs. pressure
- Cell and System Design
  - Tune electrode fabrication process for further loading reduction
  - Build, test, and iterate on design for 1L/min AEM stack and system prototype utilizing partners materials
  - Present final design in prototype internal gate review

Summary

- **Relevance:** The goal of this effort is to produce a high-performance anion exchange membrane water electrolyzer (AEM-WE) with PGM electrodes
- **Approach:**
  - Optimization of anode ionomer for improved stability and conductivity vs. current commercially available materials. Verify through in-cell steady-state and accelerated test parameters.
  - Synthesize highly active PbRu OER catalysts with minimal PGM content. Transfer technology to commercial catalyst manufacturer for scale-up and yield improvement.
  - Develop a prototype laboratory scale AEM system capable of 1L/min hydrogen flow rate.
  - Utilize cheaper materials of construction for cell stack and system design to further reduce total $/kg H_2.
- **Collaborations:**
  - Georgia Tech: Development of a stable, anode ionomer through the use of short block, low molecular weight block copolymers providing efficient channel conduction.
  - Washington University: Refine composition of PbRu pyrochlore OER catalysts, while maintaining high activity. Support degradation analysis of ionomer and technology transfer of catalyst synthesis to Pajarito Powder.
  - Pajarito Powder: Implement and refine synthesis process developed at Washington University for scale-up to 50-100g batch sizes. Provide cost estimation for 1kg scale production volumes.
- **Proposed Future Work:**
  - Continue synthesis and scale-up of highly active, low PGM OER catalysts.
  - Synthesize additional anode ionomer for accelerated and long-term durability testing.
  - Optimize cathode and anode GDEs to realize additional loading reductions.
  - Integrate all materials and operating modes into optimal cell and system configuration for prototype review.