PROTON
THE LEADER IN ON SITE GAS GENERATION.

Economical Production of Hydrogen Through Development of Novel, High Efficiency Electrocatalysts for Alkaline Membrane Electrolysis

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Organization: Proton OnSite
Date: June 18th,2014

Project ID: PD094

Overview

Timeline

- Project Start: 20 Feb 2012
- Project End: 21 April 2015
- Percent complete: 55%

Budget

- Total Funding Spent*
  - $487,000
- Total Project Value
  - $1,150,000
- Cost Share Percentage
  - 0% (SBIR)

*as of 3/31/14

Barriers

- Barriers addressed

  G: 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

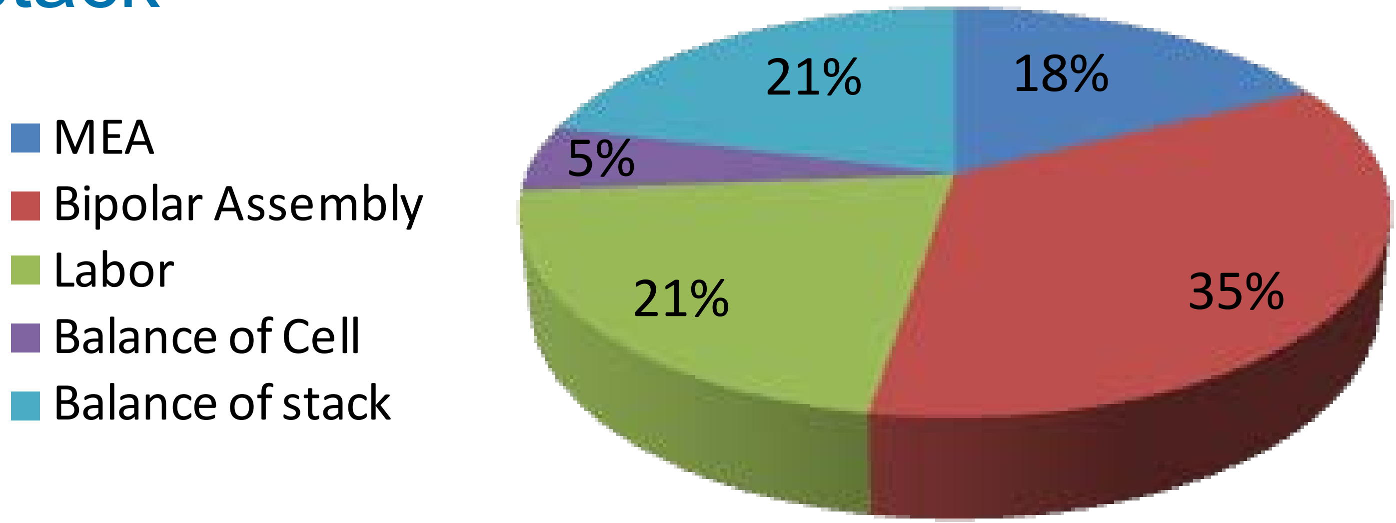
- Illinois Institute of Technology

Collaborators

- Sandia National Labs

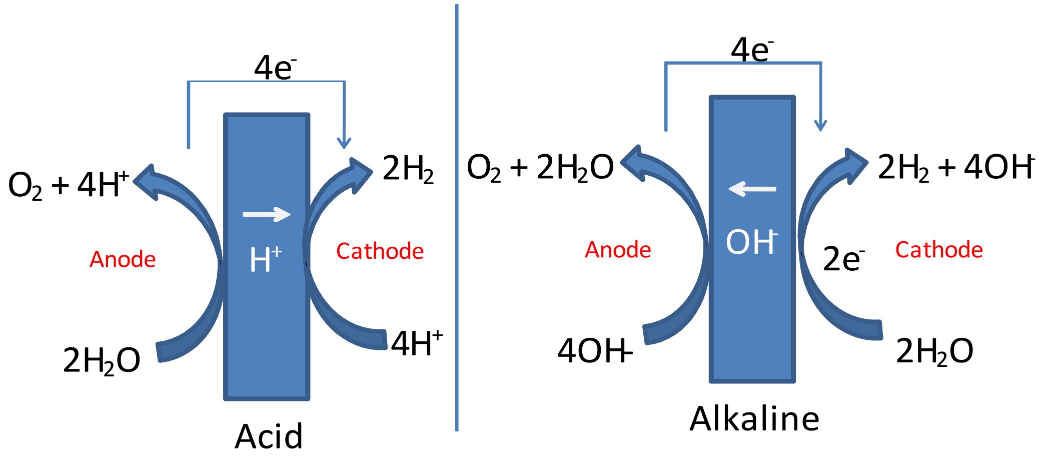
Relevance: Capital Cost

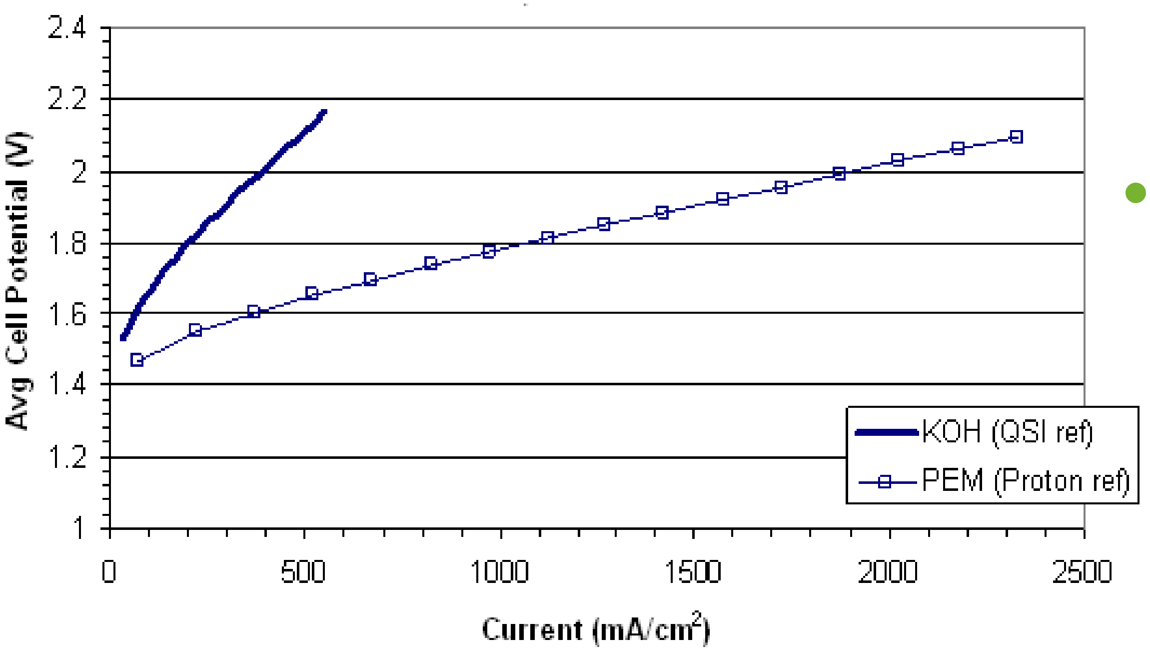
- Bipolar assembly still represents highest cost of PEM stack



- Alkaline media enables transition from titanium to stainless steel: eliminates 75% of part cost
  - Also should enable lower cost catalysts
- Saves ~$.11/kg capital cost with H2A assumptions
  - Current PGM costs, 500 units/year, 1500 kg/day

Relevance: Project Concept

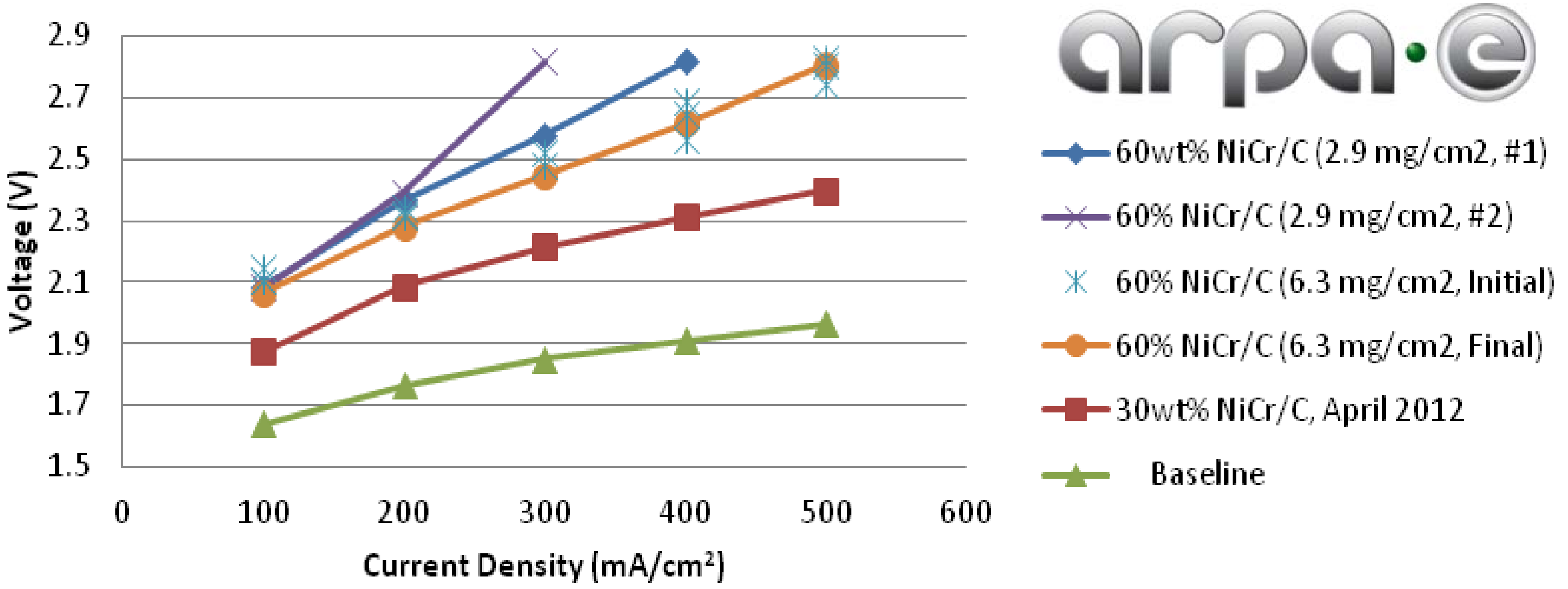




- Alkaline membranes provide benefits of both PEM and KOH
- Efficiency should be between existing technologies
- AEM membranes gaining stability

Relevance: Catalyst Status

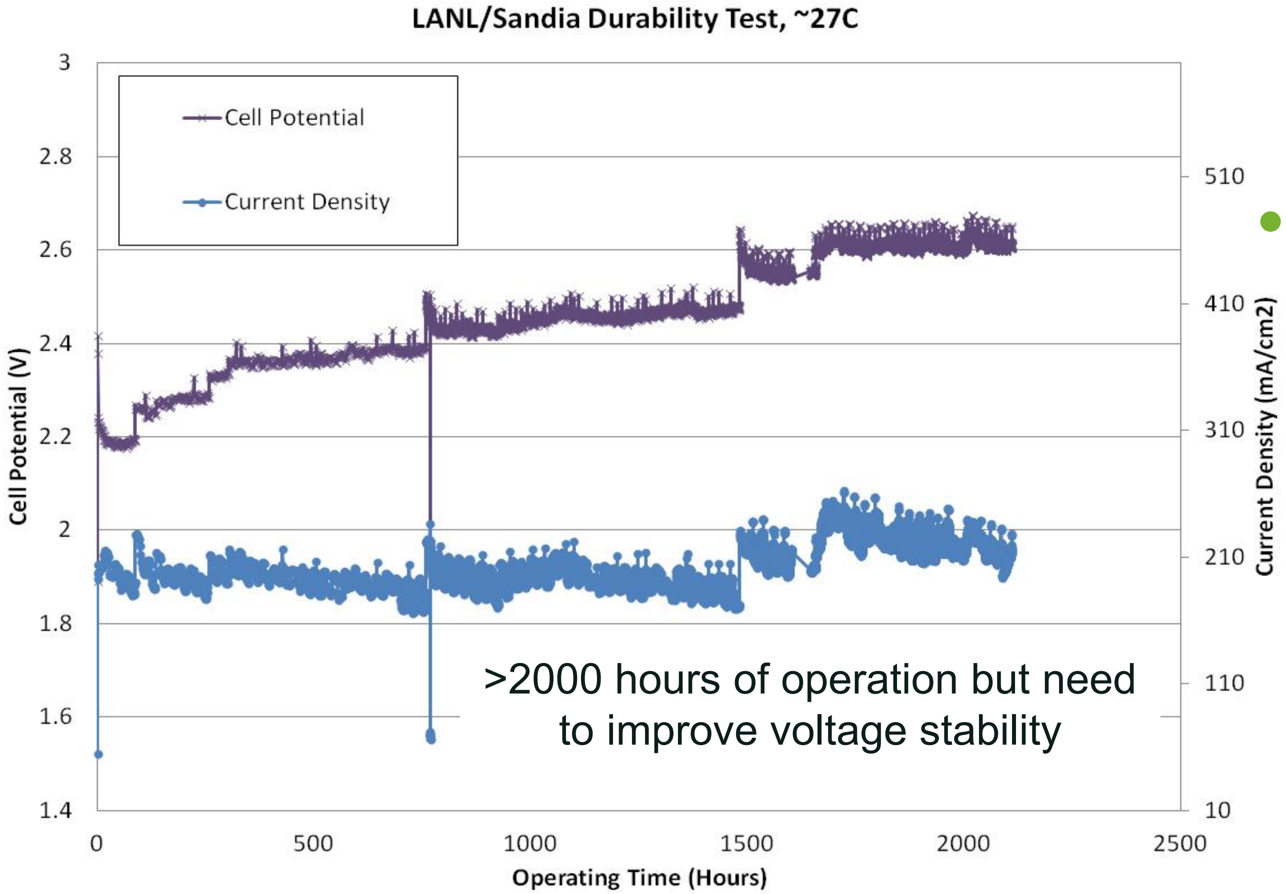
- Traditional Ni-based catalysts have not yet translated from solution to ionomer



- Note: catalyst is only 6% of cost in PEM system
- Intermediate solution can still enable significant flow field and stack cost savings with AEM technology

Relevance: Membrane Status

- Proton has become test bed for electrolysis AEMs
  - Testing protocol and electrode/cell designs established
  - Need characterization of degradation mechanisms



>2000 hours of operation but need to improve voltage stability

- ARPA-E results, highest stability AEMs to date

Relevance: Commercialization Strategy

- Fueling represents a high need for cost reduction but need near term markets and product strategy as well
- Hydrogen replacing helium in lab applications
  - Less dependent on efficiency, higher risk tolerance at small scale
  - Highly price sensitive market
- Leverages Proton's existing product re-design effort
  - Prototype AEM system to be built based on new design
- Product cost analysis to be performed on final configuration

System Configuration for AEM

Relevance: Long Term Value Proposition

- Hydrogen via electrolysis is ideally suited for:
  - Transportation fuel
  - Grid-buffering and energy storage
  - High value chemical streams
  - Green production of fertilizer
  - Supplement to natural gas for higher efficiency
- PEM technology can meet short term goals
  - Parallel efforts in cost reduction ongoing
- AEM technology leverages MW scale designs and can be inserted as technology matures

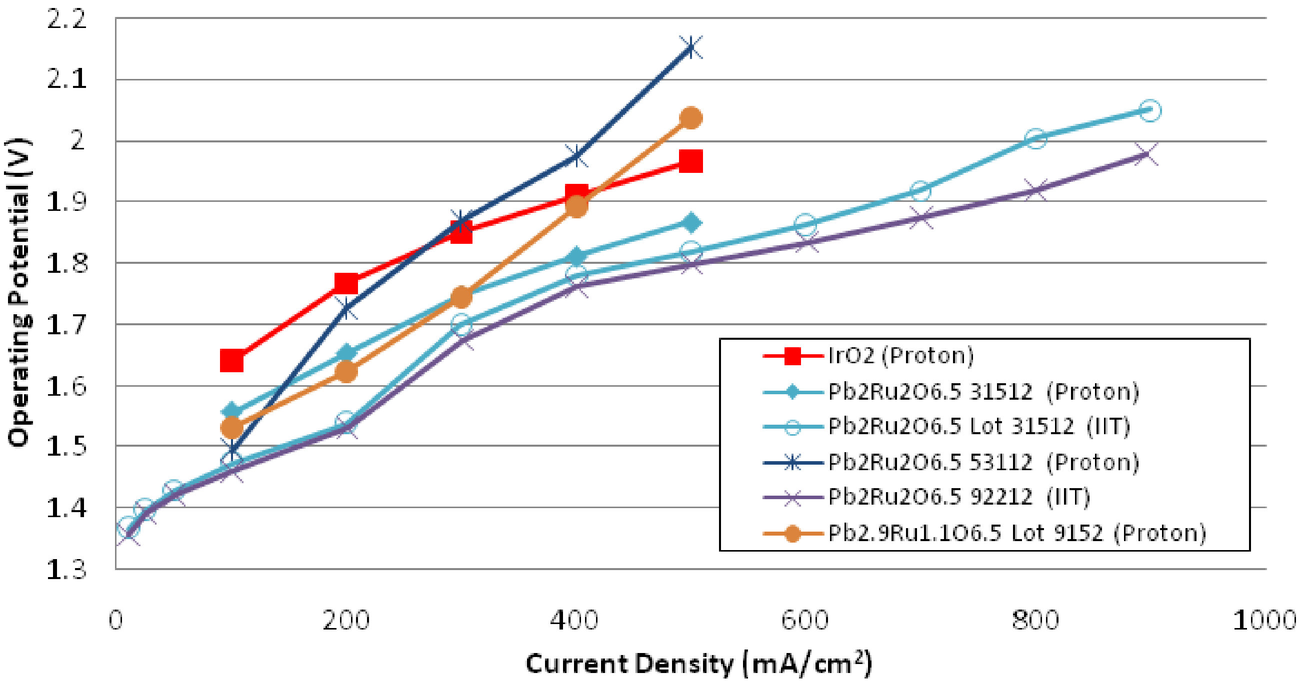
Approach
Task Breakdown

- Task 1.0 Catalyst Development
  - Subtask 1.1 Synthesis of new compositions
  - Subtask 1.2 Characterization of physical properties
- Task 2.0 Membrane Development
  - Subtask 2.1 Synthesis of AEM membrane
  - Subtask 2.2 Characterization through 2D NMR
- Task 3.0 Electrode Development & Testing
  - Subtask 3.1 Membrane Electrode Assembly
  - Subtask 3.2 Gas Diffusion Electrode
  - Subtask 3.3 Testing and Post Operation Assessment

Catalyst Approach

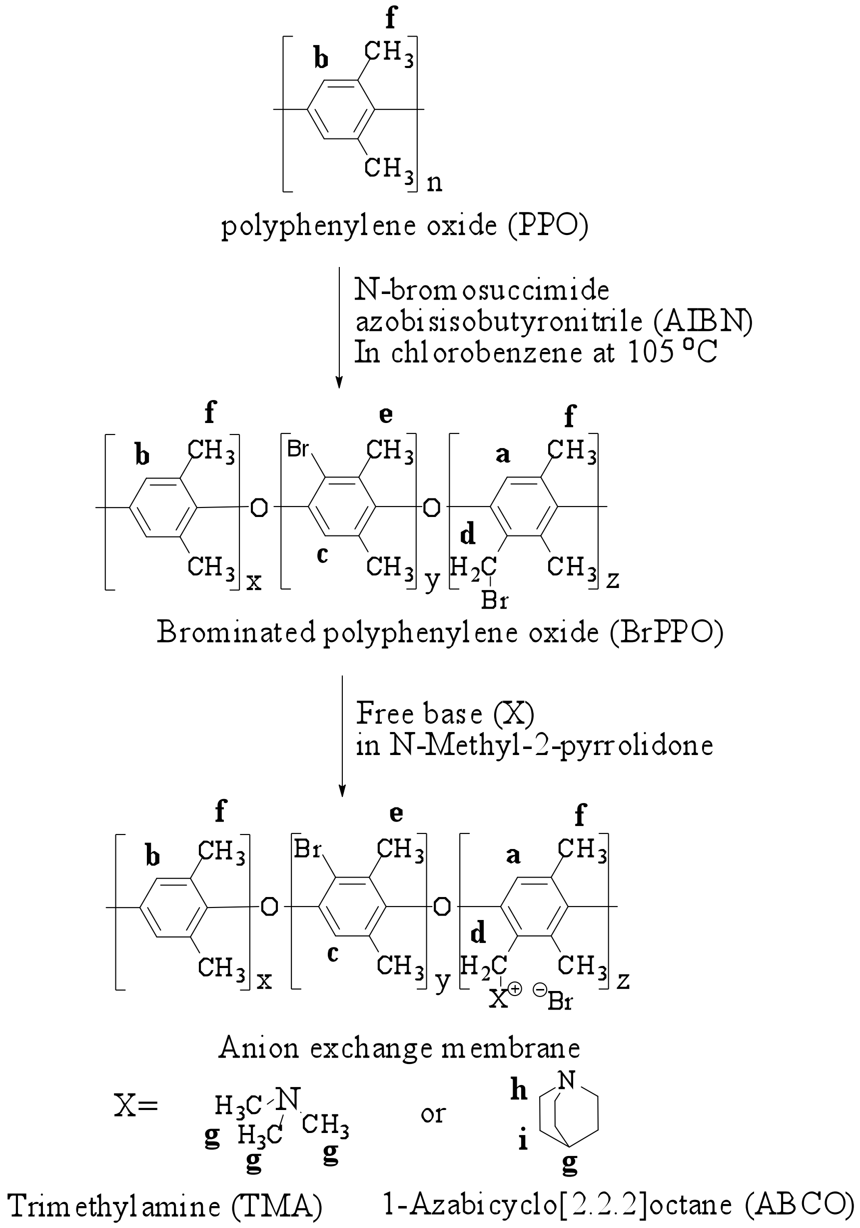
- Leverage pyrochlore class of catalysts ($A_2B_2O_{6\text{-}7}$)
  - Good kinetics for OER, stable in base
  - Able to make as nanoparticles
- Investigate compounds with A = Bi, Pb; B = Ru, Ir

Phase I Results



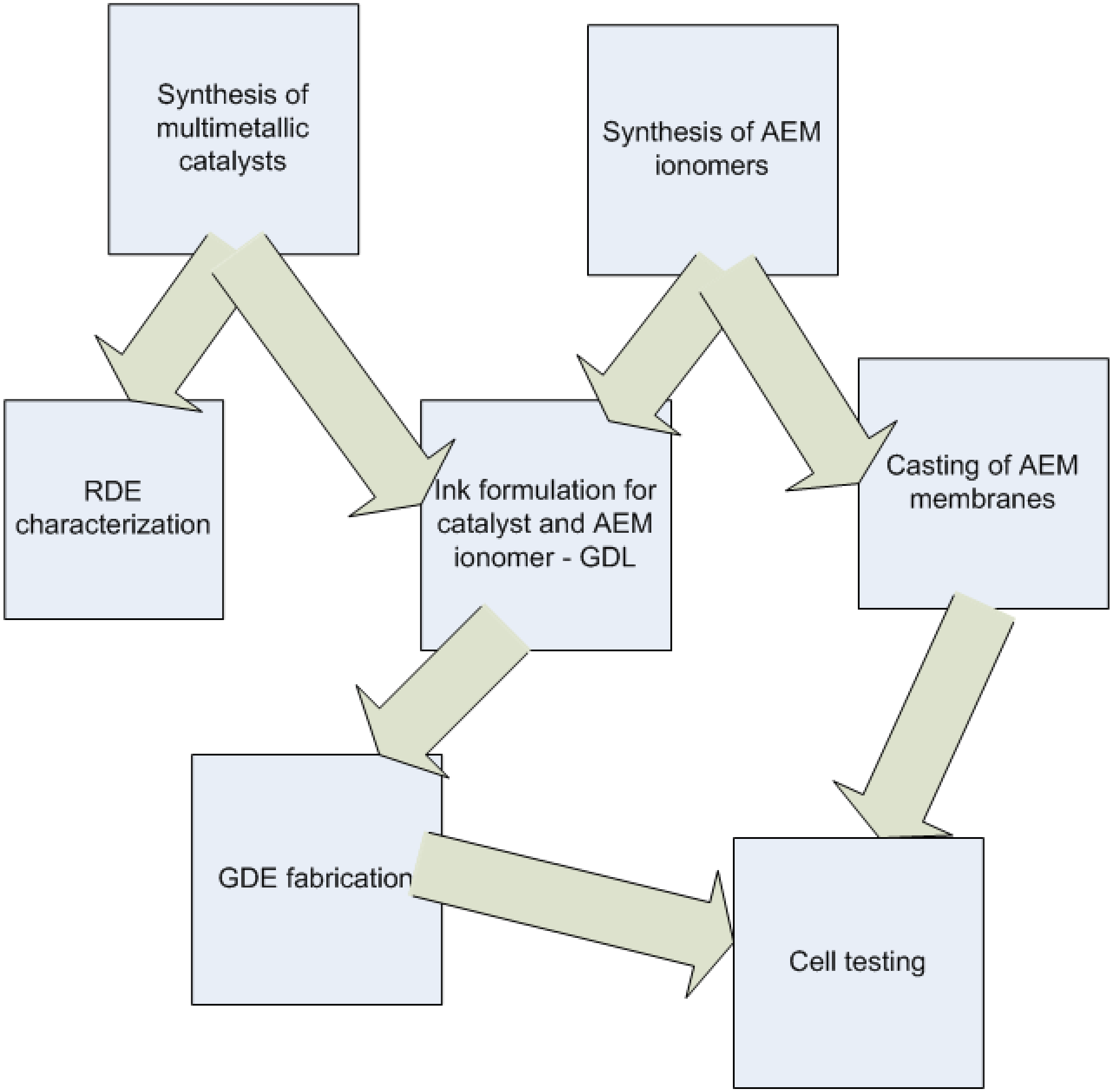
Membrane Approach

- IIT development of alternate polymers
- Leverage NMR for degradation studies
- Continue to evaluate Sandia/LANL materials



Approach: Materials Integration

- Materials will move to Proton configuration against baseline as progress is made
- Perform post-testing analysis

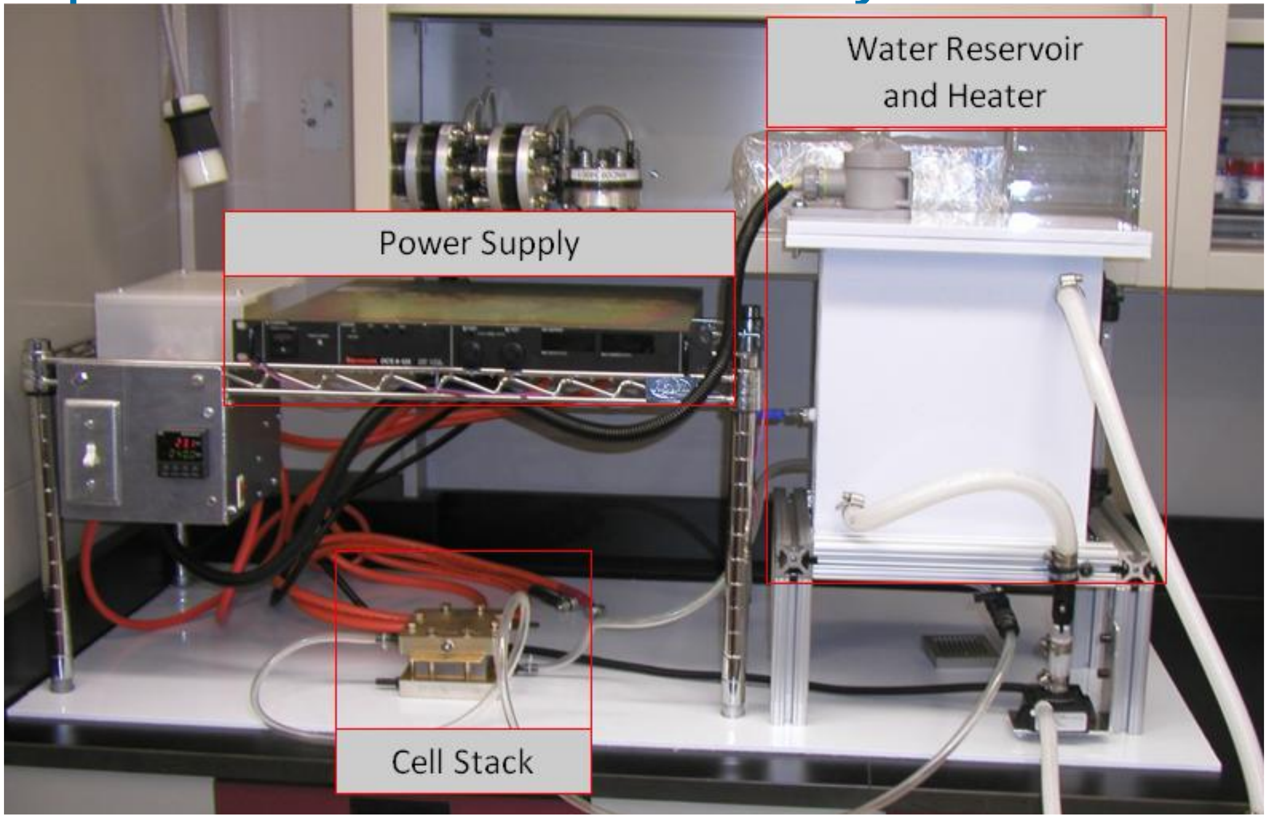


Approach
Task Breakdown

- Task 4.0 Stack Design and Fabrication
  - Subtask 4.1 Cell Stack Materials Evaluation
  - Subtask 4.2 Cell Stack Design Scale-up
- Task 5.0 System Design and Fabrication
  - Subtask 5.1 System Materials Evaluation
  - Subtask 5.2 System Scale-up
  - Subtask 5.3 System Operation
  - Subtask 5.4 Full-Scale Durability Testing

Approach: Stack Design & Development

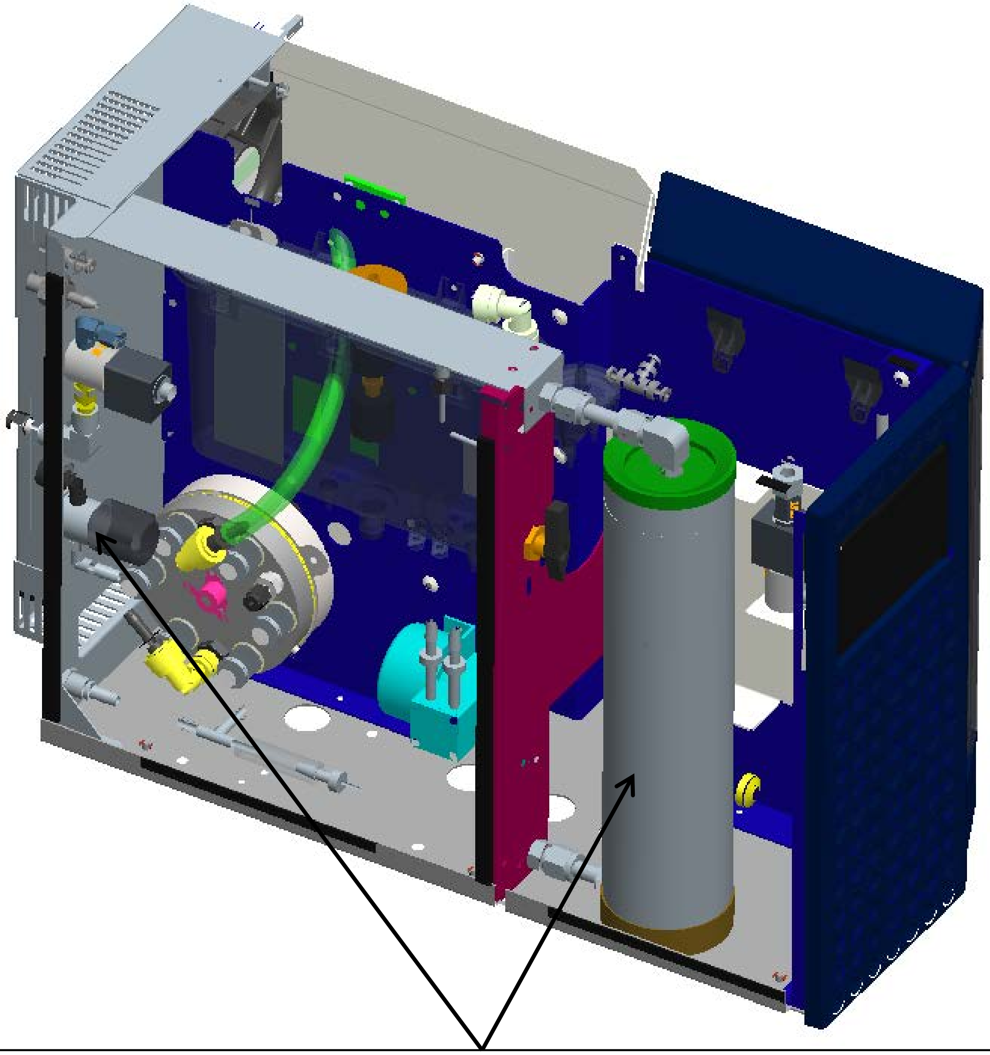
- Alternative materials of construction will be evaluated in terms of strength, hydrogen embrittlement, and cost.
  - Examples include nickel, aluminum, steel
- Candidates down-selected will be bench-tested for performance and durability.



AEM Bench-Test allows for quick screening of materials identified for evaluation.

Approach: AEM System Development

- System materials will be replaced with cheaper alternatives
  - Hydrogen phase separators, plumbing
- Will also serve as test station for durability tests
- Proof of concept for cost reduced product



316L SS Pressure Vessels, valves, and H_2 plumbing will be replaced with cheaper materials

Approach: Milestones

Task Number	Milestone Description	Due Date	% Completed
1.1.1	Synthesis, characterization, and delivery of large (5-10g) batch of low Ru – content lead ruthenate and bismuth ruthenate catalysts	10/15/2013	100%
1.1.2	Screening of initial ionomer compositions	1/15/2014	75%
1.2	Process development for reversal of carbonate contamination	7/15/2014	25%
1.3	Report elucidating fundamental degradation pathways in AEMs with different cations under electrolyzer test conditions as ascertained using 2D NMR spectroscopy (COSY, HMBC, HMQC)	11/14/2014	25%
2.1.1	Complete 200 hour durability testing with down-selected catalysts	11/30/2013	100%
3.1	Using baseline membrane and catalysts, recommend approach for electrode fabrication and attachment	12/30/2013	50%
3.2	Identify optimal MEA for full-scale operational testing.	4/23/2014	25%
4.1.1	Complete material assessment of alkaline compatible stack materials (Cost and strength)	6/28/2014	10%
4.2.1	Finish CAD drawings and sizing calculations for a 1 LPM hydrogen flow rate cell stack	7/30/2014	100%
5.2.1	Complete concept review of methods for CO_2 management within system, including method from 1.2	9/15/2014	10%
5.2.2	Generate complete CAD model for lab scale alkaline system	12/15/2014	25%

Technical Accomplishments: Catalyst Development

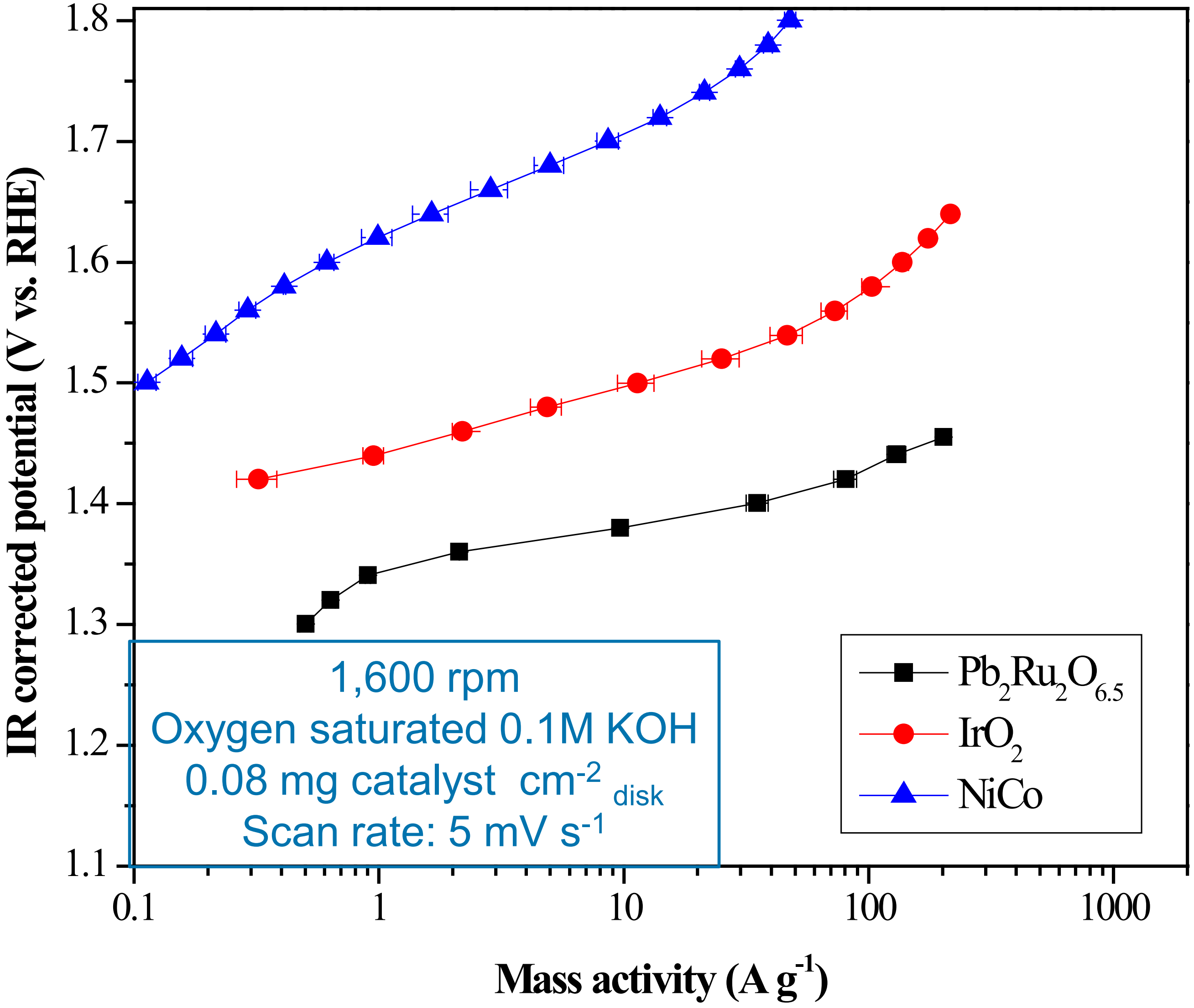
- Successfully synthesized catalysts with higher activity

RDE results:

OER activity (1.5 V vs. RHE) of NiCo electrocatalyst = 0.11±0.01 A/g;

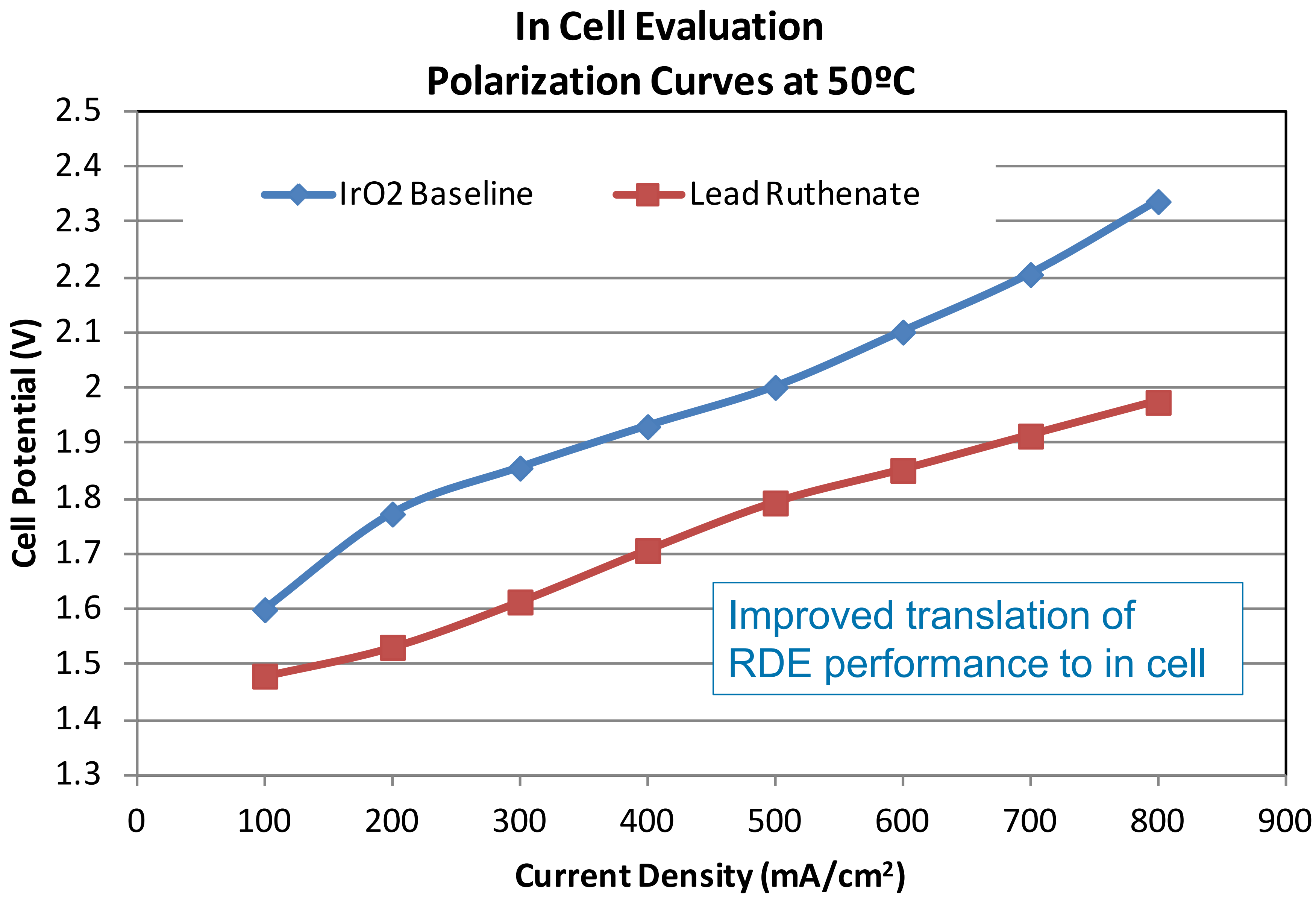
100 times less than IrO_2 (10 A/g)

2000 times less than $Pb_2Ru_2O_{6.5}$ (202 A/g).



1,600 rpm
Oxygen saturated 0.1M KOH
0.08 mg catalyst cm^{-2}$_{disk}$
Scan rate: 5 mV s^{-1}

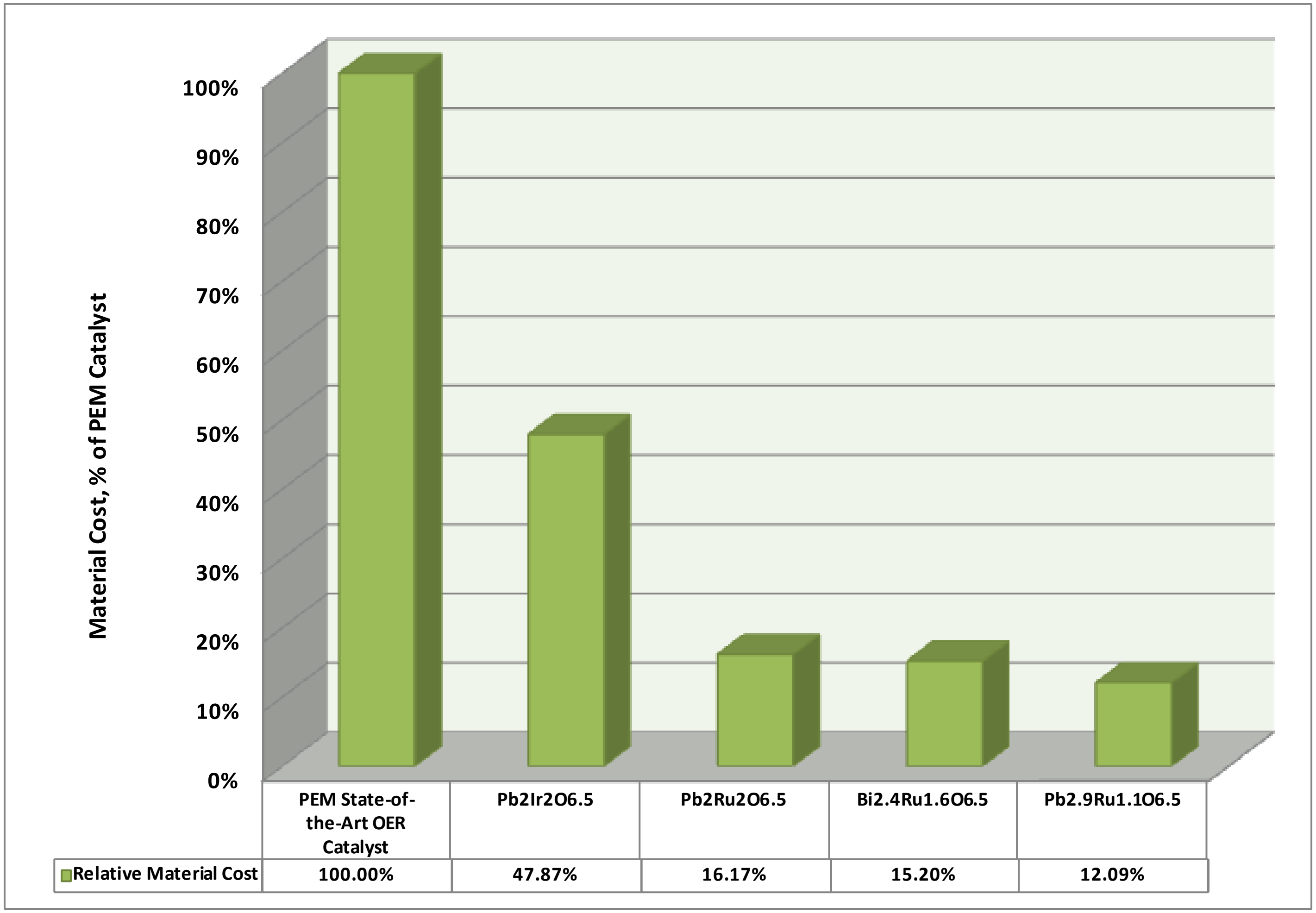
Catalyst: In Cell Measurements



Improved translation of RDE performance to in cell

Catalyst Performance vs. Cost

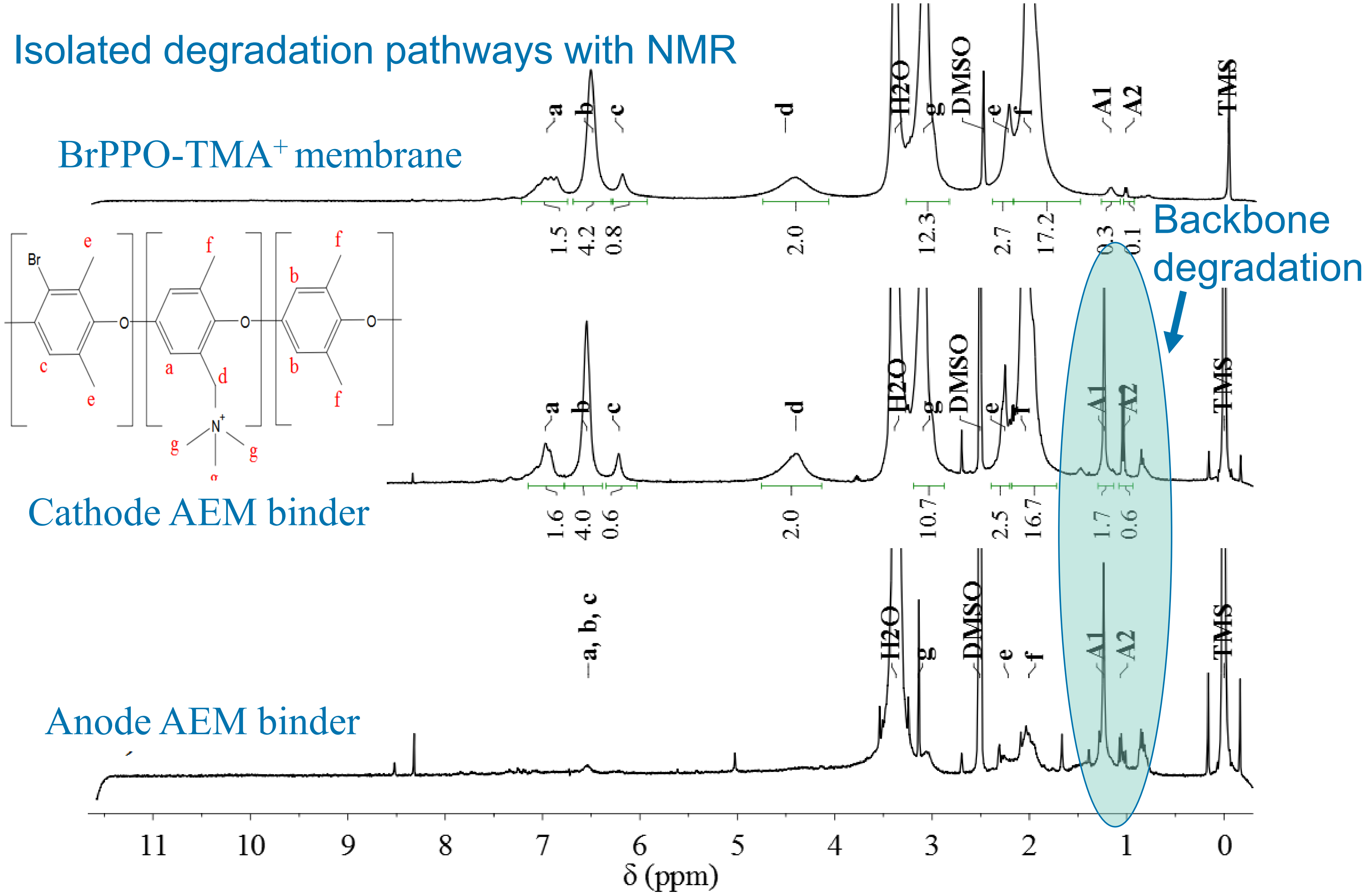
- >80% material cost reduction over baseline OER catalyst
  - Optimum compositions of lead and bismuth ruthenates
  - Better utilization achieved with a more effective GDE structure



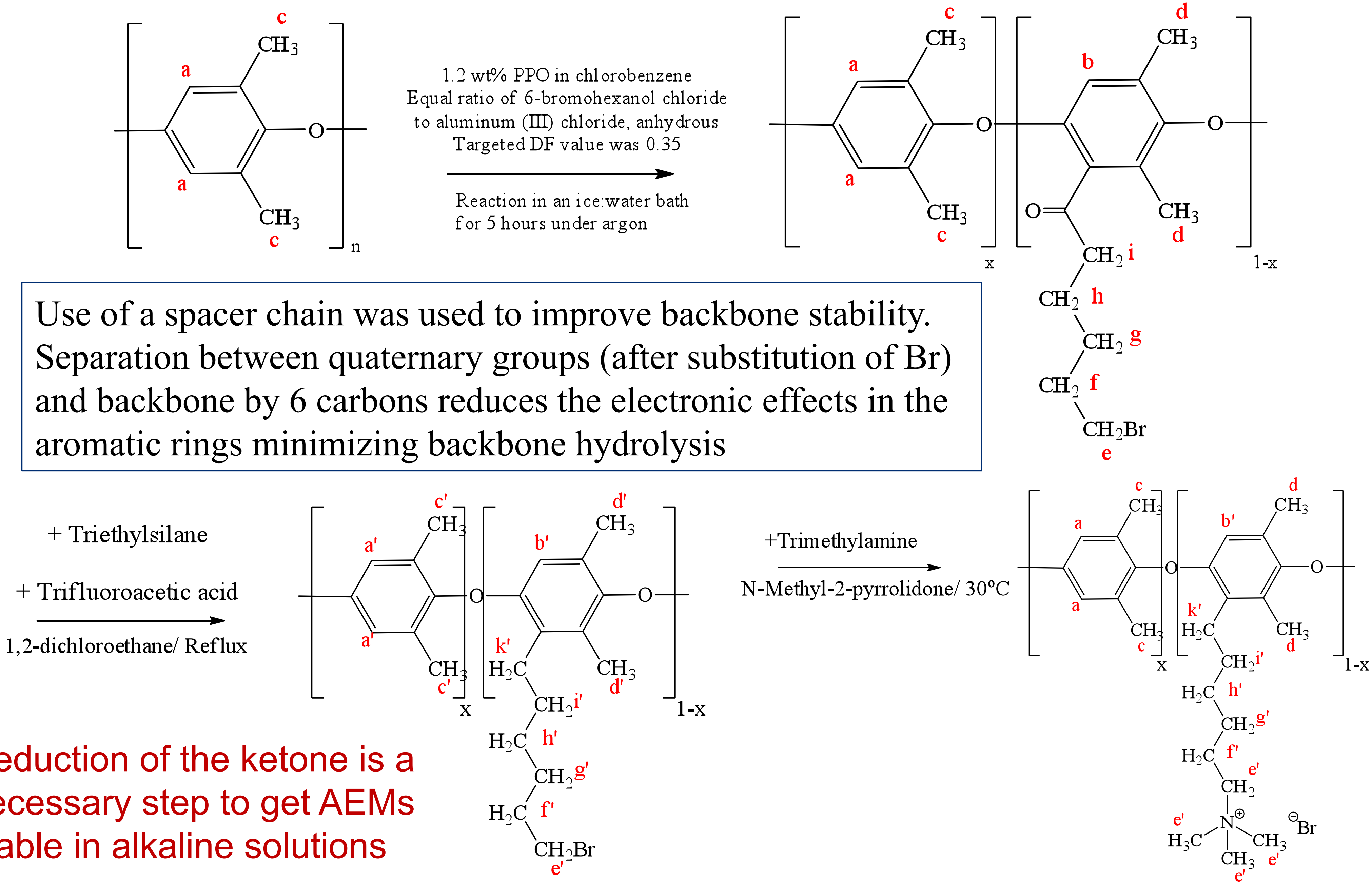
	PEM State-of-the-Art OER Catalyst	Pb2Ir2O6.5	Pb2Ru2O6.5	Bi2.4Ru1.6O6.5	Pb2.9Ru1.1O6.5
🟩 Relative Material Cost	100.00%	47.87%	16.17%	15.20%	12.09%

Technical Accomplishments: Membrane

Isolated degradation pathways with NMR



Binder Synthesis for Improved Stability



1.2 wt% PPO in chlorobenzene
Equal ratio of 6-bromohexanol chloride to aluminum (Ⅲ) chloride, anhydrous
Targeted DF value was 0.35

Reaction in an ice:water bath for 5 hours under argon

+ Triethylsilane
+ Trifluoroacetic acid
1,2-dichloroethane/ Reflux

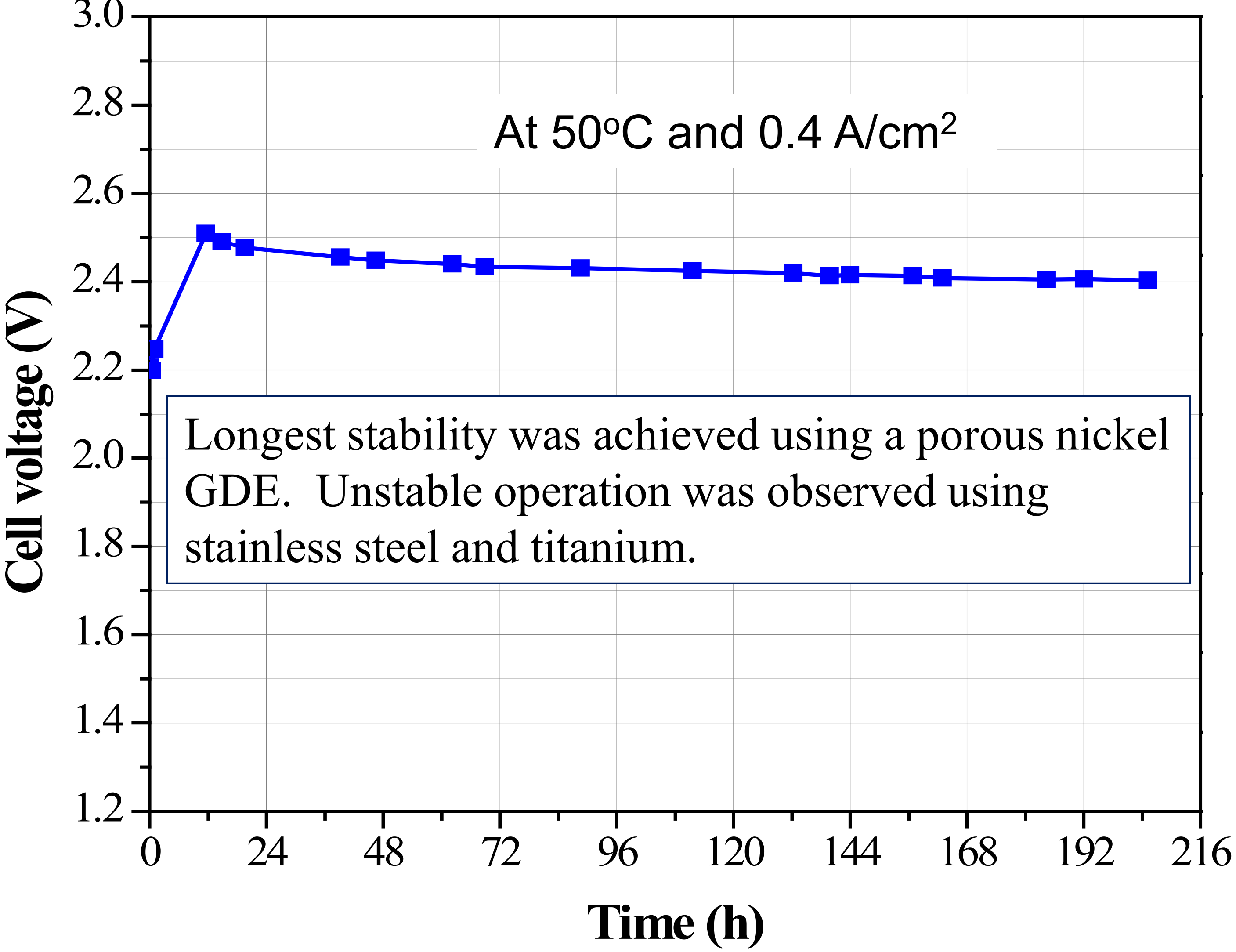
+Trimethylamine
N-Methyl-2-pyrrolidone/ 30°C

Use of a spacer chain was used to improve backbone stability. Separation between quaternary groups (after substitution of Br) and backbone by 6 carbons reduces the electronic effects in the aromatic rings minimizing backbone hydrolysis

Reduction of the ketone is a necessary step to get AEMs stable in alkaline solutions

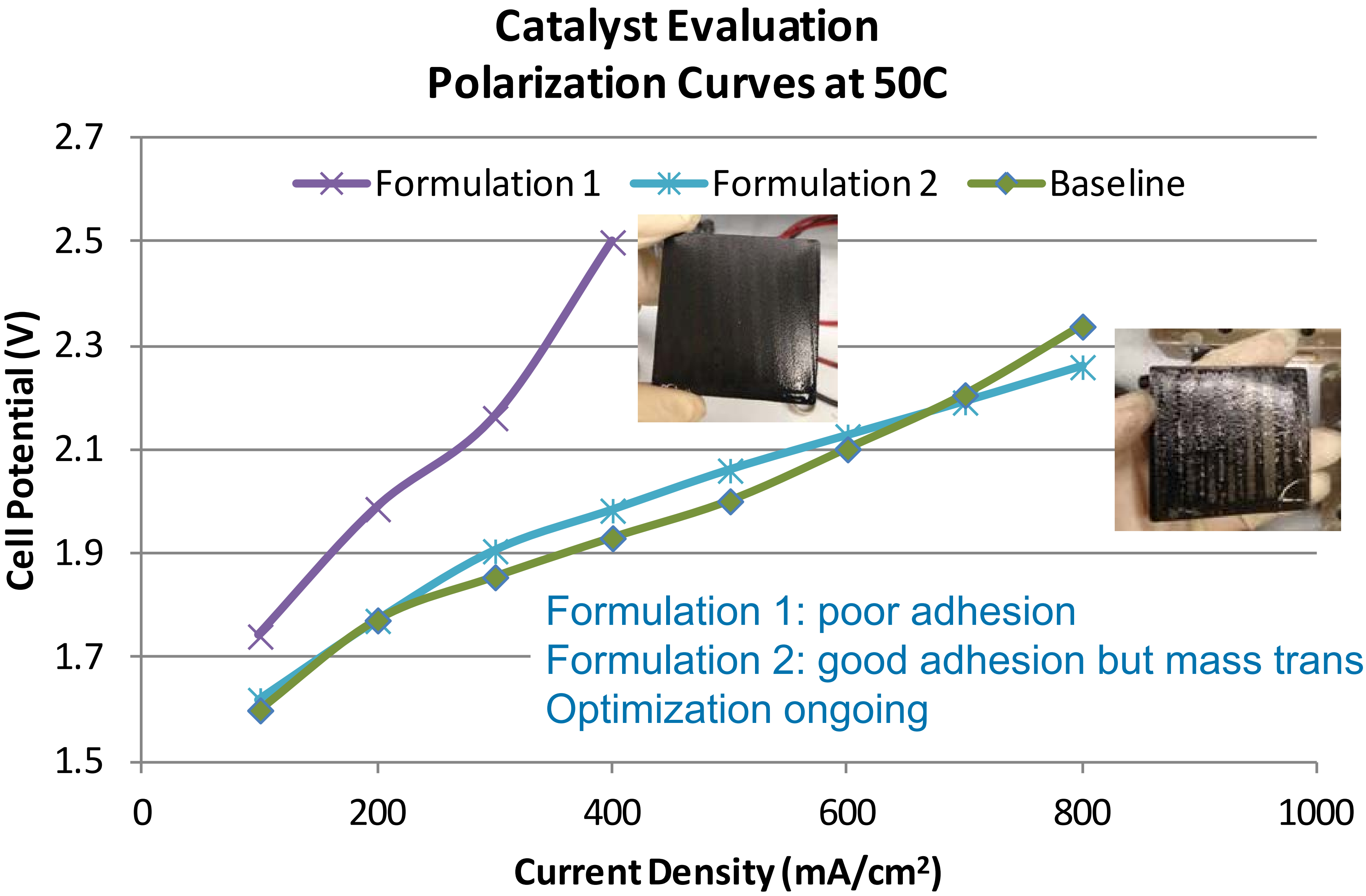
Technical Accomplishments

- Task 3: Electrode Development and Testing
  - Successfully fabricated stable anode GDEs in the AEM cell



Longest stability was achieved using a porous nickel GDE. Unstable operation was observed using stainless steel and titanium.

GDE Added Binder Formulations

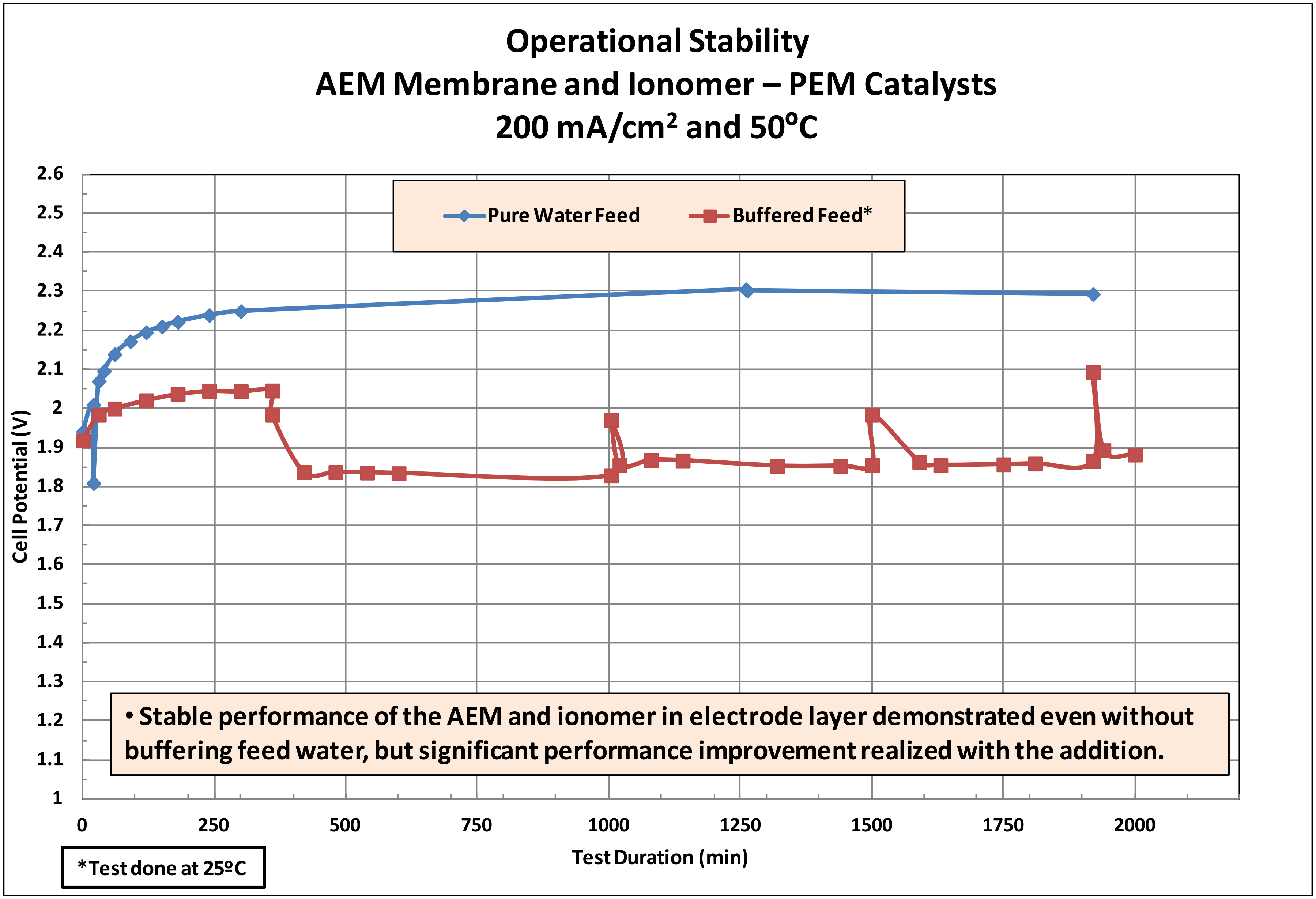


Formulation 1: poor adhesion

Formulation 2: good adhesion but mass transport issues

Optimization ongoing

Impact of Carbonate Addition

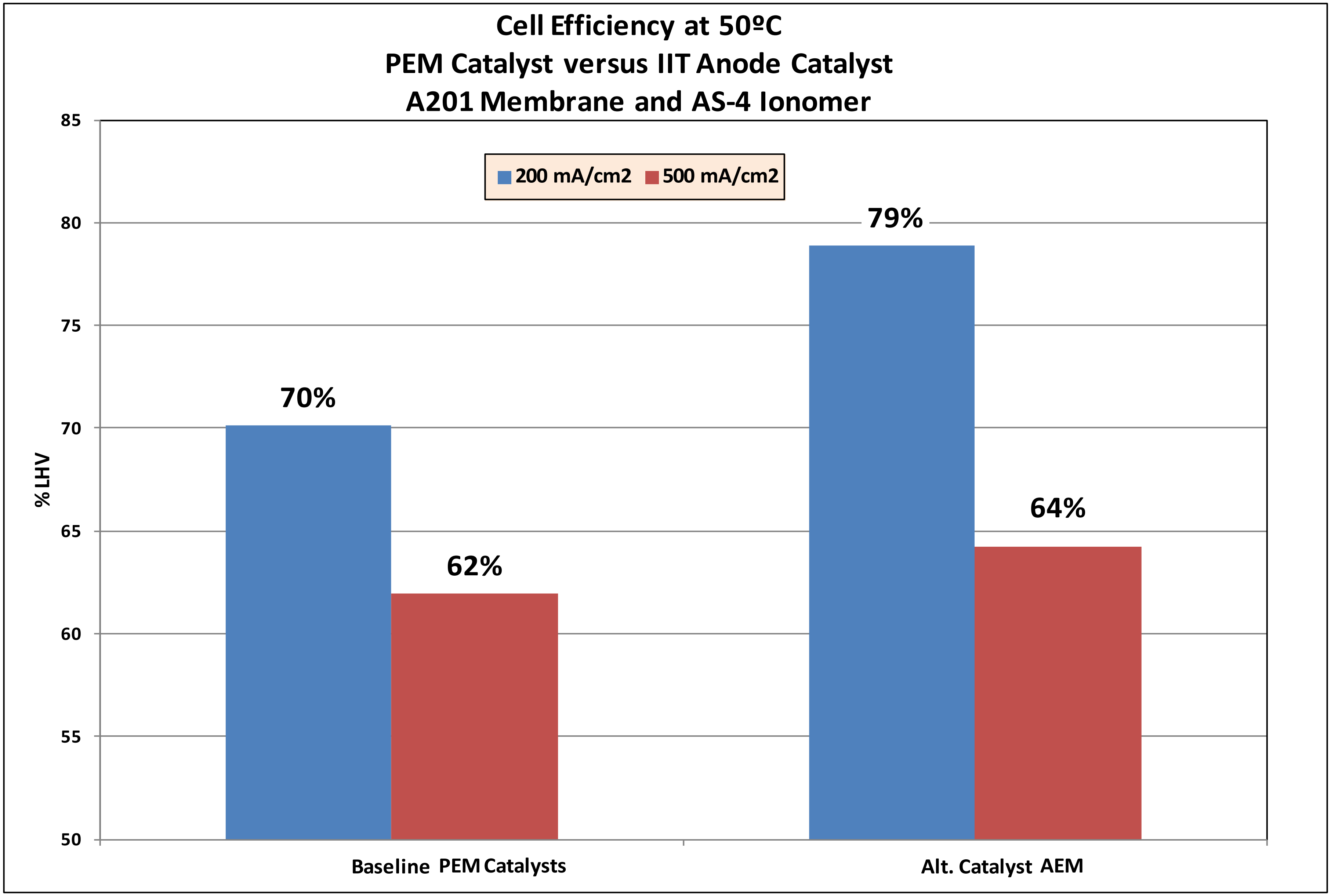


Operational Stability
AEM Membrane and Ionomer – PEM Catalysts
200 mA/cm² and 50°C

- Stable performance of the AEM and ionomer in electrode layer demonstrated even without buffering feed water, but significant performance improvement realized with the addition.

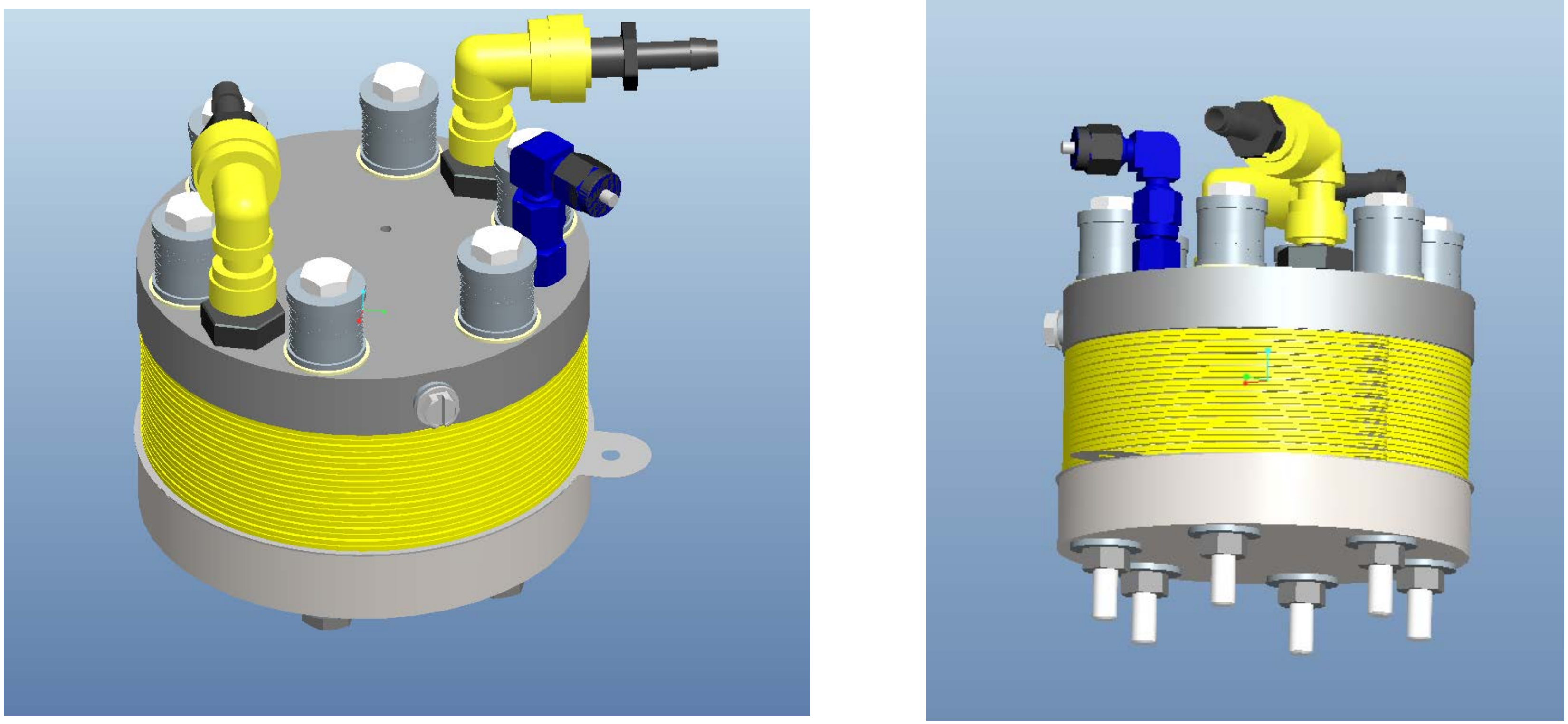
*Test done at 25ºC

Performance vs. Previous Baseline



Technical Accomplishments

- Task 4: Stack Design
  - Modeling of stack complete. Flow modeling initiated.
  - Strength calculations on alt. materials initiated.



1L/min cell stack design

Future Work: IIT

- Continue development of alternate binders and membranes
  - Optimize separately to distinguish effects
  - Start with ionomer and Tokuyama A201
- Characterize decomposition mechanisms using 2-D NMR and use to iterate on binder and membrane synthesis
- Evaluate impact of cross-linking on membrane stability
- Determine differences in degradation modes for anode and cathode feed modes
- Perform corrosion study for titanium, stainless steel and nickel porous plates
- Provide samples to Proton for durability testing at differential pressure

Future Work: Proton

- **Cell Stack Development**
  - Complete strength calculations and hydrogen uptake analysis on alternate materials.
  - Provide feedback to IIT on material testing for iterations
  - Compare to Sandia membrane baseline for stability
  - Order down-selected cell materials and stack embodiment hardware
  - Test new stack configuration for performance and impact on previously reported durability
  - Conduct multi-cell operational test to simulate pilot run and assess reproducibility.
- **System Development**
  - Conduct material characterizations
  - Order system components for prototype demonstration
  - Conduct steady-state operational testing of complete stack/system
    - Evaluate durability with and without carbonate in the water loop

Collaborators

- Illinois Institute of Technology:
  - Catalyst and ionomer synthesis and screening
  - 2-D NMR for ionomer/membrane degradation studies
  - Fundamental characterization
- Sandia National Lab
  - Supply of ionomer and membrane to Proton
  - Best performing class of materials from ARPA-E project as baseline for study

ILLINOIS INSTITUTE
OF TECHNOLOGY

Sandia
National
Laboratories

Summary of Previous Year Comments and Responses

- No comparisons were made to known state-of-the-art materials with RDE

Answer: RDE data and full cell data was shown for lead ruthenate cataysts vs. iridium oxide catalysts. Nickel data was added to the 2014 slides.

- The extent of collaboration with IIT on membranes was not clear.

Answer: IIT has been involved actively in the synthesis and evaluation of several anion exchange membranes. Some results are shown here.

- Need more structural characterization of pyrochlores.

Answer: Catalysts were evaluated measuring BET, conductivity, and OER activity which provides enough information to decide if they are viable. Scope and budget do not allow for more fundamental characterization.

- There should be a focus on why certain materials exhibit low surface area.

Answer: Differences in synthesis method likely impacted surface areas.

- Should reduce the catalyst development work and focus on membrane performance and durability issues.

Answer: Have shifted more focus (at IIT) to synthesis of AEMs and stability (both as membrane and solubilized AEM binder). However, the work as proposed and approved by the proposal reviewers needs to be completed.

Summary

- **Relevance:** Demonstrates technology pathway to reducing cell stack capital cost and resulting hydrogen production cost for further market penetration
- **Approach:** Synthesize a stable OER catalyst to enable low cost flow fields for cheaper AEM operation
- **Technical Accomplishments:**
  - Promising catalyst and membrane/ionomer compositions identified , improvement demonstrated
  - 2D NMR to understand degradation mechanisms
  - 200 hour durability test successfully completed for anode GDE
  - System layout and stack flow modeling completed
- **Collaborations:**
  - Illinois Institute of Technology: Screening and synthesis of lead ruthenate pyrochlore catalyst. Development of stable ionomer being pursued.
  - Sandia: Casting additional membranes of best performing ionomers to date
- **Proposed Future Work:**
  - Optimize cathode and anode GDEs to increase cell efficiency, while maintaining operational stability
  - Reduce cost of stack and system components for total electrolyzer reduction in cost
  - Electrode and stack scale-up
  - Manufacturing cost reduction study and refined H2A model $/kg cost analysis

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- Chris Arges
- Javier Parrondo
- Cy Fujimoto (Sandia)