PROTON
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# Economical Production of Hydrogen through Development of Novel, High Efficiency Electrocatalysts for Alkaline Membrane Electrolysis

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Organization: Proton OnSite

Date: May 15, 2013

Project ID: PD094

# Overview

## Timeline

- Project Start: 20 Feb 2012
- Project End: 19 Nov 2012
- Percent complete: 100% (Phase II pending)

## Budget

- Total project funding
  - DOE share: $1,150,000
- Funding for FY13
  - DOE share: $500,000 (pending)

## Barriers

- Barriers addressed
  G: Capital Cost

| Table 3.1.5 Technical Targets: Central Water Electrolysis Using Green Electricity [a,b] | | | | |
|---|---|---|---|---|
| Characteristics | Units | 2011 Status [c] | 2015 Target [d] | 2020 Target [e] |
| Hydrogen Levelized Cost (Plant Gate) [f] | $/kg $H_2$ | 4.10 | 3.00 | 2.00 |
| Total Capital Investment [b] | $M | 68 | 51 | 40 |
| System Energy Efficiency [g] | % | 67 | 73 | 75 |
| | kWh/kg $H_2$ | 50 | 46 | 44.7 |
| Stack Energy Efficiency [h] | % | 74 | 76 | 78 |
| | kWh/kg $H_2$ | 45 | 44 | 43 |
| Electricity Price [i] | $/kWh | From AEO '09 | $0.049 | $0.031 |

## Partners

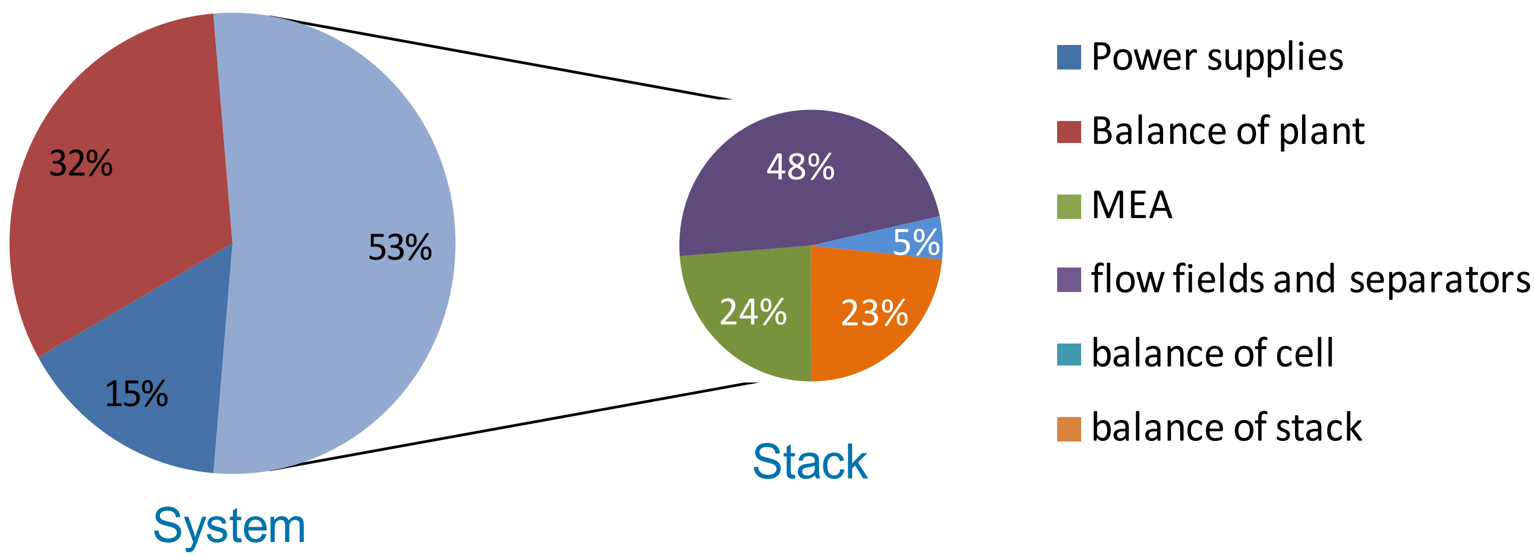
- Illinois Institute of Technology

# Relevance: Project Objectives

- Demonstrate high activity of pyrochlore catalysts for oxygen evolution
- Optimize catalyst composition and microstructure
- Form and characterize new anion exchange membranes and demonstrate acceptable conductivity for electrolysis
- Process promising membrane and catalyst materials into MEAs
- Scale up to a relevant stack active area and height and operate in a relevant environment.

# Relevance: Cost

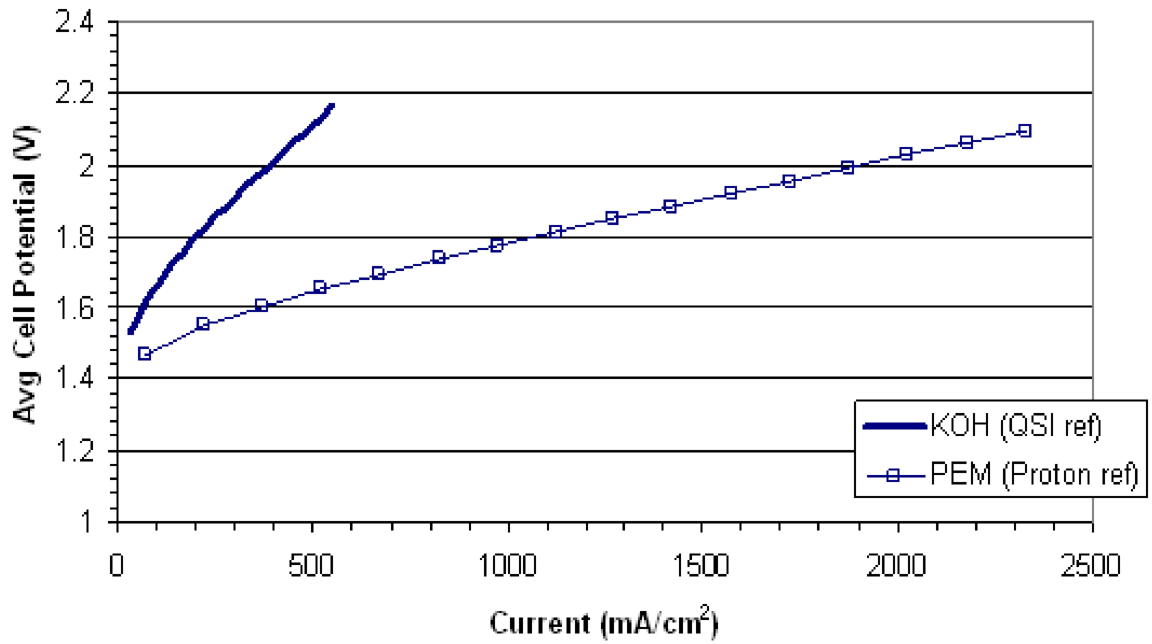
- Metal flow fields and separators represent almost half of stack cost




- Alkaline media enables transition from titanium to stainless steel: eliminates 75% of part cost
- Also enables less expensive catalysts

# Relevance: Efficiency

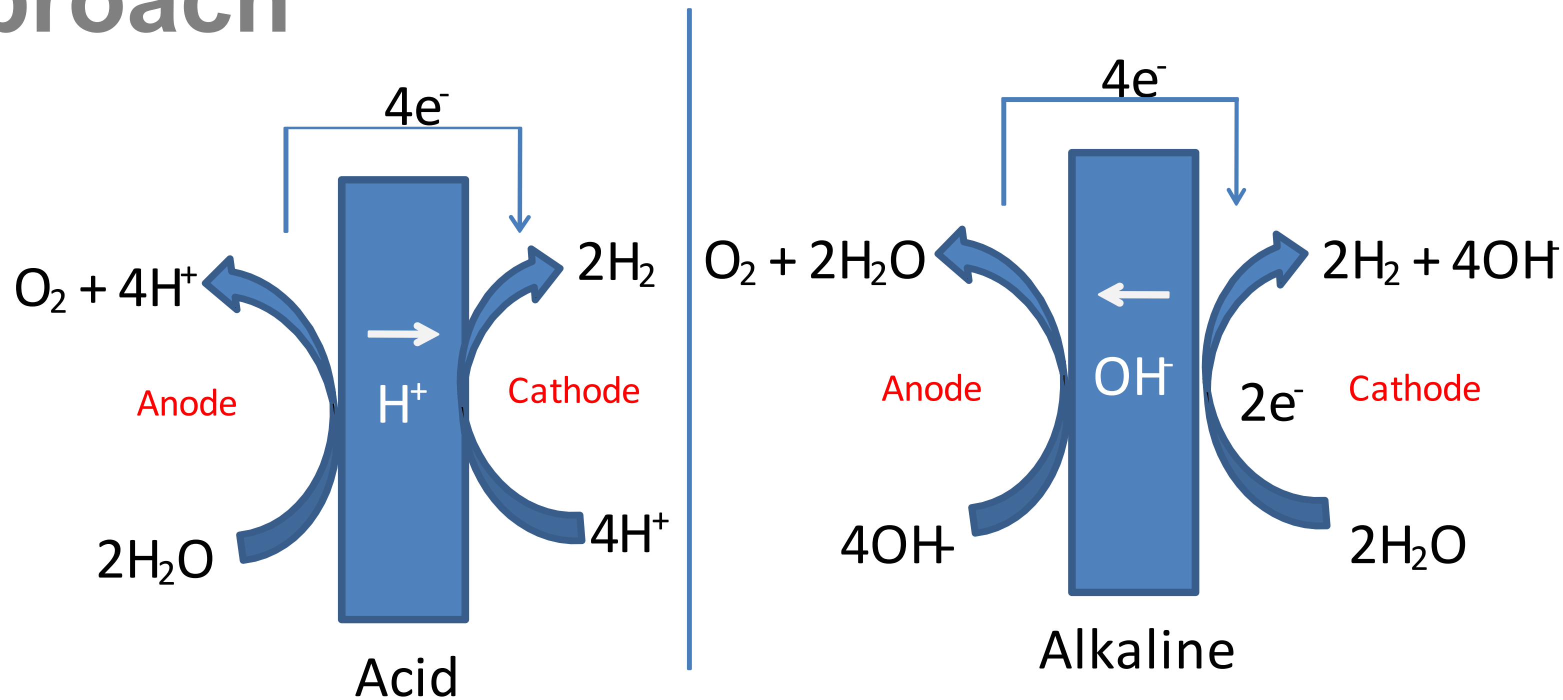
- Liquid KOH electrolyte systems much less efficient than membrane-based systems
- Expect AEM hybrid to fall between existing technologies
- Advanced catalysts and membranes help to close gap



# Top Level Approach

- Task 1.0 Catalyst Development
  - 1.1 – Catalyst Synthesis
  - 1.2 – Catalyst Characterization
- Task 2.0 Membrane Development
  - 2.1 – Membrane Synthesis
  - 2.2 – Membrane Characterization
- Task 3.0 MEA Testing
  - 3.1 – Manufacturing Development
  - 3.2 – Electrochemical Characterization
  - 3.2 – Post Operational Assessment
- Task 4.0 Program Management

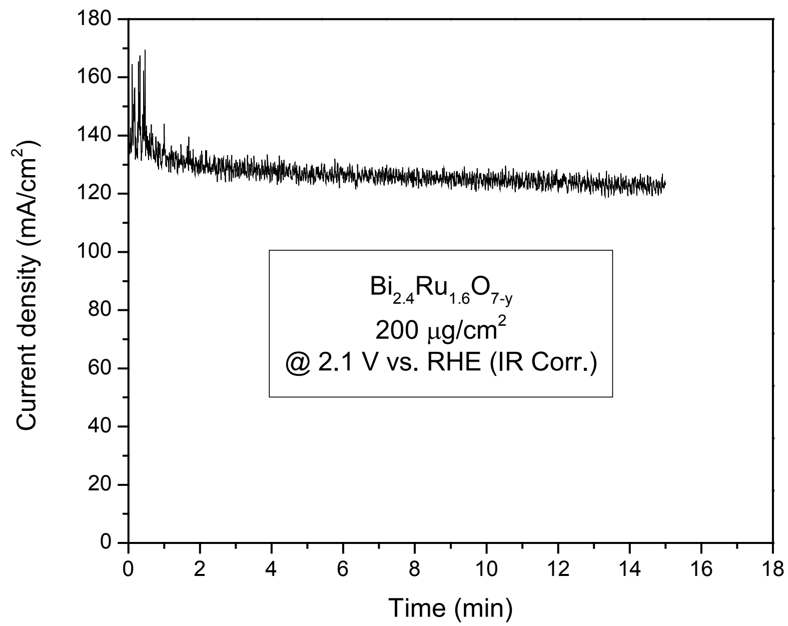
# Approach




- Water management is a key consideration in determining operating point
- Phase separation easier with anode feed
- ARPA-E work shows 500 $mA/cm^2$ achievable with no water mass transport issues

# Approach

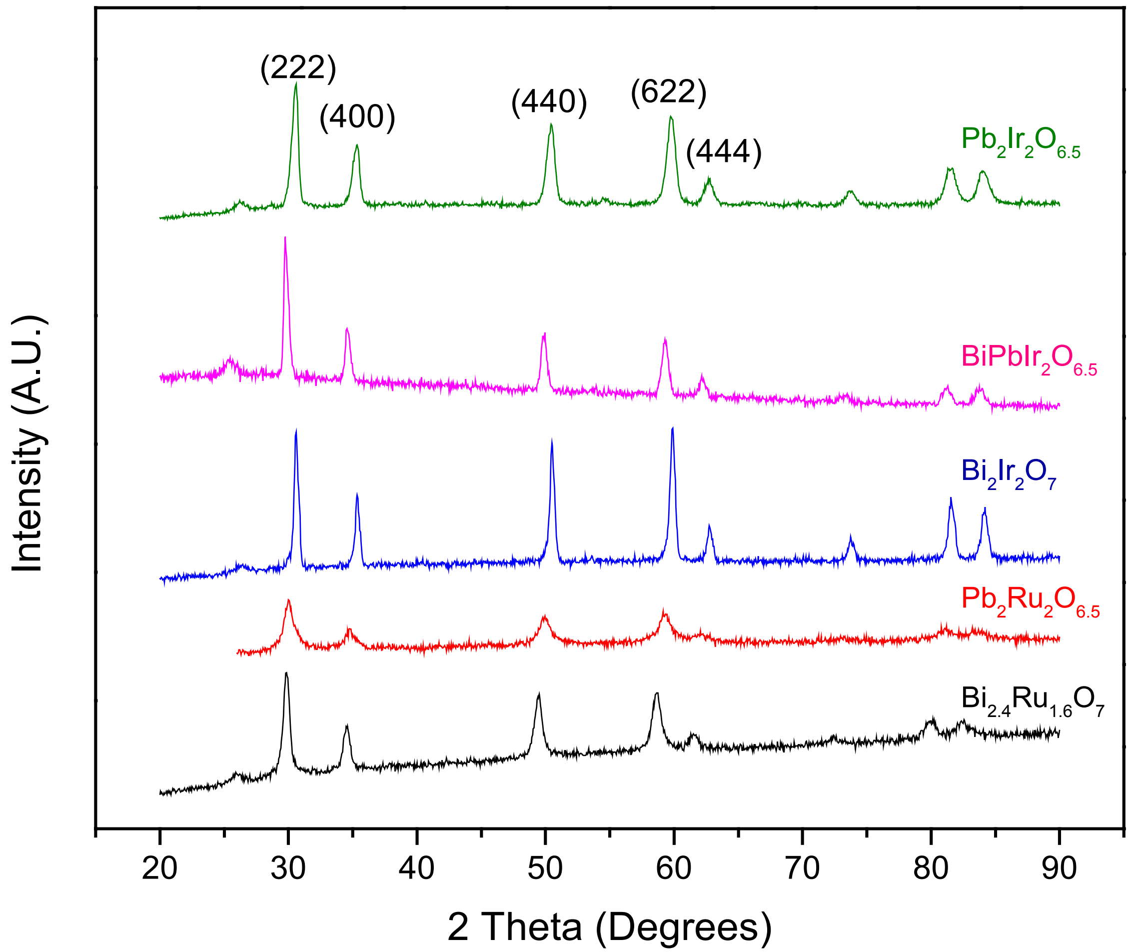
- Leverage pyrochlore class of catalysts ($A_2B_2O_{6-7}$)
  - Good kinetics for OER
  - Stable in base
  - Able to make as nanoparticles
- Investigate compounds with A = Bi, Pb; B = Ru, Ir



# Technical Accomplishments: Phase 1

| Task | Task Description | Progress Notes | Completion |
|---|---|---|---|
| 1.0 | Catalyst Development | • Synthesized desired pyrochlores and proved structure with XRD | 100% |
| 2.0 | Membrane Development | • Focused on development of Tokuyama for catalyst screening<br>• Investigated 2 additional polysulfone derivatives | 100% |
| 3.0 | MEA testing | • Process trials completed for improved electrode adhesion and stability<br>• Cells tested for up to 200 hours | 100% |
| 4.0 | Program Management | • Project reporting completed<br>• Phase II proposal completed with internal funds | 100% |

# Technical Accomplishments: Synthesis

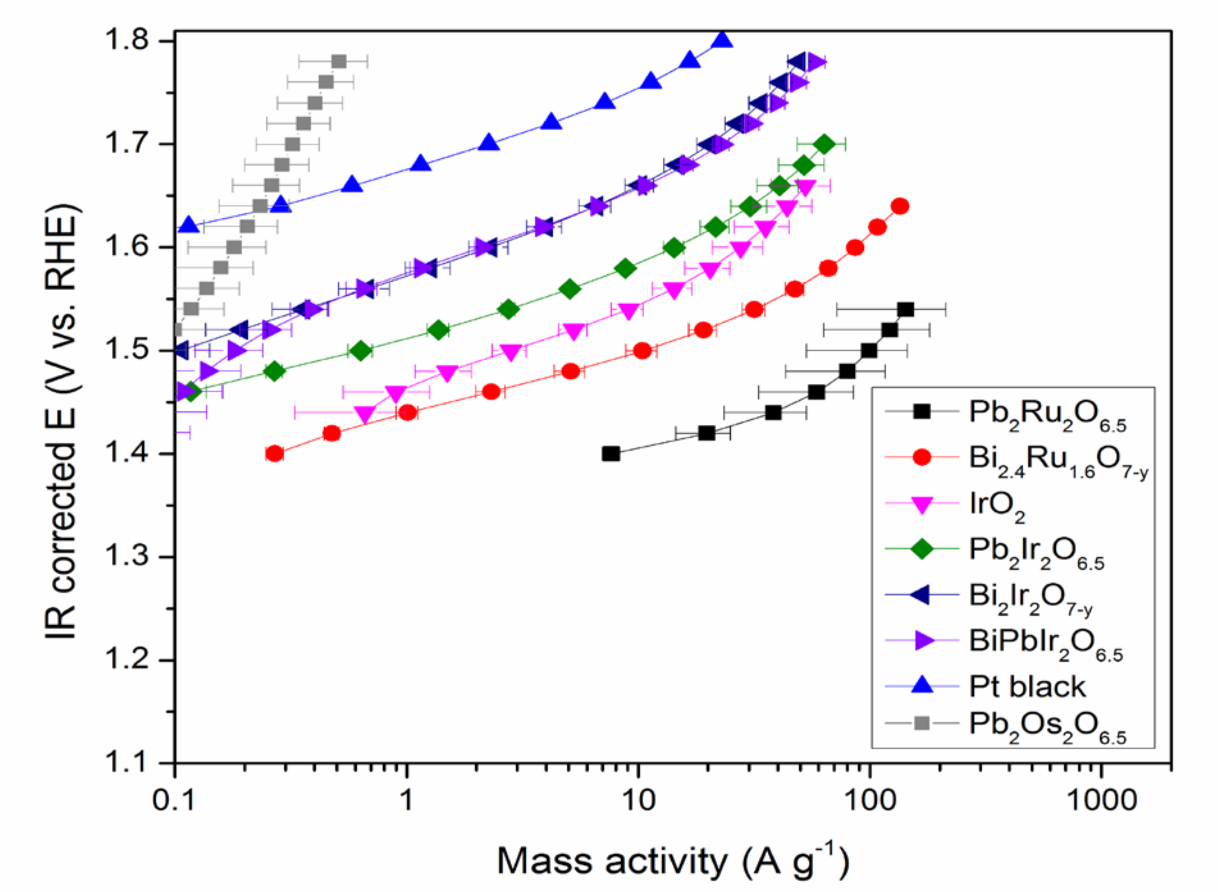



| Catalyst | B.E.T. surface area ($m^2/g$) | Electronic conductivity S/cm |
|---|---|---|
| $Pb_2Ru_2O_{6.5}$ | 99±4 | 87 |
| $Bi_{2.4}Ru_{1.6}O_7$ | 7.8±0.2 | 63 |
| $Pb_2Ir_2O_{6.5}$ | 1.2±0.1 | 73±7 |
| $Bi_2Ir_2O_7$ | 0.4±0.1 | 56±6 |
| $BiPbIr_2O_{6.5}$ | 0.4±0.1 | 75±7 |
| $Pb_2Os_2O_{6.5}$ | 0.8±0.3 | |

- Desired compositions successfully made
- Surface area of some compositions still low

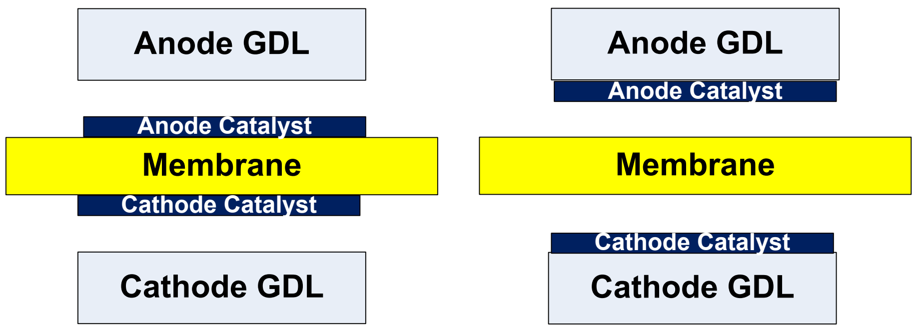
# Technical Accomplishments: Bench Tests

- Mass activity shows good promise even with some catalysts at 10% desired surface area

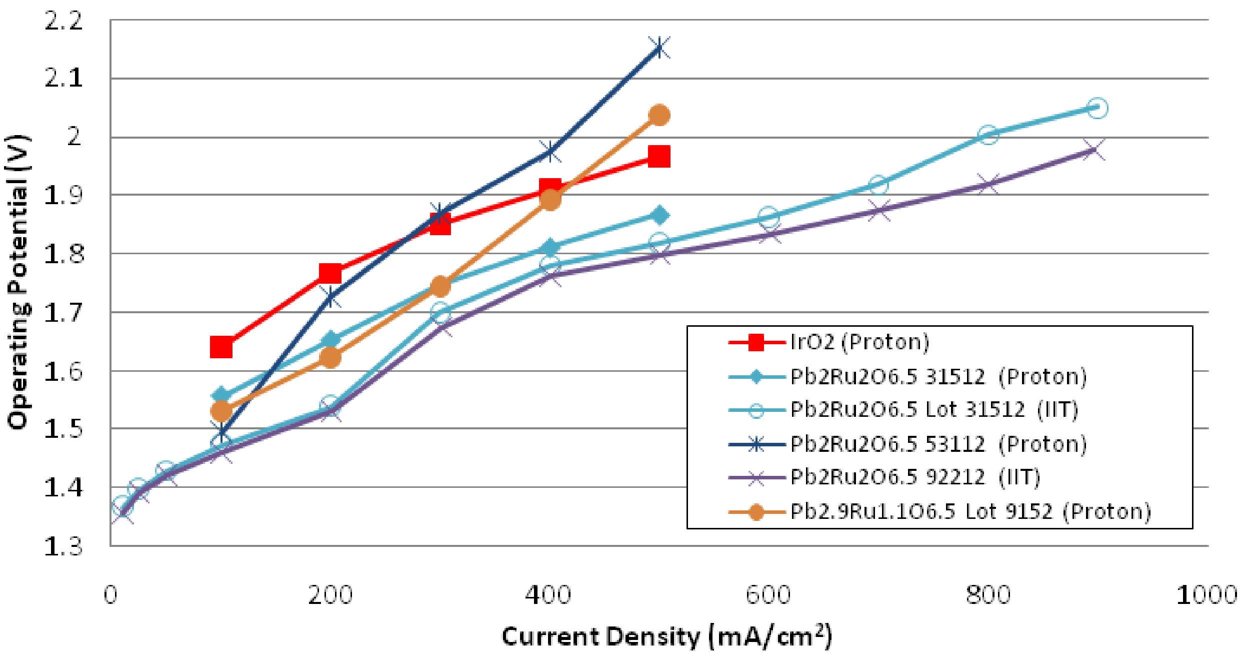


# Technical Accomplishments: Electrode and Cell Fabrication

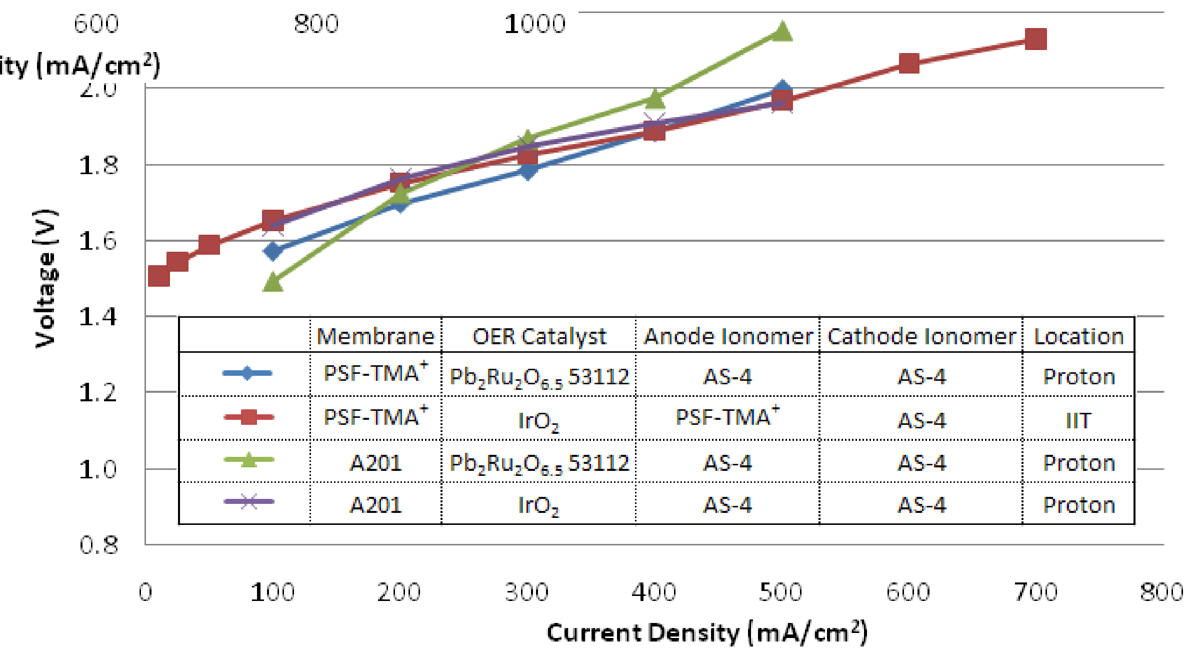
- GDE approach leveraged to mitigate stress on membrane
- Ionomer formulation and technique leveraged from ARPA-E program
- Cell design modified for thinner/stiffer membranes



# Technical Accomplishments: Stack Testing




- RDE shows good translation to full cell
- IIT membranes show similar performance to commercial AEM

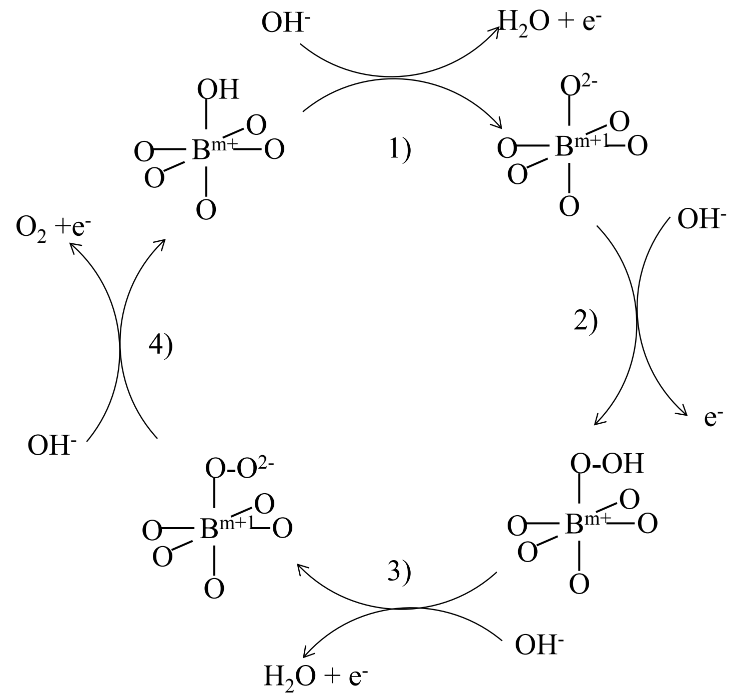



| | Membrane | OER Catalyst | Anode Ionomer | Cathode Ionomer | Location |
|---|---|---|---|---|---|
| (blue diamond) | PSF-TMA+ | $Pb_2Ru_2O_{6.5}$ 53112 | AS-4 | AS-4 | Proton |
| (red square) | PSF-TMA+ | $IrO_2$ | PSF-TMA+ | AS-4 | IIT |
| (green triangle) | A201 | $Pb_2Ru_2O_{6.5}$ 53112 | AS-4 | AS-4 | Proton |
| (purple x) | A201 | $IrO_2$ | AS-4 | AS-4 | Proton |

# Technical Accomplishments: Modeling

- D-band orbital theory and density functional theory used to explain activity trends
- Larger metal-adsorbate repulsion ($V^2$) leads to lower OER activity

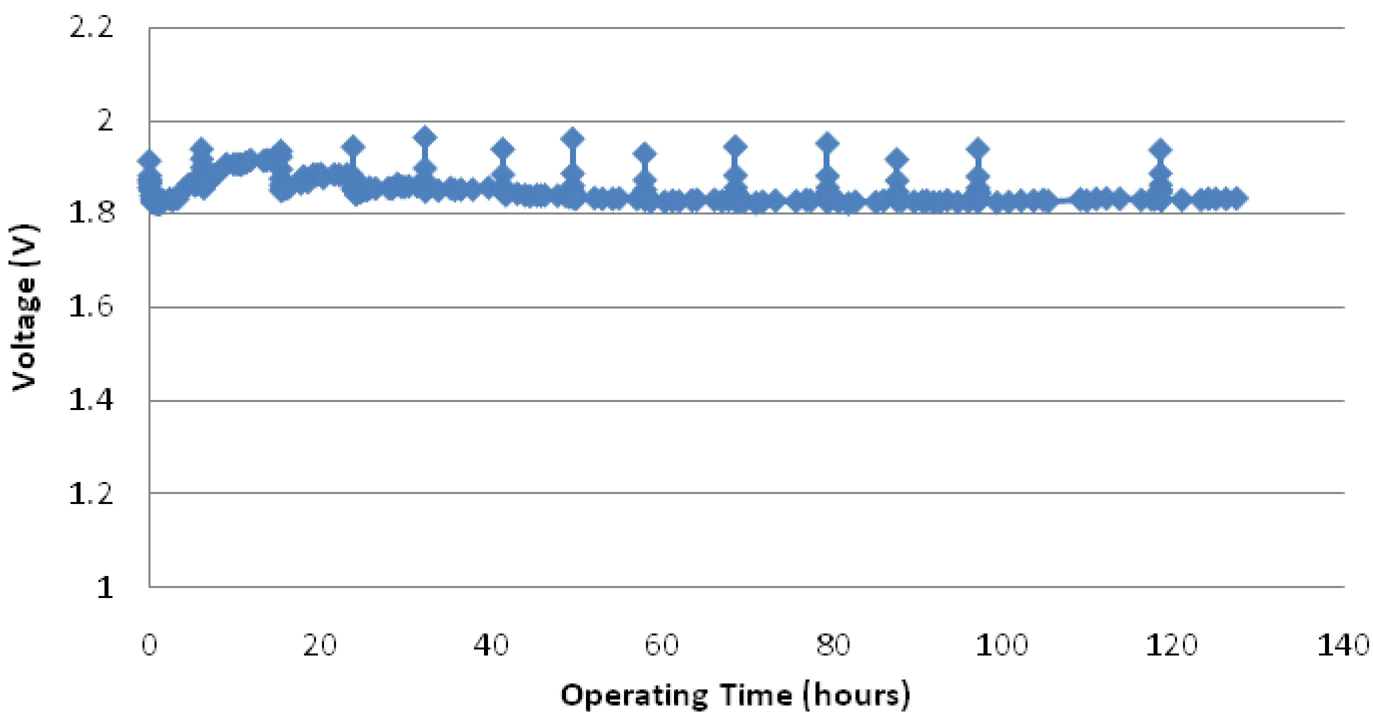
| Catalyst | B cation | d band center* ($\varepsilon_d$, eV) | $V^2_{ad}$* | $i_m$(A/g) | $i_s$(A/m$^2$) |
|---|---|---|---|---|---|
| $Pb_2Ru_2O_{6.5}$ | Ru | -1.41 | 3.87 | 100±40 | 1.0±0.5 |
| $Bi_{2.4}Ru_{1.6}O_{6.9}$ | Ru | -1.41 | 3.87 | 10±2 | 1.3±0.2 |
| $Pb_2Ir_2O_{6.5}$ | Ir | -2.11 | 4.45 | 0.6±0.1 | 0.5±0.1 |
| $Bi_2Ir_2O_{6.8}$ | Ir | -2.11 | 4.45 | 0.11±0.03 | 0.3±0.1 |
| $BiPbIr_2O_{6.5}$ | Ir | -2.11 | 4.45 | 0.18±0.06 | 0.5±0.2 |
| $Pb_2Os_2O_{6.5}$ | Os | ------ | 5.13 | 0.08±0.03 | 0.1±0.05 |



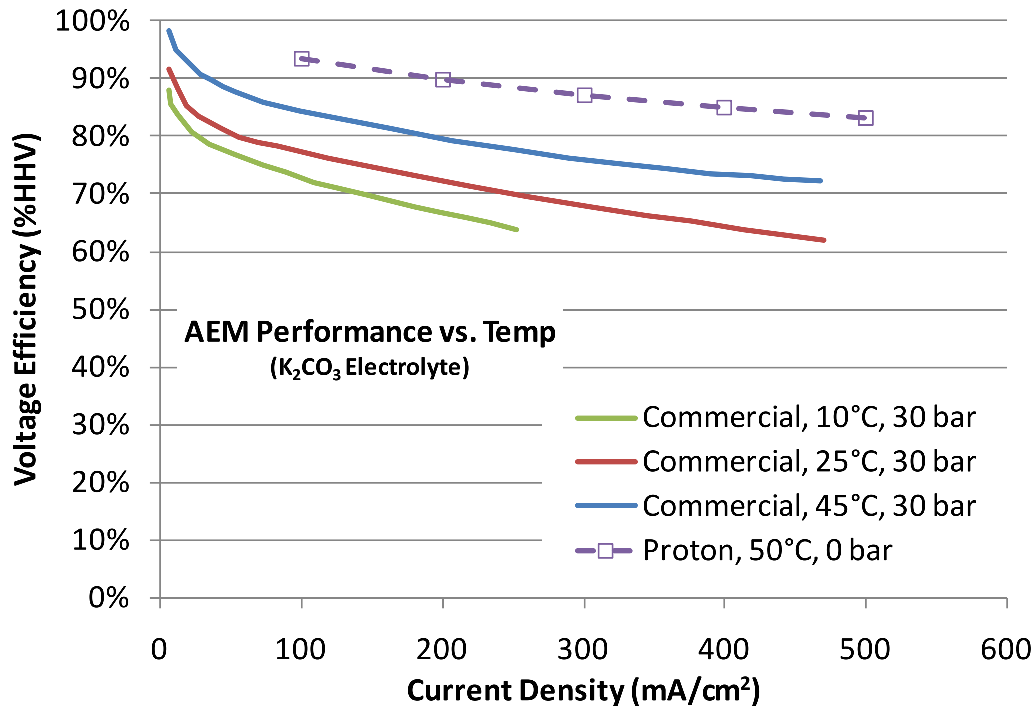

Proposed mechanism

# Technical Accomplishments: Durability

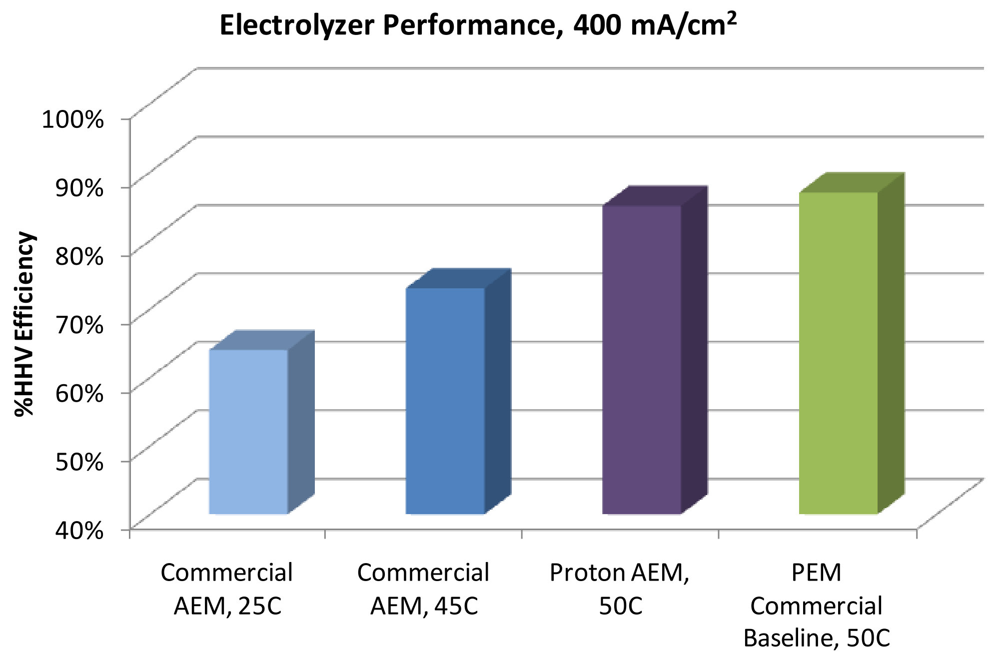
- Voltage stability good with carbonate recirculation
- Phase II will focus on pure water



# Comparison to State of the Art




- Exceeds existing AEM and approaches legacy PEM performance

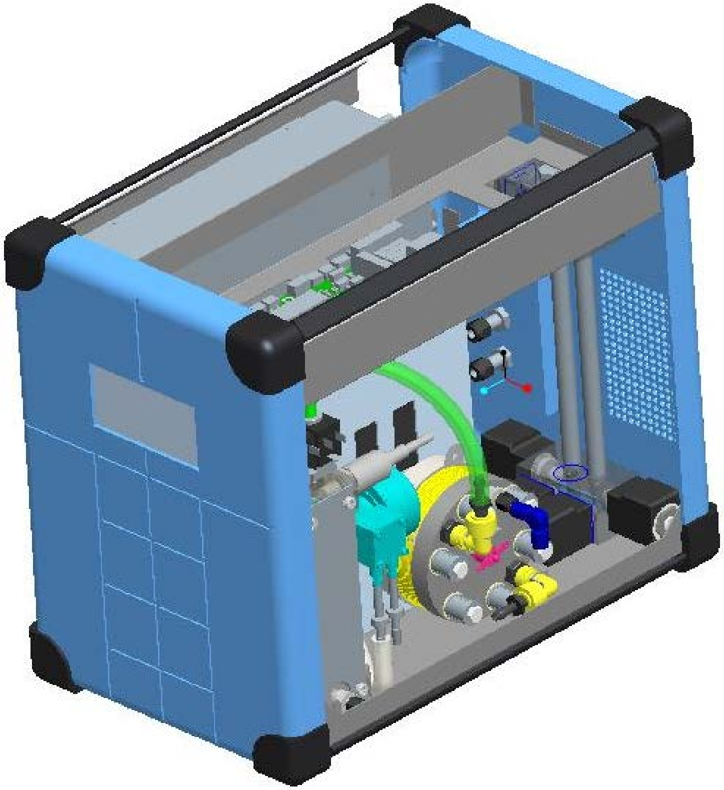


# Collaboration

- IIT major subcontractor on Phase 1
  - Catalyst synthesis and structural characterization
  - Molecular bonding theory
- Phase II to focus on continued synthesis optimization of particle size and composition
- Tuning of properties for membrane and ionomer stability

# Future Work:

- Determine influence of composition on pyrochlore microstructure, physical properties, and activity
- Determine the impact of key AEM properties (conductivity, water uptake, gas crossover) on AEM performance and synthesize optimized AEMs
- Complete system trade study of electrolyte vs. cost and stability and develop prototype lab system
- Provide a product cost analysis for lab scale and large scale AEM electrolysis systems



# Summary

- **Relevance:** Alternate electrolysis chemistry for capital cost reduction
- **Approach:** Leverage AEM expertise to reduce cell part cost with efficient catalyst and membrane materials to offset lower operating current
- **Technical Accomplishments:**
  - Improved OER and model development for improved prediction
  - Initial membrane performance equivalent to baseline
  - Stability of AEM electrolysis and improvement over existing technology
- **Collaborations:**
  - IIT: Catalyst and membrane synthesis; modeling
- **Proposed Future Work:**
  - Leverage model to optimize catalyst performance
  - Optimization of membrane properties for stable performance
  - System prototype and cost analysis