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# Non-Platinum Group Metal OER/ORR Catalysts for Alkaline Membrane Fuel Cells and Electrolyzers

P. I. Name: Nemanja Danilovic

Organization: Proton OnSite

Date: May 15, 2015

Project ID: FC-133

# Overview

## Timeline

- Project Start: 15 Feb 2015
- Project End: 15 Nov 2015
- Percent complete: ~30%

## Budget

- Total project funding
  - DOE share: $150,000

## Partners

- Rutgers University:
  - Charles Dismukes (PI)
  - Graeme Gardner
  - Karin Calvinho

## Barriers

- Barriers addressed
  - G: Capital Cost (Electrolyzer + Fuel Cell)

**Table 3.4.7.a Technical Targets: Portable Power Fuel Cell Systems (<2 Watt)[a]**

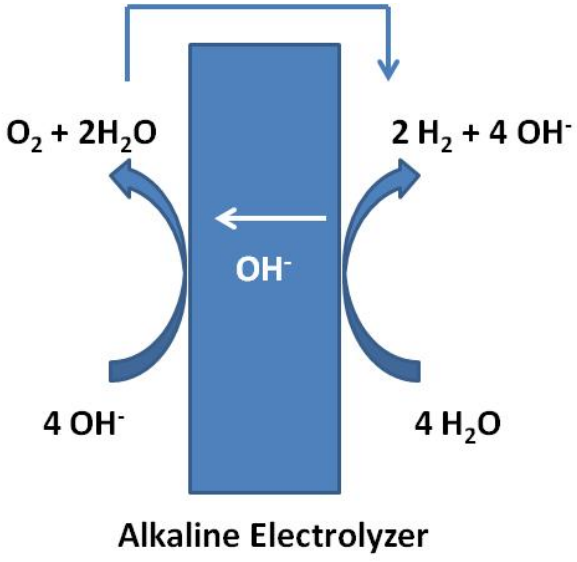
| Characteristic | Units | 2011 Status | 2013 Targets | 2015 Targets |
|---|---|---|---|---|
| Specific power[b] | W/kg | 5 | 8 | 10 |
| Power density[b] | W/L | 7 | 10 | 13 |
| Specific energy[b,c] | Wh/kg | 110 | 200 | 230 |
| Energy density[b,c] | Wh/L | 150 | 250 | 300 |
| Cost[d] | $/system | 150 | 130 | 70 |
| Durability[e,f] | hours | 1,500 | 3,000 | 5,000 |
| Mean time between failures[f,g] | hours | 500 | 1,500 | 5,000 |

**Table 3.1.4 Technical Targets: Distributed Forecourt Water Electrolysis Hydrogen Production [a, b, c, l]**

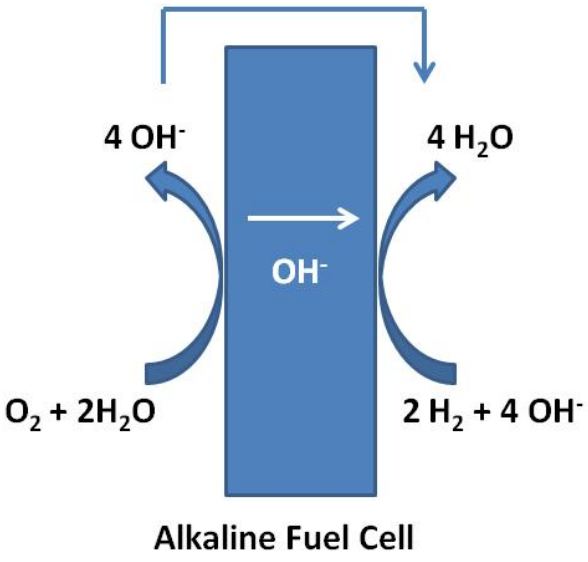
| Characteristics | Units | 2011 Status | 2015 Target | 2020 Target |
|---|---|---|---|---|
| Hydrogen Levelized Cost [d] (Production Only) | $/kg | 4.20 [d] | 3.90 [d] | 2.30 [d] |
| Electrolyzer System Capital Cost | $/kg<br>$/kW | 0.70<br>430 [e, f] | 0.50<br>300 [f] | 0.50<br>300 [f] |
| System Energy Efficiency [g] | % (LHV)<br>kWh/kg | 67<br>50 | 72<br>46 | 75<br>44 |
| Stack Energy Efficiency [h] | % (LHV)<br>kWh/kg | 74<br>45 | 76<br>44 | 77<br>43 |
| Electricity Price | $/kWh | From AEO 2009 [i] | From AEO 2009 [i] | 0.037 [j] |

# Project Goal

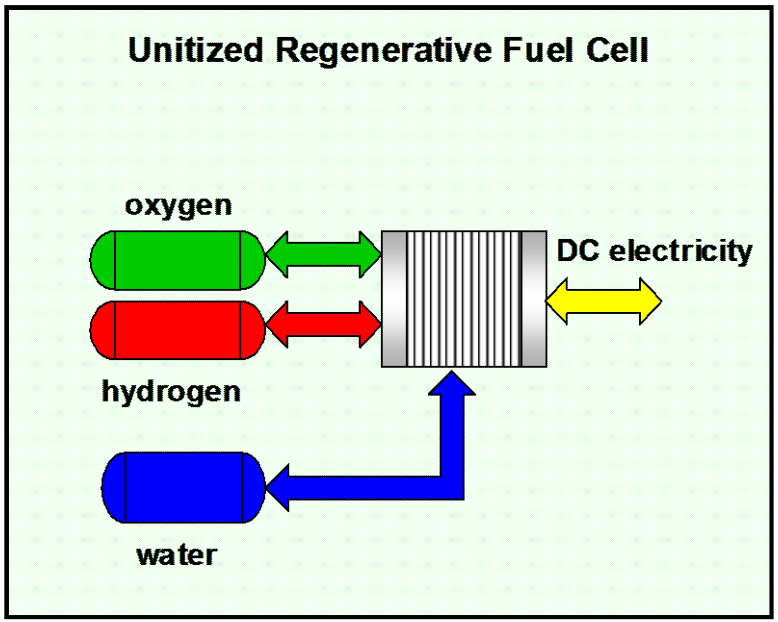
- Anion exchange membrane (AEM) based unitized regenerative fuel cell (URFC)
- Non-platinum group metal (PGM)-based oxygen electrode



Alkaline Electrolyzer

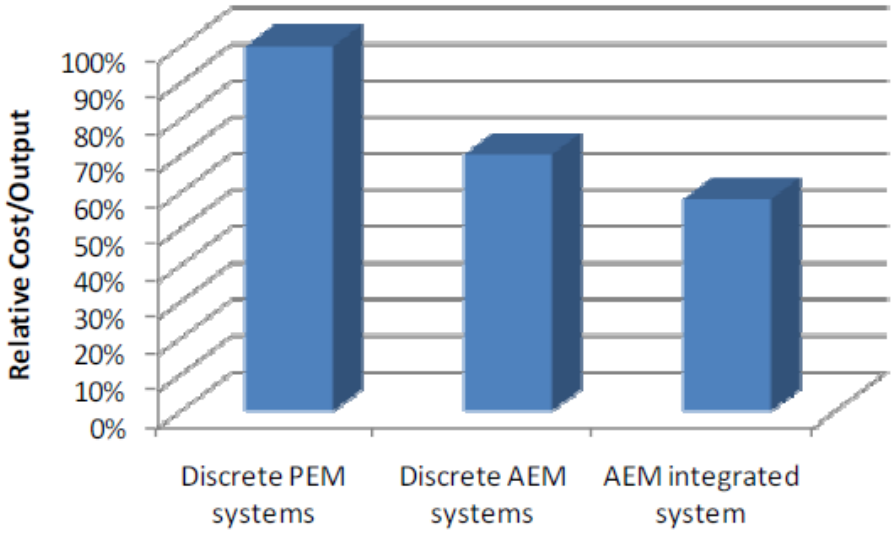


Alkaline Fuel Cell



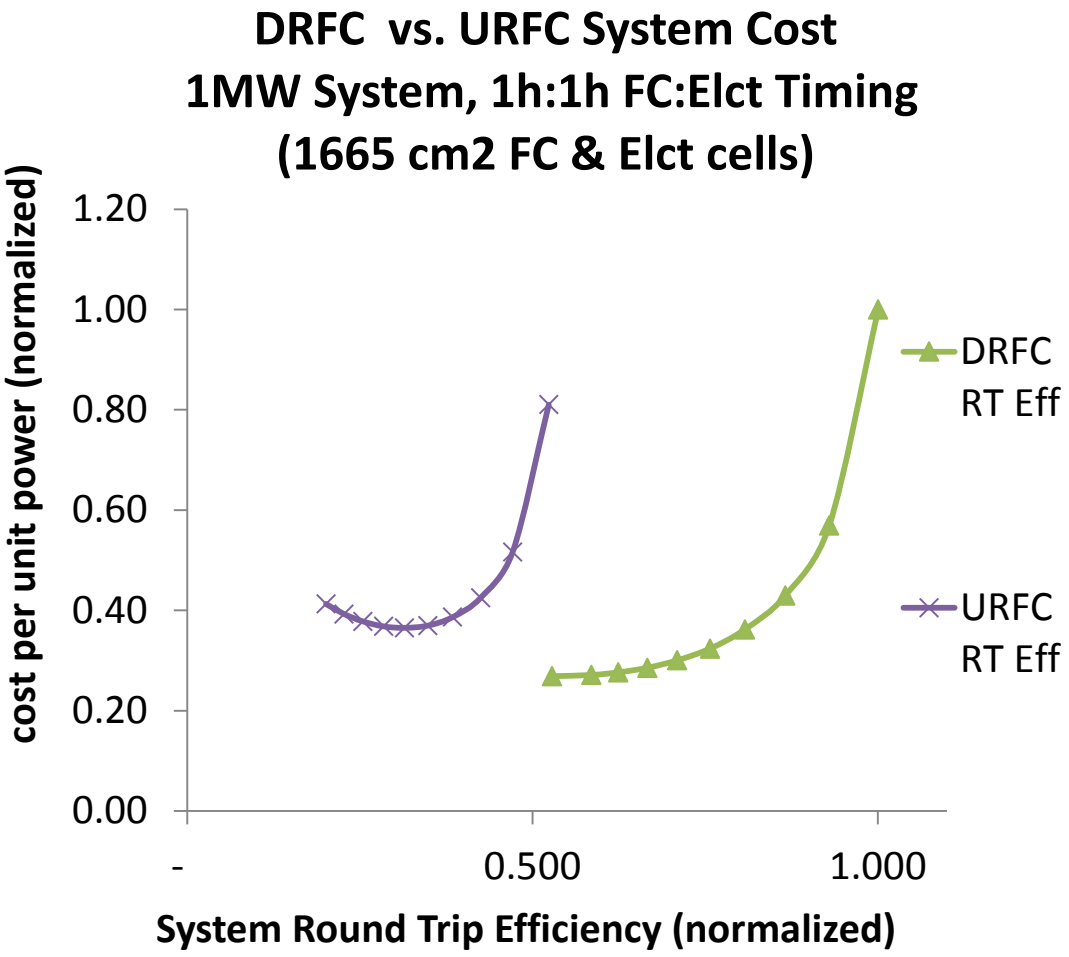
# Relevance

- Stacks are the largest cost components of RFCs
  - Integrated approach should make significant $ impact
- Precious metal content
  - Decrease or eliminate PGM metals in electrodes
- Membrane electrode assembly cost
  - Anion exchange (AEM) vs proton exchange (PEM) membranes
- Balance of stack component cost
  - Reduction in cost using stainless steel vs valve metal components



# Relevance: Energy Storage

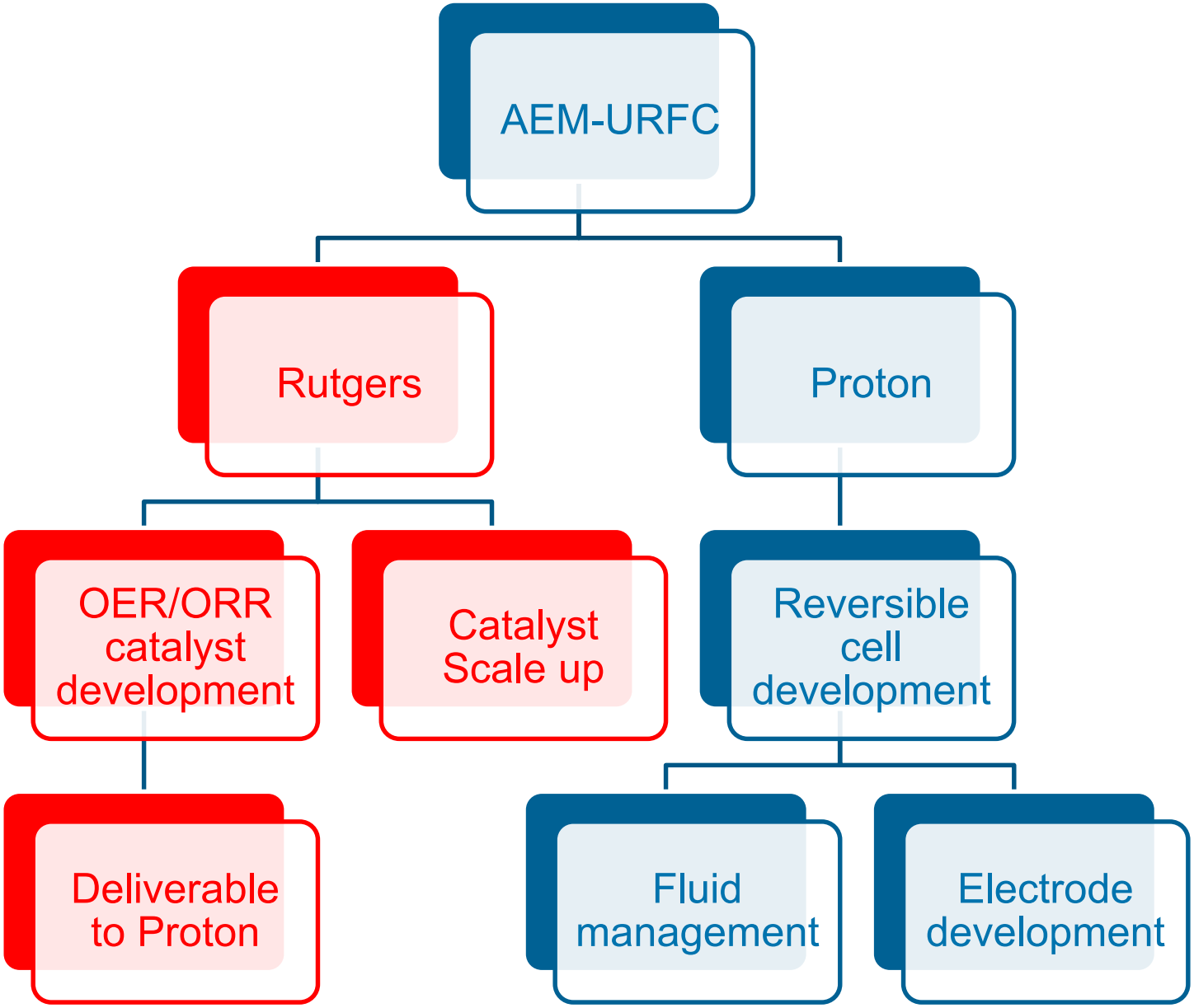
- Costs need to be significantly reduced to enable energy markets
  - Energy capture and supply
  - Auxiliary power units
  - Backup power
  - Load leveling
  - Peak shaving
- URFC traditionally sacrifices operating efficiency for capital cost
  - AEM chemistry opens up broader range of catalysts



# Relevance: Project Objectives

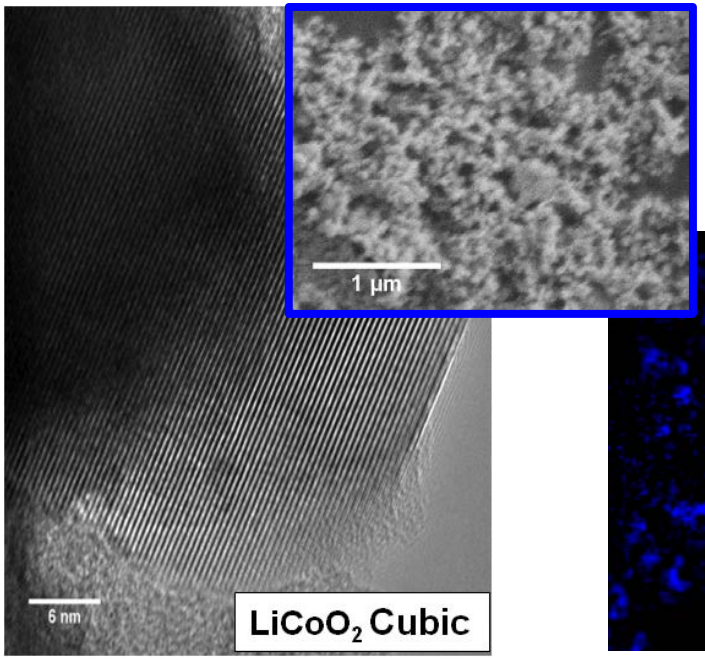
- Baseline AEM-URFC cell
  - Optimize flow fields and gas diffusion layers (GDL)
  - Optimize catalyst layers ($O_2$ and $H_2$)
- Develop non-PGM bifunctional oxygen catalyst
- Demonstrate feasibility
- Demonstrate cyclability (fuel cell ↔ electrolysis)
- Demonstrate stability
  - 200 hrs of run time

# Approach

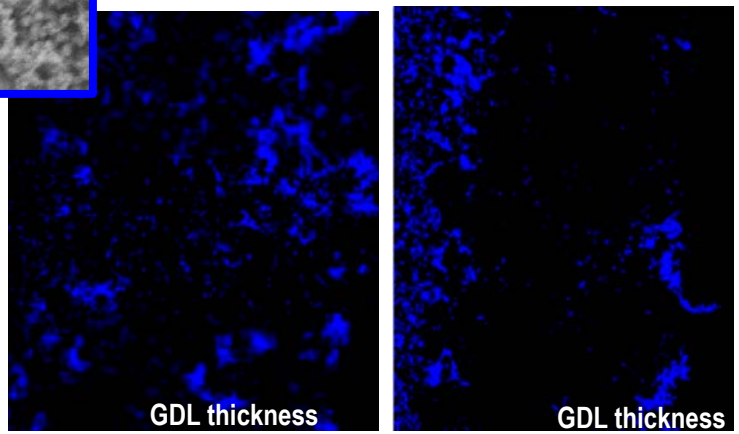

AEM-URFC
Rutgers
Proton
OER/ORR catalyst development
Catalyst Scale up
Reversible cell development
Deliverable to Proton
Fluid management
Electrode development

# Approach

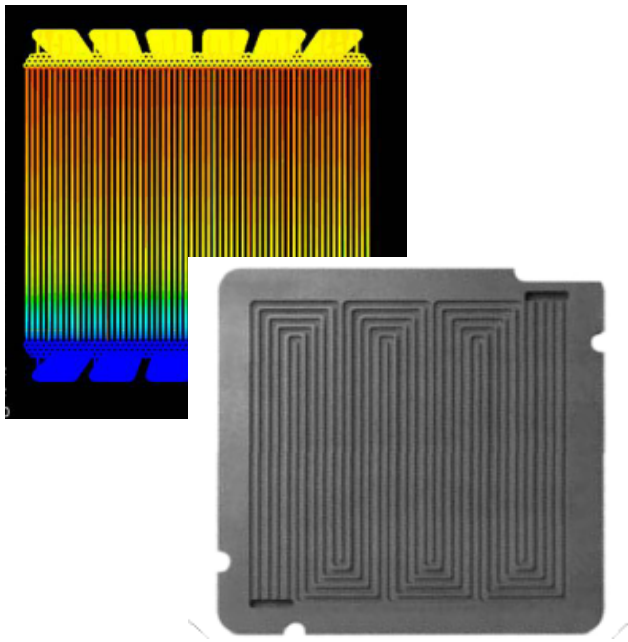
- Catalyst (Rutgers):
  - Based on cubic $LiCoO_2$
  - Tune OER/ORR activity by varying A and B site dopants
- AEM-URFC cell (Proton)
  - Water management
  - Flowfield
  - Wetproofing
  - Catalyst layer integration




Preliminary data on $LiCoO_2$



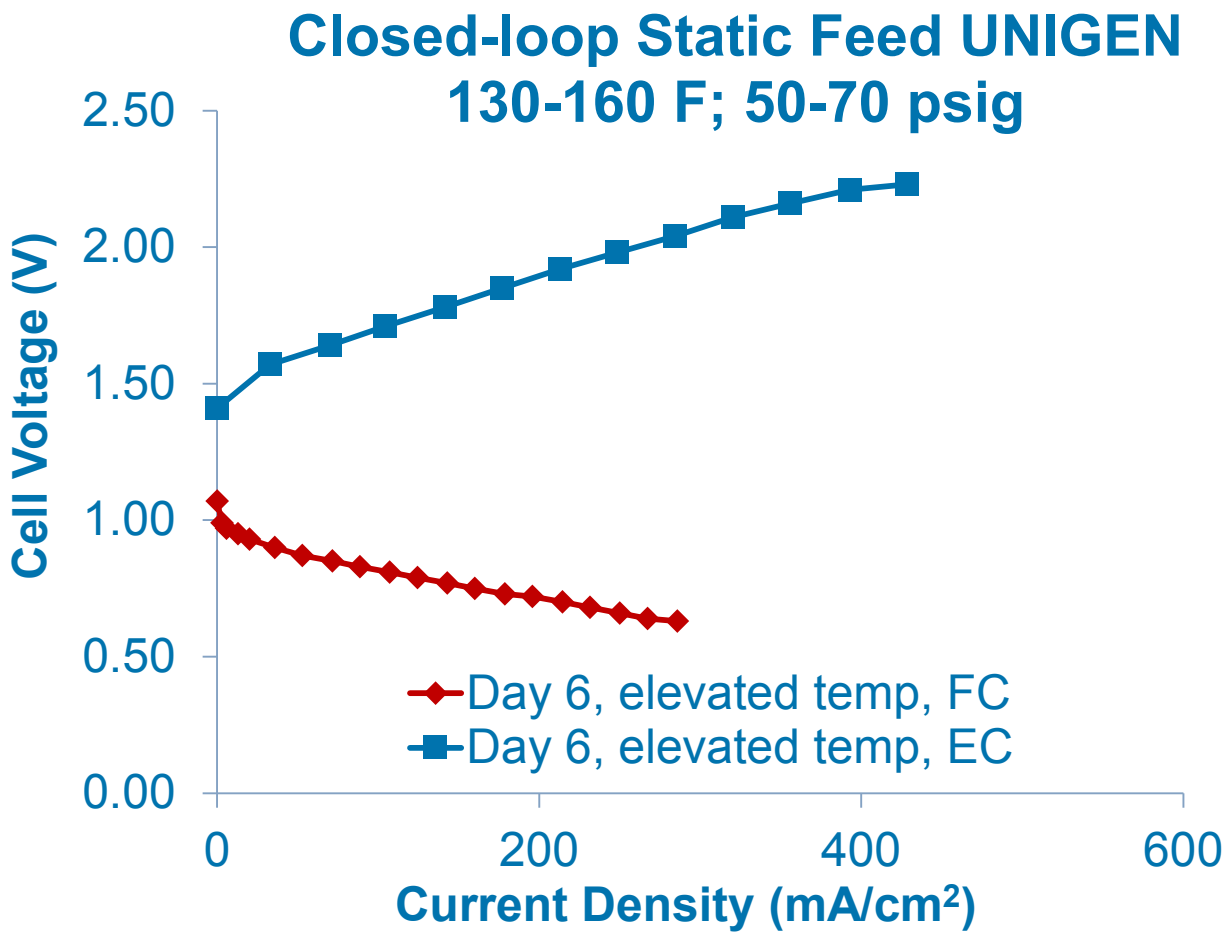

Water management optimization



Flowfield Design

# Approach: Leveraging Previous Work

- Leverage Proton PEM URFC experience from DARPA/NASA/NSF programs in AEM application:
  - Flowfields
  - Wetproofing
  - OER/ORR catalyst philosophy
  - Test stands
- Leverage AEM experience from ARPA-E and other programs



# Objectives

| Task description and significance achievements | Completion |
|---|---|
| Cubic phase $LiBCoO_2$ *(B=Mn⁺, etc)* synthesized and screened | 25% |
| Electrochemical screening of synthesized materials in RDE | 25% |
| Development of URFC cell | 100% |
| Optimization of flowfields for fuel cell and electrolysis operation | 50% |
| Baselining PGM catalyst materials in fuel cell and electrolysis | 100% |
| Evaluation of non-PGM $O_2$ electrodes | 10% |
| Durability testing of non-PGM $O_2$ electrodes | 10% |

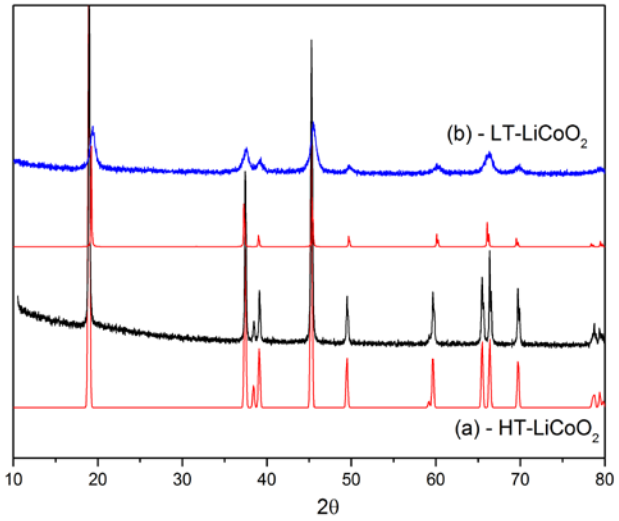
# Technical Accomplishments

- **Catalyst Development**
  - Scaled up synthesis of $LiCoO_2$
  - Performance verified at Proton
  - Multiple B-site doped $LiBCoO_2$ (B=Mn…) synthesized and characterized by RDE
- **Cell Development**
  - Cell geometry and architecture defined for 25 $cm^2$ cells
  - Verified to function in fuel cell and electrolysis operation
  - Flowfield optimization and wet proofing initiated
- **URFC Testing**
  - Baseline performance obtained in fuel cell and electrolysis mode for Pt | Pt catalyst (PGM baseline)
  - Baseline electrolysis performance for $LiCoO_2$ and 600 hrs stability test completed

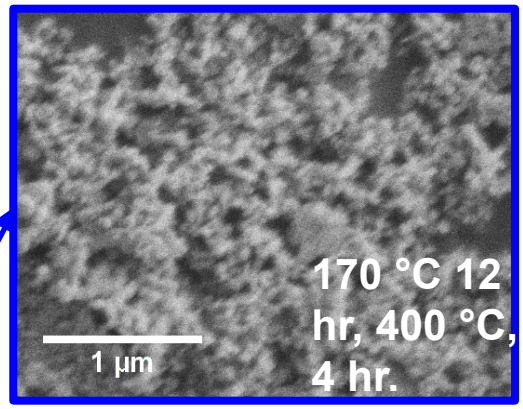
# Technical Accomplishments: Synthesis

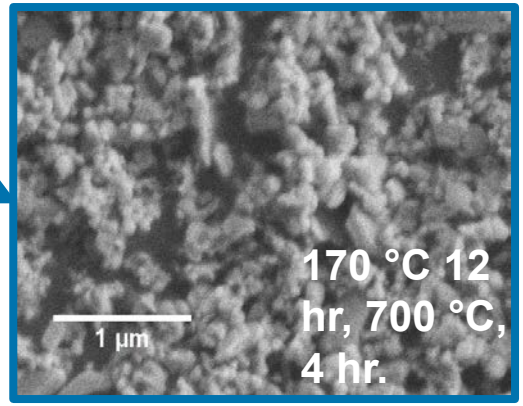
- Sol-gel synthesis employed for high phase purity and higher surface area catalysts

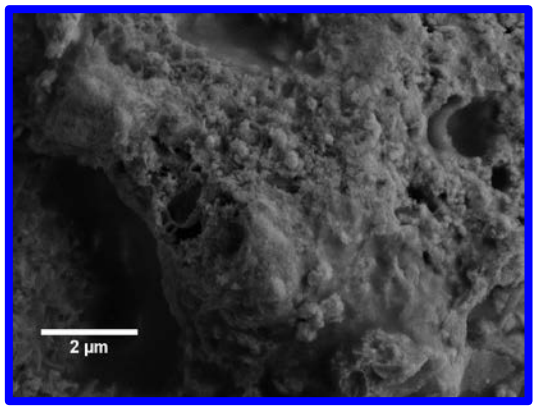
## Sol-Gel Synthetic Routes




$Li_2NO_3 + Co(NO_3)_2 + CH_4N_2O(urea) + C_6H_8O_7(citric\ acid) + H_2O$



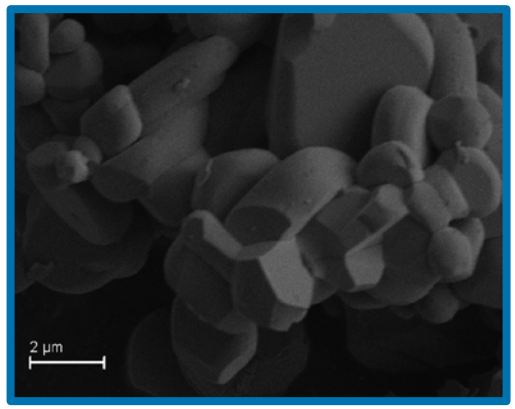




## Solid State Synthesis

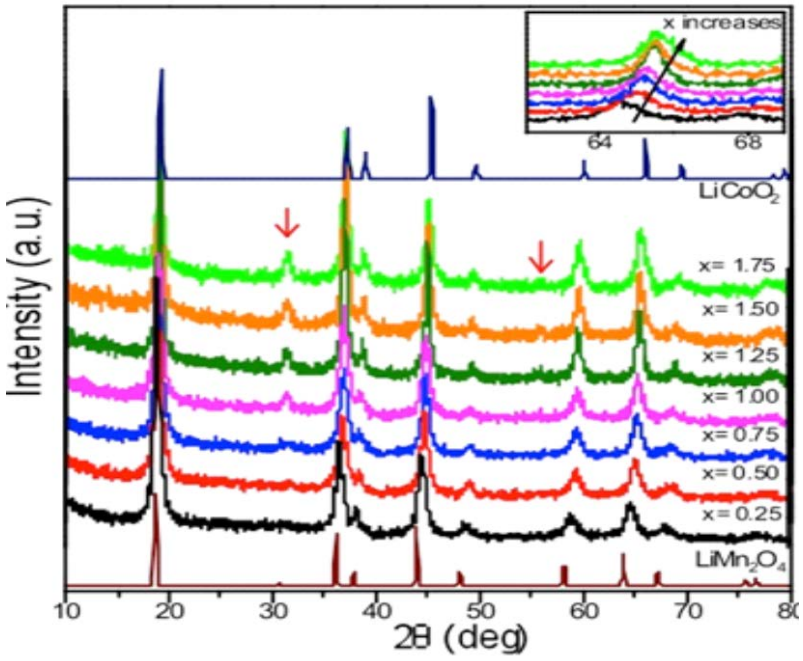
$Li_2CO_3 + CoCO_3$ (grinding)

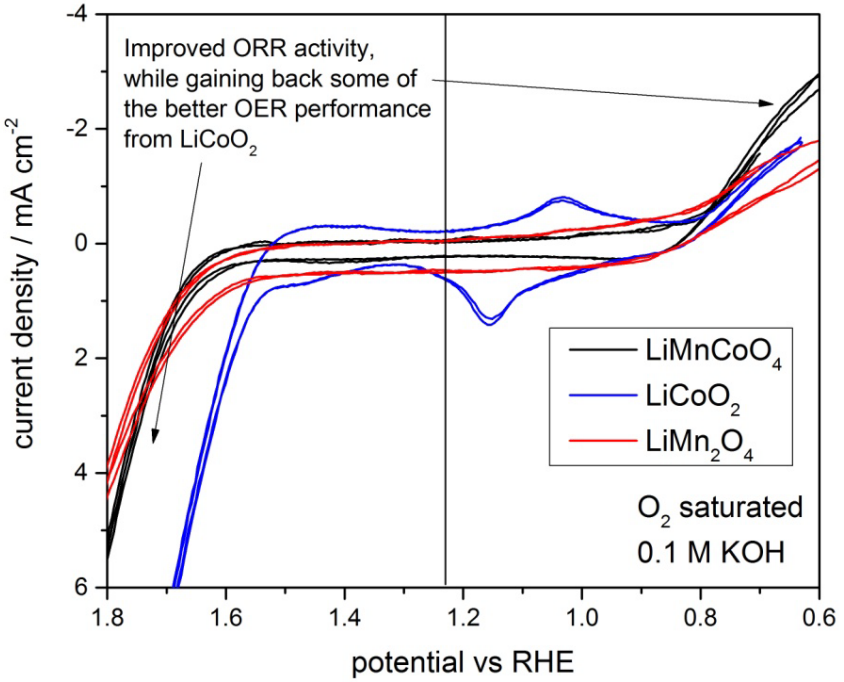
**400 °C, 72 hr.** **800 °C, 12 hr.**



# Technical Accomplishments: Non-PGM OER/ORR catalysts

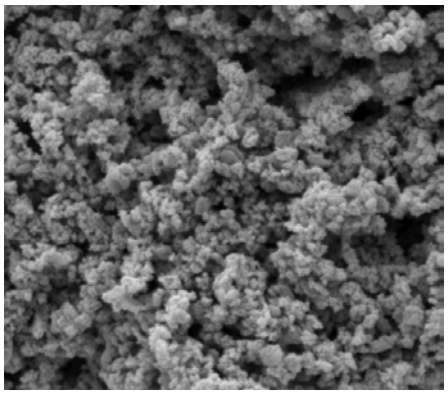
- Synthesized well-defined non-PGM $O_2$ catalysts based on $LiCoO_2$ and $LiMn_2O_4$ families
  - Large batches by sol-gel method achieved high surface area
- Tuned OER and ORR activity by B site substitution
  - $LiMn_{2-x}Co_xO_4$ ($0 < x < 1.5$)

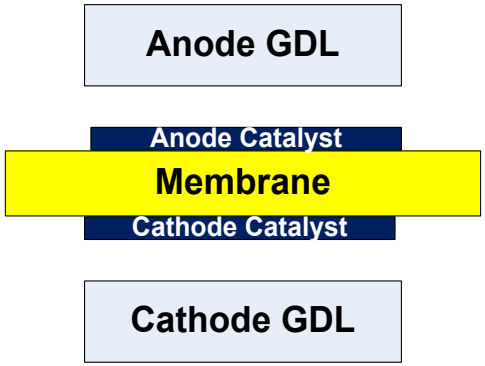


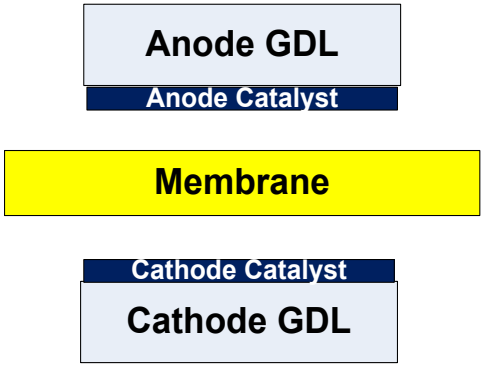



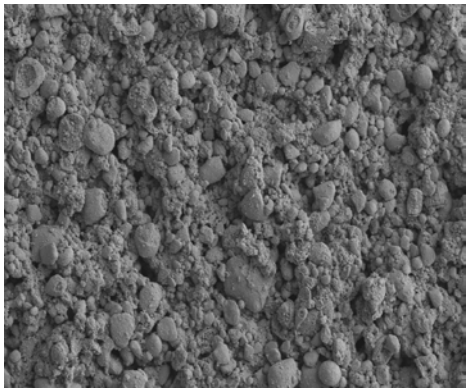
# Technical Accomplishments: GDE Manufacture and Integration

- Rutgers non-PGM materials integrated in GDE ink and sprayed to make electrodes for electrolysis testing
- CCM based approach pending





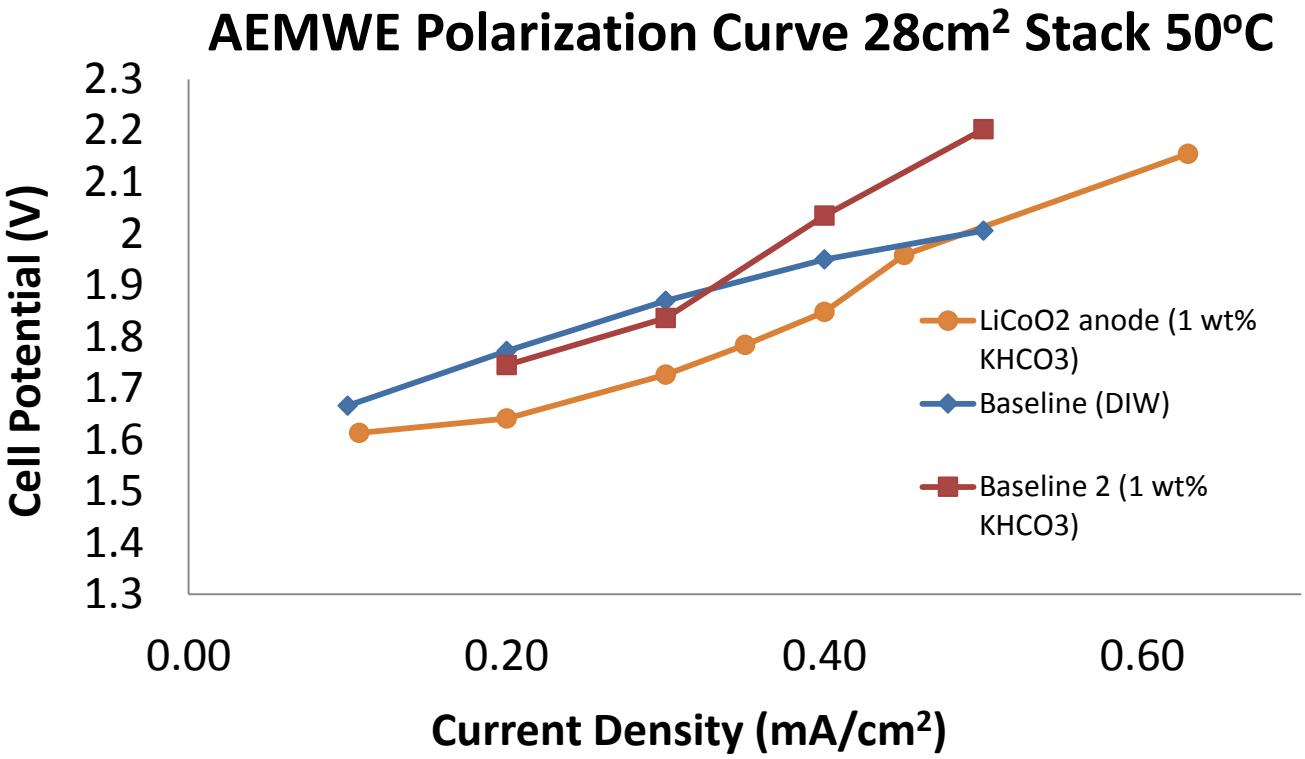



Catalyst coated membrane (CCM)

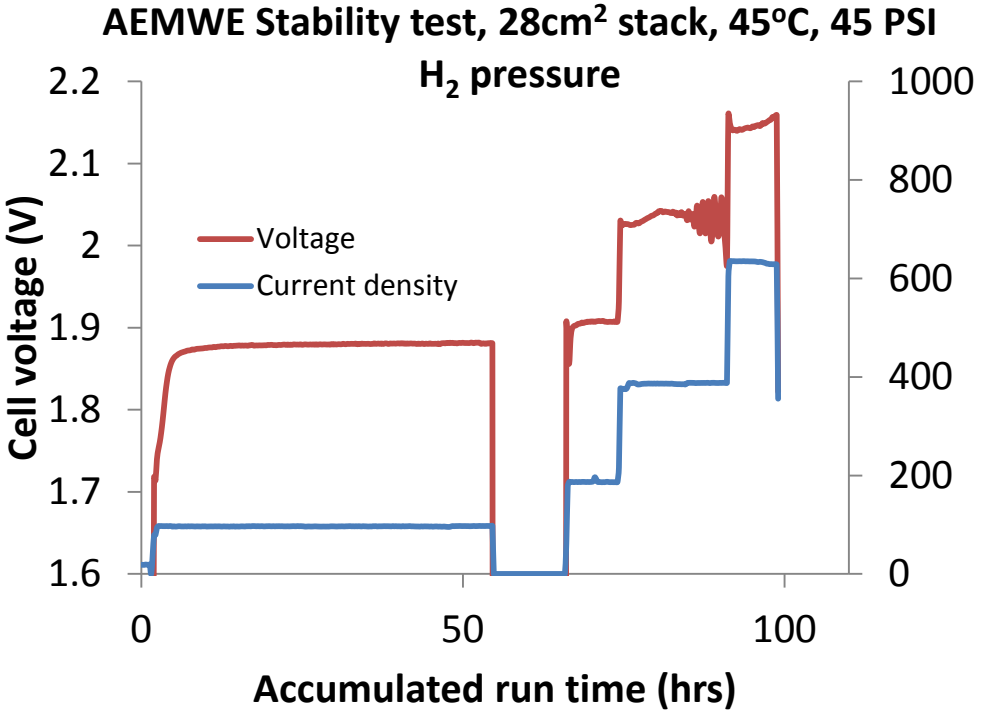
Gas diffusion electrodes (GDE)

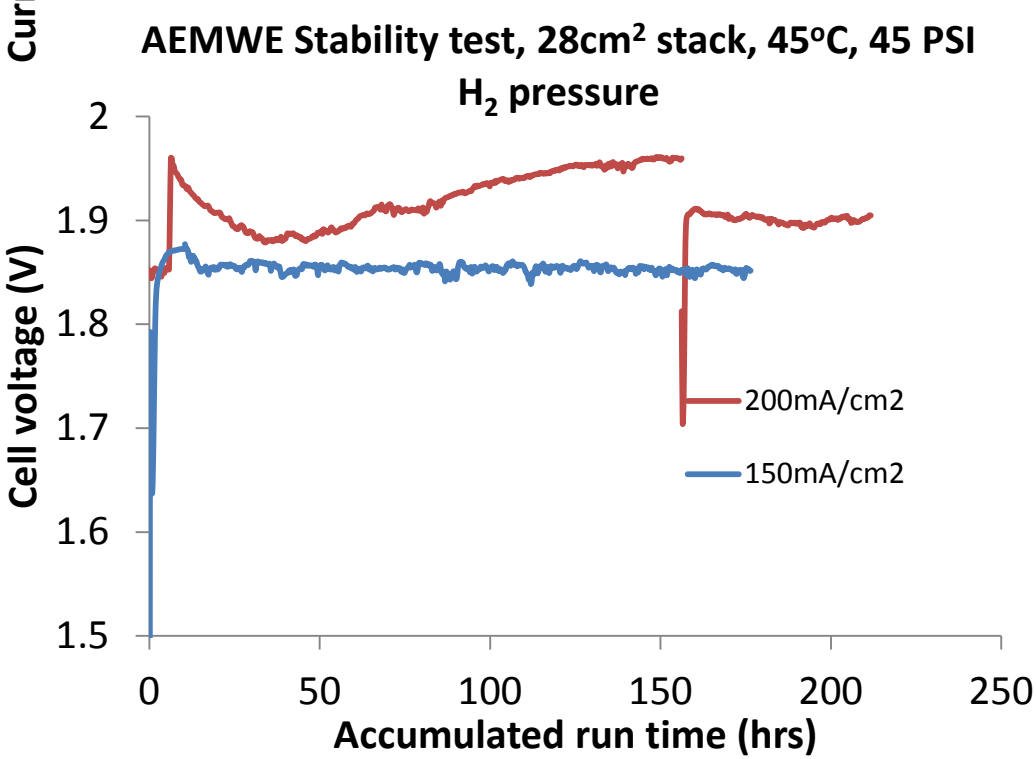
# Technical Accomplishments: Non-PGM OER Performance Screening




- Anode DI water or bicarbonate feed
- Equivalent Pt cathodes
- Improved performance over baseline anode catalyst

# Technical Accomplishments
# Non-PGM $O_2$ Catalyst Durability Test

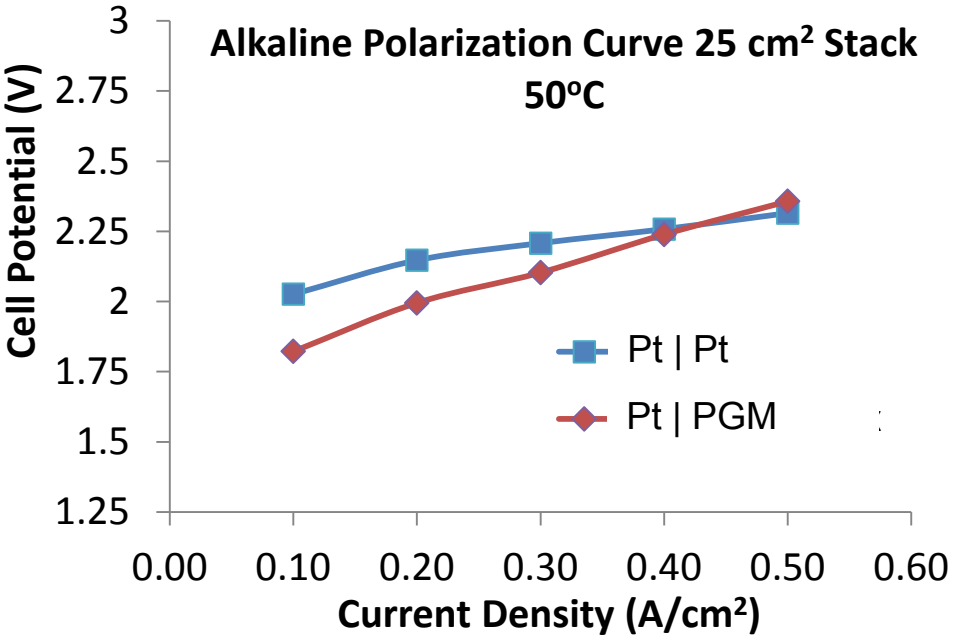


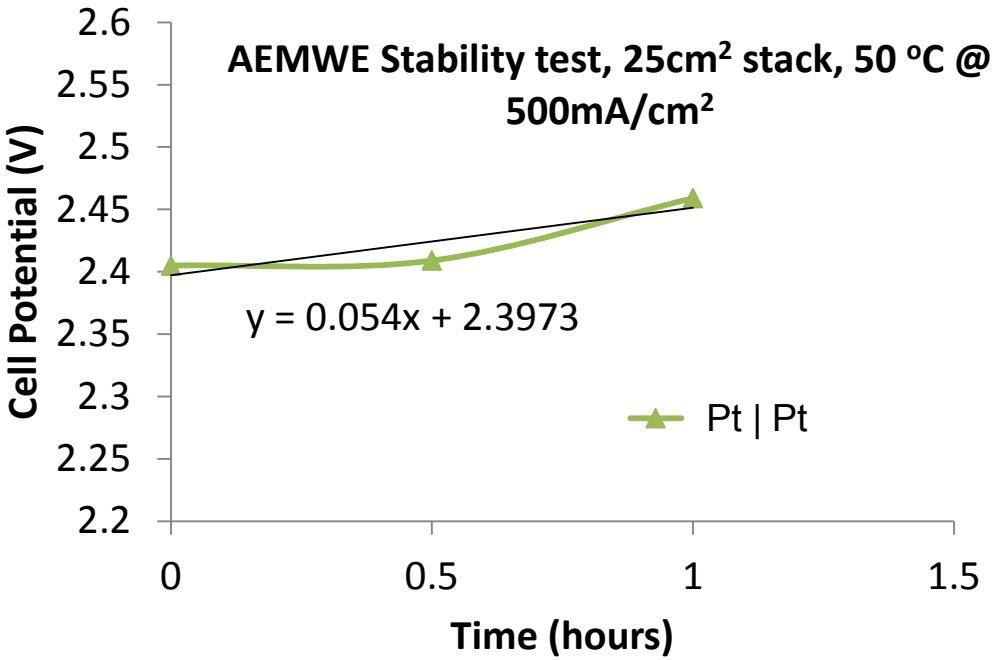




- 28cm² cell commercial platform
- Stainless steel and carbon BOP
- 1wt% $KHCO_3$ anode feed
- Cumulative run time of 550 hrs
- Apparent drift at high current densities

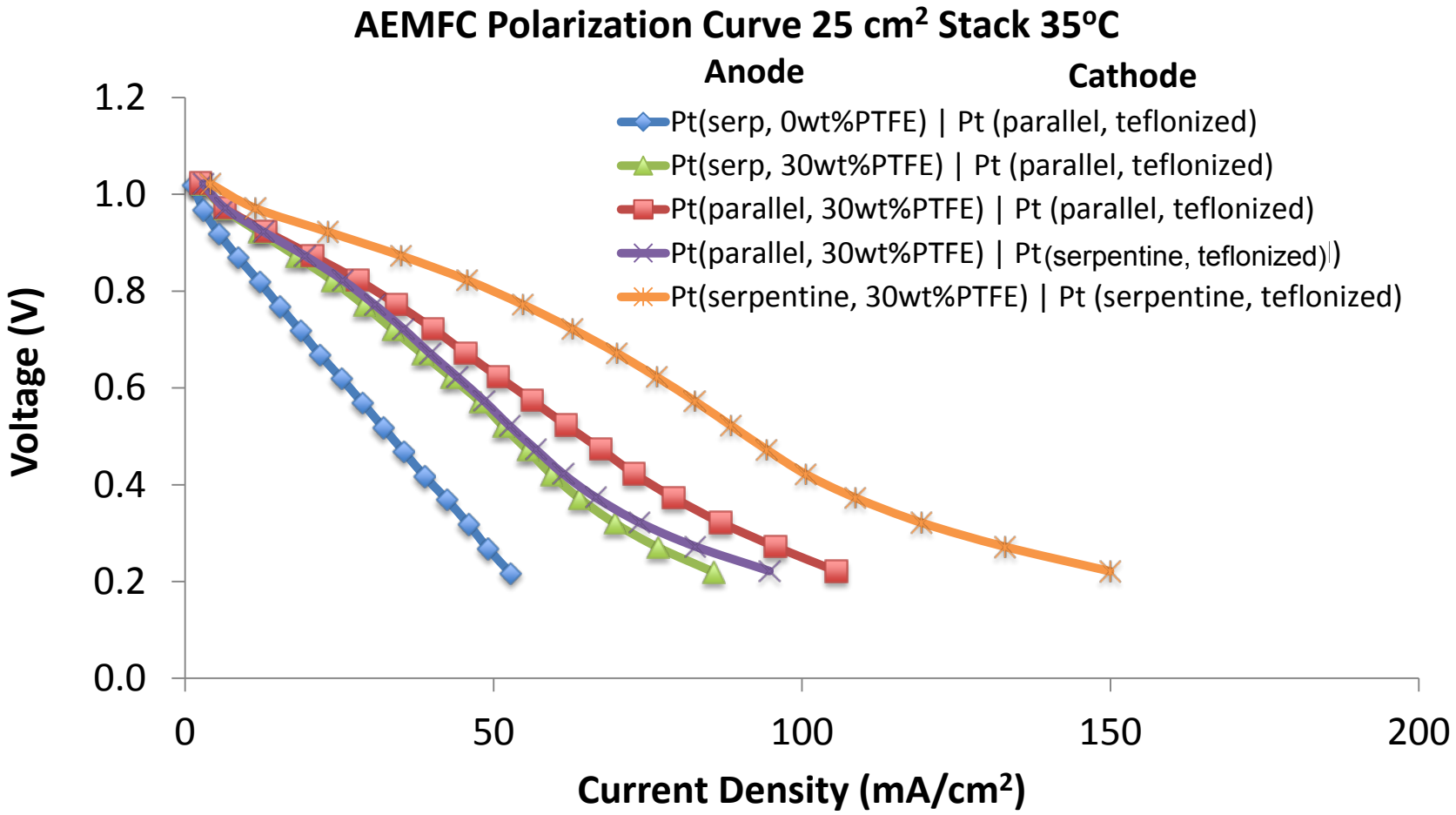
# Technical Accomplishments: URFC cell baselining - Electrolysis

- 25cm$^2$ non-proprietary cell platform
- Deionized water feed on the anode side ($O_2$ electrode)
- Baseline vs conventional PGM anode catalyst
- Little difference at higher current densities points to other rate limiting steps



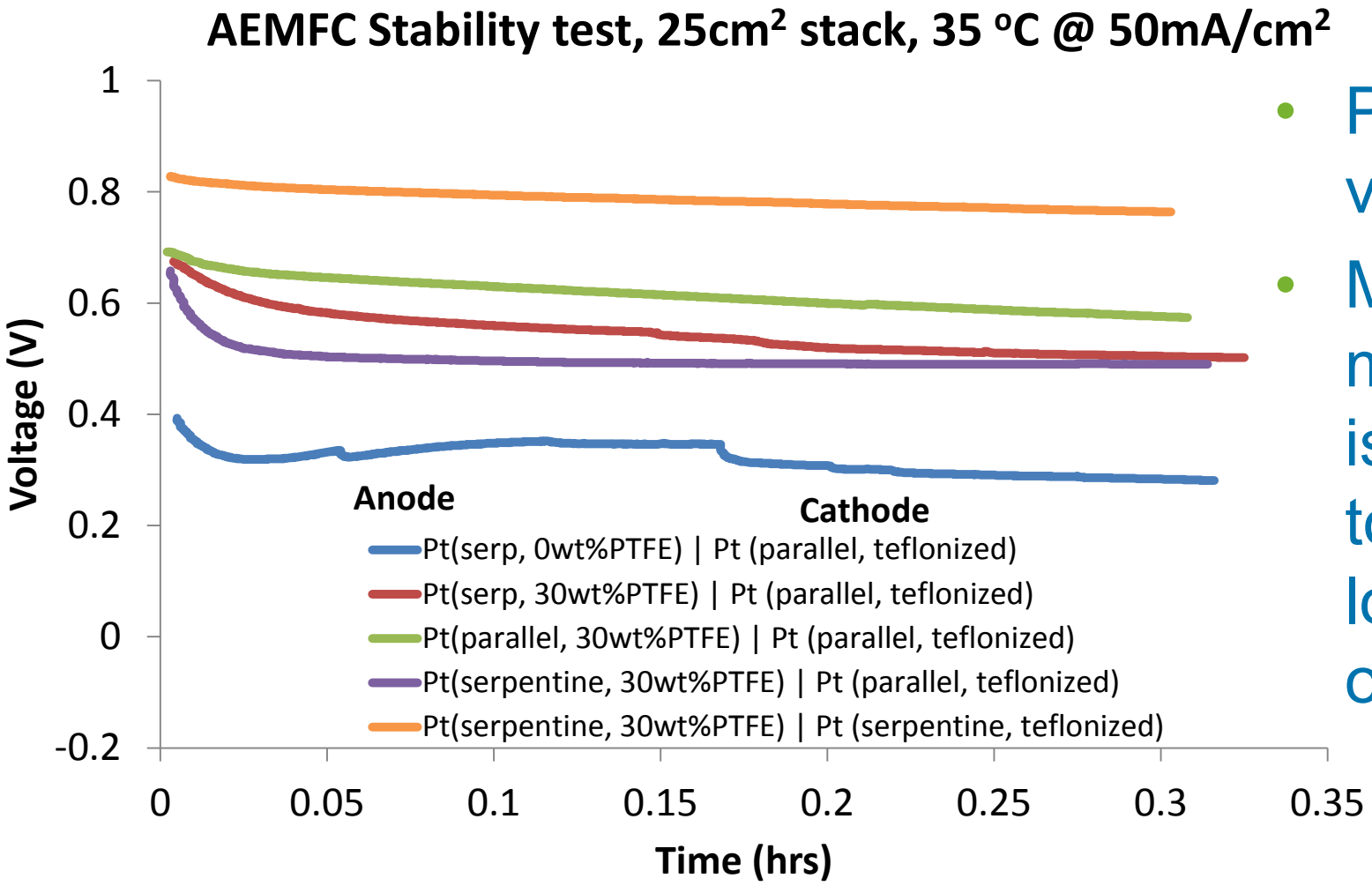



# Technical Accomplishments: URFC cell baselining – Fuel Cell




- 25 $cm^2$ non-proprietary cell platform
- Underhumidified $H_2$, overhumidified $O_2$: high flow rates

# Technical Accomplishments: URFC cell baselining – Fuel Cell




- Performance vs. stability
- May have water management issues - need to resolve for longer term operation

# Future Work

- **Balance of Phase I:**
  - Test non-PGM Rutgers catalyst in URFC
    - Stability and cyclability data
  - Investigate CCM based approach
  - Incorporate advanced $H_2$ electrode catalyst
  - Investigate alternative membranes

- **Proposed work for Phase II:**
  - Development of 28cm$^2$ URFC platform
  - Multi cell stack
  - Scale up fabrication of non-PGM catalyst materials
  - Long term cycling and stability performance

# Collaborations

- Rutgers University
  - Synthesis of ~ 2 gram batches of non-PGM oxygen catalysts
    - Cubic $LiCoO_2$ and spinel $LiMn_2O_4$
      - B site dopants (transition metal cations)
      - N doping into O site
  - OER/ORR activity and stability screening with RDE in near neutral, NaOH (pH 14) and potassium bicarbonate
  - Supplemental characterization

# Summary

- **Relevance:** Demonstrates non-PGM AEM based URFC for reduced capital cost system and higher market penetration
- **Approach:** Optimize cell design and non-PGM catalyst activity for fuel cell and electrolysis operation with an anion exchange membrane
- **Technical Accomplishments:**
  - >500 hour durability test successfully completed for non-PGM electrolysis anode GDE
  - Baseline PGM feasibility demonstrated in 25 $cm^2$ test cell in both electrolysis and fuel cell operation
- **Collaborations:**
  - Rutgers University: non-PGM catalyst synthesis and screening
- **Proposed Future Work:**
  - Test non-PGM Rutgers catalyst in URFC
  - Investigate CCM based approach
  - Incorporate advanced $H_2$ electrode catalyst
  - Incorporate membrane improvements