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

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Organization: Proton OnSite

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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]

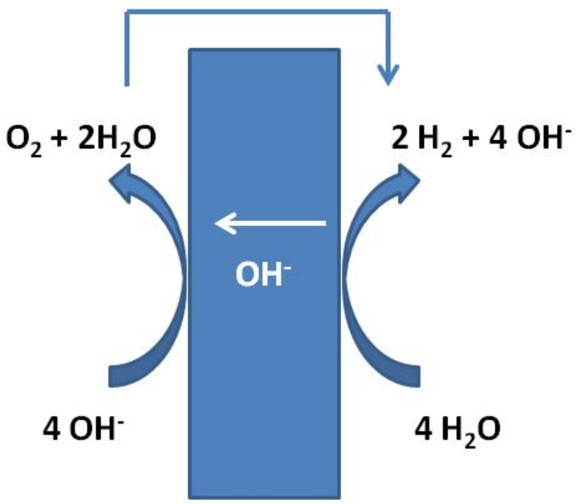
Characteristic	Units	2011 Status	2013 Targets	2015 Targets
Specific power[b]	W/kg	5	8	10
Power density[b]	W/L	7	10	13
Specific energy[b,c]	Wh/kg	110	200	230
Energy density[b,c]	Wh/L	150	250	300
Cost[d]	$/system	150	130	70
Durability[e,f]	hours	1,500	3,000	5,000
Mean time between failures[f,g]	hours	500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

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

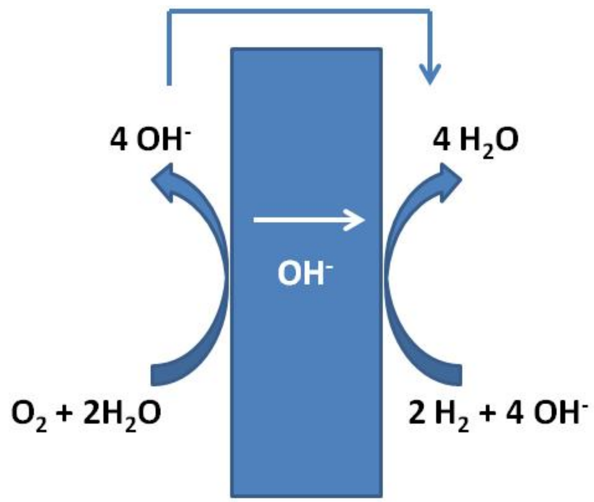
Characteristics	Units	2011 Status	2015 Target	2020 Target
Hydrogen Levelized Cost[d] (Production Only)	$/kg	4.20[d]	3.90[d]	2.30[d]
Electrolyzer System Capital Cost	$/kg $/kW	0.70 430[e, f]	0.50 300[f]	0.50 300[f]
System Energy Efficiency[g]	% (LHV)	67	72	75
	kWh/kg	50	46	44
Stack Energy Efficiency[h]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

Project Goal

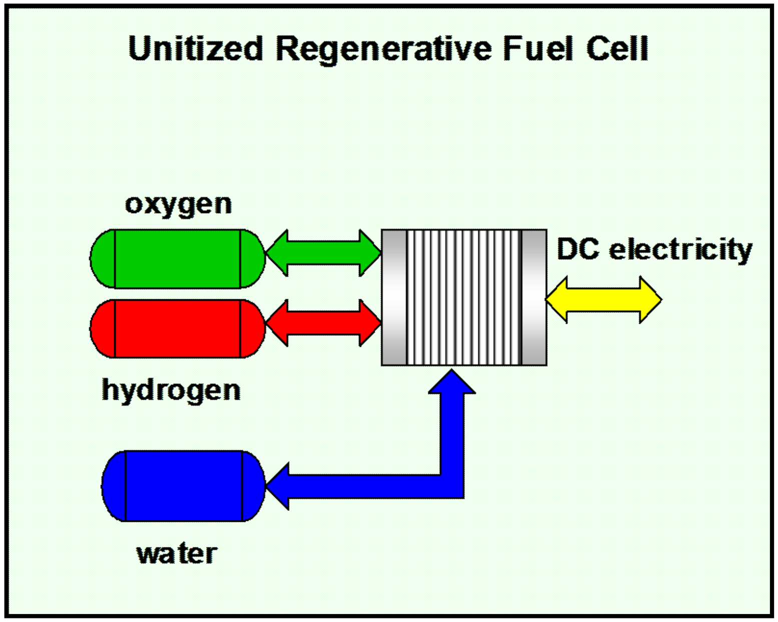
- Anion exchange membrane (AEM) based unitized regenerative fuel cell (URFC)
- Non-platinum group metal (PGM)-based oxygen electrode



Alkaline Electrolyzer

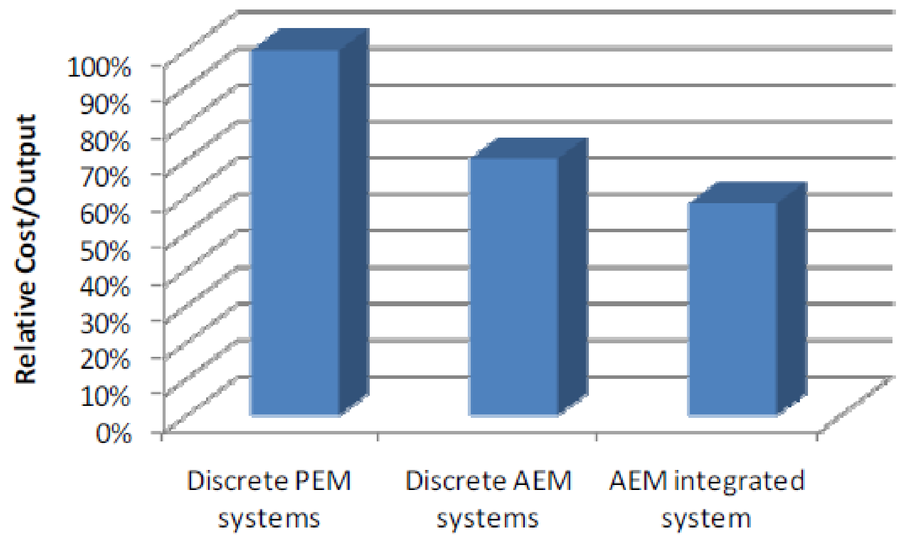


Alkaline Fuel Cell



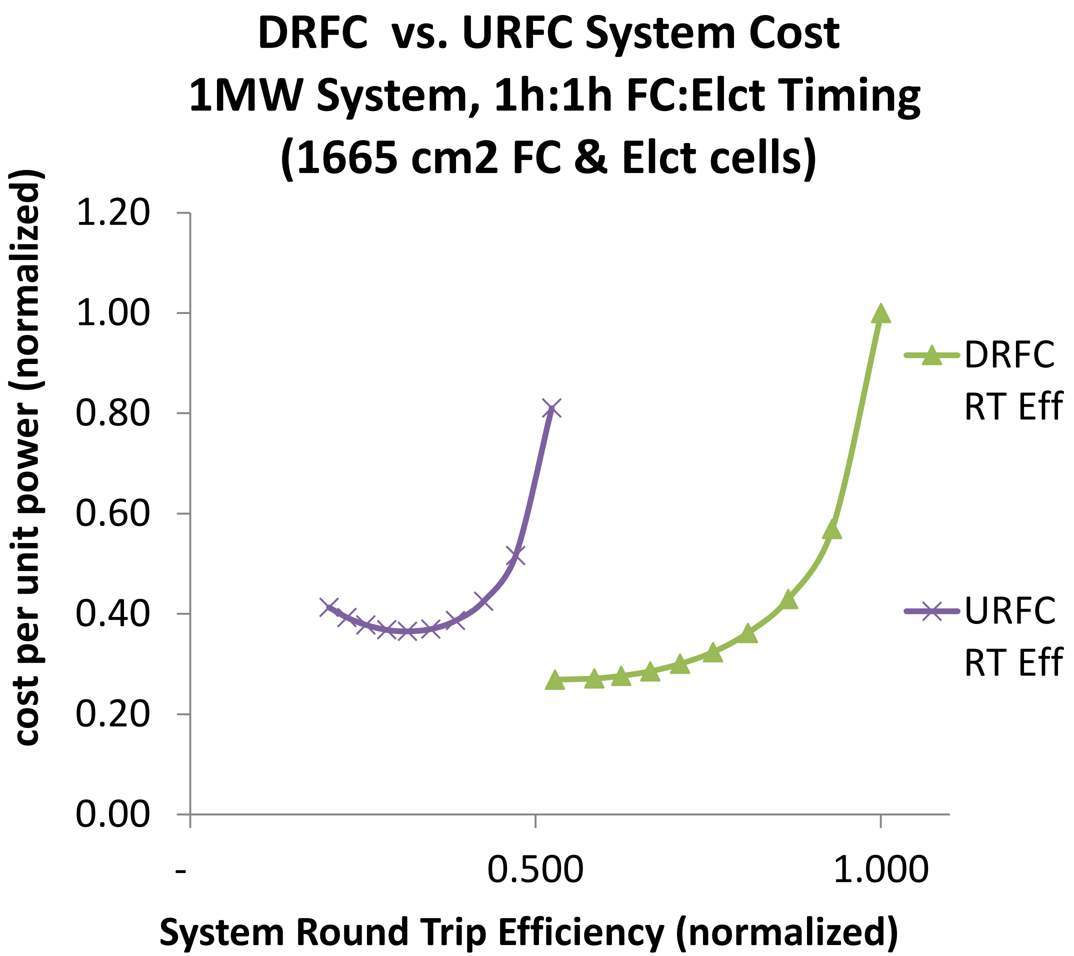
Relevance

- 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

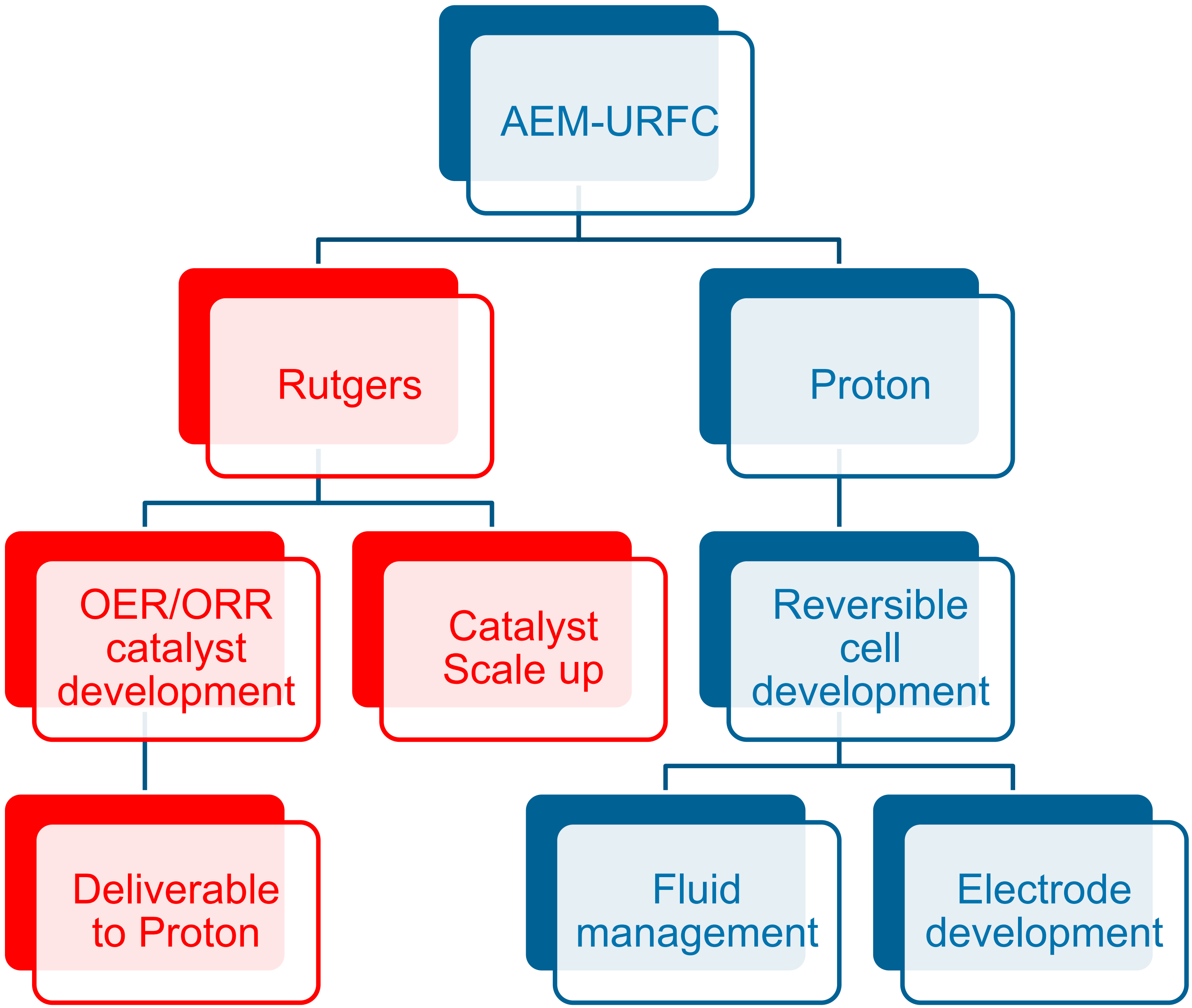
- Costs need to be significantly reduced to enable energy markets
  - Energy capture and supply
  - Auxiliary power units
  - Backup power
  - Load leveling
  - Peak shaving
- URFC traditionally sacrifices operating efficiency for capital cost
  - AEM chemistry opens up broader range of catalysts



Relevance: Project Objectives

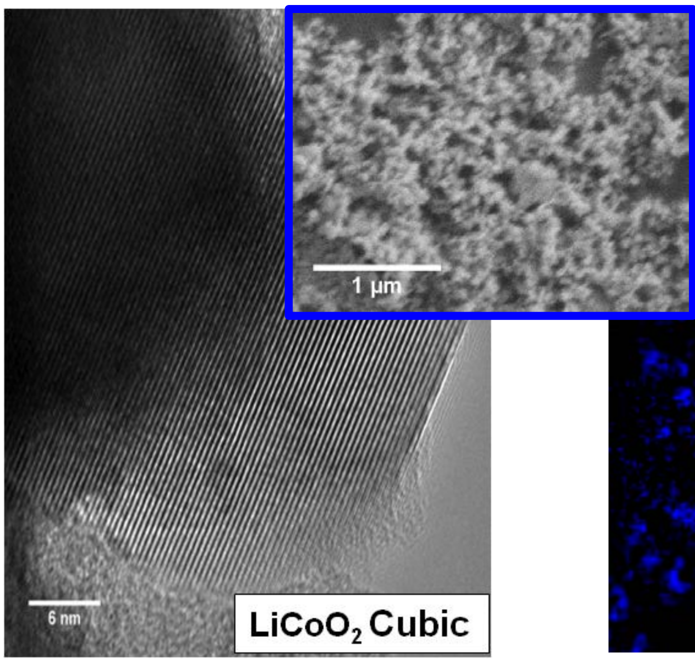
- Baseline AEM-URFC cell
  - Optimize flow fields and gas diffusion layers (GDL)
  - Optimize catalyst layers (O_2 and H_2)
- Develop non-PGM bifunctional oxygen catalyst
- Demonstrate feasibility
- Demonstrate cyclability (fuel cell ↔ electrolysis)
- Demonstrate stability
  - 200 hrs of run time

Approach

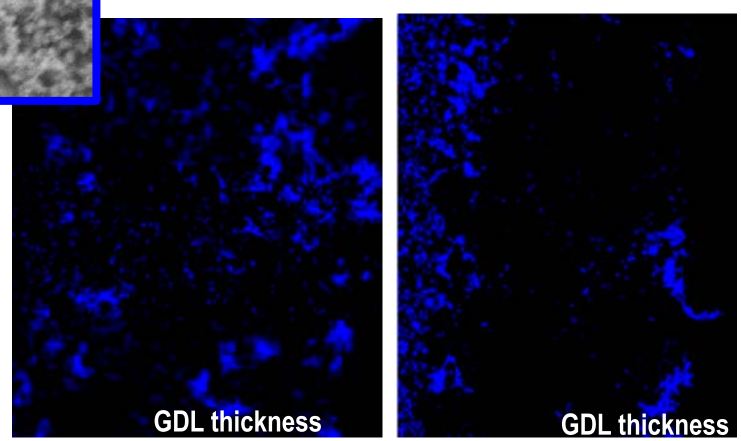

AEM-URFC
Rutgers
Proton
OER/ORR catalyst development
Catalyst Scale up
Reversible cell development
Deliverable to Proton
Fluid management
Electrode development

Approach

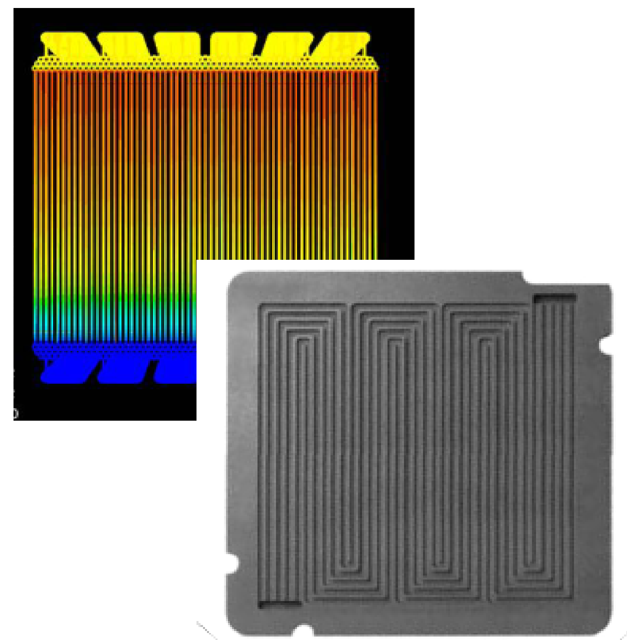
- Catalyst (Rutgers):
  - Based on cubic $LiCoO_2$
  - Tune OER/ORR activity by varying A and B site dopants
- AEM-URFC cell (Proton)
  - Water management
  - Flowfield
  - Wetproofing
  - Catalyst layer integration



Preliminary data on $LiCoO_2$



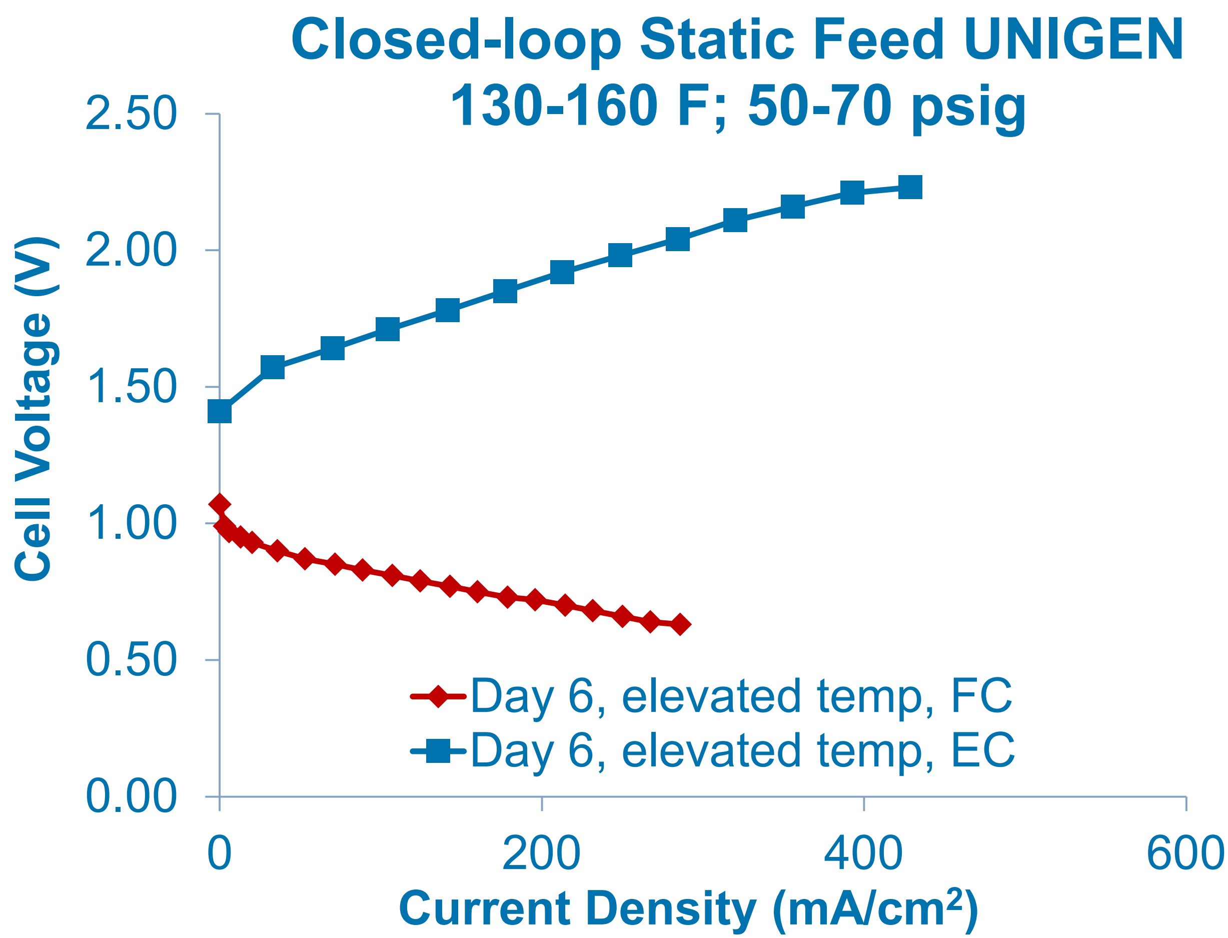
Water management optimization



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%

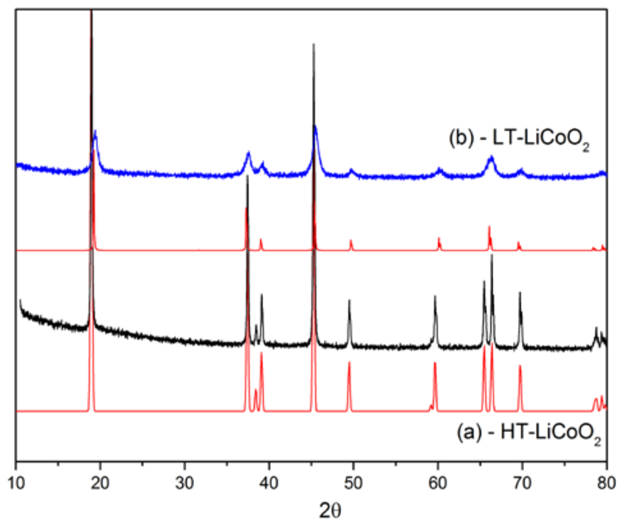
Technical Accomplishments

- **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

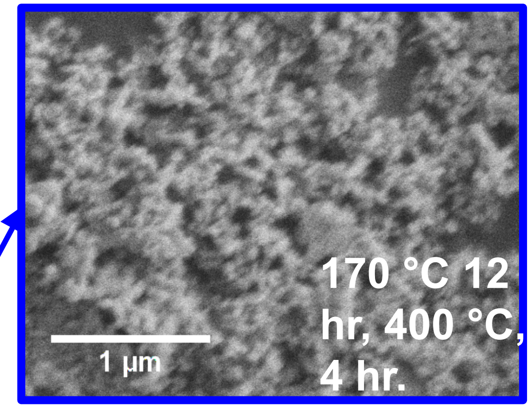
Technical Accomplishments: Synthesis

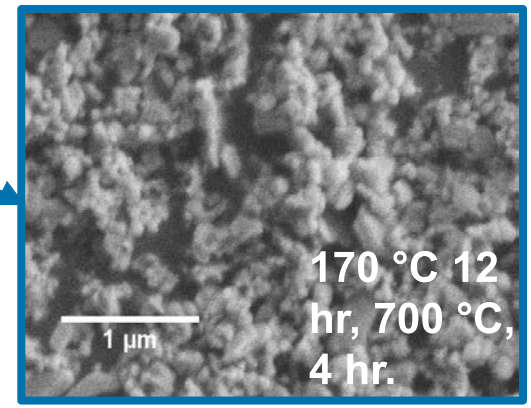
- Sol-gel synthesis employed for high phase purity and higher surface area catalysts

Sol-Gel Synthetic Routes



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



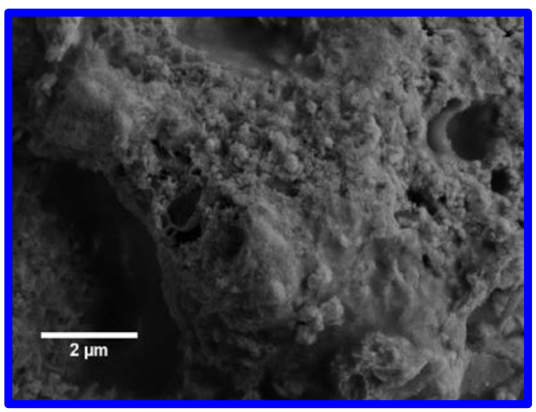


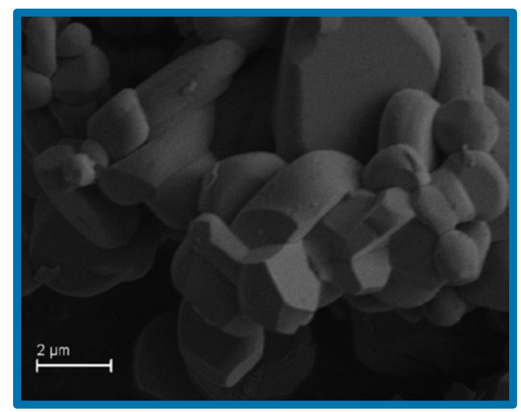
Solid State Synthesis

Li_2CO_3 + $CoCO_3$ (grinding)

400 °C, 72 hr.

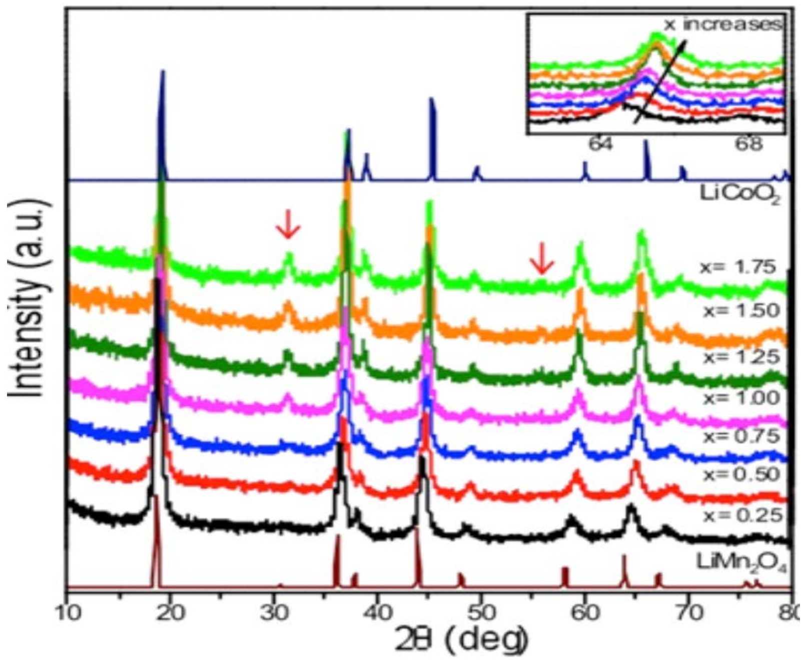
800 °C, 12 hr.

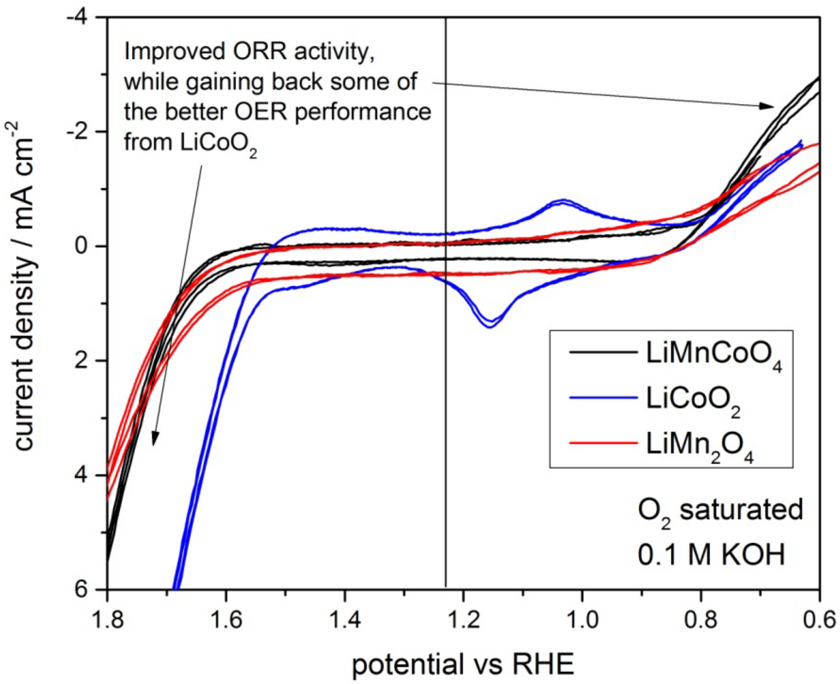




Technical Accomplishments: Non-PGM OER/ORR catalysts

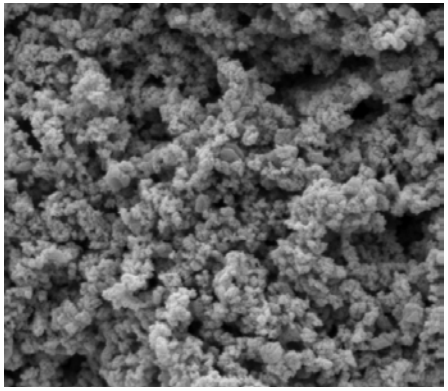
- Synthesized well-defined non-PGM O_2 catalysts based on $LiCoO_2$ and $LiMn_2O_4$ families
  - Large batches by sol-gel method achieved high surface area
- Tuned OER and ORR activity by B site substitution
  - $LiMn_{2-x}Co_xO_4$ ($0 < x < 1.5$)

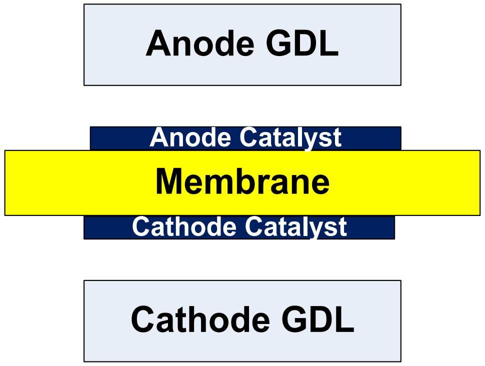




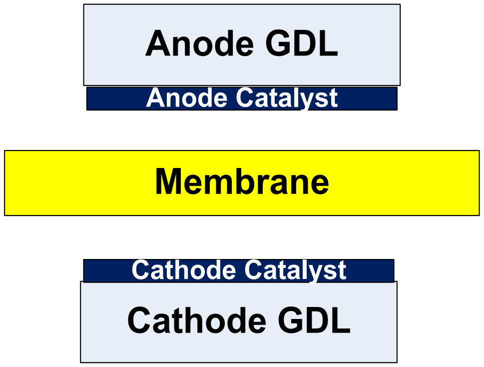
Technical Accomplishments: GDE Manufacture and Integration

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

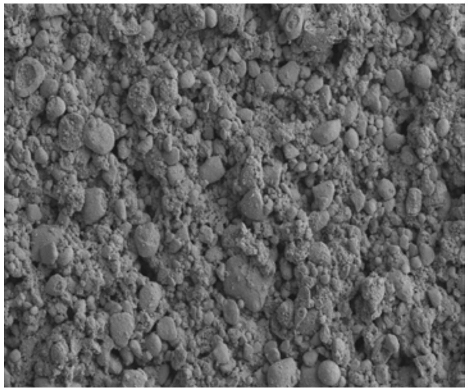




Catalyst coated membrane (CCM)



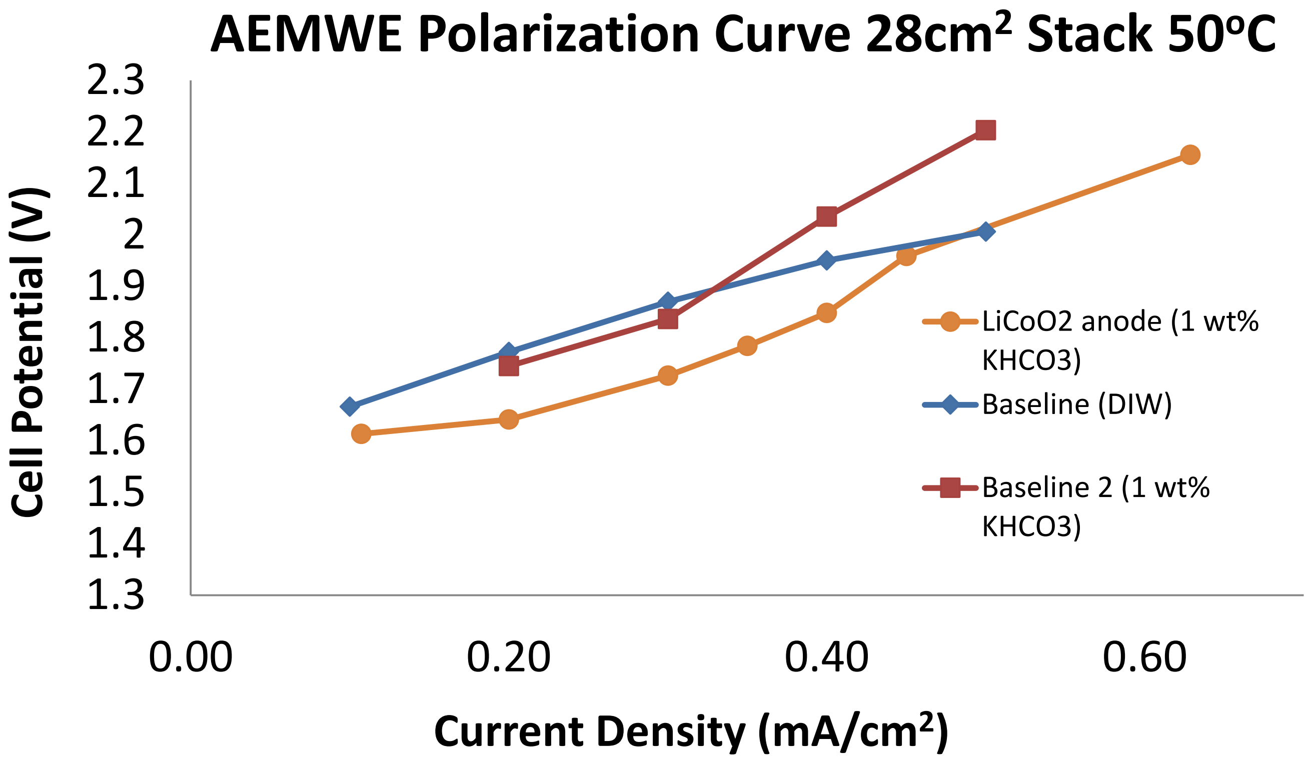
Gas diffusion electrodes (GDE)



PROTON ON SITE

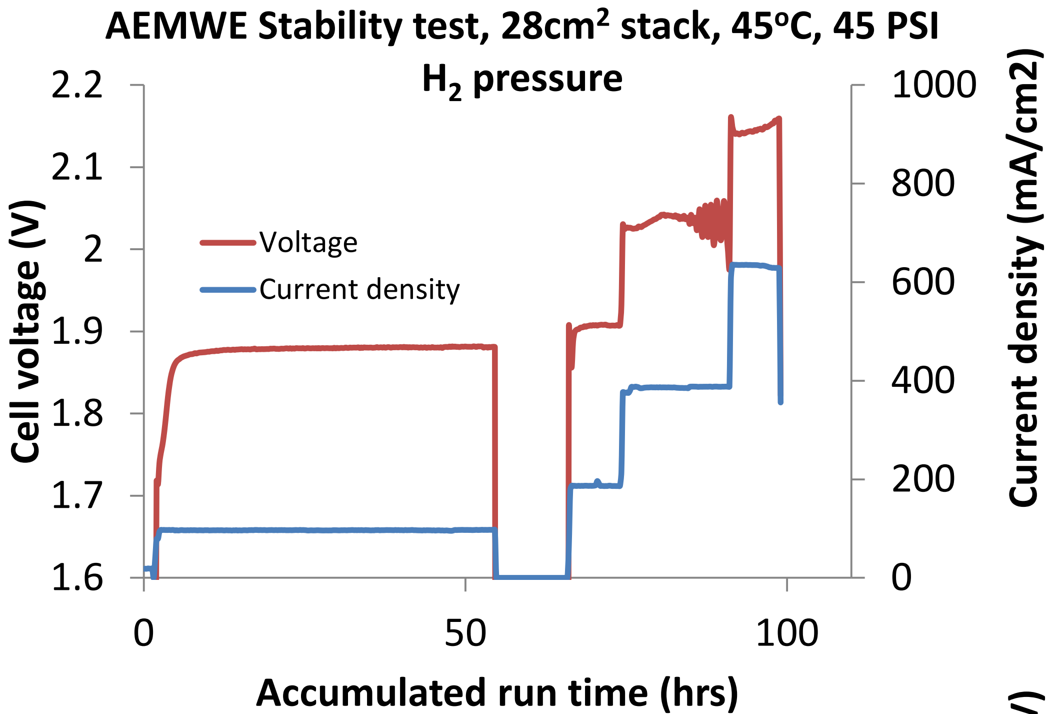
RUTGERS UNIVERSITY

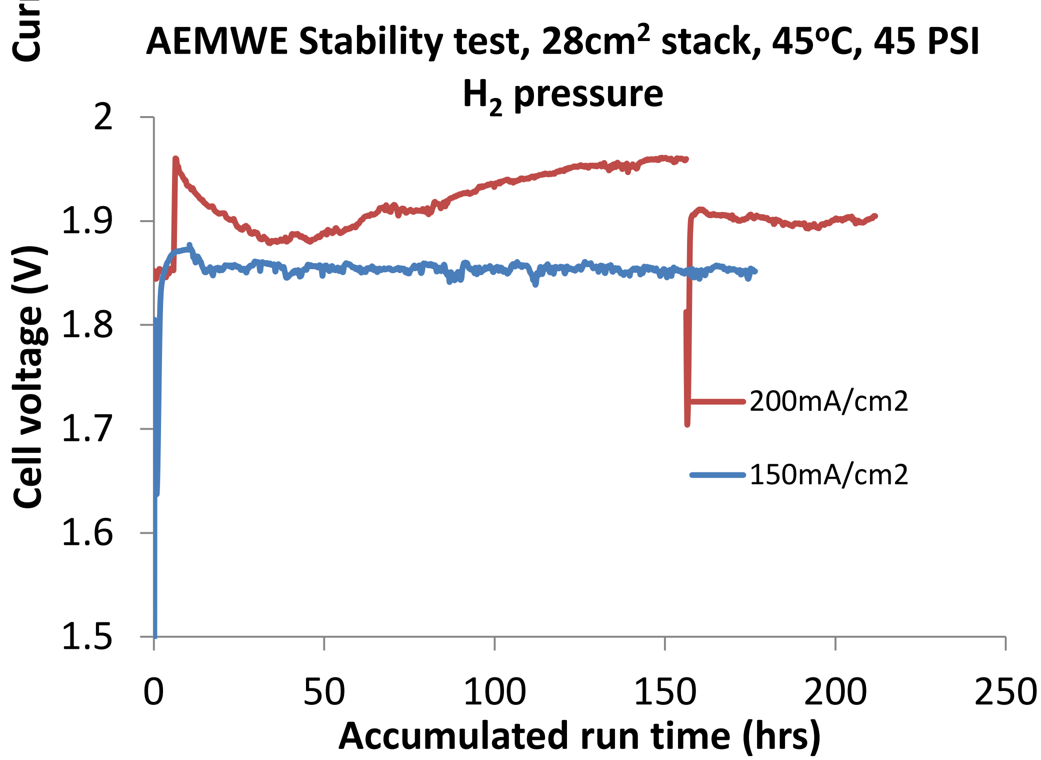
Technical Accomplishments: Non-PGM OER Performance Screening



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

Technical Accomplishments Non-PGM O_2 Catalyst Durability Test

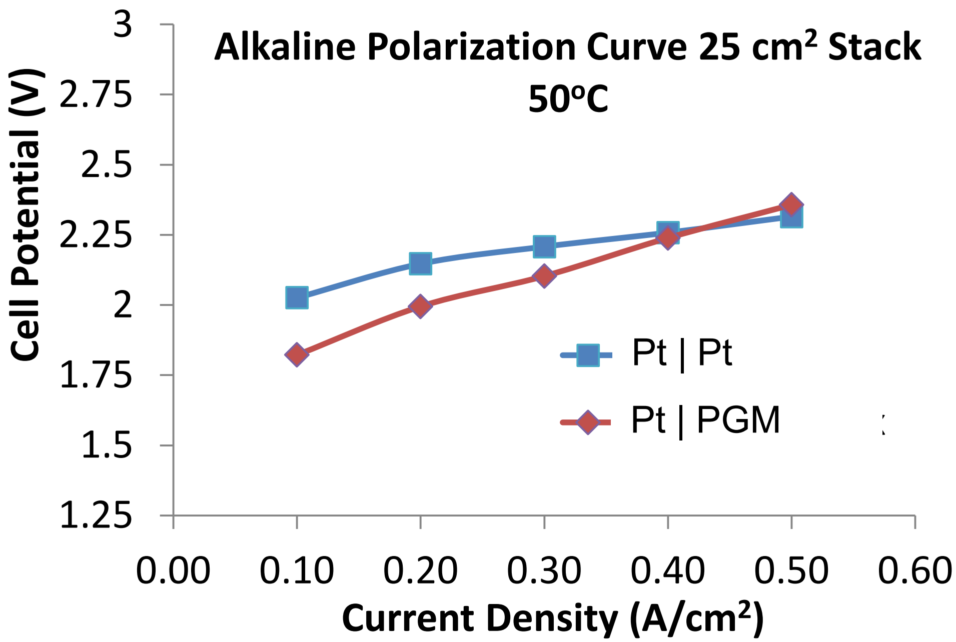


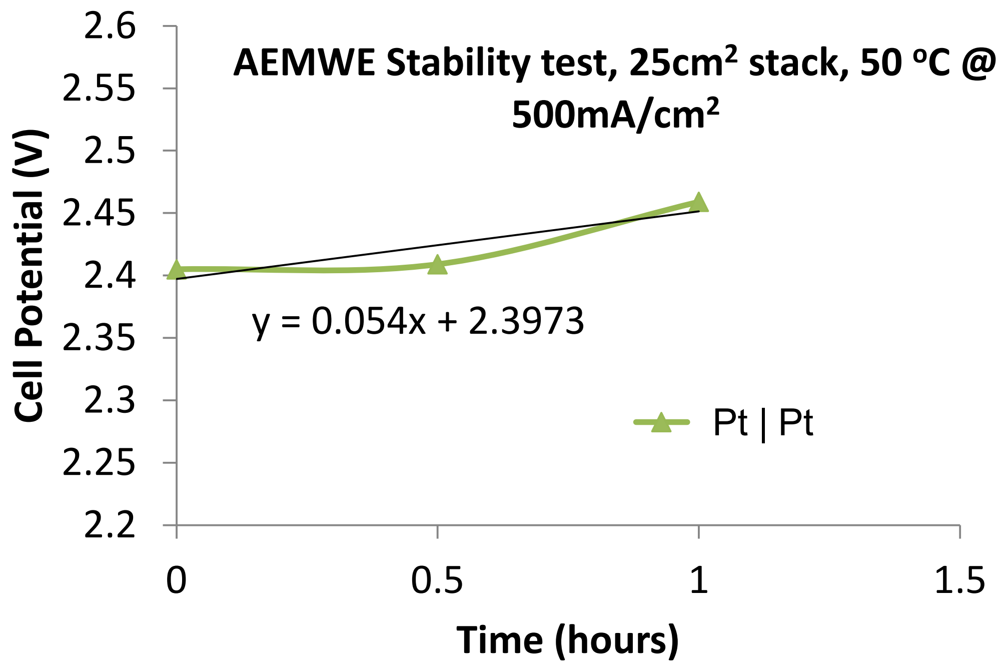


- $28cm^2$ cell commercial platform
- Stainless steel and carbon BOP
- 1wt% $KHCO_3$ anode feed
- Cumulative run time of 550 hrs
- Apparent drift at high current densities

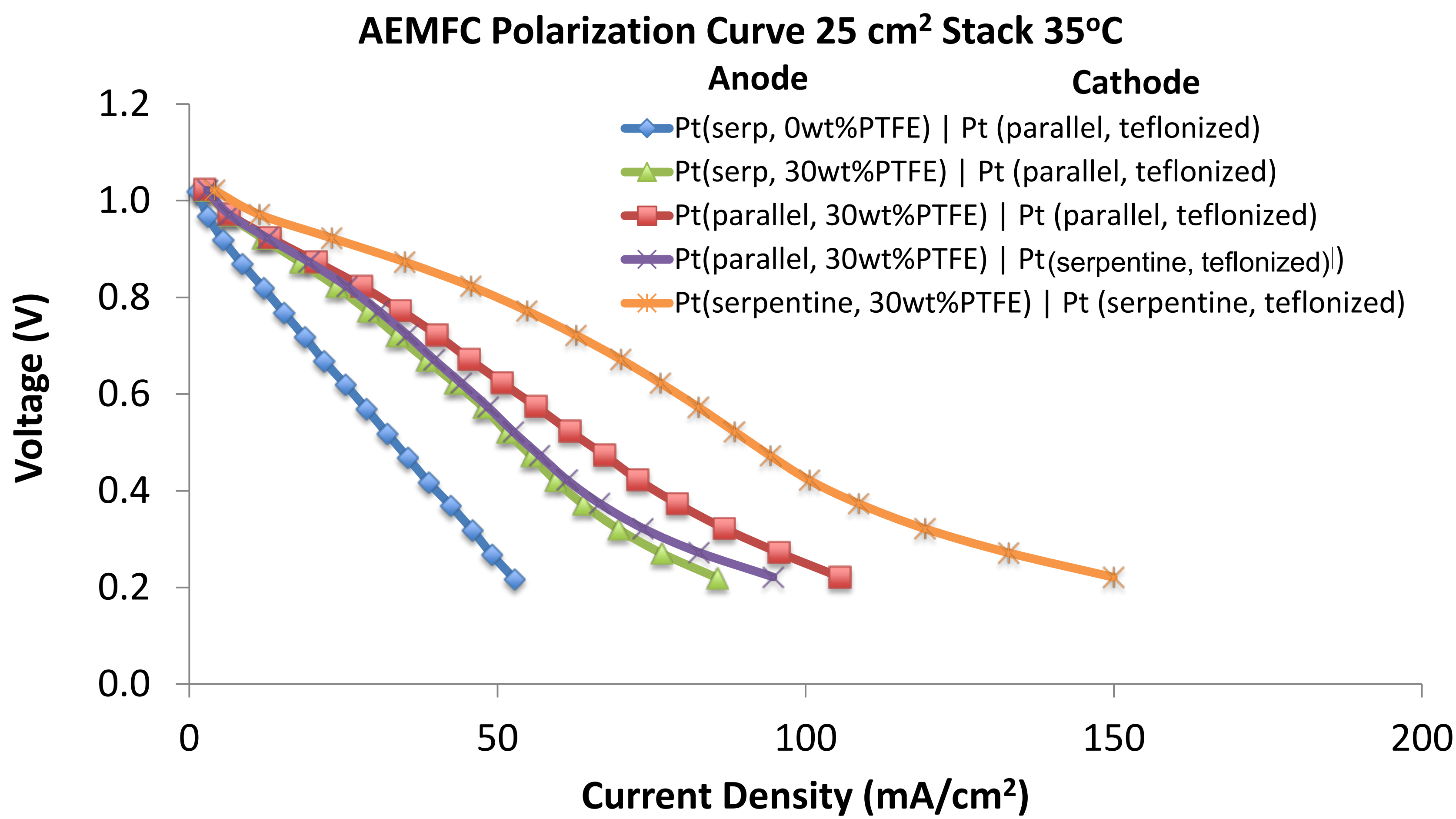
Technical Accomplishments: URFC cell baselining - Electrolysis

- 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



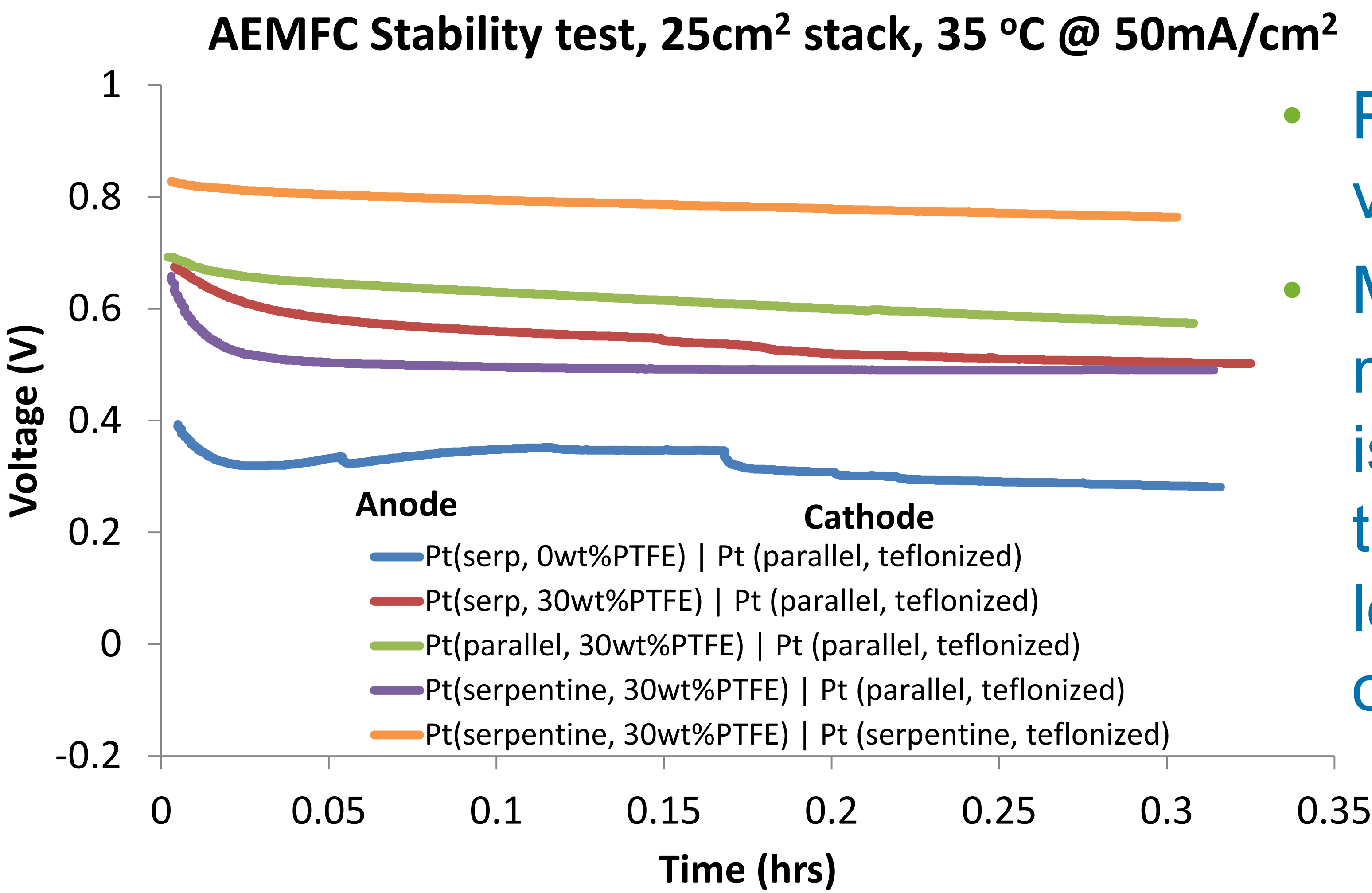


Technical Accomplishments: URFC cell baselining – Fuel Cell



- 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