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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: ~85%

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]

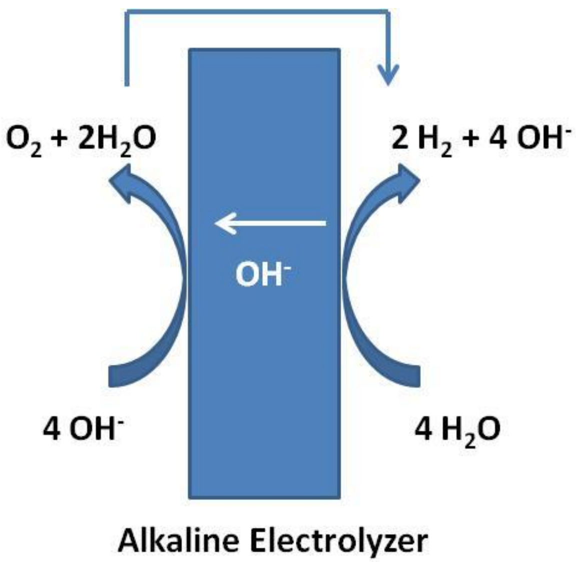
Characteristic	Units	2011 Status	2013 Targets	2015 Targets
Specific power[b]	W/kg	5	8	10
Power density[b]	W/L	7	10	13
Specific energy[b,c]	Wh/kg	110	200	230
Energy density[b,c]	Wh/L	150	250	300
Cost[d]	$/system	150	130	70
Durability[e,f]	hours	1,500	3,000	5,000
Mean time between failures[f,g]	hours	500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

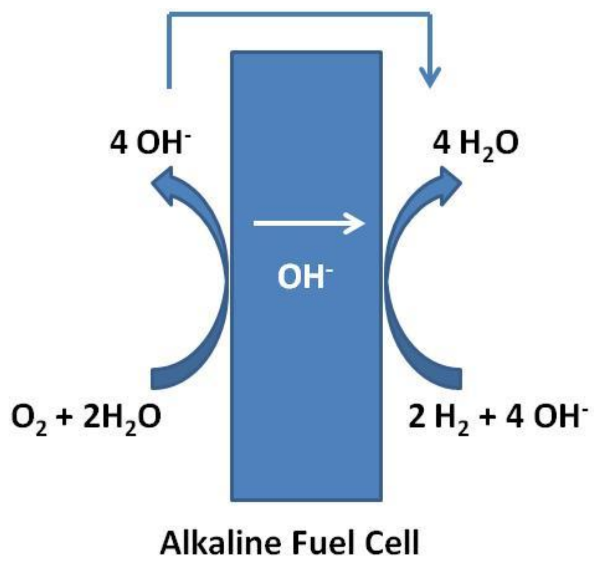
Table 3.1.4 Technical Targets: Distributed Forecourt Water Electrolysis Hydrogen Production [a, b, c, l]

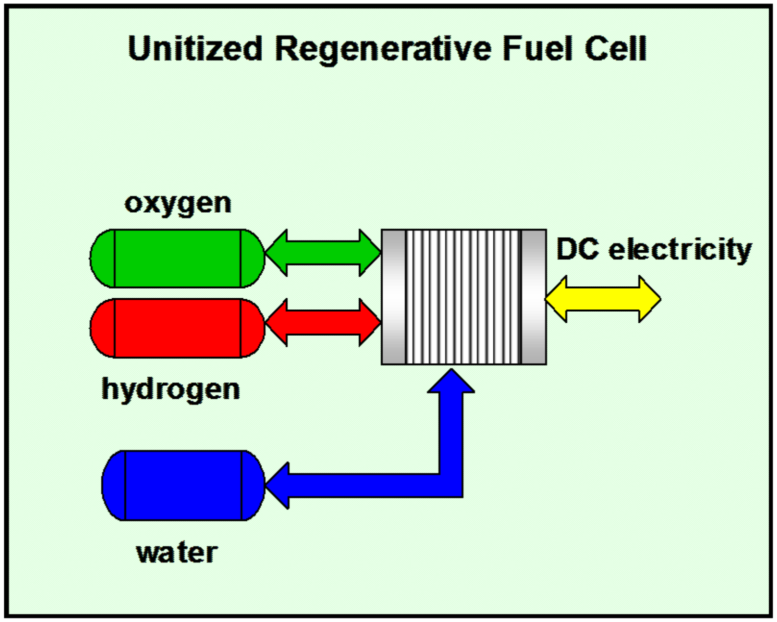
Characteristics	Units	2011 Status	2015 Target	2020 Target
Hydrogen Levelized Cost[d] (Production Only)	$/kg	4.20 [d]	3.90 [d]	2.30 [d]
Electrolyzer System Capital Cost	$/kg $/kW	0.70 430 [e, f]	0.50 300 [f]	0.50 300 [f]
System Energy Efficiency [g]	% (LHV)	67	72	75
	kWh/kg	50	46	44
Stack Energy Efficiency [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- Phase 1

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

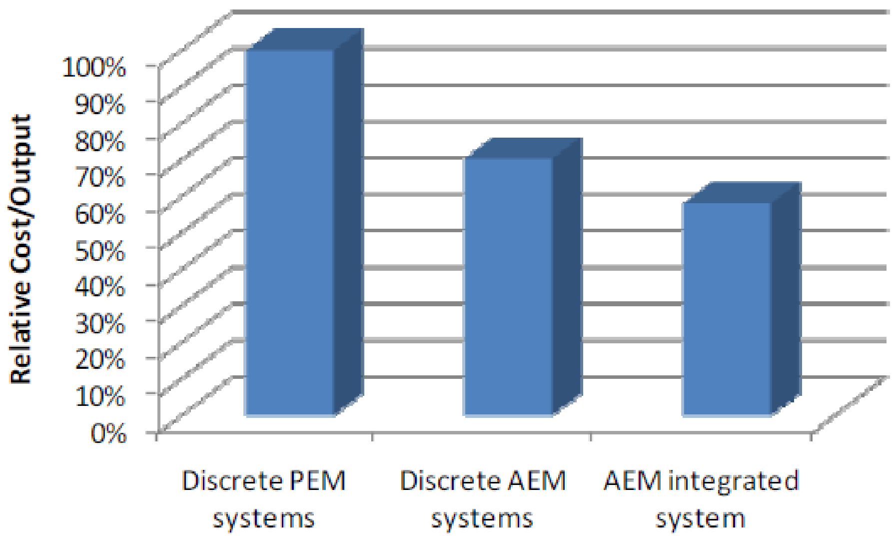






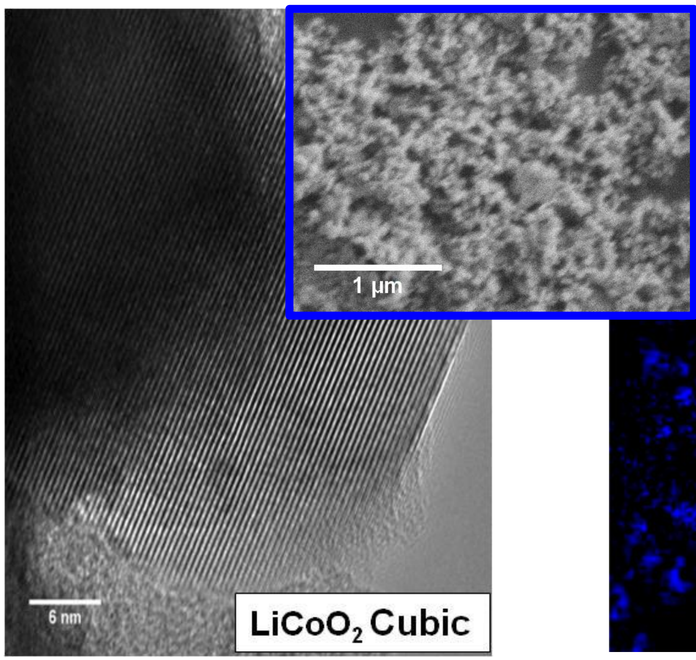
Relevance

- 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

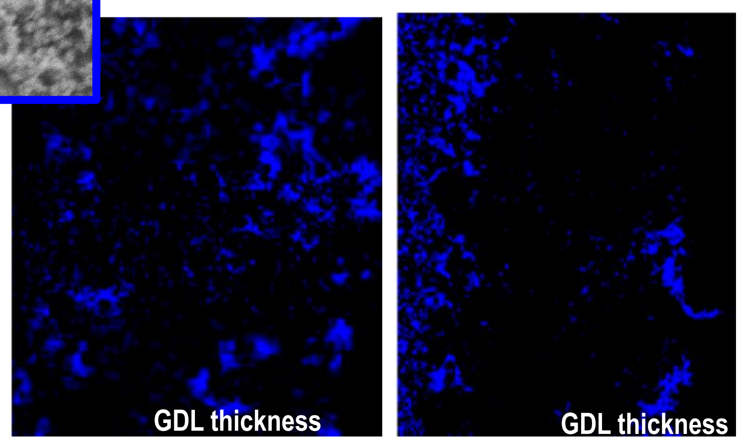


Approach

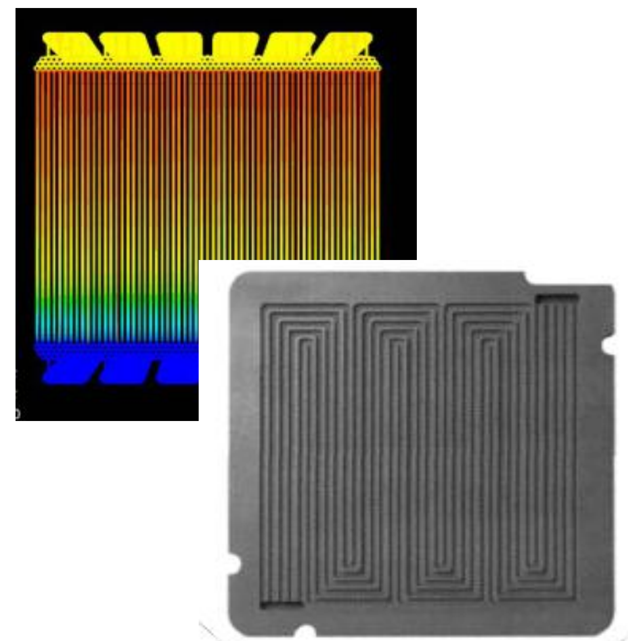
- Catalyst (Rutgers):
  - Based on cubic $LiCoO_2$
  - Tune OER/ORR activity by varying A and B site dopants
- AEM-URFC cell (Proton)
  - Water management
  - Flowfield
  - Wetproofing
  - Catalyst layer integration



Preliminary data on $LiCoO_2$



Water management optimization



Flowfield Design

Objectives

Task description and significance achievements	Completion
Cubic phase *$LiBCoO_2$ ($B=Mn^+$, etc)* synthesized and screened	100%
Electrochemical screening of synthesized materials in RDE	75%
Development of URFC cell	100%
Optimization of flowfields for fuel cell and electrolysis operation	75%
Baselining PGM catalyst materials in fuel cell and electrolysis	100%
Evaluation of non-PGM O_2 electrodes	75%
Durability testing of non-PGM O_2 electrodes	100%

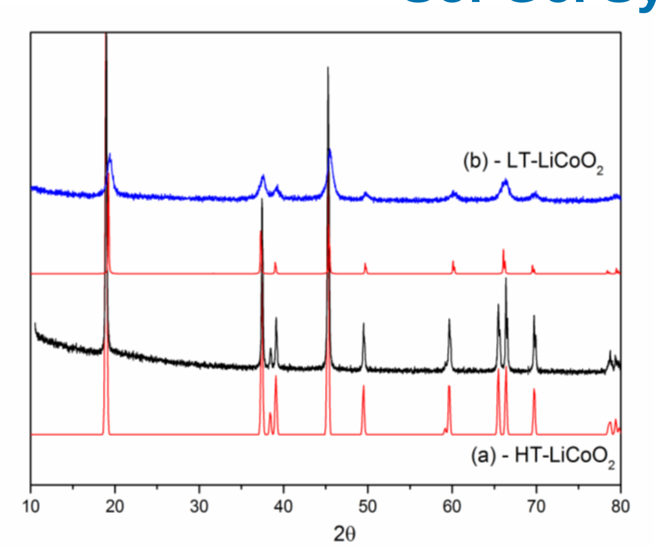
Technical Accomplishments

- **Catalyst Development**
  - Synthesis, performance and reproducibility at 5 grams verified at Proton for $LiCoO_2$
  - Multiple A and B-site doped $ABCoO_2$ (A=Mg, Zn; B=Mn) synthesized and characterized by RDE
- **Cell Development**
  - Defined flowfield geometry and fabricated stainless steel hardware for O_2 side.
  - Flowfield optimization and wet proofing conducted
- **URFC Testing**
  - Baseline performance obtained in fuel cell and electrolysis mode for Pt | Pt catalyst (PGM baseline)
  - Baseline electrolysis performance for $LiCoO_2$ and 1300 hrs stability test completed
  - Preliminary Fuel cell and electrolysis data obtained for $LiCoO_2$

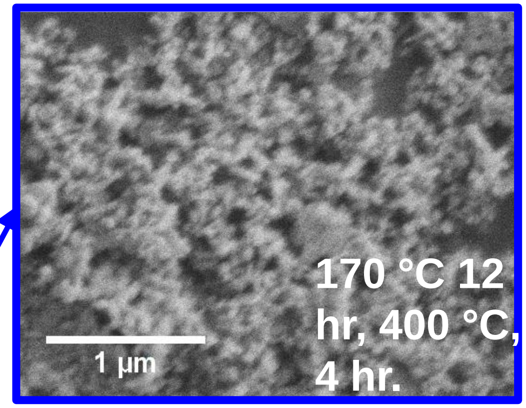
Technical Accomplishments: Synthesis

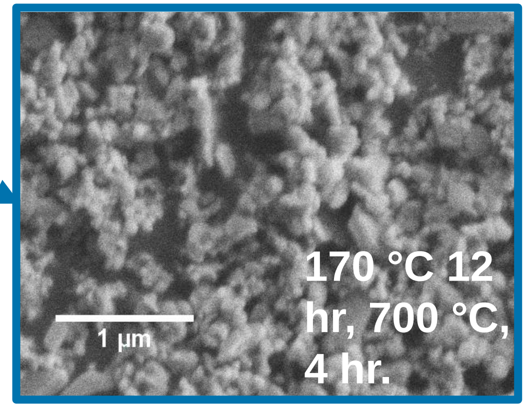
- Sol-gel synthesis employed for high phase purity and higher surface area catalysts

Sol-Gel Synthetic Routes



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

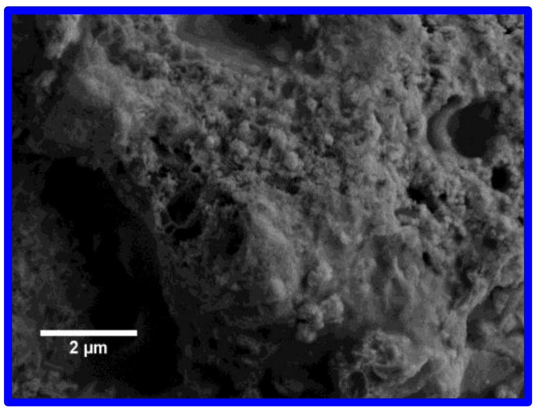




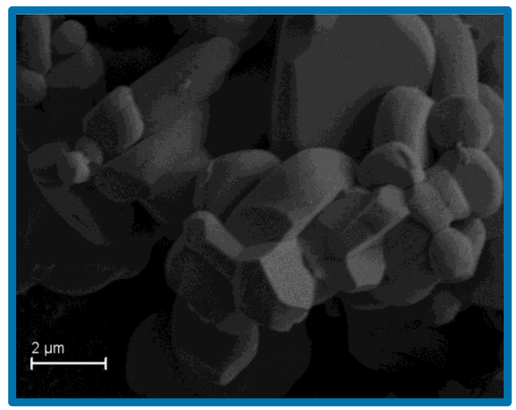
Solid State Synthesis

Li_2CO_3 + $CoCO_3$ (grinding)

400 °C, 72 hr.

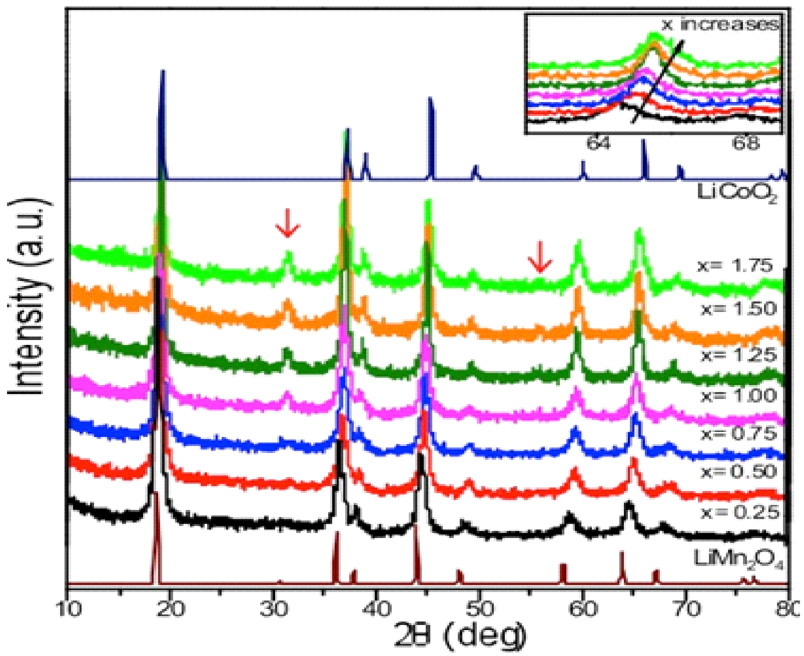


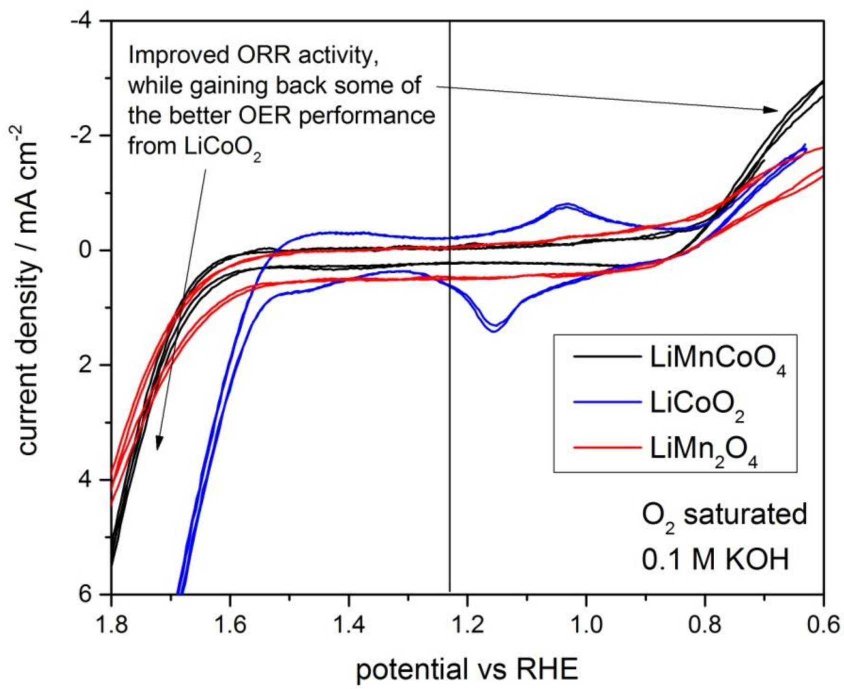
800 °C, 12 hr.



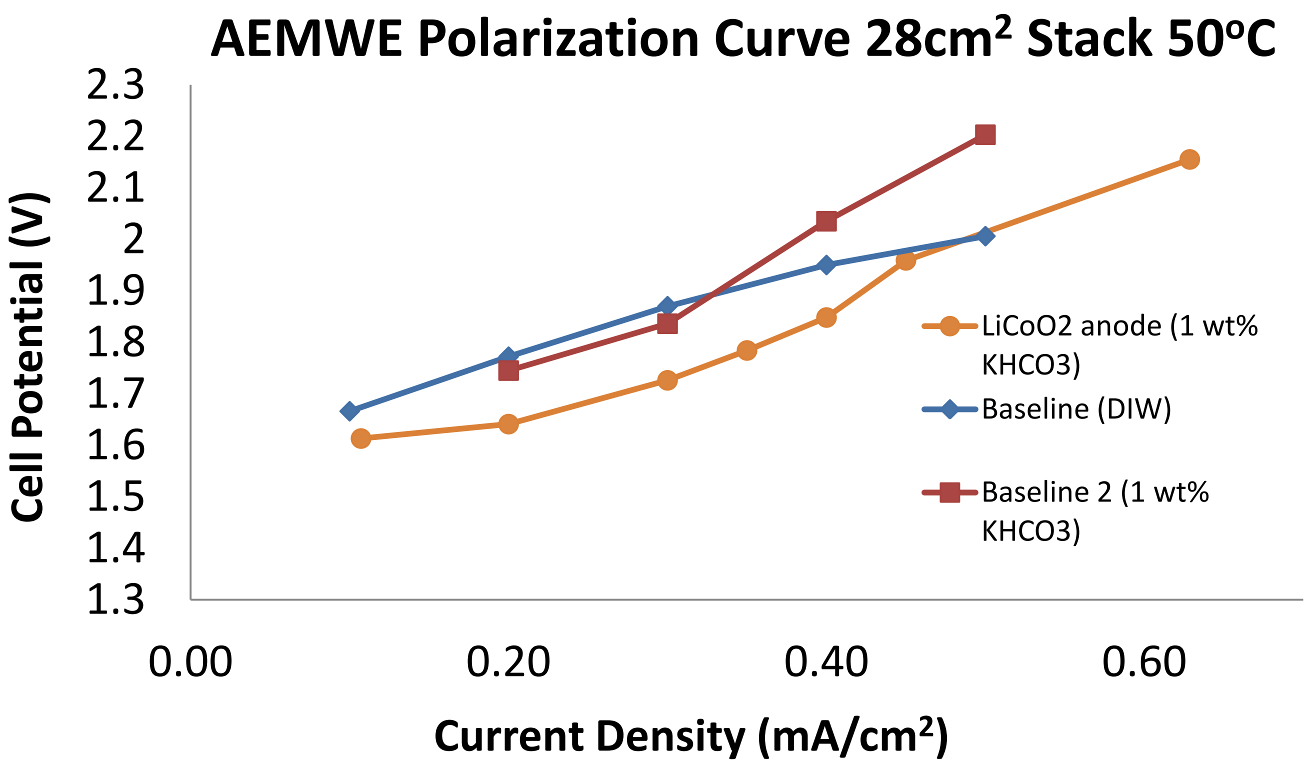
Technical Accomplishments: Non-PGM OER/ORR catalysts

- 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)



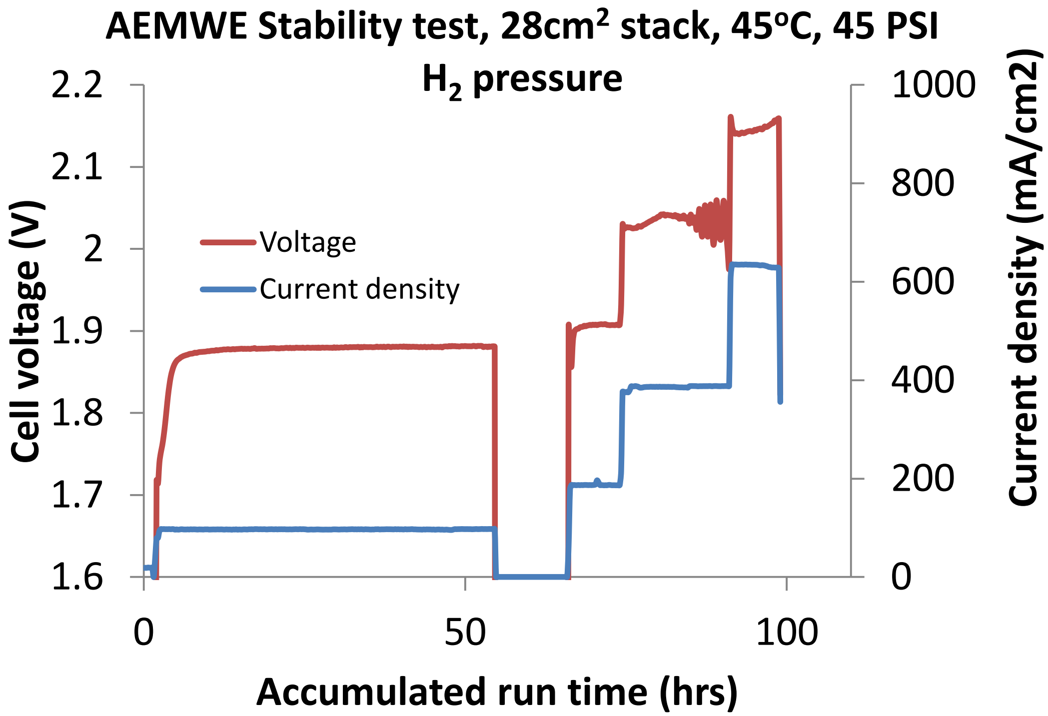


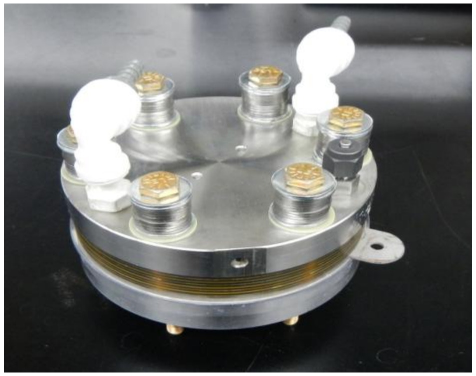
Technical Accomplishments: Non-PGM OER Performance Screening

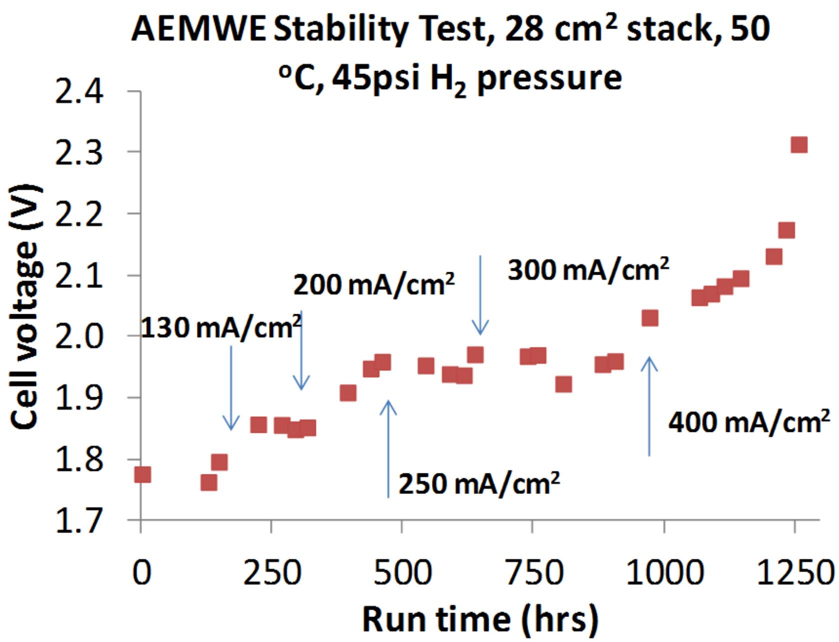


- Anode DI water or bicarbonate feed
- Equivalent Pt cathodes
- Improved performance over baseline anode catalyst

Technical Accomplishments
Non-PGM O_2 Catalyst Durability Test



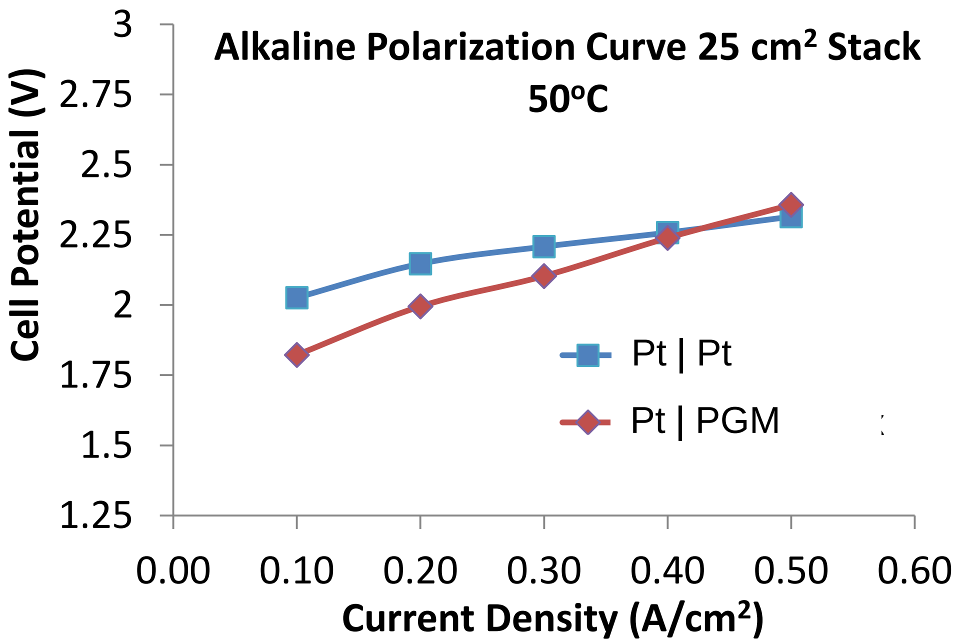


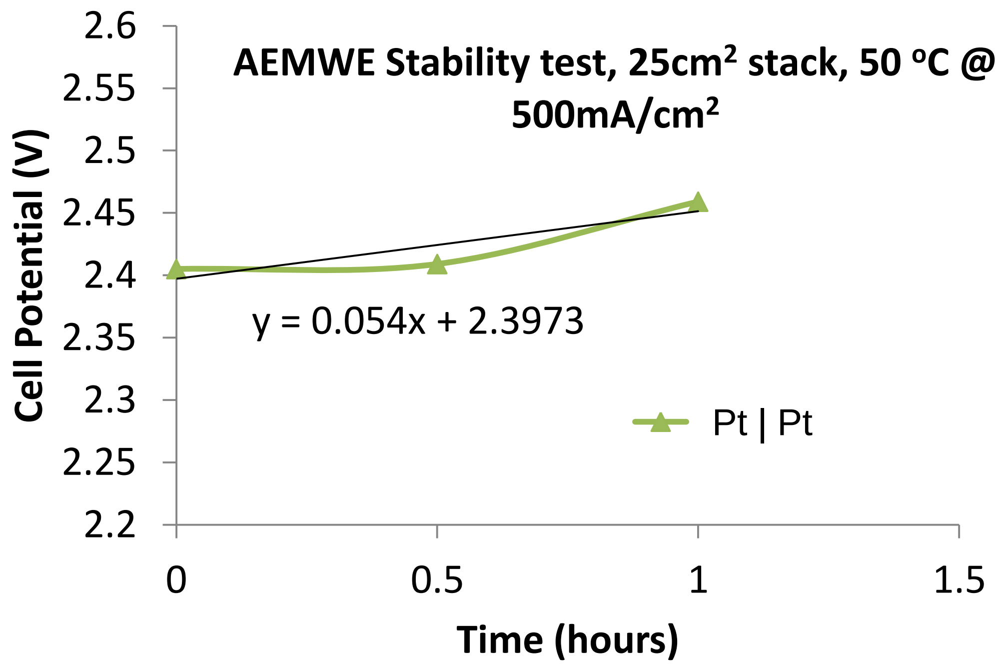


- $28cm^2$ cell commercial platform
- Stainless steel and carbon BOP
- 1wt% $KHCO_3$ anode feed
- Cumulative run time of 1300 hrs
- Apparent drift at high current densities

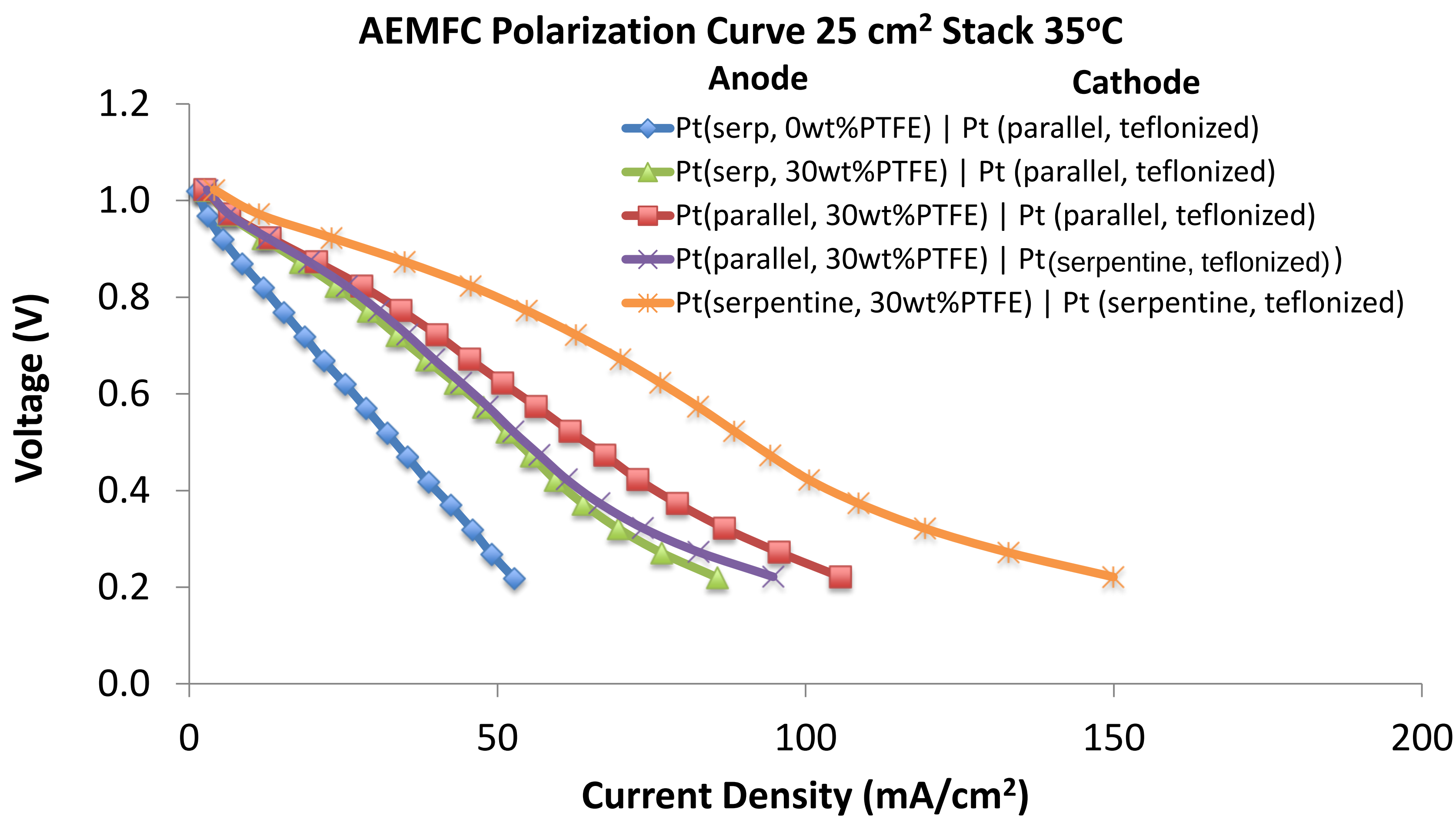
Technical Accomplishments: URFC cell baselining - Electrolysis

- $25cm^2$ 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



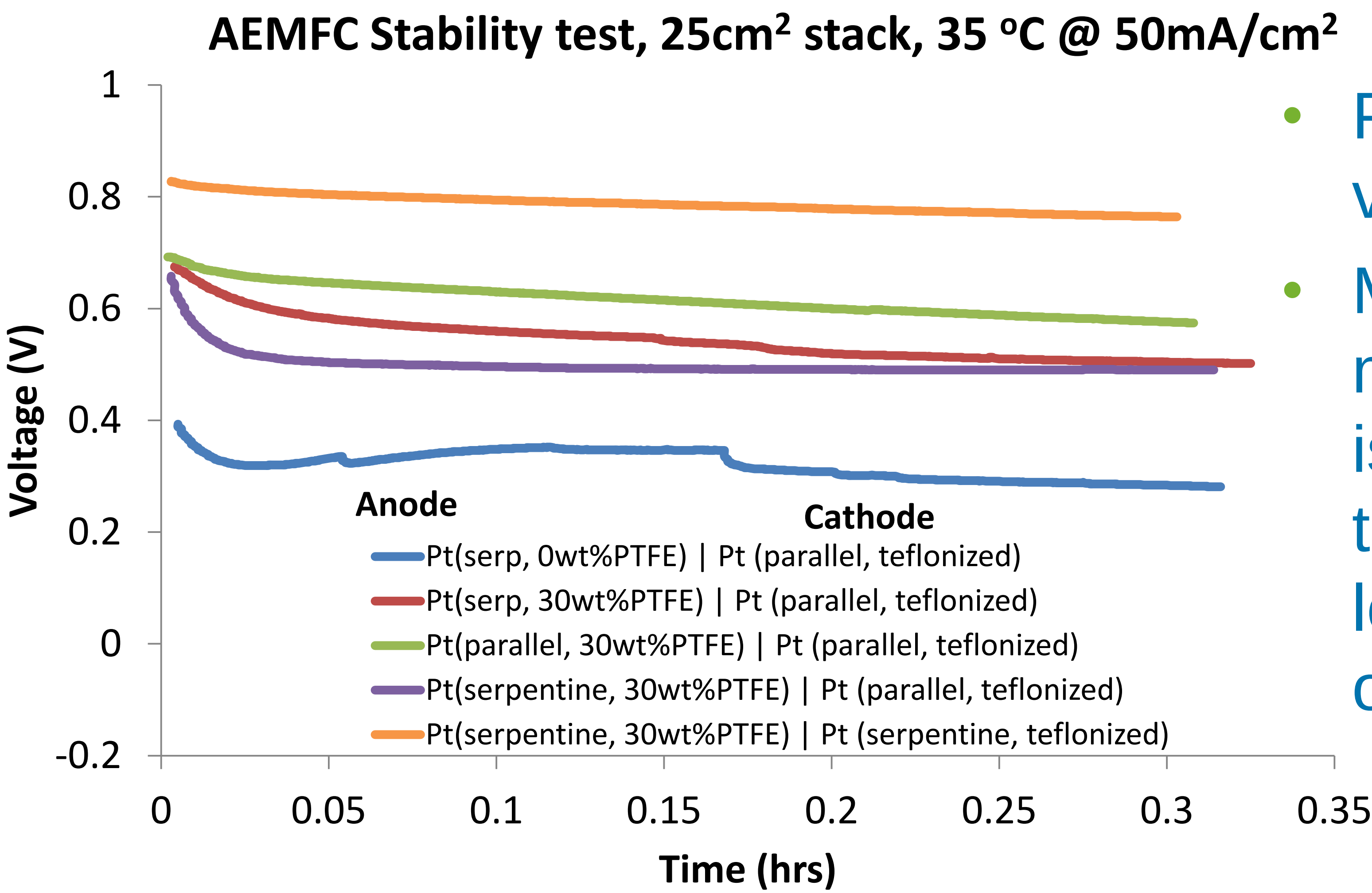


Technical Accomplishments: URFC cell baselining – Fuel Cell



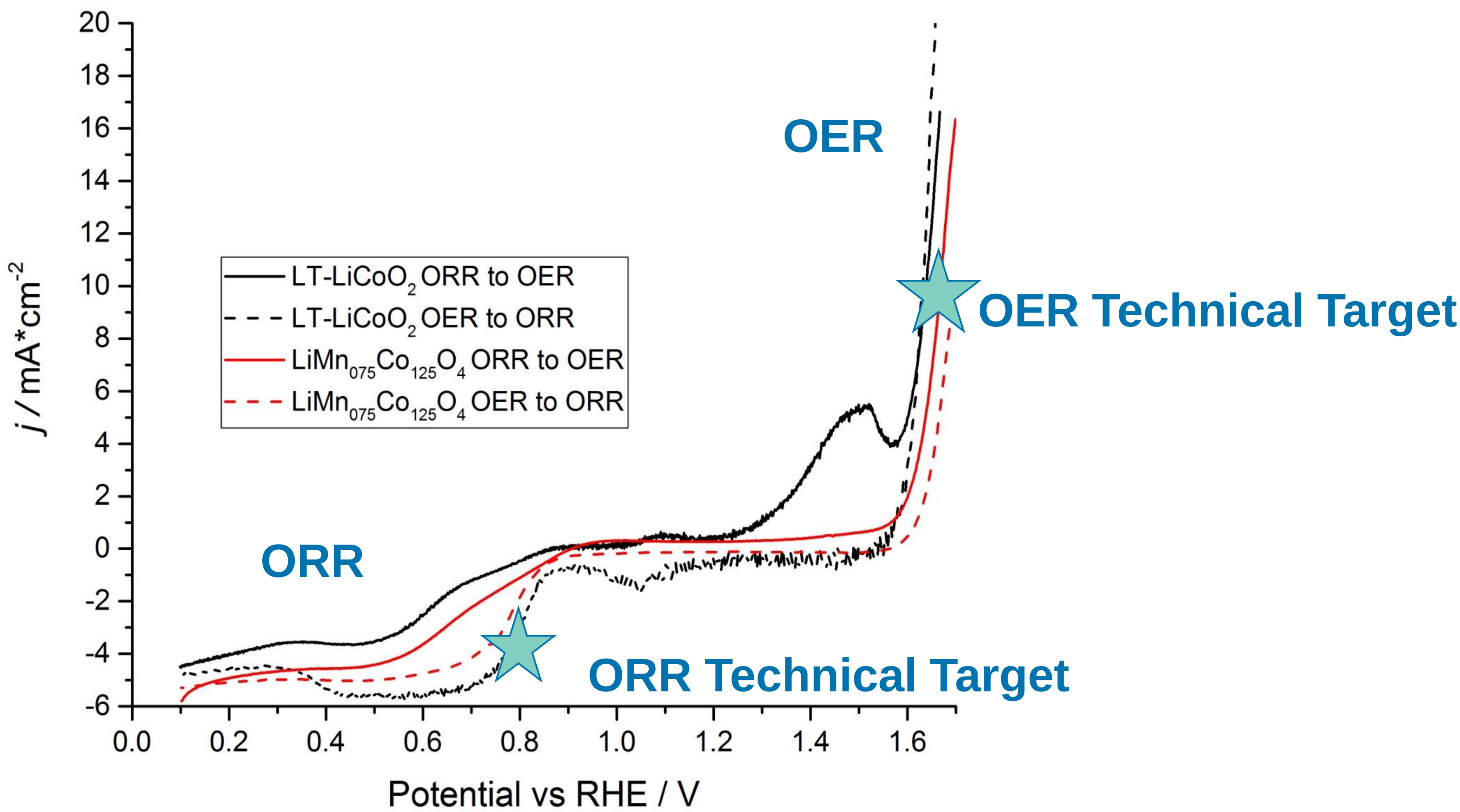
- 25 cm^2 non-proprietary cell platform
- Underhumidified H_2, overhumidified O_2: high flow rates

Technical Accomplishments: URFC cell baselining – Fuel Cell



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

Rutgers non-PGM cycling data

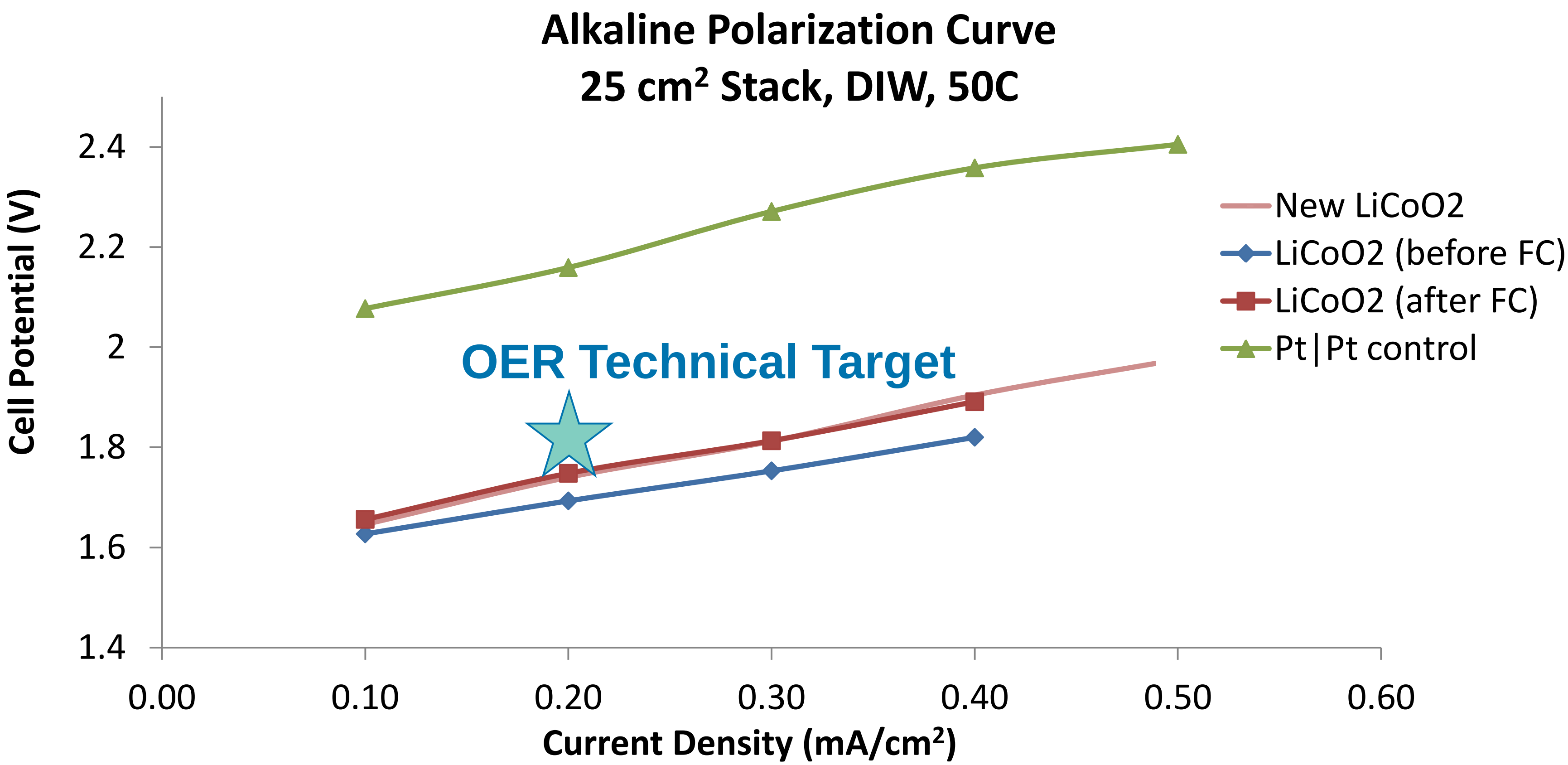


- Rutgers evaluated ORR and OER activity of two non-PGM oxide compounds. Meets OER and ORR, RDE technical targets.
- Initial sweep direction affects activity OER –> ORR vs ORR –> OER
- Electrolysis followed by fuel cell testing is better than fuel cell followed by electrolysis

Electrode and cell configurations fabrication

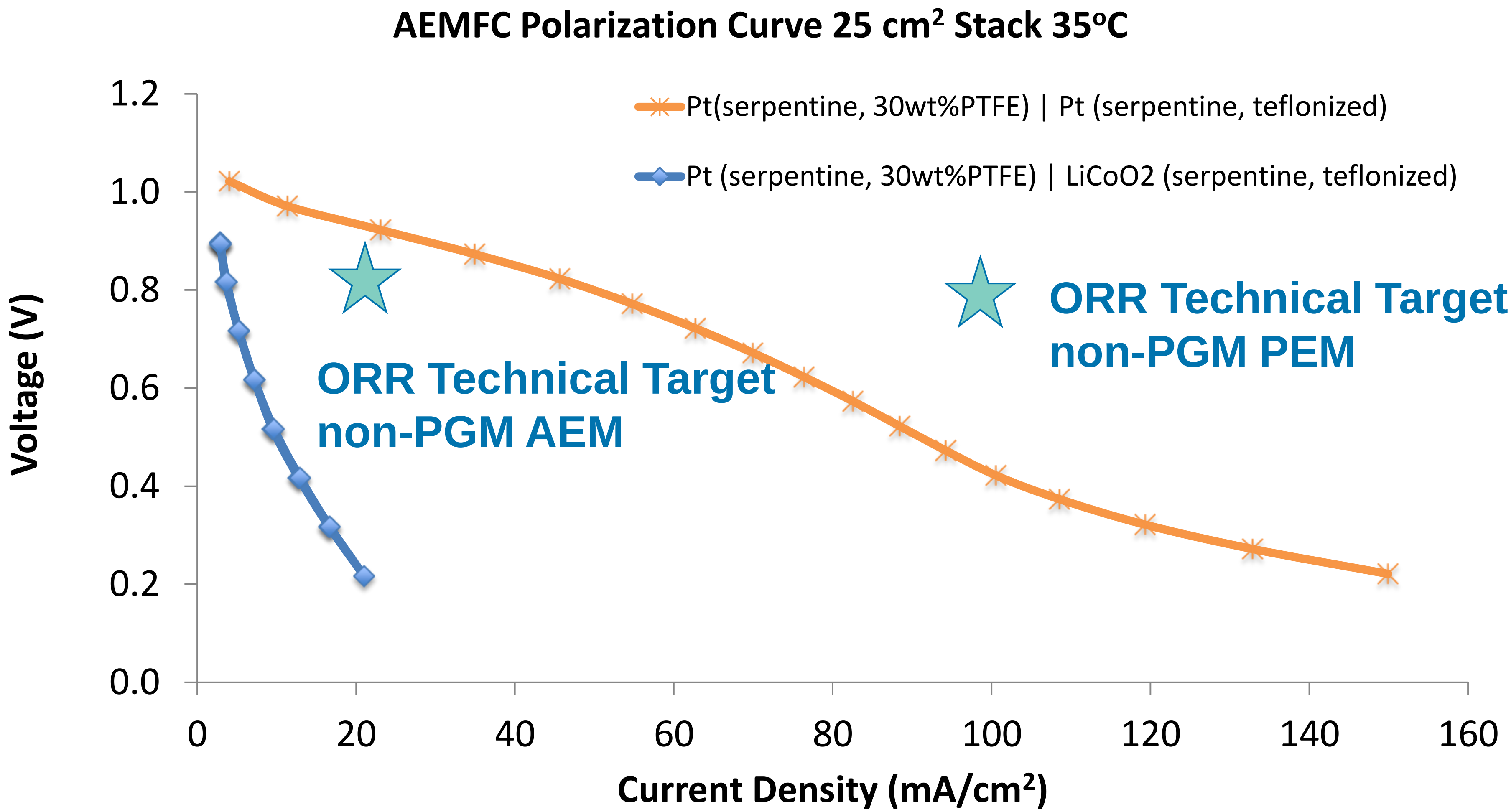
- 25cm^2 test stacks that integrates baseline data and cell design:
  - Serpentine flow channels H_2 and O_2 electrodes
  - Stainless steel serpentine flow channel fabricated, and passivated. Used for cycling tests.
  - Teflonized carbon paper and teflonized Ti porous plate GDLs used to improve water management

$LiCoO_2$ anode



- Before and after FC test, denotes first electrolysis test followed by fuel cell testing, then electrolysis again
- Meets OER technical target in MEA configuration

FC polarization curve



- Does not meets ORR technical target in MEA configuration that was based on PEM non-PGM materials (MYRD&D).
- Propose new target as half of Pt baseline

Proton and Rutgers next steps

- Improve MEA FC performance ORR
  - Focus on improving water transport through GDL
  - Evaluate improved cathode catalyst
- Promote advanced cathode catalyst to 28cm^2 retest with $LiCoO_2$ anode for long term stability
- Conduct 10 cycles using new cathode, $LiCoO_2$ anode (last remaining milestone)
- Rutgers:
  - Evaluate cycling effects on $LiCoO_2$
  - Evaluating anion and cation dopants on ORR/OER activity

More information

- AMR poster:
  - http://www.hydrogen.energy.gov/pdfs/review15/fc133_danilovic_2015_p.pdf