Energy Materials Network
U.S. Department of Energy

HydroGEN
Advanced Water Splitting Materials

High-Performance Ultralow-Cost Non-Precious Metal Catalyst System for AEM Electrolyzer

P. I. Hoon T. Chung
Los Alamos National Laboratory

Project ID p158

NREL · BERKELEY LAB · Sandia National Laboratories · INL Idaho National Laboratory · Lawrence Livermore National Laboratory · SRNL

Project Overview

Project Partners

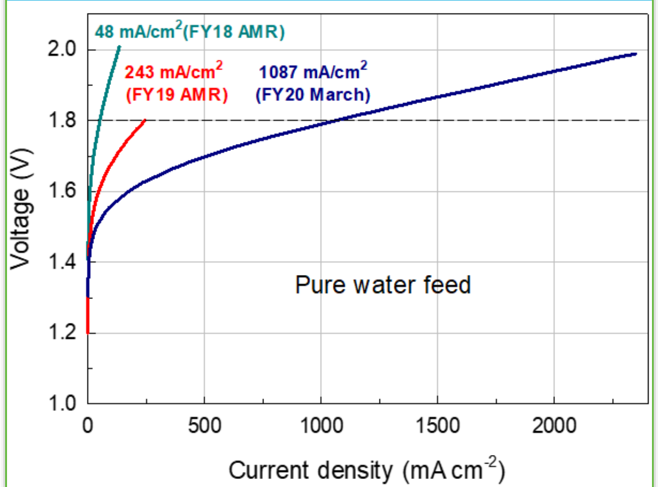
Hoon T. Chung, Los Alamos National Laboratory
Barr Zulevi, Pajarito Powder, LLC

Award #	2.2.0.402
Year 3 Start Date Year 3 End Date	10/01/2019 09/30/2020
Year 3 DOE Share* Year 3 Cost Share Year 3Total Funding	$250 K $ 28 K $278 K

Project Vision

The key challenge in anion exchange membrane (AEM) electrolyzer is to achieve high performance without feeding any salt or alkaline solutions to the electrodes. In this project, we are developing PGM-free OER catalyst with high performance in the alkaline solution-free AEM water electrolyzer.

22 times improvement achieved since FY2018 AMR in current density at 1.8 V



Project Impact

By eliminating most expensive PEM electrolyzer components, AEM technology offers > 75% stack cost reduction. This opens a pathway to meeting the DOE H_2 production cost target of < $2/kg.

** this amount does not cover support for HydroGEN resources leveraged by the project (which is provided separately by DOE)*

Approach- Summary

Project Motivation

Since early 2000s, LANL has contributed significantly in the design and performance of PGM-free cathode catalysts for PEFCs. Pajarito Powder, LLC (PPC) is a venture-backed US manufacturer of electrochemical materials including catalysts. Leveraging expertise of both institutions, this project has been initiated.

Key Impact

Metric	State of the Art	Proposed
AEM water electrolyzer performance	2.7 A/cm^2 at 1.8 V	2.8 A/cm^2 at 1.8 V
AEM water electrolyzer durability	Degradation rate of 1.7 mV/hr for ~ 200 hours at a current density of 200 mA/cm^2 with NiFe PGM-free catalyst	Degradation rate of 0.1 mV/hr for ~ 500 hours at a current density of 400 mA/cm^2 with perovskite PGM-free catalyst

Barriers

- Cost:
  - ✓ Expensive materials: platinized titanium flow filed; Nafion® membrane; PGM-catalysts for PEM electrolyzers
  - ✓ Efficiency: High overpotential for HER and OER catalysts

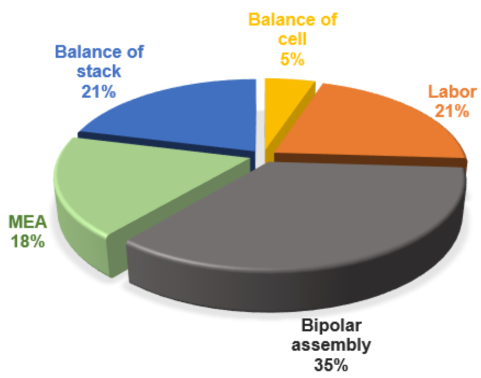
Partnerships

PPC is a partner of this project. Their expertise is in (i) mass-production of catalysts, (ii) fabrication of MEAs, and (iii) AEM electrolyzer test. Catalyst developed by LANL will be tested by PPC in AEM electrolyzer and be produced scaled-up of 25 g/batch.

Relevance & Impact: H_2 Production for <$2/kg

- AEM electrolysis *vs. PEM electrolysis*: significant cost reduction:
  - ✓ PGM catalysts → PGM-free catalysts
  - ✓ Titanium bipolar assembly→ stainless steel bipolar assembly
  - ✓ Nafion®perfluorinated membrane → hydrocarbon membrane

K. Ayers, AMR presentation PD094, 06/2014

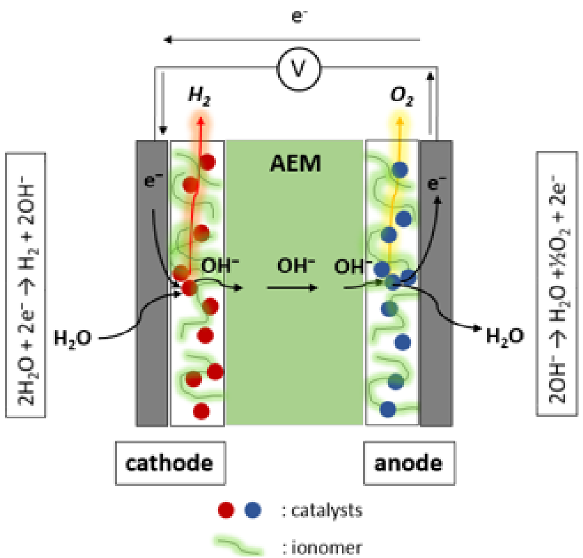


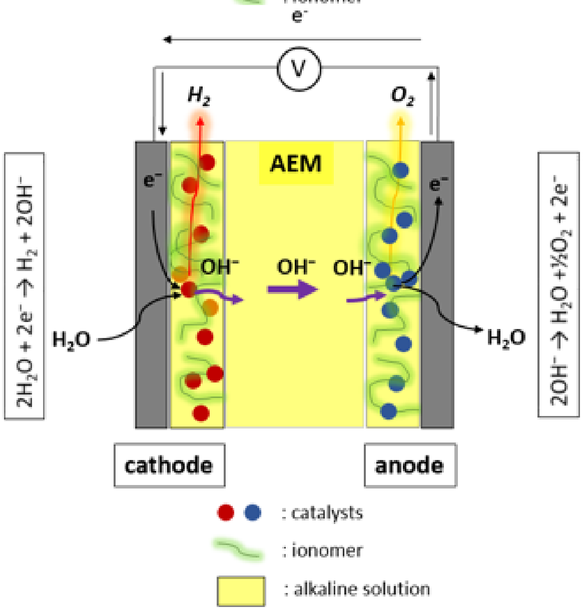
- Bipolar assembly and MEA represents highest cost of PEM stack
- Alkaline media enables transition from titanium to stainless steel: eliminates 75% of part cost and also enables lower cost catalysts

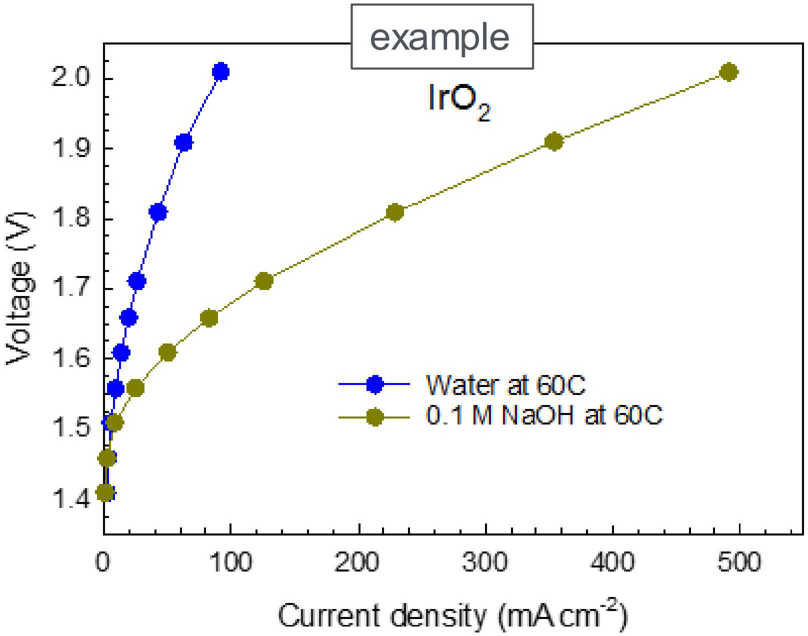
- AEM electrolysis *vs. Alkaline electrolysis*: compact size; less corrosive environment:
  - ✓ Corrosive alkaline solution → water
  - ✓ Low gas purity → high gas purity
  - ✓ Low current generation → high current density

AEM *water* electrolysis has combined advantages of both PEM and alkaline electrolysis: the best system to meet the H_2 production cost target of < 2 $/Kg of H_2

Relevance: Development of Pure Water-feed AEM Electrolyzer





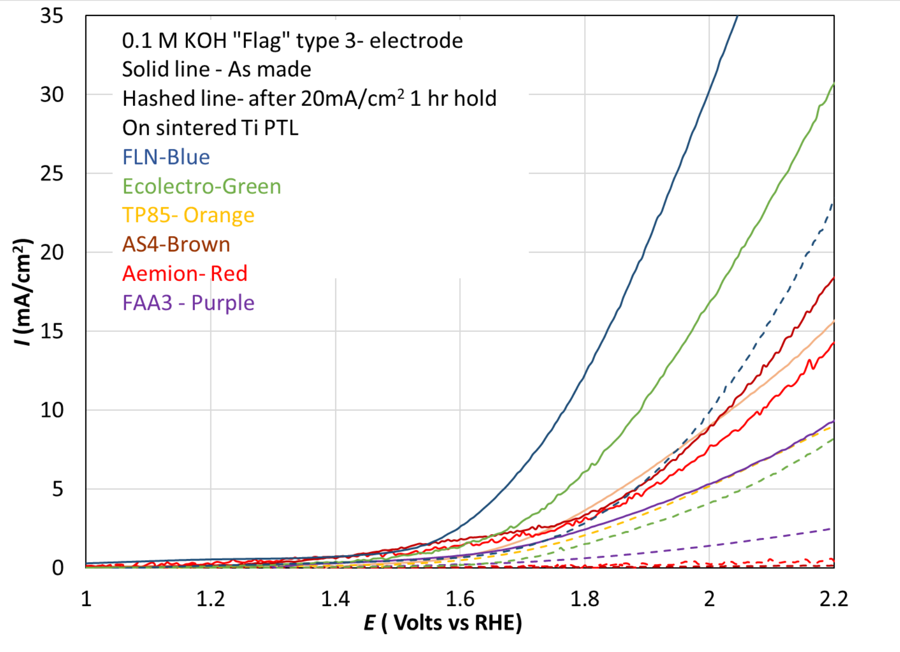


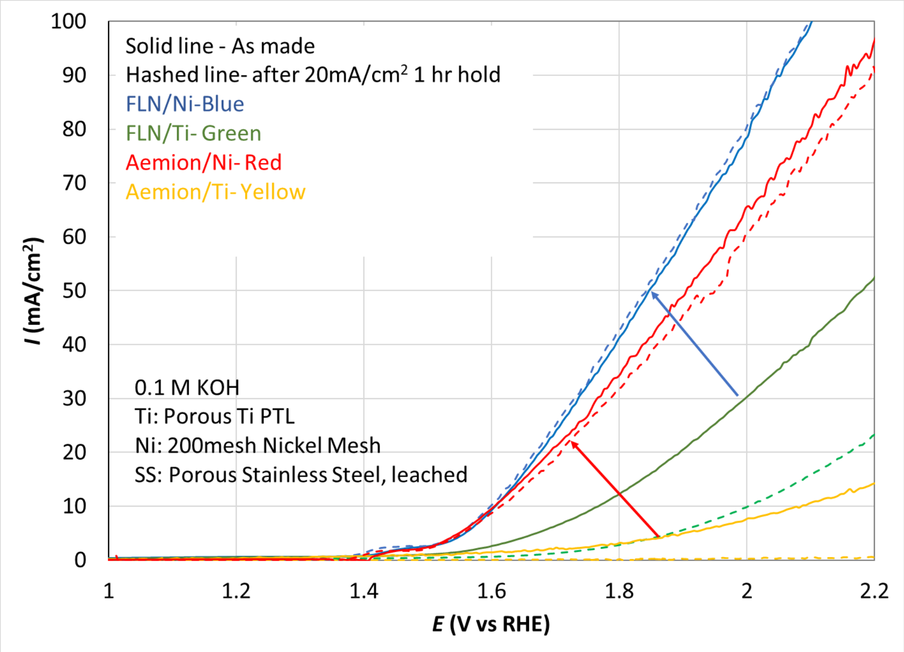
Alkaline solution-feed leads to higher AEM electrolyzer performance compared to water-feed AEM electrolyzer → Development of high performance water-feed AEM electrolyzer is challenging.

FY20 Quarterly Progress Measures

Date	Quarterly Progress Measures	Status
December 2019 (Fy20 Q1)	Optimize test conditions for catalyst/ionomer interactions using ambient pressure x-ray photoelectron spectroscopy (XPS)	**Completed** (see slide **)
March 2020 (Fy20 Q2)	Synthesize perovskite OER catalyst that has particle size < 10 nm using a supercritical drying method, and demonstrate 500 mA/cm^2 at 1.8 V in a pure water-feeding (e.g., no added salt or base) AEM electrolyzer. The durability target is 0.5 mV/hr.	**Performance and durability targets met and exceeded** (see slides 10, 11)
June 2020 (Fy20 Q3)	PPC delivers 25 gr batch of scaled up catalyst that is developed by LANL with higher than 25 m^2/gr BET surface area and activity great than 90% of small batch scale catalysts.	**On track**
September 2020 (Fy20 Q4)	Demonstrate 1 A/cm^2 at 1.8 V in a pure water-feeding (e.g., no added salt or base) AEM water electrolysis with PGM-free, carbon-free OER catalyst. The durability target is 0.1 mV/hr based on testing for 500 hour at a current density of ≥400 mA/cm^2.	**On track**

Accomplishment : Ionomer Effect and Ni-Mesh PTL

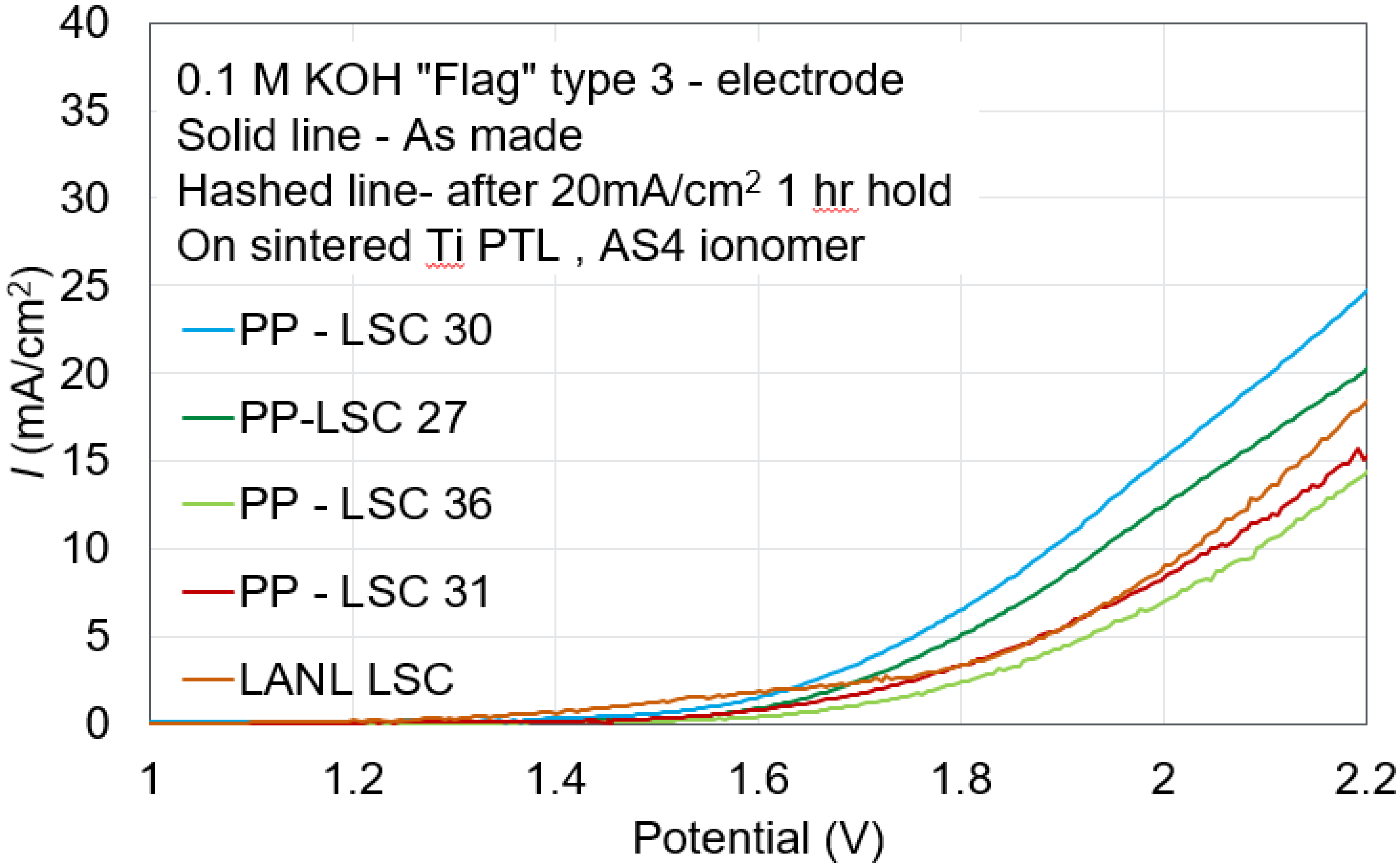




- 3 - Electrode "Flag" type electrode testing of catalyst/Ionomer/PTL interactions
- Ionomer significantly impacts OER performance
- Ni-mesh porous transport layer (PTL) exhibits much higher OER performance than expensive titanium(Ti) PTL → Ni PTLs to be employed in AEM electrolyzer

PAJARITO POWDER FUEL CELL CATALYSTS

Accomplishments: Catalyst Scale Up

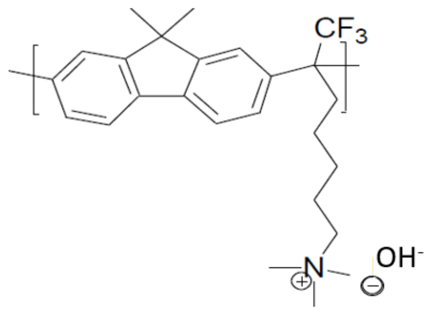


- Catalyst technology is transferred to Pajarito Powder from LANL and scale upsynthesis preliminary results are demonstrated
- OER performance of LSC catalysts synthesized by Pajarito Powder match or exceed LANL LSC catalyst performance

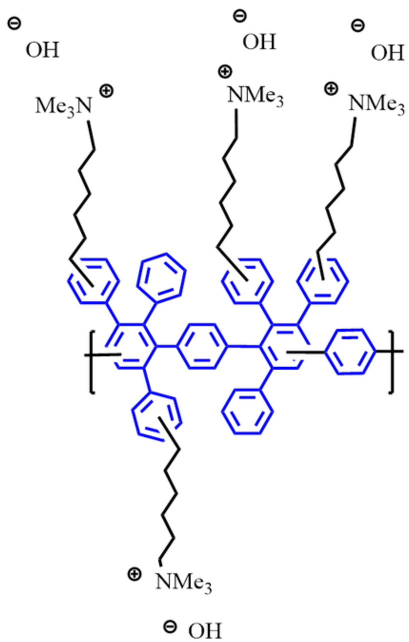
PAJARITO POWDER
FUEL CELL CATALYSTS

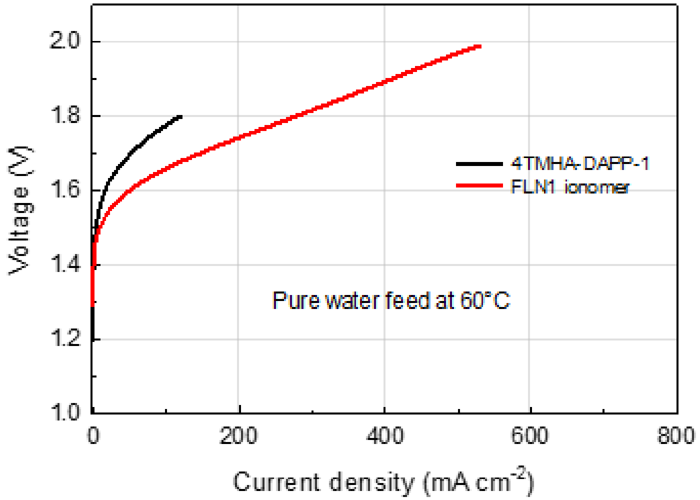
Accomplishment: Catalyst-Ionomer Interaction Effect

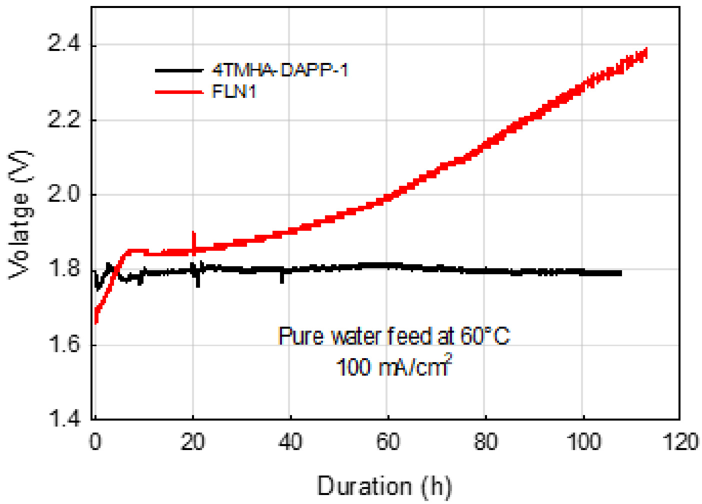
FLN1



4TMHA-DAPP-1



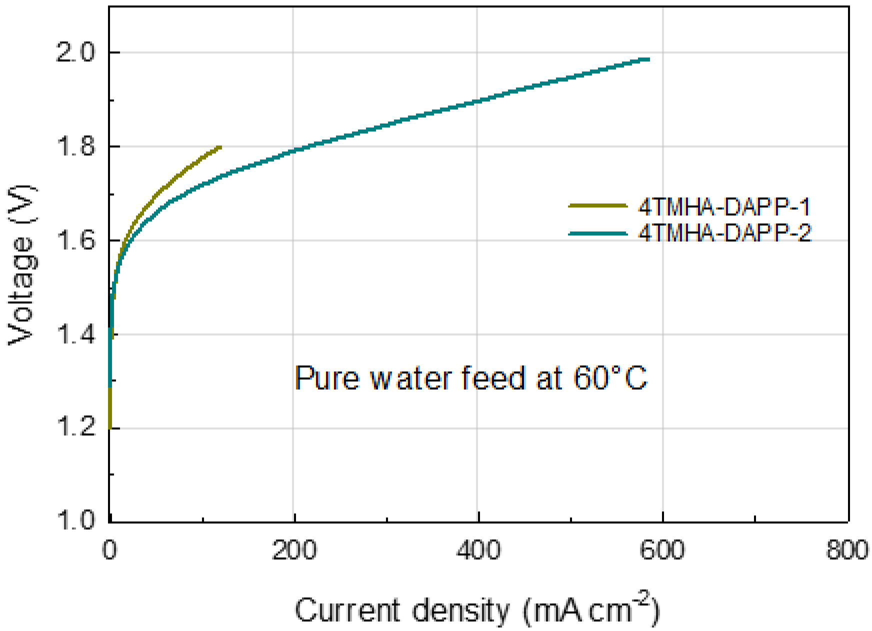


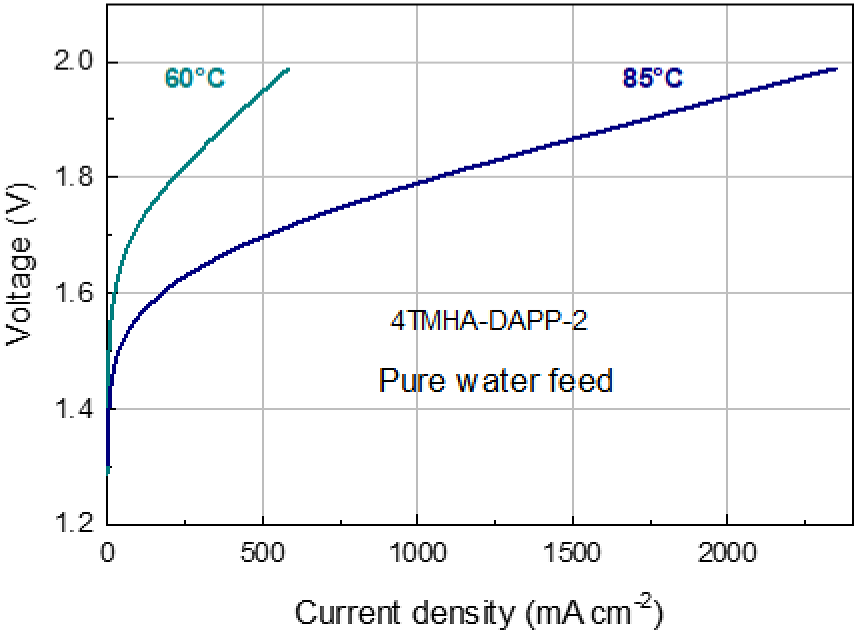


- FLN1 demonstrates higher initial performance but lower durability than 4TMHA-DAPP-1

→ indicating understanding the catalyst-ionomer interaction critical particularly for durability

Accomplishment: AEM Electrolyzer Performance

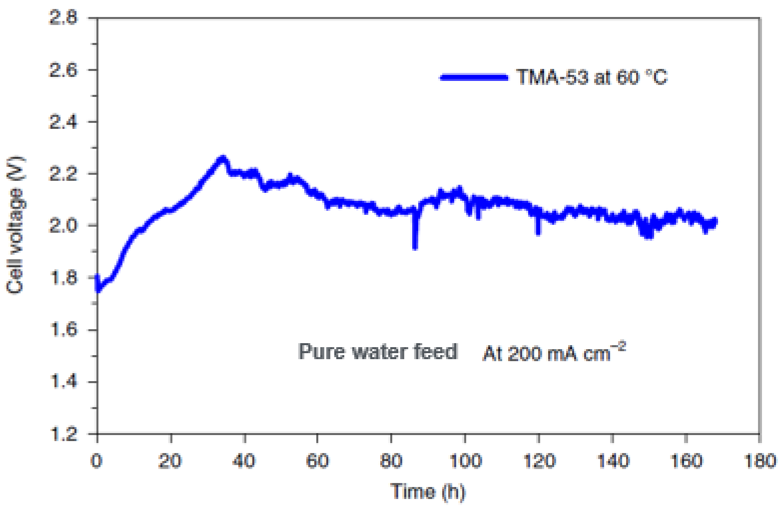




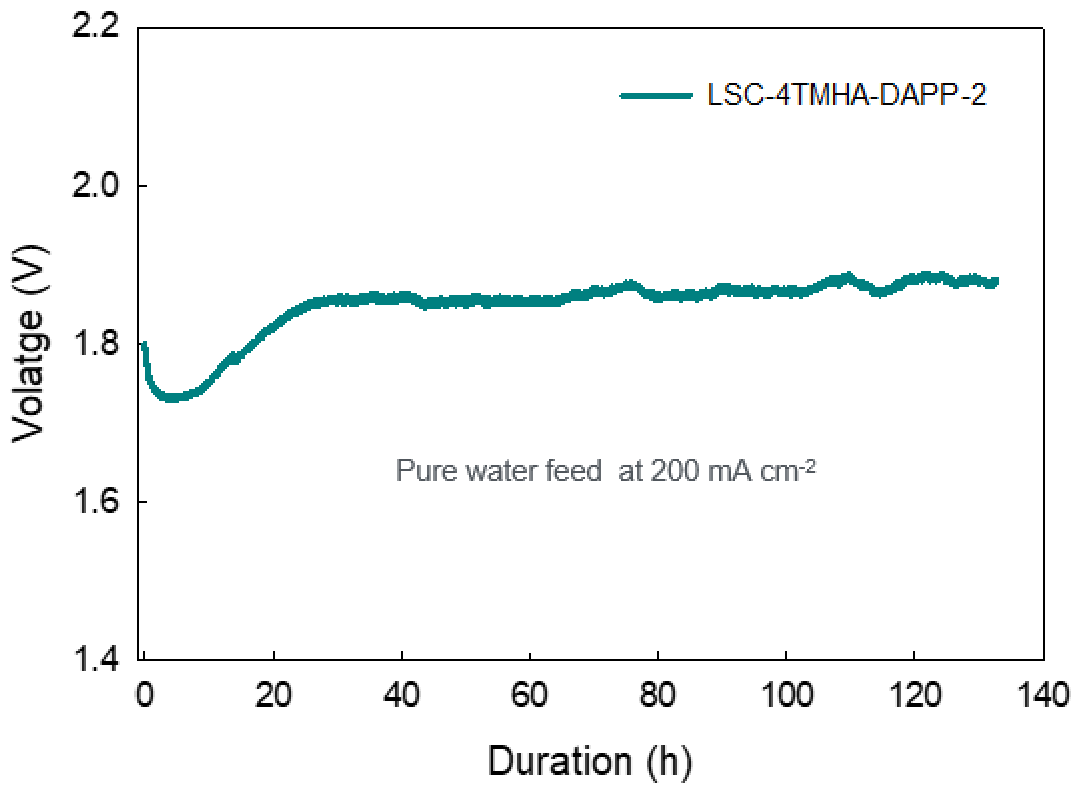
- Higher IEC ionomer (4TMHA-DAPP-2) enhances AEM electrolyzer performance than lower IEC ionomer (4TMHA-DAPP-1)
- Temperature has a huge impact on AEM electrolyzer performance
- Current density of 1.04 A/cm^2 is achieved at 1.8 V at 85°C

Accomplishment: AEM Electrolyzer Durability

State-of-the-art durability with PGM-free catalyst

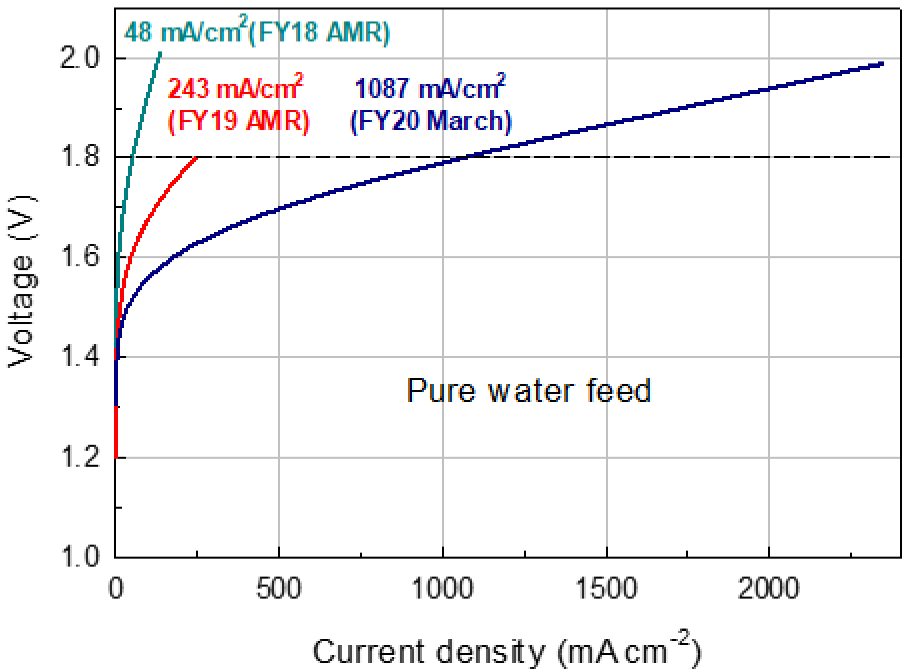


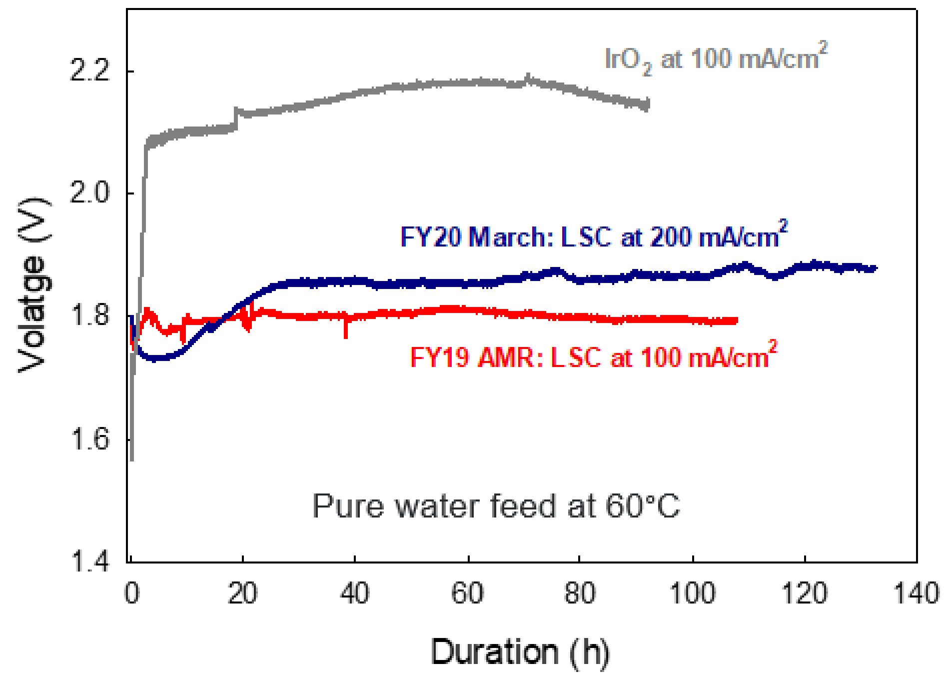
Y. S. Kim *et al* **10.1038** *Nature Energy* (2020)



- ~0.2 mV/hr degradation rate is demonstrated at 200 mA/cm^2 after initial pre-conditioning for 100 hour durability test with LSC-4TMHA-DAPP-2 catalyst-ionomer
- LSC-4TMHA-DAPP-2 catalyst-ionomer demonstrates higher performance and durability than state-of-the-art NiFe-TMA-53 catalyst-ionomer

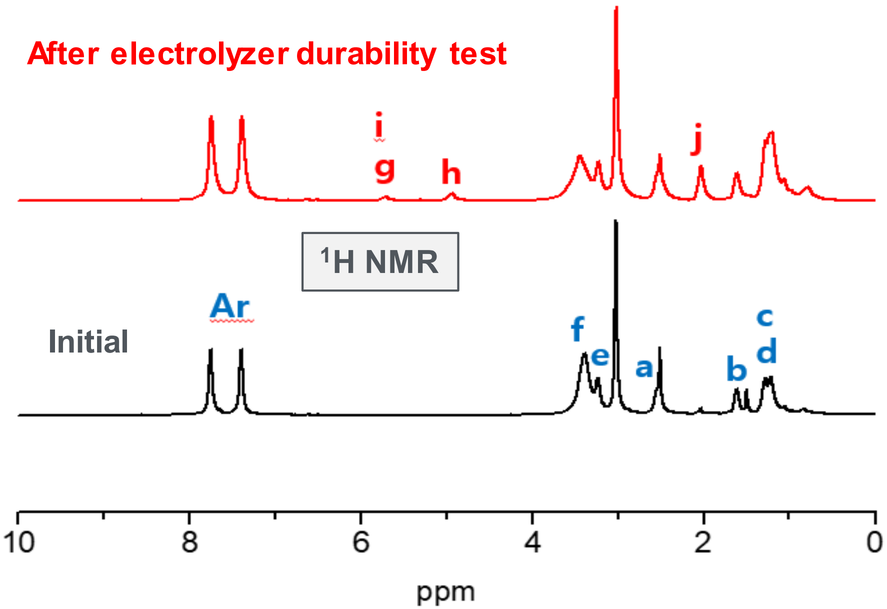
Accomplishment: Progress since FY19 AMR

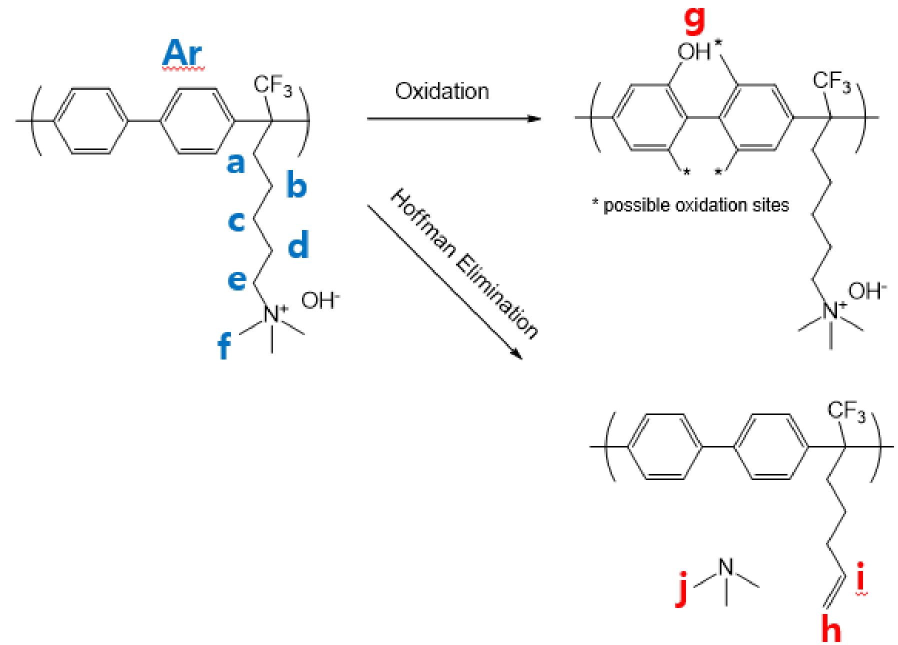


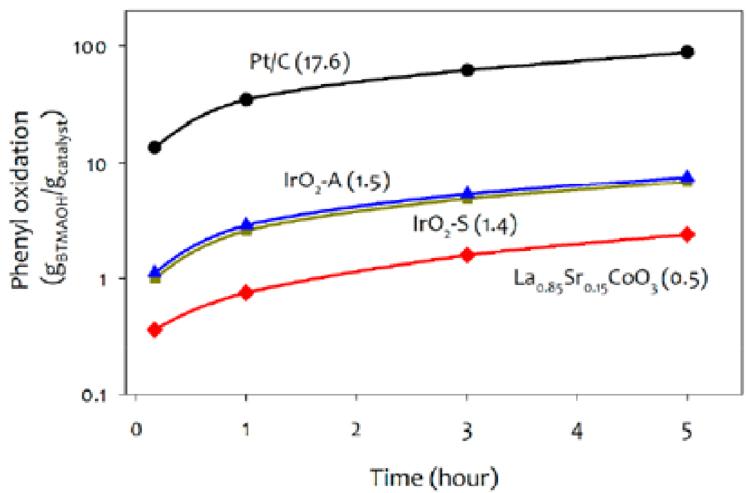


- Noticeable progress in AEM performance and durability have been achieved since FY19 AMR

Accomplishment: Catalyst-Ionomer Interaction



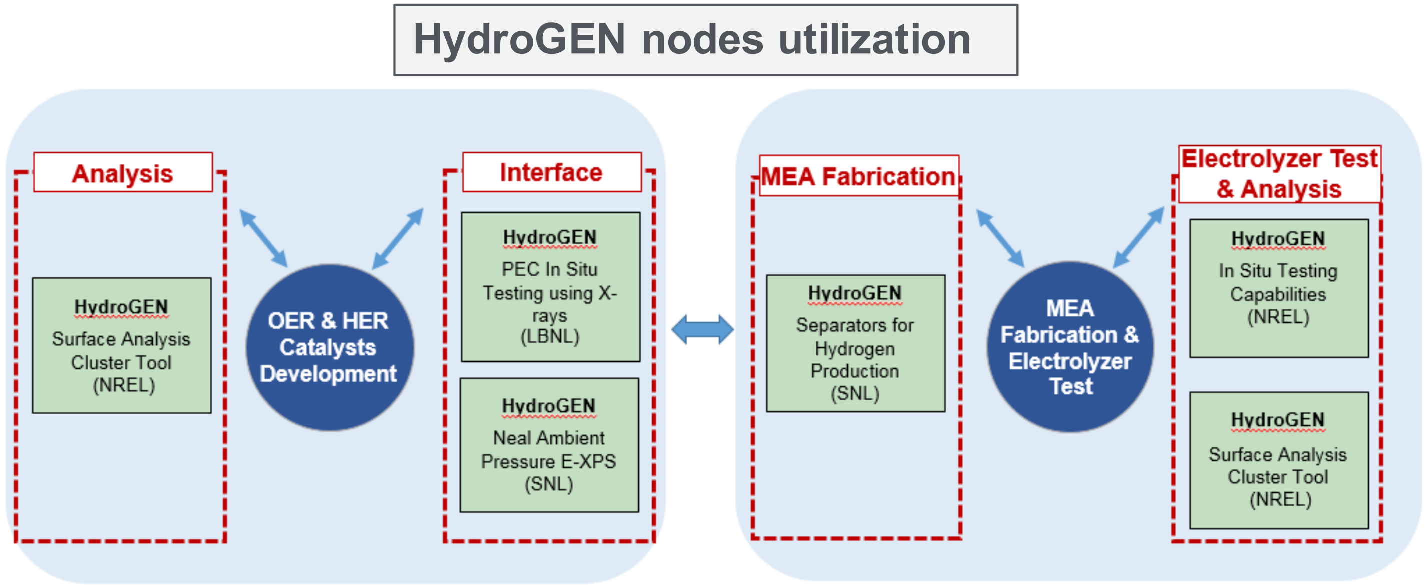




D. Li *et al* **116**, F1096 *ACS Appl. Mater. & Interface* (2019)

- Two ionomer degradations, (i) phenyl oxidation (ii) Hoffman elimination, are identified by ¹H NMR for BPN ionomer in the durability tested AEM → causes for AEM performance degradation
- Catalysts impact phenyl oxidation significantly
- Catalyst – ionomer interaction is key parameter for improving performance and durability of AEM electrolyzers

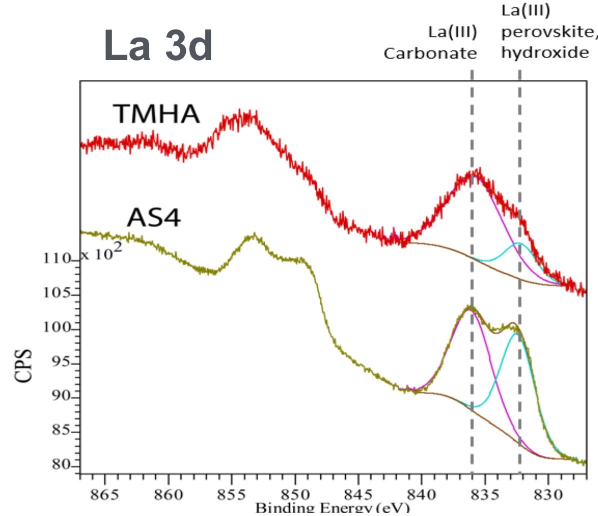
Collaboration: Effectiveness

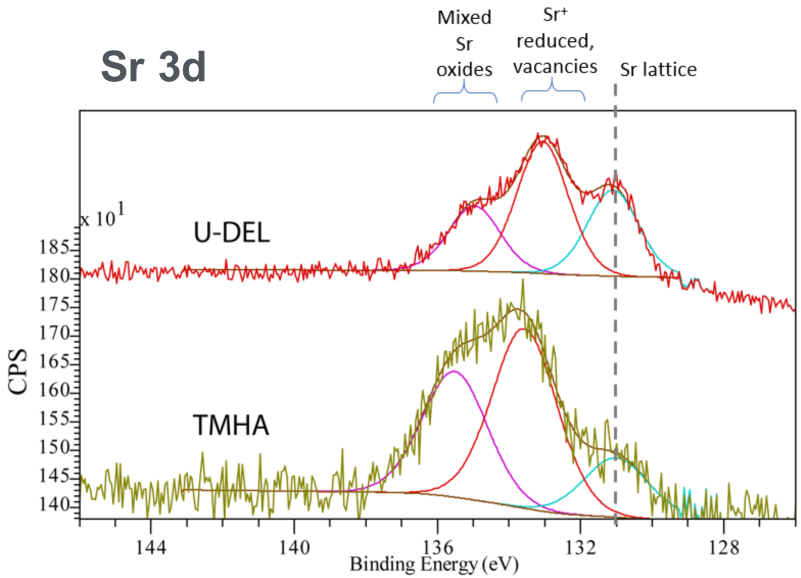


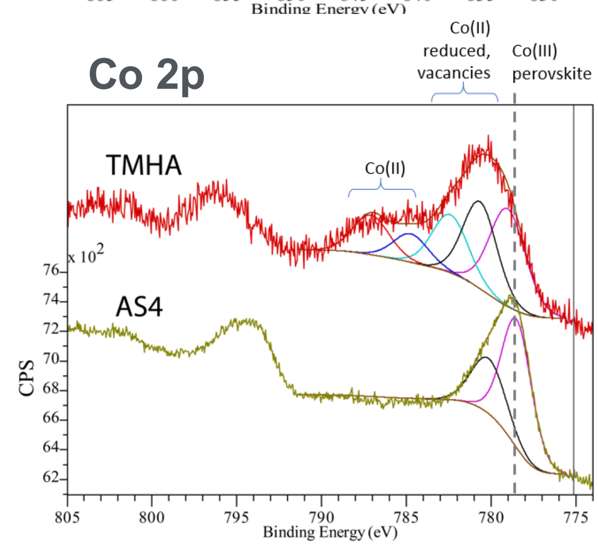
Node	PI	Task
Separator for Hydrogen Production	Cy Fujimoto (SNL)	Anion exchange membranes and ionomer synthesis
In situ Testing Capabilities for Hydrogen Generation	Guido Bender (NREL)	AEM water electrolysis test
Surface Analysis Cluster Tool	Craig Perkins (NREL)	Composition analyses for fresh and tested AEM electrolyzer electrodes with XPS/UPS
PEC In Situ and Operando Testing Using X-rays	Walter Drisdell (LBNL)	In situ and operando characterization of catalyst/ionomer-membrane interfaces
Near Ambient Pressure Electrochemical X-Ray Photoelectron Spectroscopy	Anthony McDaniel (SNL)	Catalyst/ionomer interaction phenomena study in conjunction with electrochemical characterization

Collaboration: Near Ambient Pressure Electrochemical XPS

SNL node: Catalyst/ionomer interaction phenomena study in conjunction with electrochemical characterization







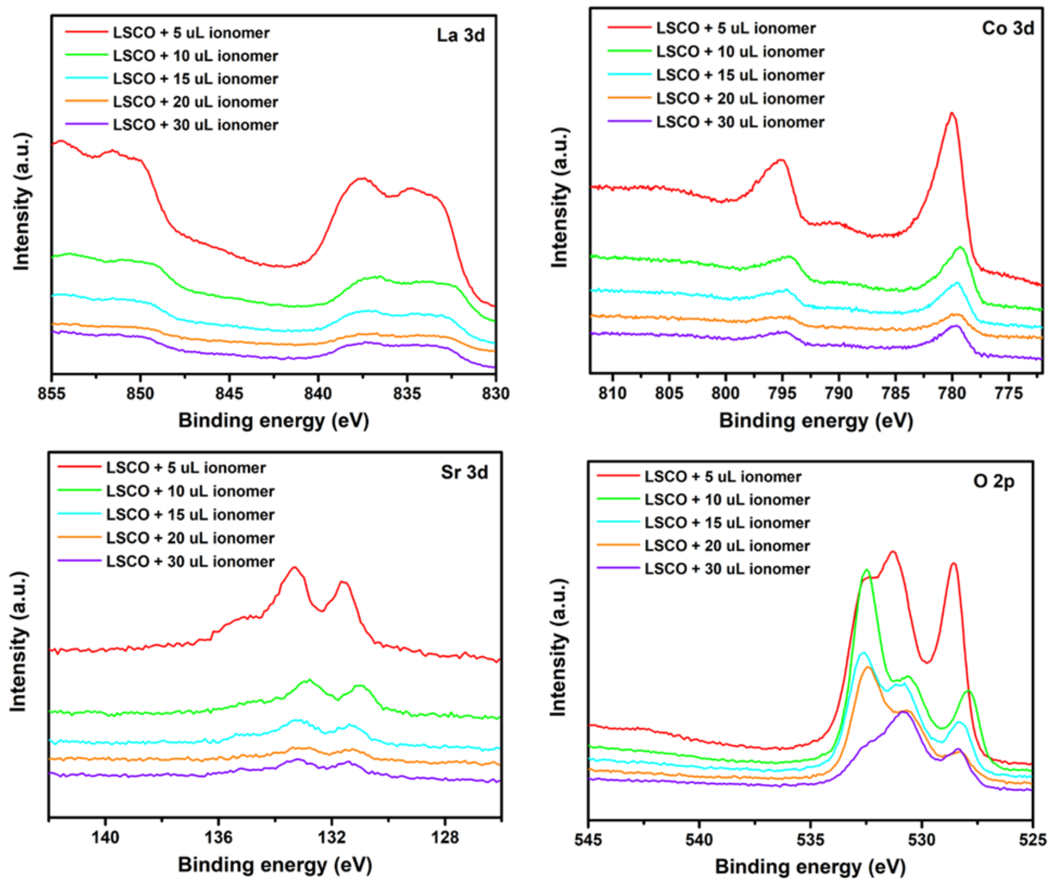
- Ionomers impact metal element XPS → AP- electrochemical XPS experiments to correlate the XPS results to electrochemical activities are going to be tested

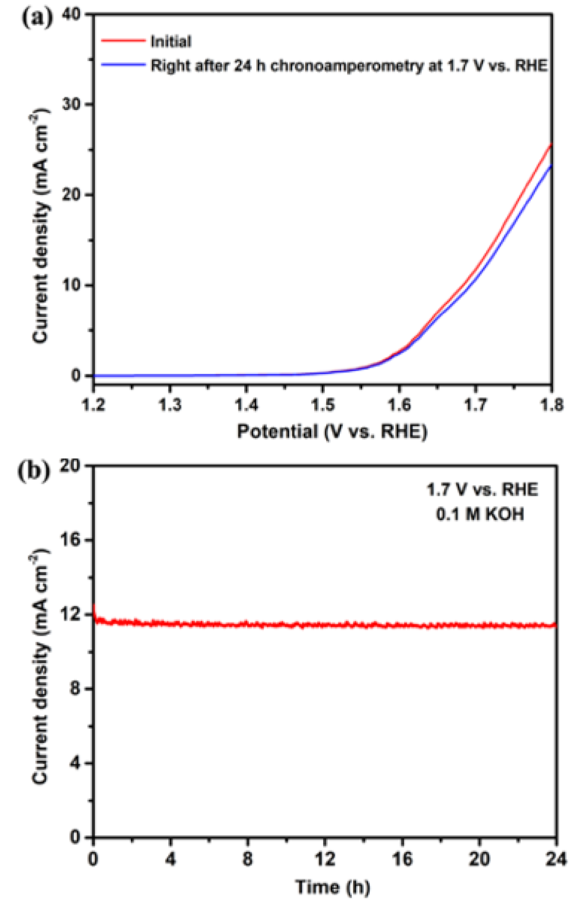
Los Alamos NATIONAL LABORATORY

Collaboration: In Situ and Operando XAS Study

LBNL node: In situ and operando characterization of catalyst/ionomer-membrane interfaces

Catalyst: $LaSrCoO_3$
Ionomer: 4TMHA-DAPP-1



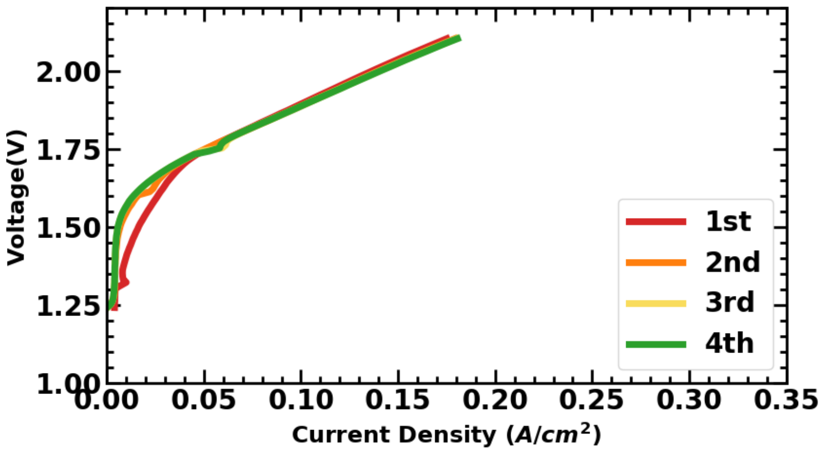


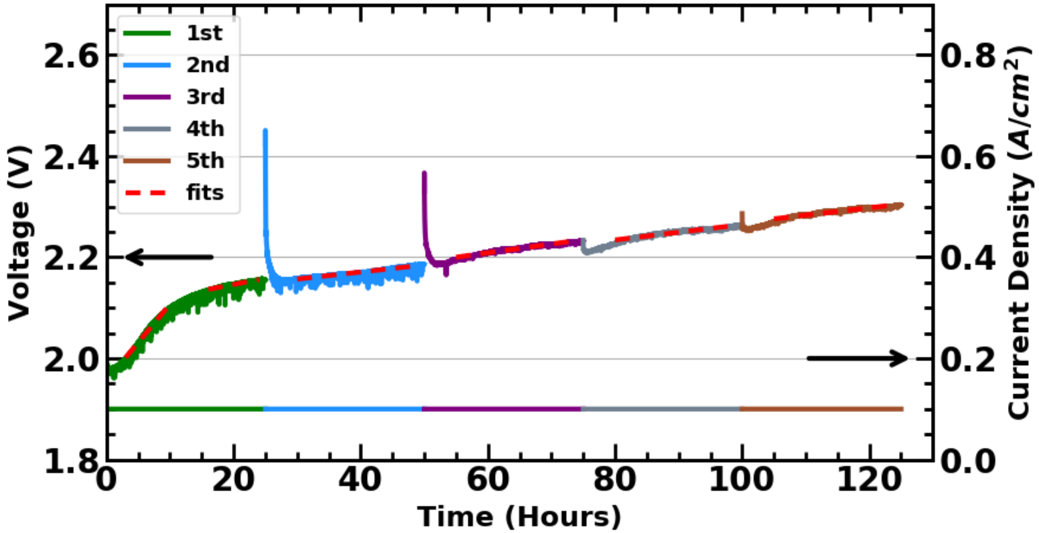
- Catalyst/ionomer ratio optimization has been finished → In situ operando XAS experiments to correlate the XPS results to electrochemical activities are going to be measured

Collaboration: In Situ and Operando XAS Study

NREL node: AEM water electrolysis test

Anode: LSC 6 mg/cm^2
Cathode: PtRu/C; 1.0 mg_{Pt}/cm^2
Ionomer: 4TMHA-DAPP-1





- Lower performance and durability are measured in NREL than in LANL
  → Gap study is in progress

Proposed Future Work

- **Fundamental study**
  - ✓ Understanding obtained from the AP XPS and in situ XAS will be utilized in catalyst optimization
  - ✓ Gap study in AEM electrolyzer performance and durability between LANL and NERL will be done
- **Catalyst development**
  - ✓ Supercritical method will be employed to reduce particle size of LSC
  - ✓ PPC will deliver 25 gr batch of catalyst that is developed by LANL with higher than 25 m^2/gr BET surface area and activity great than 90% of small batch scale catalysts
- **AEM electrolyzer test**
  - ✓ Ni-mesh porous transport layer (PTL) exhibits much higher OER performance than expensive titanium(Ti) PTL → Ni PTL is going to be employed in AEM electrolyzer
  - ✓ Achieved the durability target of 0.1 mV/hr based on testing for 500 hour at a current density of ≥400 mA/cm^2

Summary

- **AEM water electrolyzer**
  - ✓ Demonstrated significantly improved AEM water electrolyzer performance since FY19 AMR from 243 mA/cm^2 to 1087 mA/cm^2 at 1.8 V
  - ✓ Excellent durability, ~ 0.2 mV/hr at 200mA/cm^2 , achieved at 60°C for 100 hours water-feed test
  - ✓ Ni mesh PTL demonstrates promising GDE electrochemical cell performance and durability
- **Catalyst-Ionomer Interaction**
  - ✓ FLN1 demonstrates higher initial performance but lower durability than 4TMHA-DAPP-1 → Understanding the catalyst-ionomer interaction is critical particularly for durability
  - ✓ Catalyst/ionomer ratio optimization for in situ operando XAS has been finished → In situ operando XAS experiments to correlate the XPS results to electrochemical activities are going to be tested
  - ✓ Ionomers change metal element XPS → AP- electrochemical XPS experiments to correlate the XPS results to electrochemical activities are going to be measured

Publications & Presentations

- **Publication**
  - Dongguo Li, Eun Joo Park, Wenlei Zhu, Qiurong Shi, Yang Zhou, Hangyu Tian, Yuehe Lin*, Alesey Serov, Barr Zulevi, Ehren Donel Baca, Cy Fujjmotr, Hoon T. Chung, Yu Seung Kim*, "Highly quaternized polystyreneionomers for high performance anion exchange membrane water electrolysers" *Nature Energy*, **2020**, http://doi.org/10.1038/s41560-020-0577-x

    * corresponding authors
- **Presentations**
  - Hoon T. Chung, "High Performance Ultralow-cost Non-Precious metal catalyst system for AEM Electrolyzer," Poster presentation at the DOE Hydrogen and Fuel Cell Program Annual Merit Review, Washington, D.C., April 2019
  - Hoon T. Chung et al., "Highly Active and Durable Perovskite OER Catalyst for Pure Water Anion Exchange Membrane Electrolysis " 236th ECS Meeting, Atlanta, GA October 2019