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

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4-30-2019

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

Project Vision

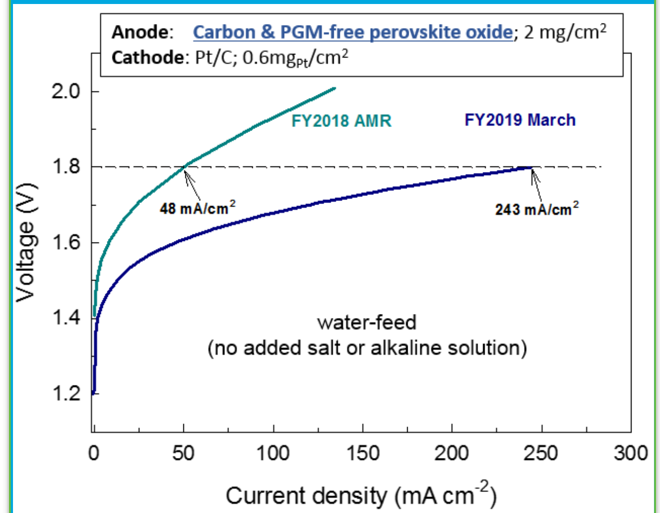
The key challenge in anion exchange membrane (AEM) electrolyzer is to achieve high performance without feeding any salt or alkaline solutions to the electrodes. In this project, we are developing PGM-free OER and HER catalysts with high performance in the alkaline solution-free AEM water electrolyzer.

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.

Award #	2.2.0.402
Year 2 Start Date Year 2 End Date	10/01/2018 09/30/2019
Year 2 DOE Share* Year 2 Cost Share Year 2 Total Funding	$500 K $ 56 K $556 K

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



** 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	200 mA/cm^2 at 2.0 V*	100 mA/cm^2 at 1.8 V
AEM water# electrolyzer durability	At 200 mA/cm^2, voltage 2.2 → 2.6 V at 27° C for 2000 hours with 3 mg/cm^2 Pt black and IrO_2*+	At 100 mA/cm^2, 1.8 V for 100 hours, the same degradation rate as that of PGM-catalysts

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.

#No added alkaline solution

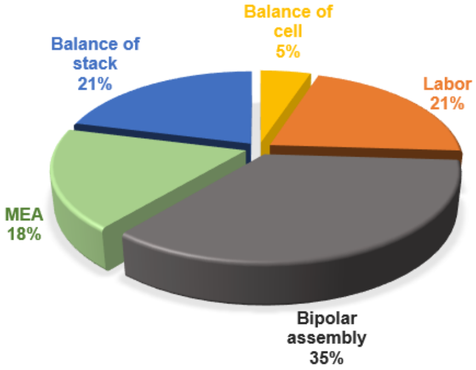
*G. Bender, AMR presentation PD147A, 06/2018; +K. Ayers, AMR presentation PD094, 06/2014

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

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

K. Ayers, AMR presentation PD094, 06/2014

PEM electrolyzer stack cost breakdown



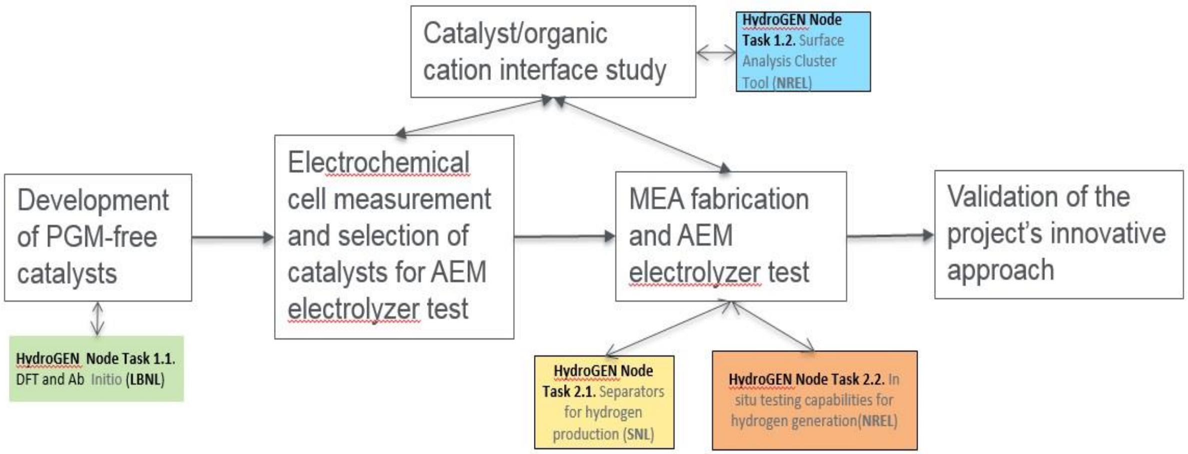
- Bipolar assembly and MEA represents highest cost of PEM stack
- Alkaline media enables transition from titanium to stainless steel: eliminates 75% of part cost and also enables lower cost catalysts

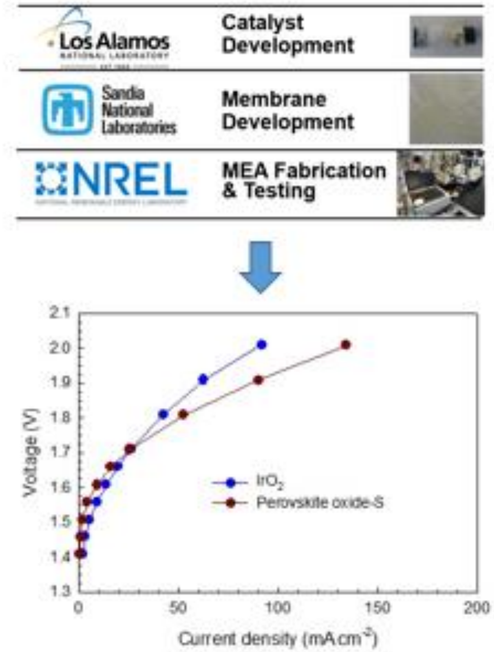
- AEM electrolysis *vs. Alkaline electrolysis*: <u>compact size; less corrosive environment</u>:
  - ✓ Corrosive alkaline solution → water
  - ✓ Low gas purity → high gas purity
  - ✓ Low current generation → high current density

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 & Impact: HydroGEN Consortium

HydroGEN nodes utilization in Phase 1





- Task 1.1 Node (DFT and Ab Initio Calculations): descriptor study for PGM-free catalysts
- Task 1.2 Node (Surface analysis cluster tools): surface analyses of catalysts and MEA
- Task 2.1 Node (Separators for hydrogen production): provision of anion exchange membranes and ionomers
- Task 2.2 Node (In situ testing capabilities): AEM electrolyzer test

HydroGEN EMN nodes facilitate this R&D and are providing critical materials and support

Approach: Phase1 Scope of Work and G/NG

NiLA HER catalyst

(1) **activity**: 34 mA/cm² at a 200 mV overpotential
(2) **durability**: less than 20% current density loss at a 200 mV overpotential
(scan rate: 200 mV/s; potential range: 0.2 and – 0.25 V; cycle number: 5,000 cycles)

Catalyst	Current density (mA/cm²) in 1.0 M NaOH	
	initial	Current density loss (%) after durability test
$Ni_{0.95}La_{0.05}$	42	19

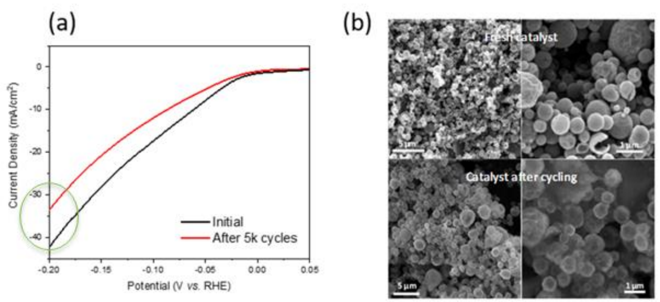


Figure 1. (a) Linearscan coltammetry (LSV) plots of $Ni_{0.95}La_{0.05}$ HER catalyst. Electrolyte: N_2-saturated 1.0 M NaOH; cell temperature: 60 °C; 1600 rpm; scan rate: 2 mV/s. (b) SEM images of $Ni_{0.95}La_{0.05}$ HER catalysts befor and after cyclic durability test.

Go/no-go decision performance for activity and durability have been achieved

Perovskite oxide OER catalyst

(1) **activity**: 5.1 mA/cm² at 1.65 V
(2) **durability**: the same degradation rate as that of IrO_2
(scan rate: 500 mV/s; potential range: 0.6 – 2.1 V; cycle number: 5,000 cycles*)

Catalyst	Current density (mA/cm²) in 0.1 M KOH		Current density (mA/cm²) In 0.1 M BTMAOH	
	initial	after 1000 cycles (1.1 – 2.1 V)	initial	after 1000 cycles (1.1 – 2.1 V)
IrO_2	5.5	1.9	1.0	0.2
Perovskite oxide-S	3.1	2.0	4.1	1.8
Perovskite oxide-A	2.5	0.9	-	-
Perovskite oxide-B	4.4	2.5	5.5	3.9
Perovskite oxide-C	3.8	2.7	6.8	5.3
Perovskite oxide-D	3.9	2.7	6.2	4.8
Perovskite oxide-E	4.1	3.4	5.2	2.7
	initial	after 1000 cycles (0.6 – 2.1 V)	initial	after 1000 cycles (0.6 – 2.1 V)
IrO_2	5.5	3.1	-	-
Perovskite oxide-F	5.2	3.4	8.3	**
Perovskite oxide-G	5.6	**		

* 5000 cycle durability test can't be done due to catalyst detachment from RDE electrode
** 1000 cycle durability test of Perovskite-F in 0.1 M BTMAOF and Perovskite-G in 0.1 M KOH can't be done due to catalyst detachment from RDE electrode

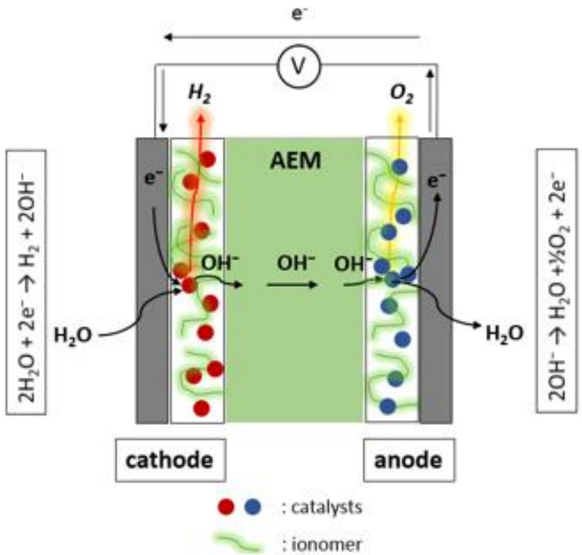
- **Go/no-go decision OER activity has been met with Perovskite-F and -G catalysts in 0.1 M KOH**
- **1000 cyclic durability test with Perovskite-F has demonstrated slightly better durability than IrO_2; 5000 cycle durability can't be done due to catalyst detachment**

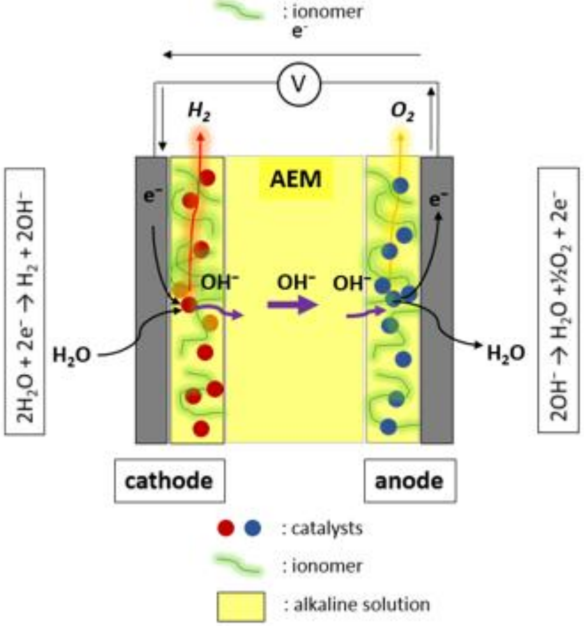
- **Focus of Phase 1**: Catalysts development was performed mostly relying on RDE activity measurement and Go/No-go was suggested with RDE activities
- **Focus of Phase 2**: Catalysts will be evaluated by AEM electrolyzers and Go/No-go performance targets are also suggested based on AEM electrolyzer performance

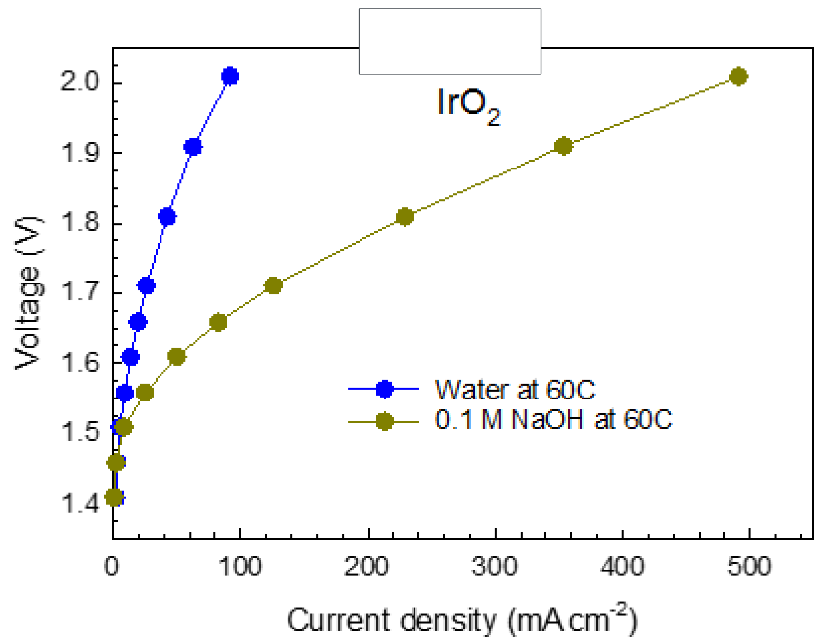
Phase2 QPMs and Go/No-go

Date	Quarterly Progress Measures and Go/No go	Status
December 2018 (Fy19 Q1), MS	Test phosphide OER catalysts in an electrochemical cell and AEM electrolysis to assess possibility for further development. The targeting activity in RDE test is 6.0 mA/cm^2 at 1.65 V in 0.1 M KOH. The highest activity with perovskite oxide catalyst was 5.6 mA/cm^2 at 1.65 V.	**Completed**
March 2019 (Fy19 Q2), MS	Synthesize NiLa(Zn) HER catalysts with high HER activity (50 mA/cm^2 at 200 mV overpotential, 50% increase from previous target) and increased surface area (45 m^2/g, 200% increase from current SA of ca. 15 m^2/g) will be chosen and scaled-up for AEM water electrolyzer tests.	**On track**
June 2019 (Fy19 Q3), MS	PPC reports several ionomer/catalyst combinations and their AEM water electrolysis results along with recommendations for next steps.	**On track**
September 2019 (Fy19 Q4), GNG	Demonstrate 100 mA/cm^2 at 1.8 V in a pure water-feeding (e.g., no added salt or base) AEM water electrolysis MEA for each PGM-free HER and PGM-free, carbon-free OER catalyst. Chronopotentiometry durability tests at 100 mA/cm^2 will be done for 100 hours, demonstrating the same degradation rate as that of PGM-catalysts (Pt; IrO_2)	**On track** **OER catalyst: performance target met and exceeded**; **HER catalyst: on track**

Water vs Alkaline Solution







With alkaline solution-feed, actual ionomer and membrane characteristics for AEM electrolyzers obscured

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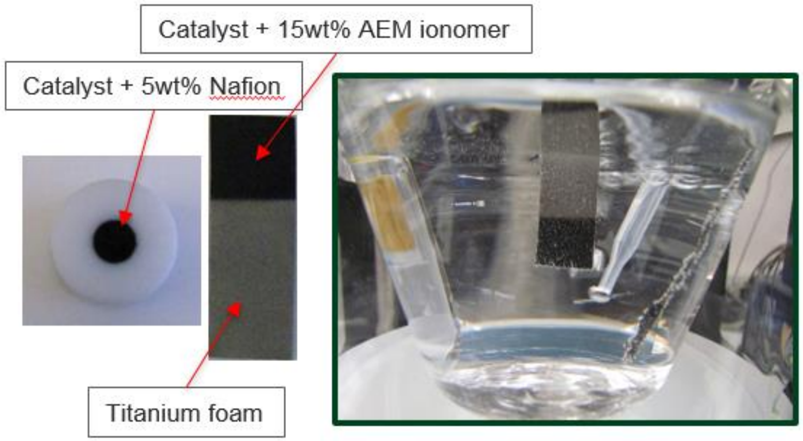
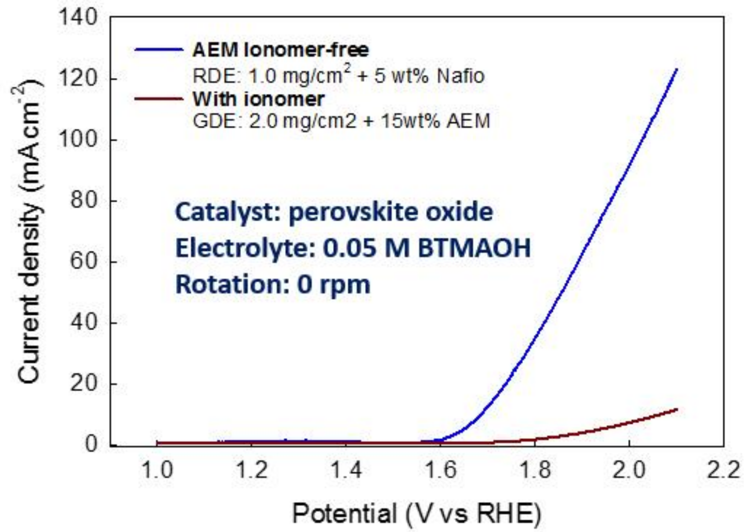
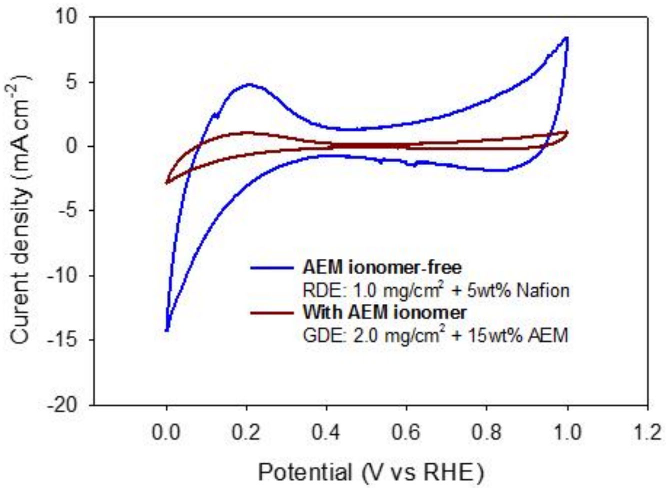
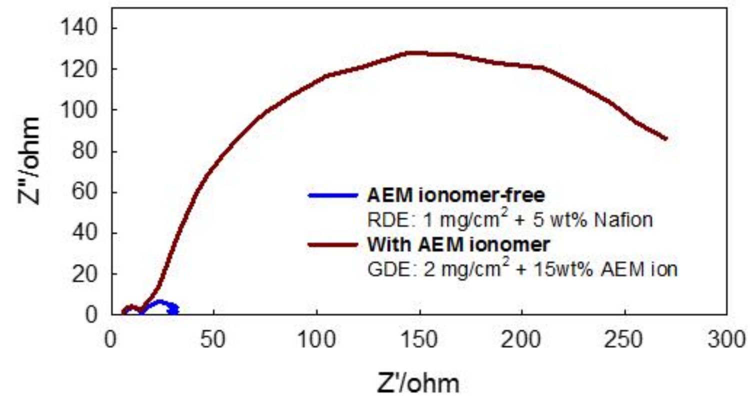
Accomplishment: GDE Electrochemical cell







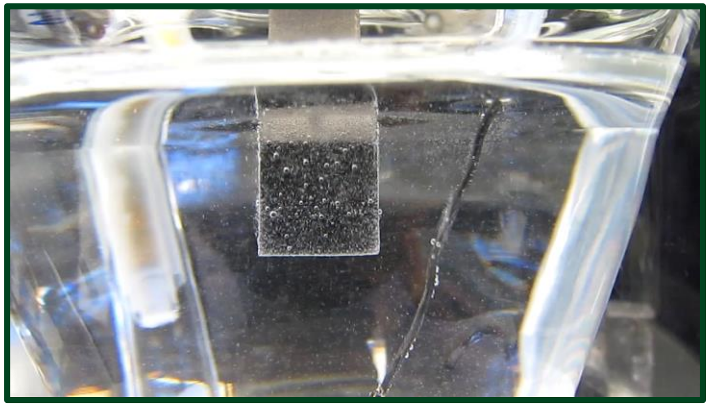


AEM ionomer significantly impeding OER performance: (i) reduced electrochemical surface area; (ii) large resistance increase

A novel RDE vs GDE electrochemical cell approach successfully accomplished in identifying AEM ionomer effect on OER performance

Advantages of GDE Electrochemical Cell

Catalyst detachment
after durability test

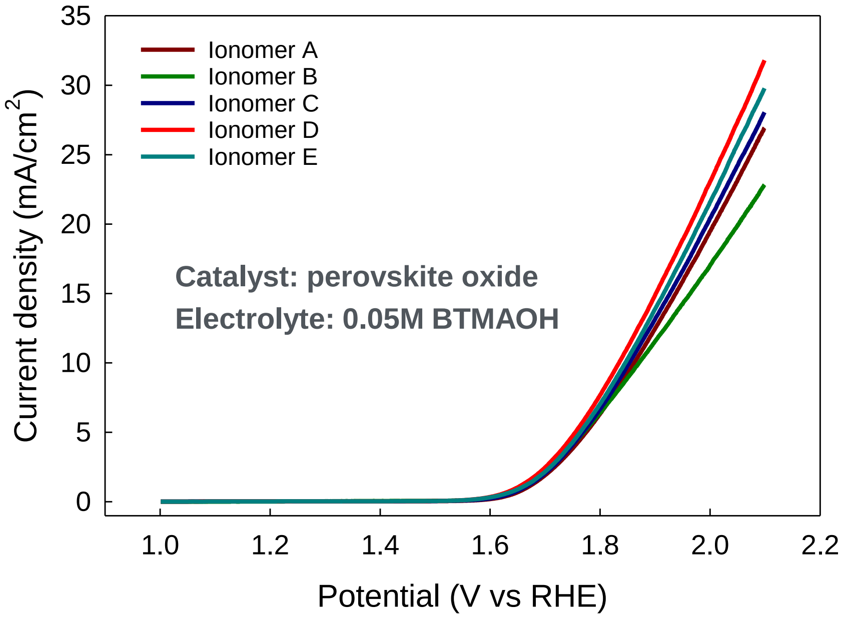


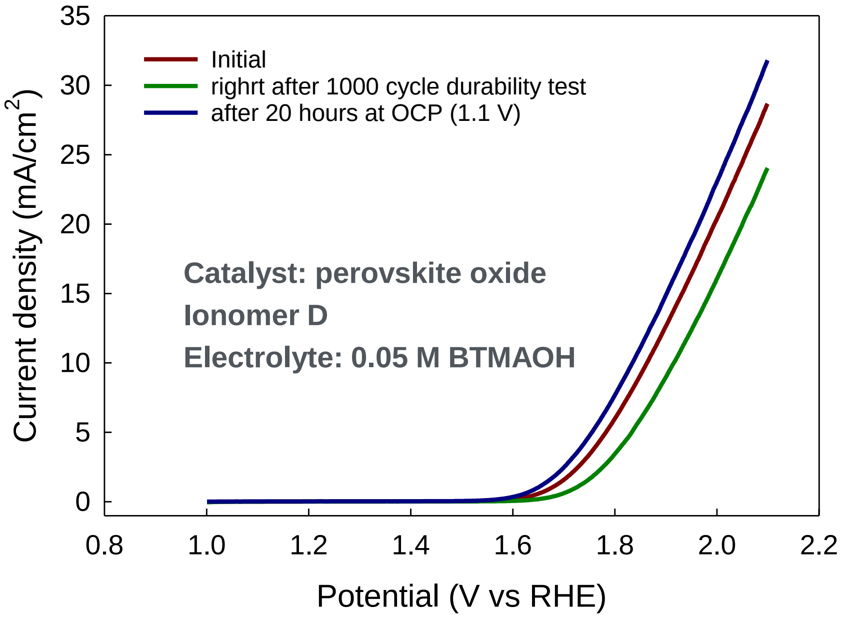
Cyclic durability test:
Catalyst: perovskite oxide
Ionomer: AEM ionomer D 15wt%
Potential: 1.2 ⟷ 2.1V
Scan rate: 500 mV/s

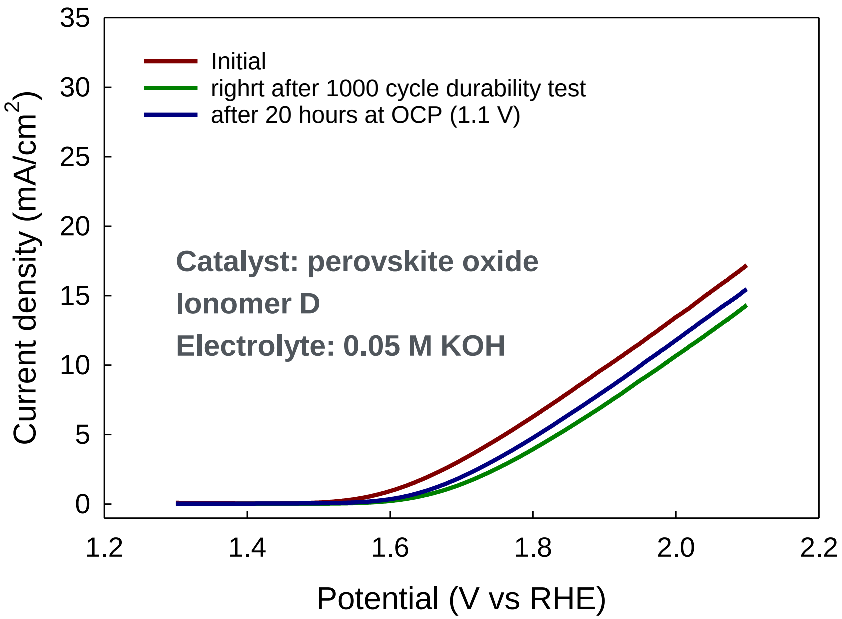
Catalyst	Ionomer (15 wt%)	Electrolyte (0.1 M BTMAOH)	Electrolyte (0.05 M BTMAOH)	Electrolyte (0.01 M BTMAOH)	Electrolyte (0.05 M KOH)
Perovskite oxide	AEM Ionomer A	√	√	√	√
	AEM Ionomer B	√	√	√	
	AEM Ionomer C	√	√	√	√
	AEM Ionomer D	√	√	√	√
	AEM Ionomer E	√	√	√	
IrO_2	AEM Ionomer A		√		

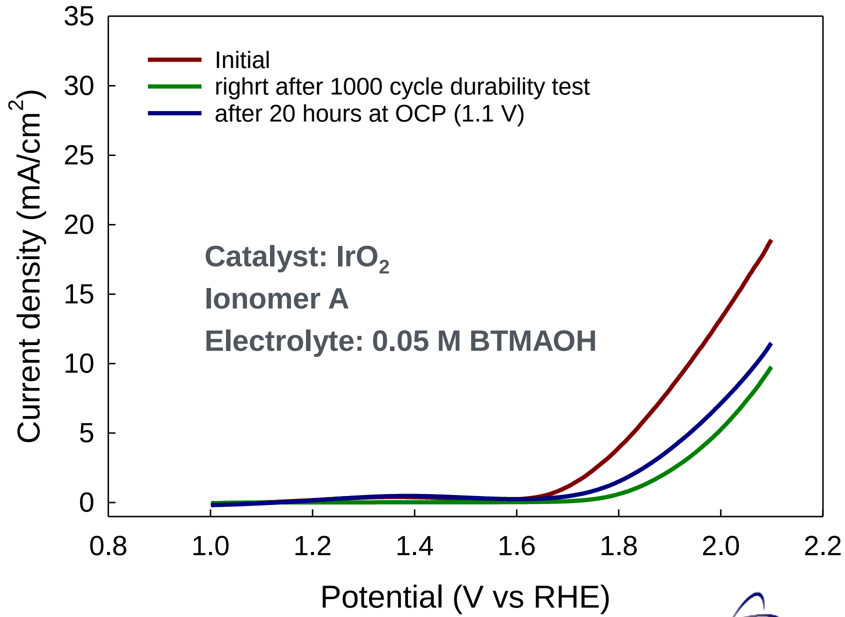
- GDE electrochemical cell securing durability test
- Enabling diverse catalyst-(ionomer; electrolyte) interaction studies

Catalyst-(ionomer; electrolyte) Interaction

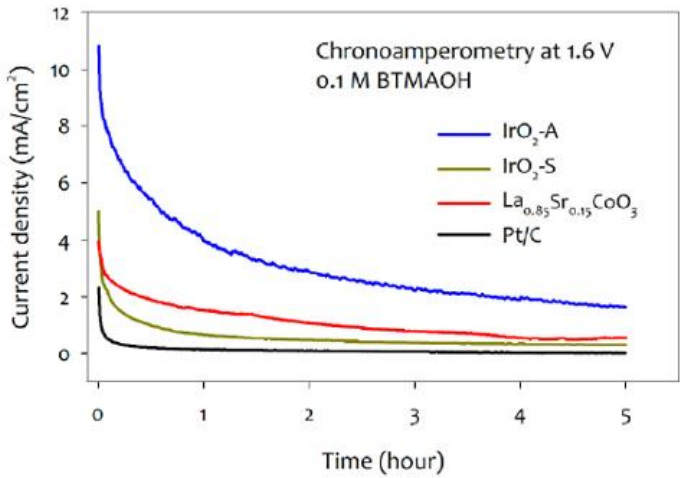


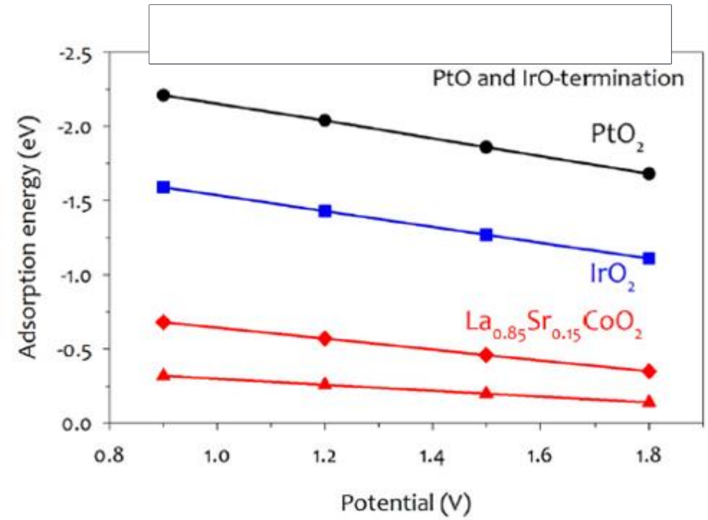


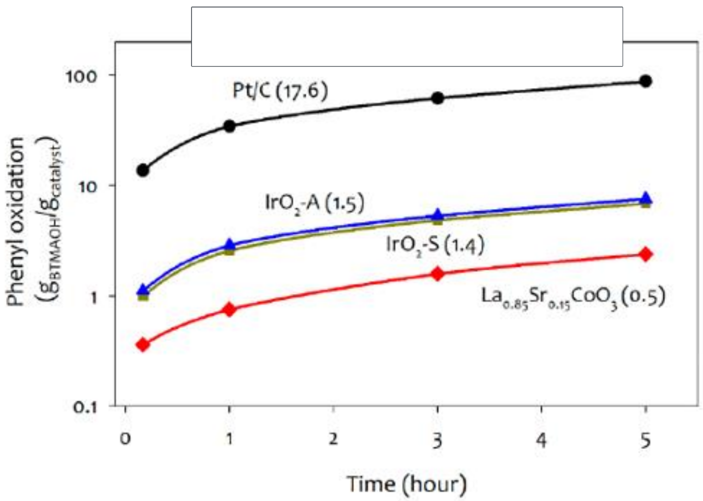


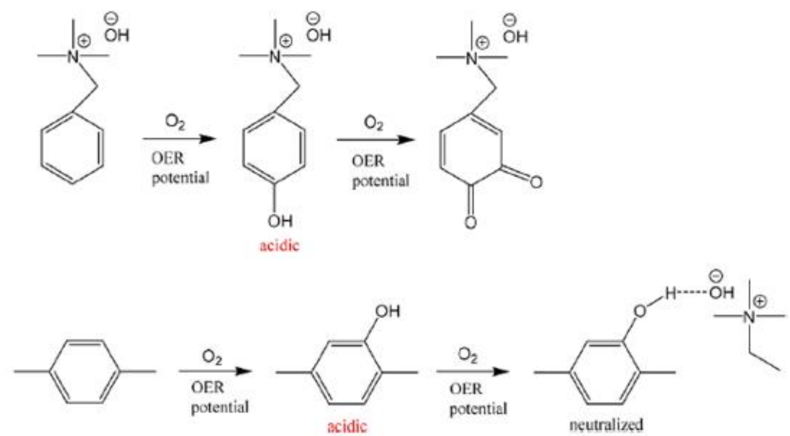


Catalyst-Ionomer Interaction



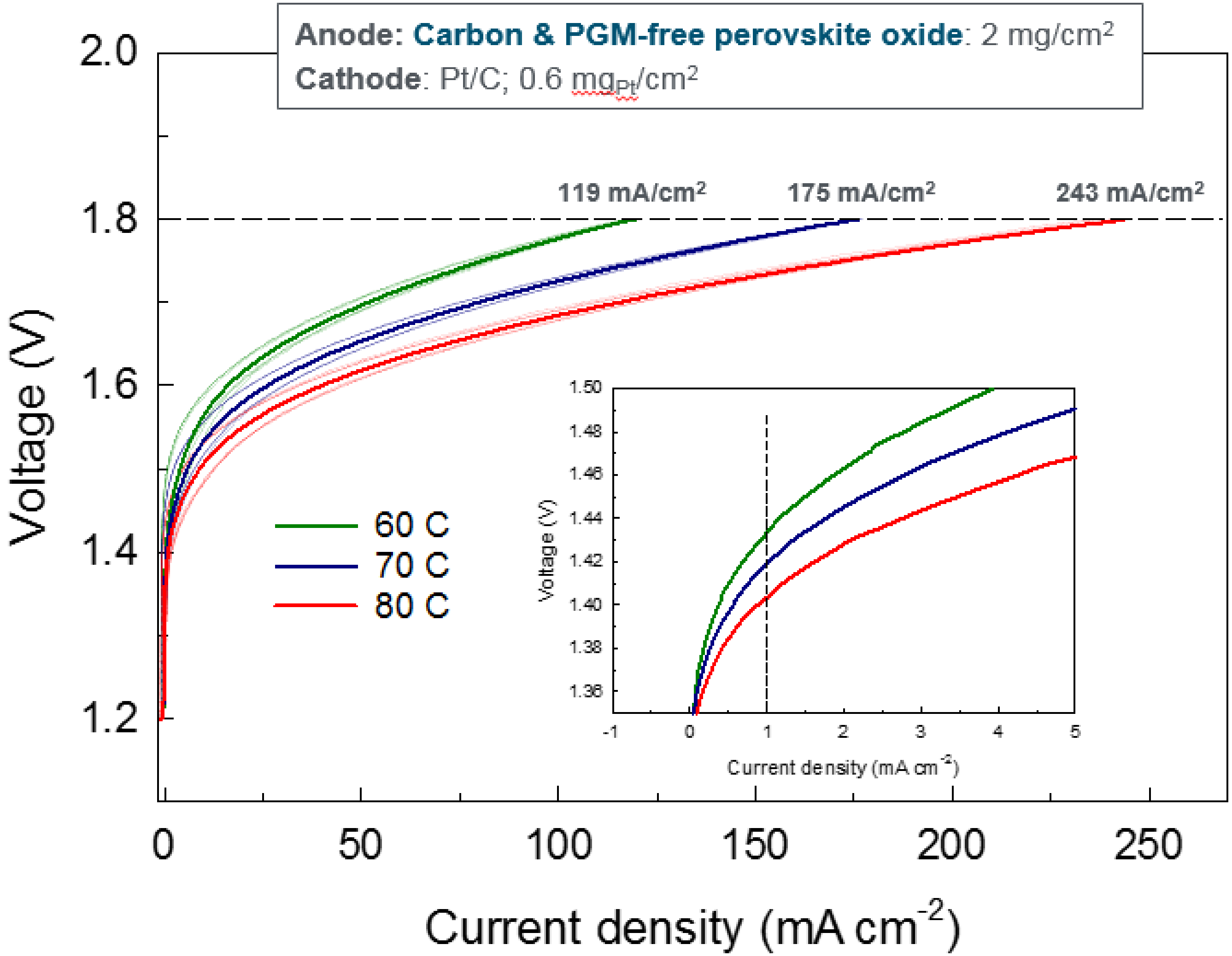






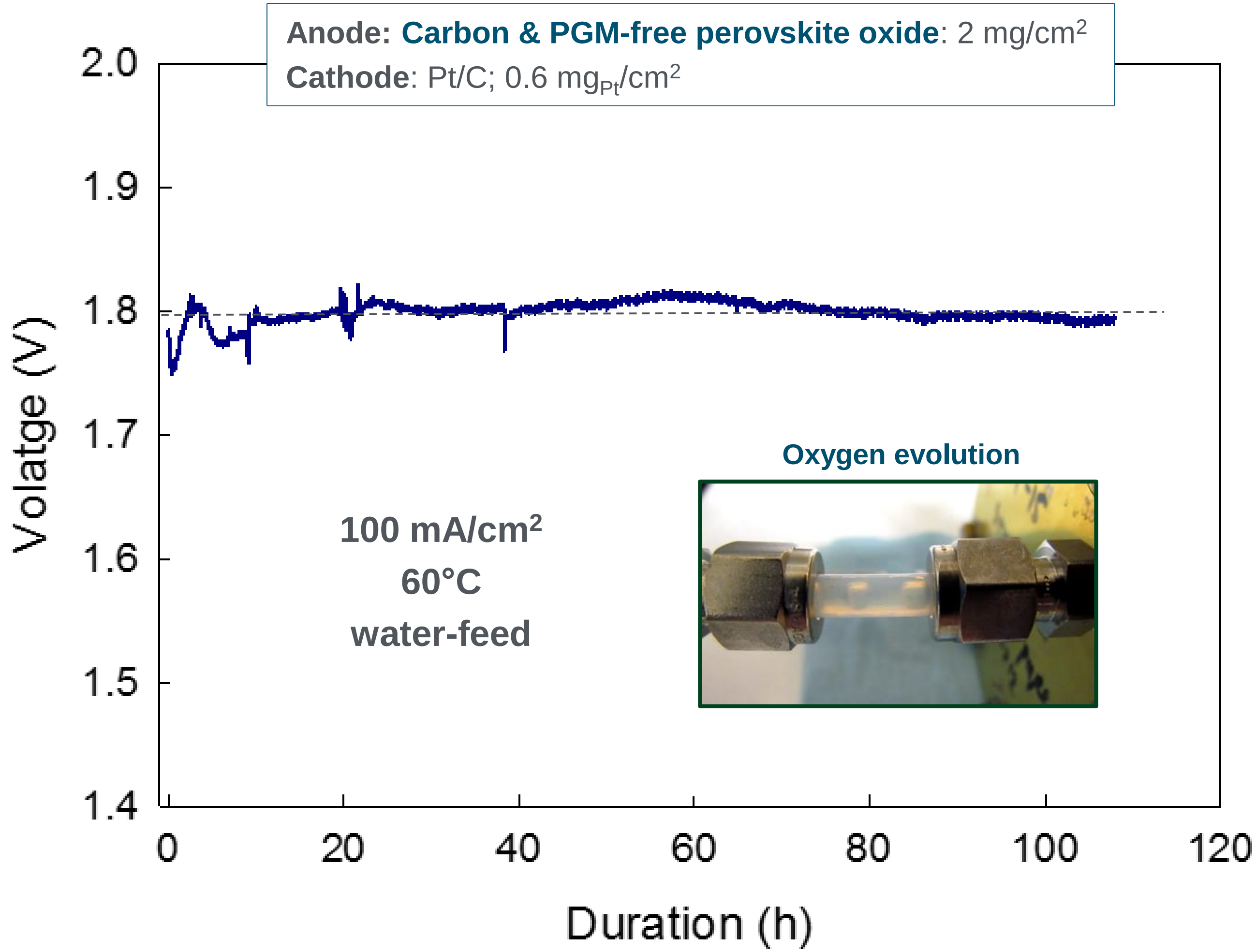
Phenyl oxidation impacts on durability

AEM Electrolyzer Performance



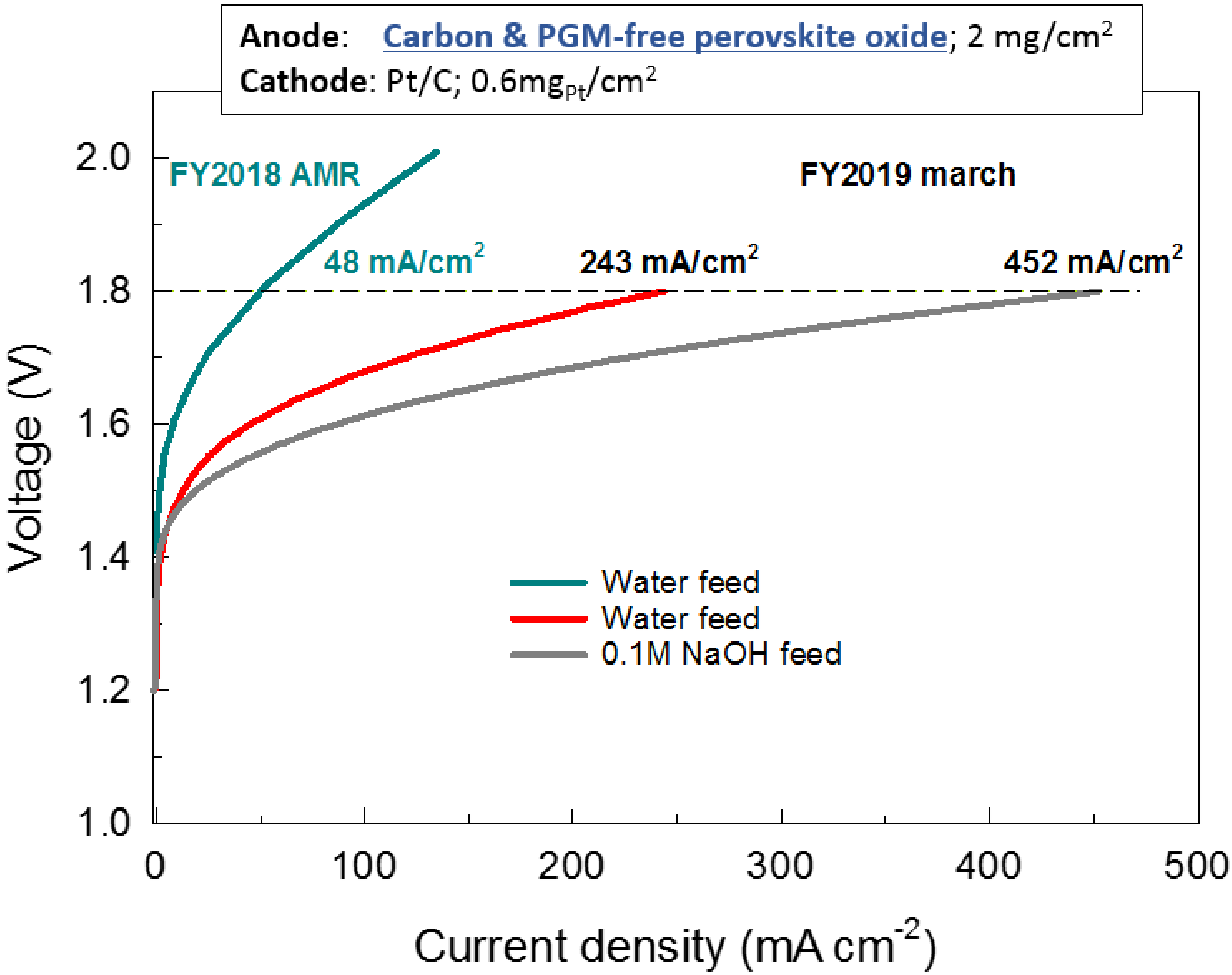
OER catalyst FY19 G/NG of 100 mA/cm² at 1.8V achieved and exceed!

AEM Electrolyzer Durability



Excellent durability demonstrated!

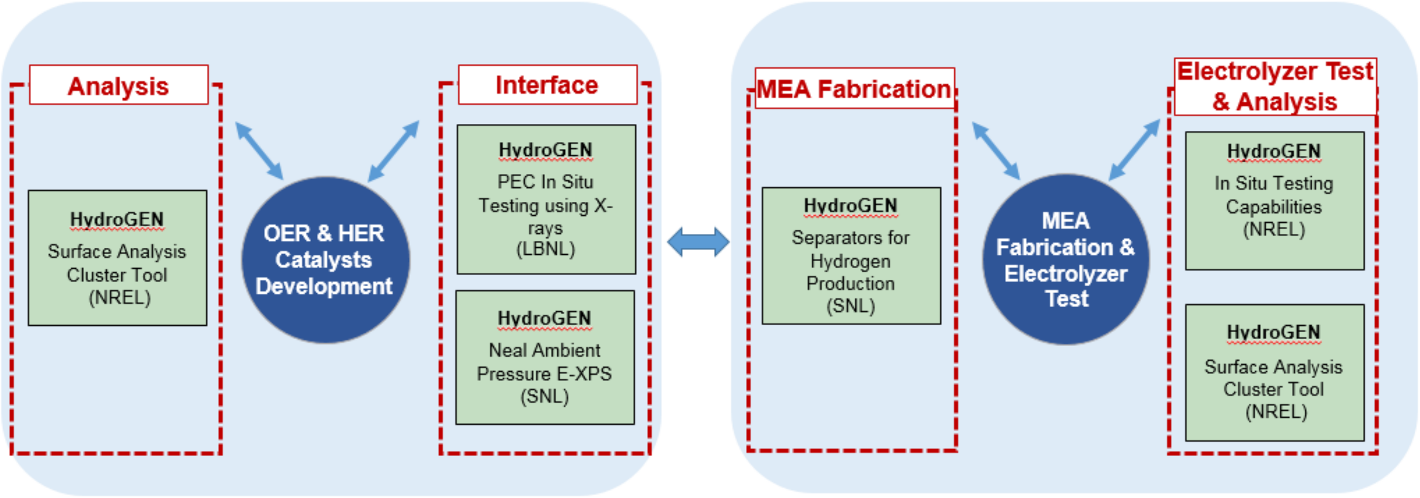
Progress: AEM Electrolyzer Performance



A big progress achieved since FY2018 AMR

Collaboration: Effectiveness

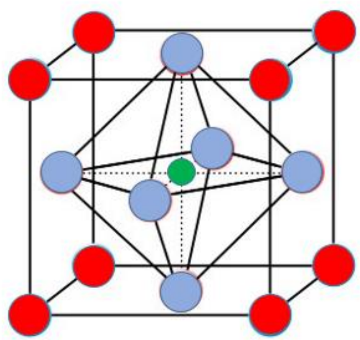
HydroGEN nodes utilization in Phase 2

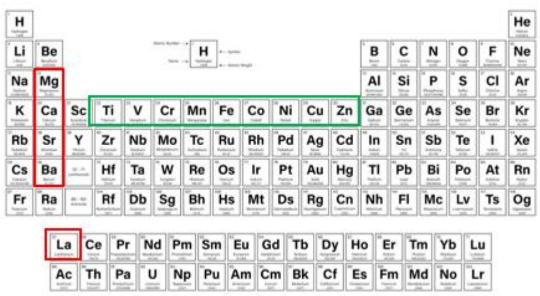


Node	PI	Task
Separator for Hydrogen Production	Cy Fujimoto (SNL)	Anion exchange membranes and ionomer synthesis
In situ Testing Capabilities for Hydrogen Generation	Guido Bender (NREL)	AEM water electrolysis test
Surface Analysis Cluster Tool	Glenn Teeter (NREL)	Composition analyses for fresh and tested 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	Farid El Gabaly (SNL)	Catalyst/ionomer interaction phenomena study in conjunction with electrochemical characterization

Proposed Future Work

- **Fundamental study**
  - ✓ Understanding the phenomena occurring at the catalyst-ionomer interface using in situ and ex situ AP-XPS and XAS
  - ✓ GDE electrochemical cell study to explore catalyst-ionomer interaction
- **Catalyst development**
  - ✓ Composition modification based on catalyst-ionomer interaction studies

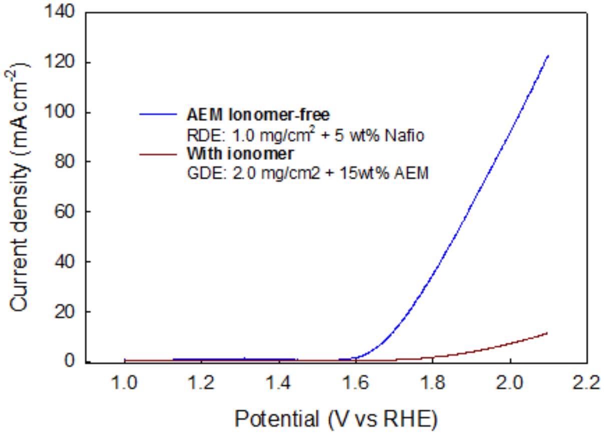




- **AEM electrolyzer test**
  - ✓ Optimizing catalyst-ionomer combination to improve performance and durability of AEM water electrolyzer

Summary

- **AEM water electrolyzer**
  - ✓ Demonstrated significantly improved AEM water electrolyzer performance compared with state-of-the-art performance, 1.77 V vs 2.0 V at 200 mA/cm^2
  - ✓ FY2019 Go/No-go performance of 100 mA/cm^2 at 1.8 V exceeded, high of 243 mA/cm^2 reached at 80°C
  - ✓ Excellent durability, nearly zero degradation in voltage at 100mA/cm^2 , achieved at 60°C for 100 hours water-feed test
- **Observation**
  - ✓ AEM ionomer significantly depressed the OER activity of the perovskite oxide catalyst
  - ✓ Identified phenyl oxidation as one of causes for AEM performance degradation
- **Research direction**
  - ✓ Understanding the catalyst-ionomer interaction is the key for improving the AEM water electrolyzer performance up to level of PEM water electrolyzer



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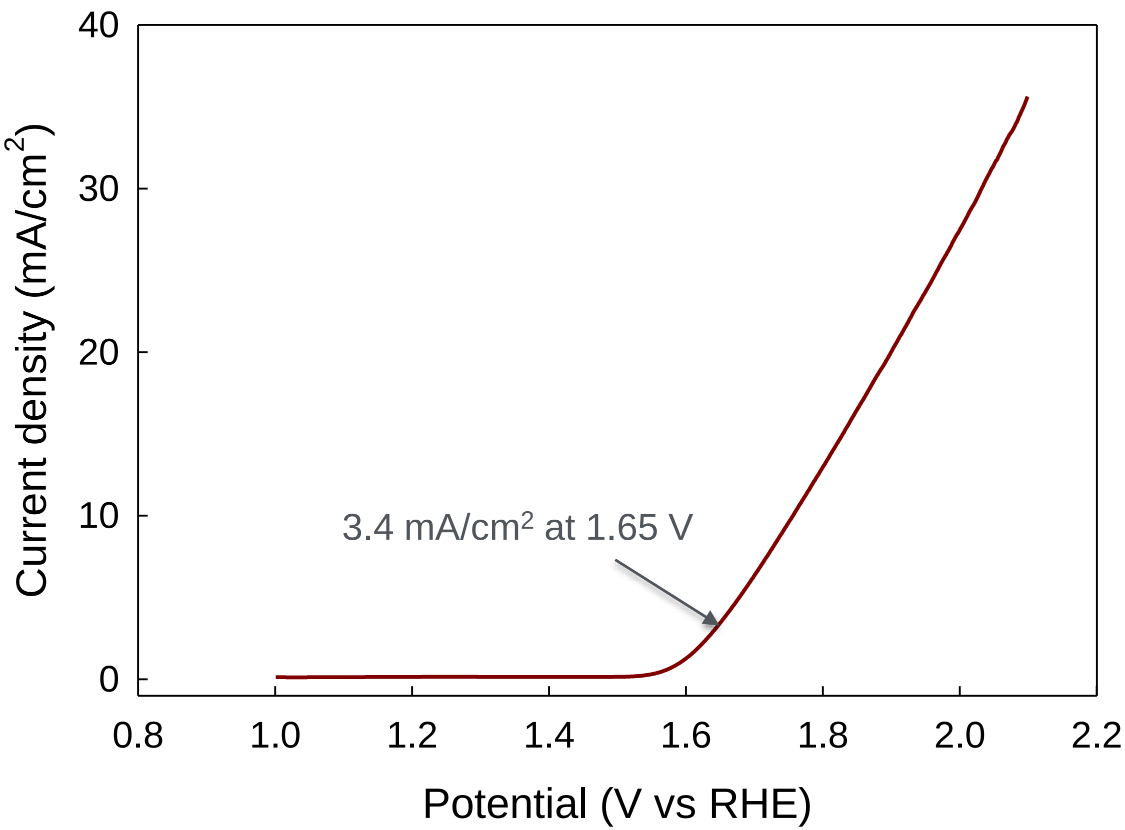
Publications & Presentations

- **Publication**
  - Dongguo Lee, Ivana Matanovic, Albert Sung Soo Lee, Eun Joo Park, Cy H Fujimoto, Hoon Taek Chung*, Yu Seung Kim*, "Phenyl Oxidation Impacts the Durability of Alkaline Membrane Water Electrolyzer" *ACS Appl. Mater. Interfaces*, **2019**, 11, pp 9696-9701

    * corresponding author
- **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., June 2018
  - Hoon T. Chung et al., "Carbon-free Perovskite Oxide OER Catalysts for AEM Electrolyzer," 233rd ECS Meeting, Seattle, WA May 2018
  - U. Martinez et al., "Spray Pyrolyzed High Surface Area Ni-Based Hydrogen Evolution Electrocatalysts for AEM Electrolyzer Applications," AiMES Meeting, Cancun, Mexico, September (2018)

Technical Back-Up Slides

OER Activity of NiP



The current density 3.4 mA/cm^2 at 1.65 V is lower that the targeting activity of 6.0 mA/cm^2 at 1.65 V

This catalyst not studied further due to low activity