HydroGEN
Advanced Water Splitting Materials

Pure Hydrogen Production through Precious-Metal-Free Membrane Electrolysis of Dirty Water

Prof. Shannon Boettcher

Department of Chemistry and Biochemistry and the Oregon Center for Electrochemistry

EE0008841

June 6-8th 2022

P187

DOE Hydrogen Program 2022 Annual Merit Review and Peer Evaluation Meeting

NREL Transforming ENERGY

BERKELEY LAB Bringing Science Solutions to the World

Sandia National Laboratories

INL Idaho National Laboratory

Lawrence Livermore National Laboratory

Project Overview

Project Partners

Shannon Boettcher, University of Oregon
HydroGEN nodes: Pivovar, Alia (NREL), Weber, Danilovic, Kusoglu (LBNL), Fujimoto (SNL)

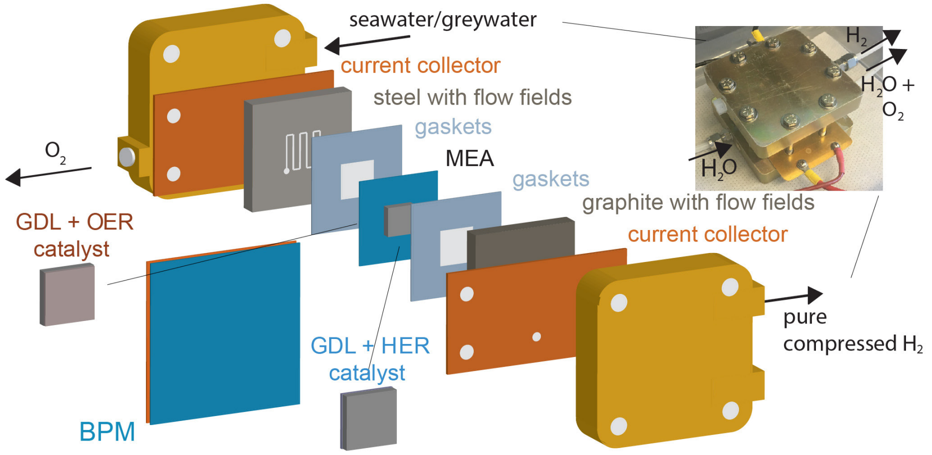
Award #	**EE0008841**
Start/End Date	4/1/20 – 3/31/23
Total Project Value* **Cost Share %**	\$0.625 M (DOE+Cost Share) 20%

Project Vision

Develop a technical understanding of performance degradation of alkaline and bipolar membrane electrolyzers in pure and dirty water and engineer impurity tolerant systems.

Project Impact

Alkaline electrolysis systems enable PGM-free devices that may be more tolerant to impurities, if appropriately designed, which would increase system longevity, allow for less-stringent input water purity, and lower costs.



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

Approach – Summary

Project Motivation

The need for ultra pure water in membrane electrolyzers increases system complexity, cost, maintenance, and failure points. We aim to design electrolyzers more intrinsically robust to ‘dirty’ water.

Barriers

- Ion exchange in membrane(s)
  - Minimize by controlling ion flow direction
- Deposition of impurities
  - Use high loadings of low-cost catalyst, control location and morphology of deposits
- Cl- oxidation
  - Maintain local basic anode

Key Impact

Metric	State of the Art	Expected Advance
BPM performance	~ 1 V at 1 A cm^{-2}	< 100 mV at 1 A cm^{-2}
Efficiency in ‘dirty’ water	N/A	< 2V at 2 A cm^{-2}
Durability in ‘dirty’ water	N/A	< 4 mV / 100 h

Partnerships

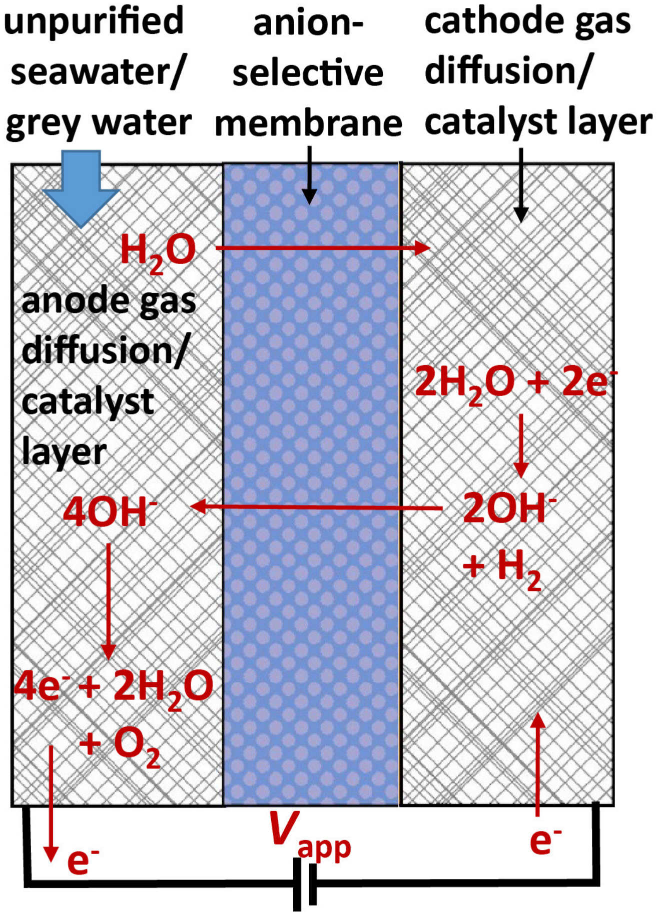
Key partners with HydroGEN network described in later section

Approach – Innovation

- We will work to control ion flow in AEM and BPM electrolyzer architectures and understand degradation modes and strategies to eliminate them.

Grace Lindquist

Dr. Sebastian Oener (DFG Fellow)



unpurified seawater/ grey water

anion-selective membrane

cathode gas diffusion/ catalyst layer

H_2O

anode gas diffusion/ catalyst layer

$2H_2O + 2e^-$

$4OH^-$

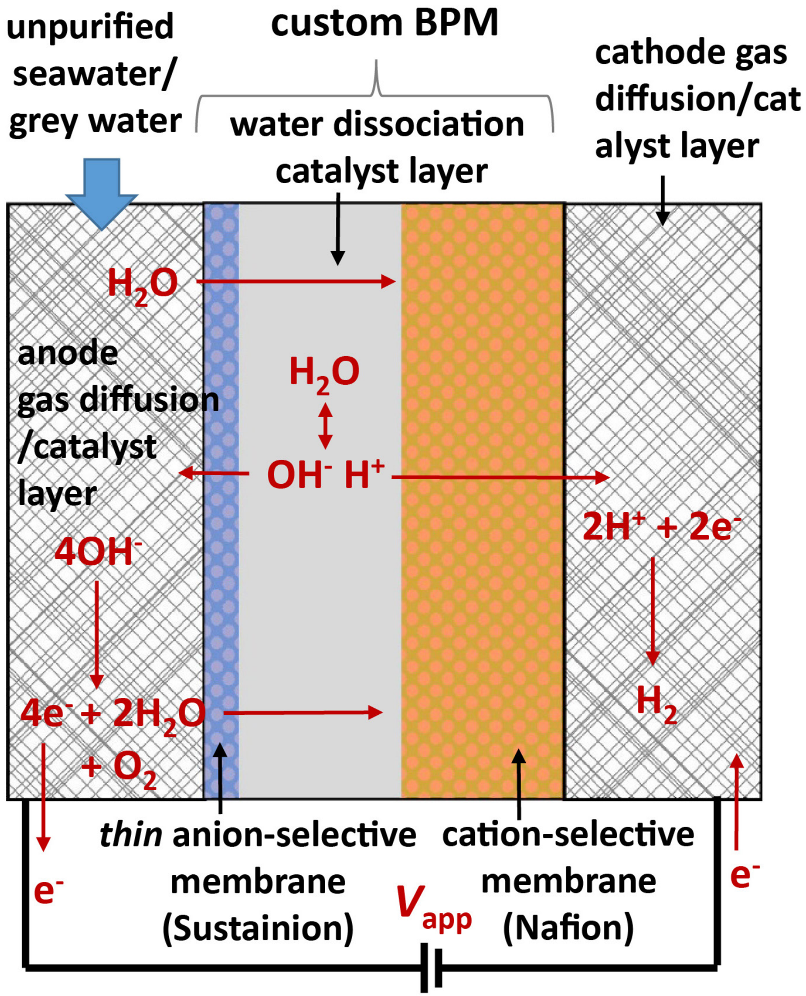
$2OH^- + H_2$

$4e^- + 2H_2O + O_2$

e^-

V_{app}

e^-



unpurified seawater/ grey water

custom BPM

water dissociation catalyst layer

cathode gas diffusion/catalyst layer

H_2O

anode gas diffusion /catalyst layer

H_2O

OH^- H^+

$2H^+ + 2e^-$

$4OH^-$

H_2

$4e^- + 2H_2O + O_2$

thin anion-selective membrane (Sustainion)

cation-selective membrane (Nafion)

e^-

V_{app}

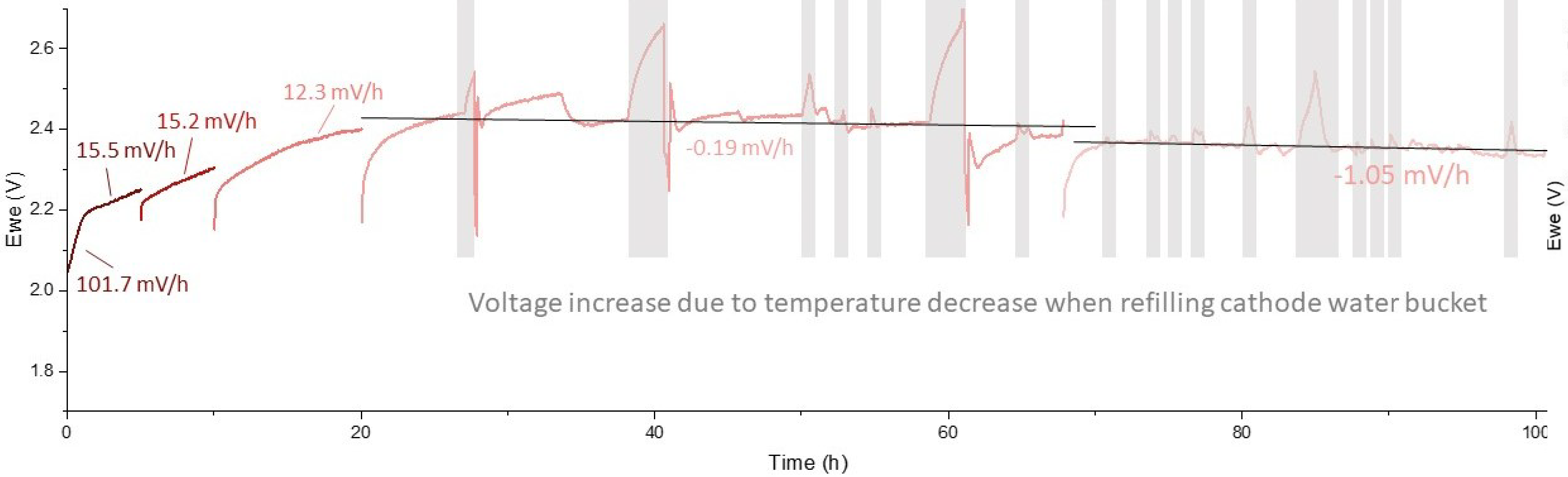
e^-

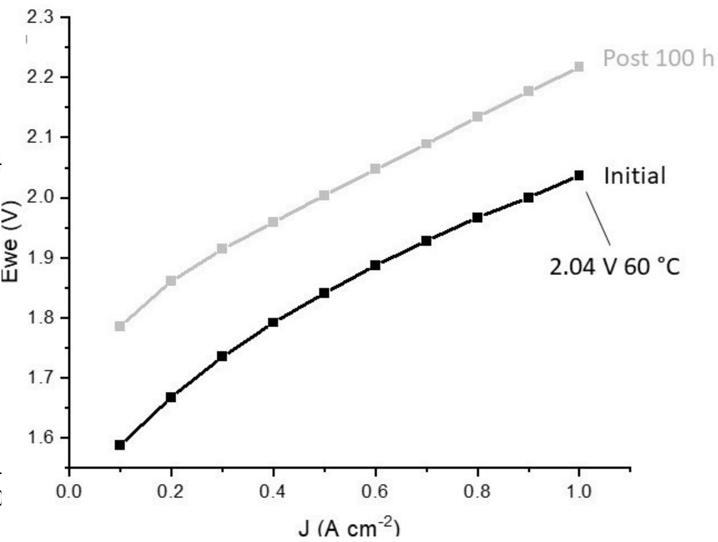
Relevance and Impact

- Program could lower costs and increase lifetime of electrolysis systems. ***Imagine*** **alkaline membrane electrolyzer with:**
  - performance equivalent to state of the art PEM
  - only earth abundant catalysts, and steel cell components
  - robust in operation in "dirty" water requiring less infrastructure and maintenance
- Project integrates broadly across HydroGEN consortium teams while leverage unique UO capabilities and experience.

Accomplishments: tap-water fed AEM operation

- **Go/No-Go Achieved**: Demonstrate AEM MEA electrolyzer performance with 1 A cm^{-2} at applied voltages ~~< 2 V~~ amended to < 2.05 V and with a voltage degradation rate of < 4 mV/h, measured for a minimum of 100 h after the initial break-in period.

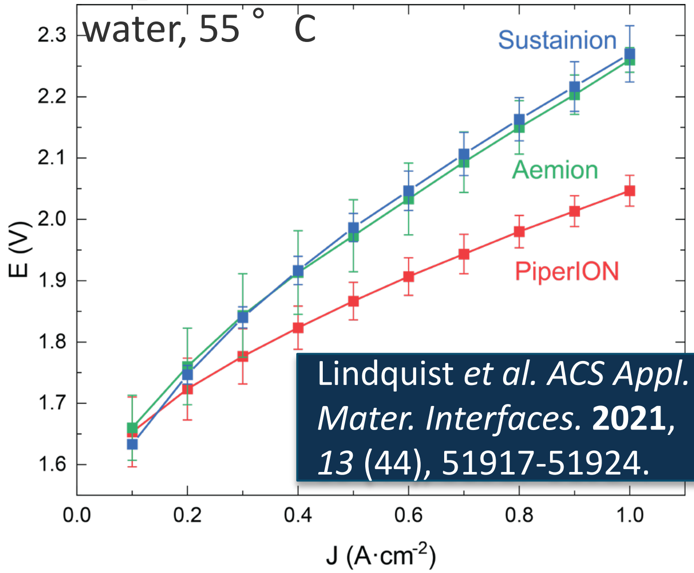




Electrolyzer fed with tap water to anode and pure water to cathode. After very high initial degradation the rate decreased and eventually lowered to a negative voltage loss. Final voltage was only ~200 mV higher after 100 h of operation.

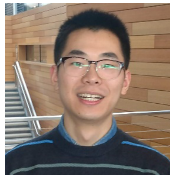
Accomplishments: anode ionomer oxidizes during operation

IrO_2 on SS anode; Pt Black on Toray cathode; Pure water, 55 ° C



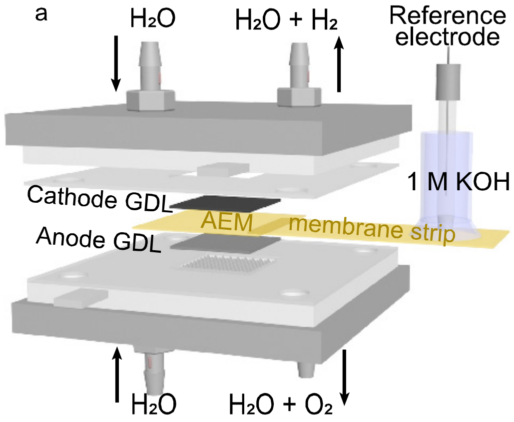
Lindquist *et al. ACS Appl. Mater. Interfaces*. **2021**, *13* (44), 51917-51924.

Grace Lindquist

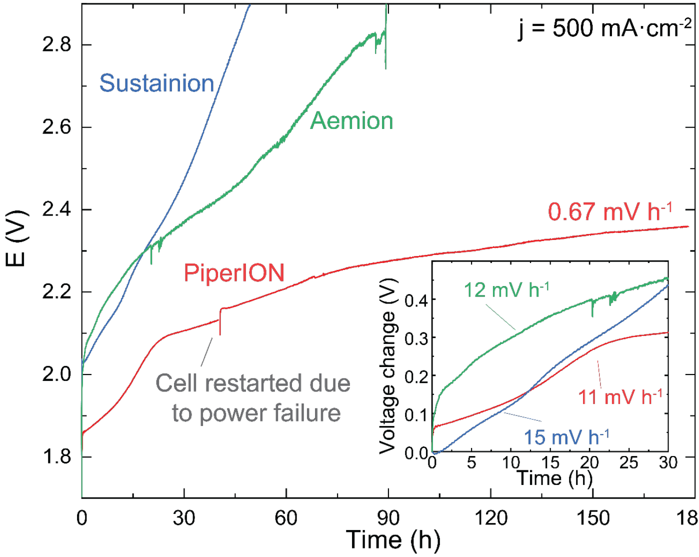


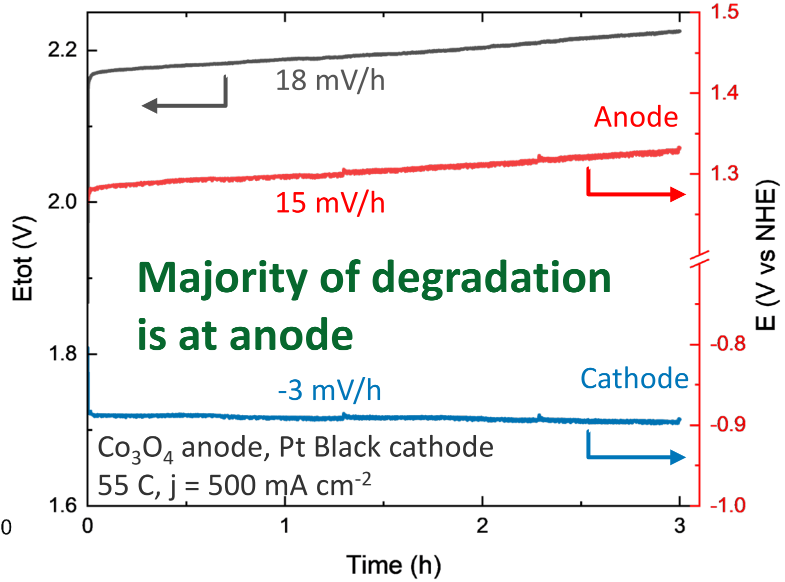
Dr. Qiucheng Xu

Xu, Q. *et al. ACS Energy Lett.* **2021**, *6* (2), 305-312.



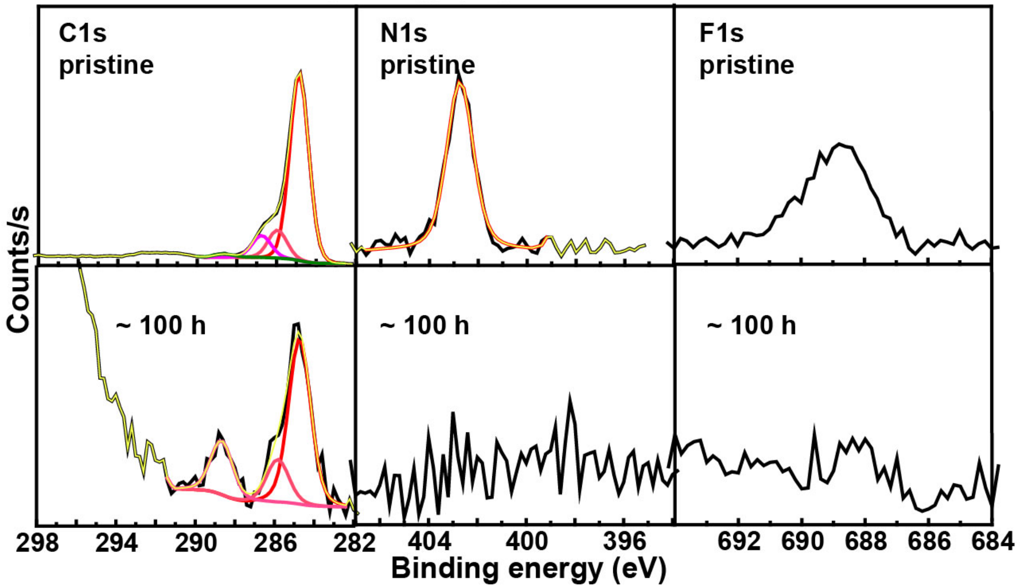
M2.1: Report comprehensive materials and electrochemical characterization of AEM electrolyzer degradation pathways



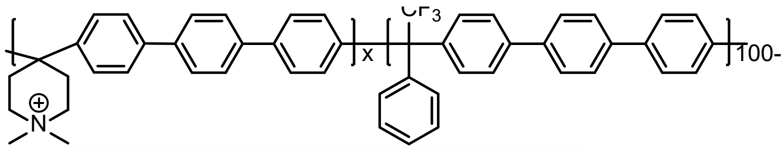


Majority of degradation is at anode

XPS shows oxidative damage



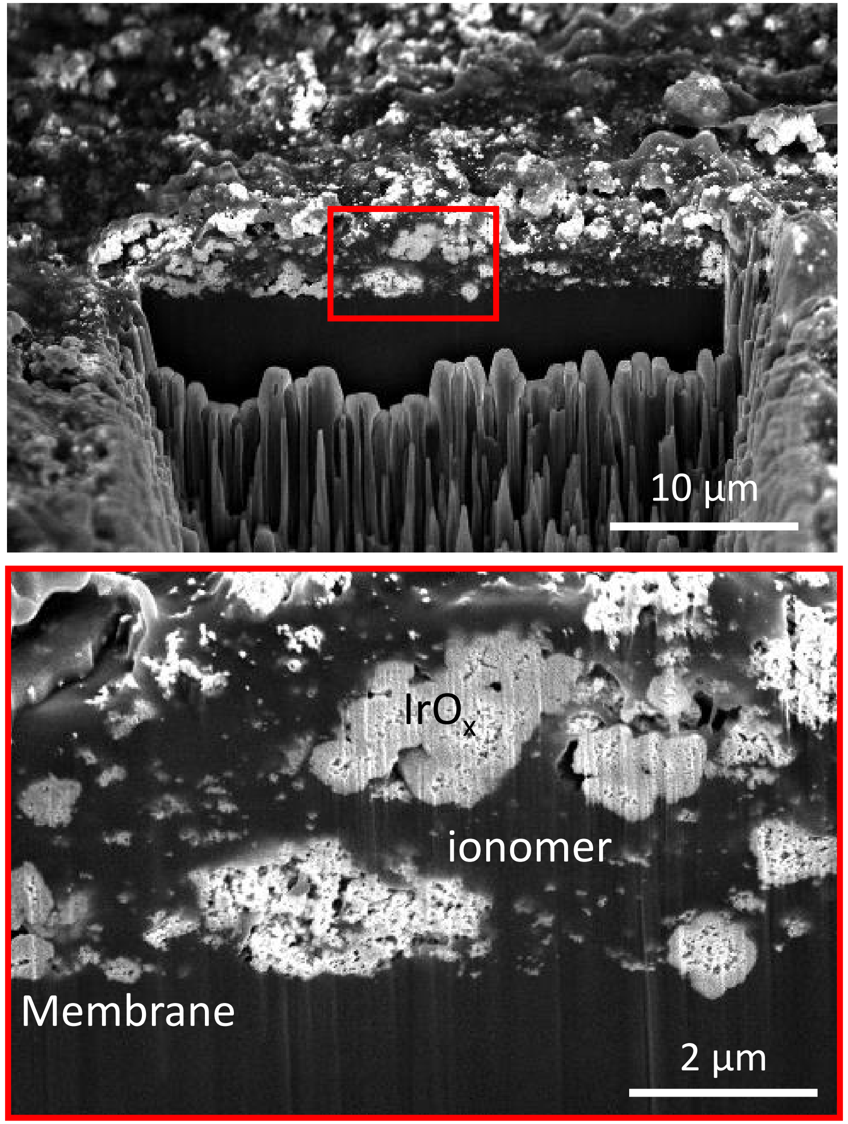
Raina Krivina



Krivina. *et al. ACS Appl. Mater Interfaces* . **2022**, *ASAP*.

Accomplishments: anode ionomer oxidizes during operation

Pristine

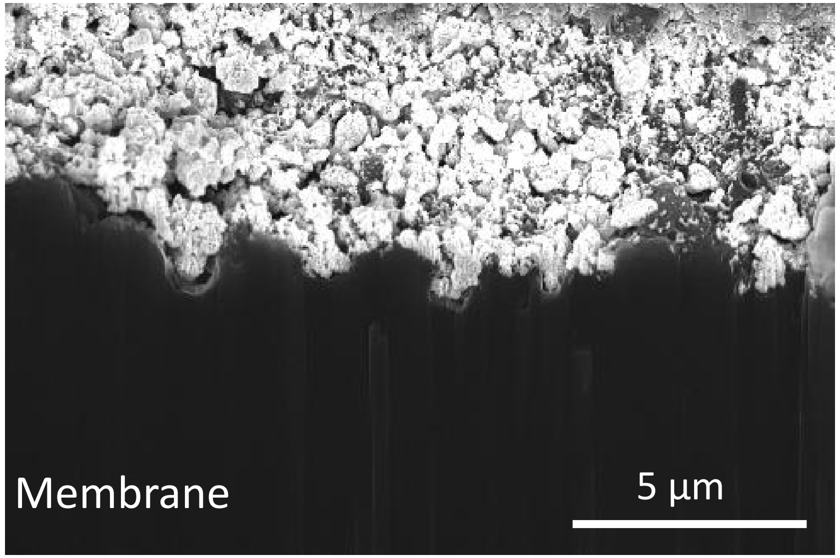


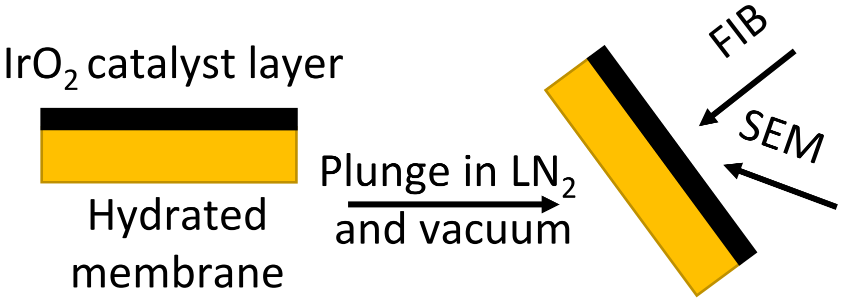
Primary degradation is occurring at anode catalyst/ionomer interface

M2.1: Report comprehensive materials and electrochemical characterization of AEM electrolyzer degradation pathways

- Ionomer oxidation is limiting

After 60 h at 1 A cm^{-2}

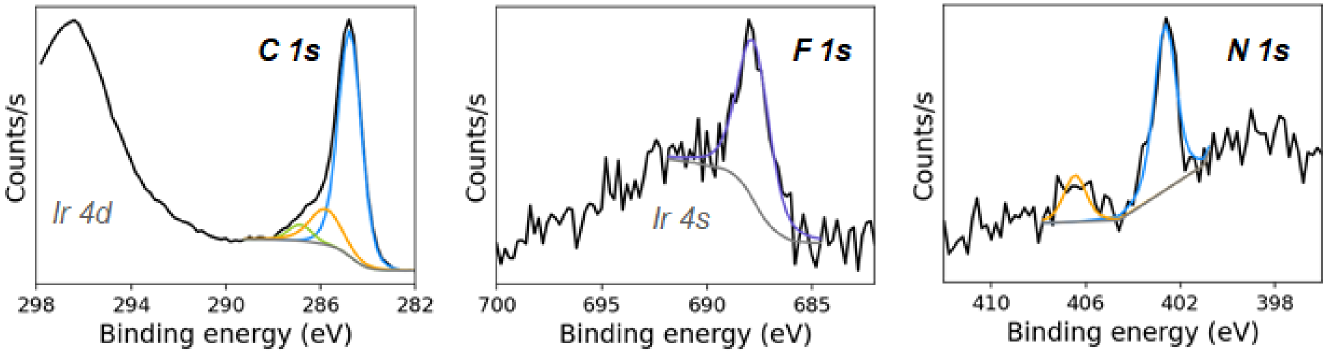


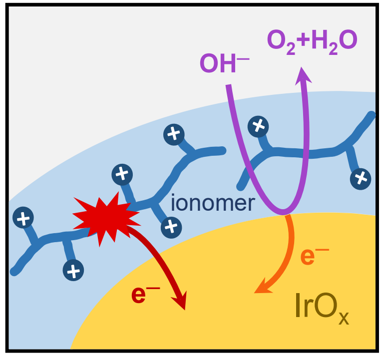


Accomplishments: ionomer oxidation can be blocked with inorganic protective layer

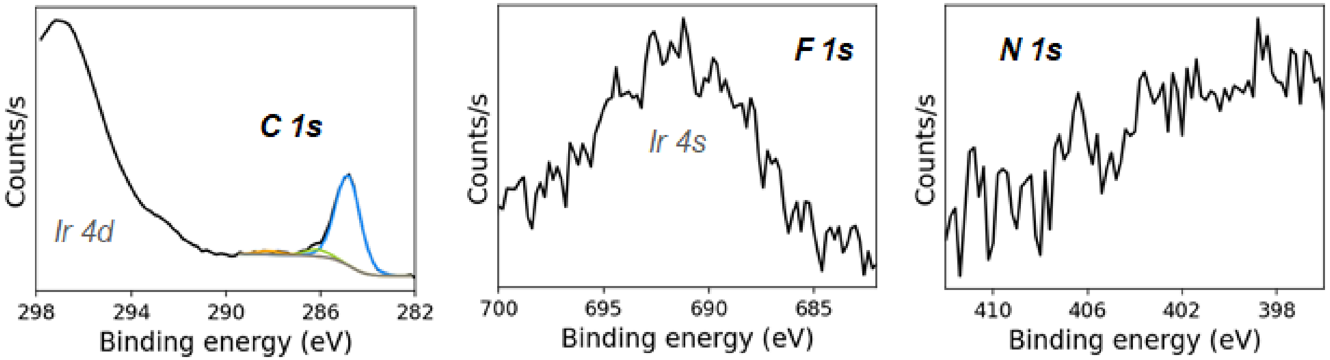
Minkyoung Kwak

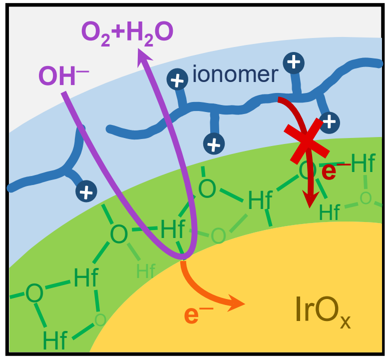
Pristine ionomer



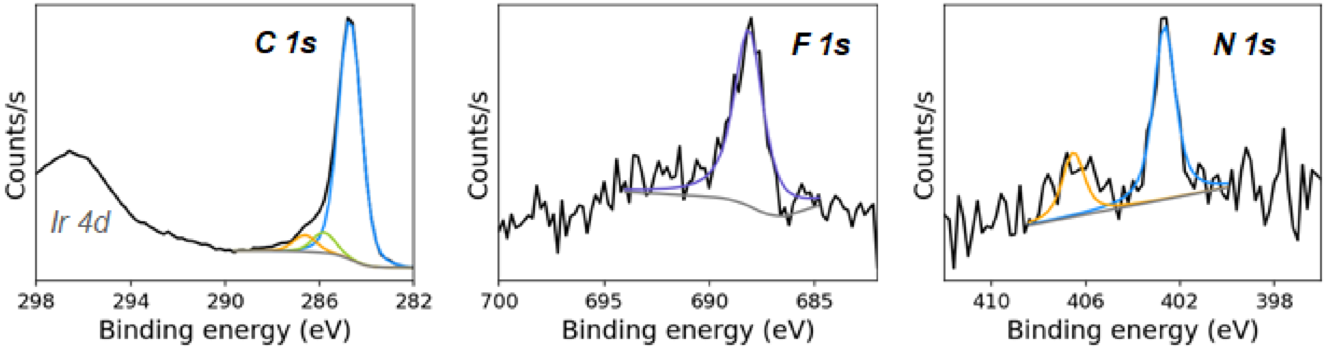


Post-operation **No** HfO_x protective layer



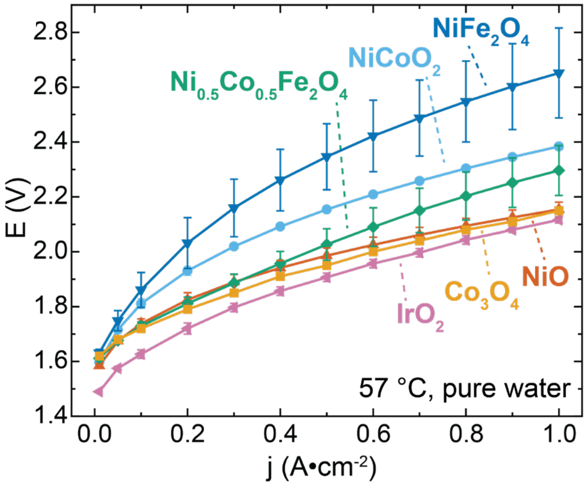


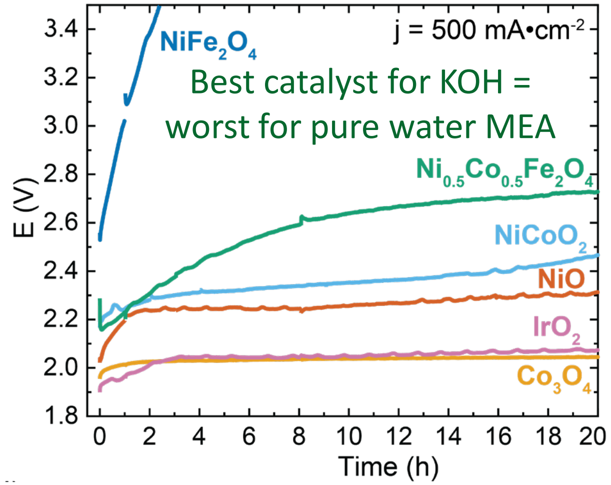
Post-operation **With** HfO_x protective layer



HfO_x coating blocks ionomer oxidation

Accomplishments: performance and durability changes with non-PGM catalysts

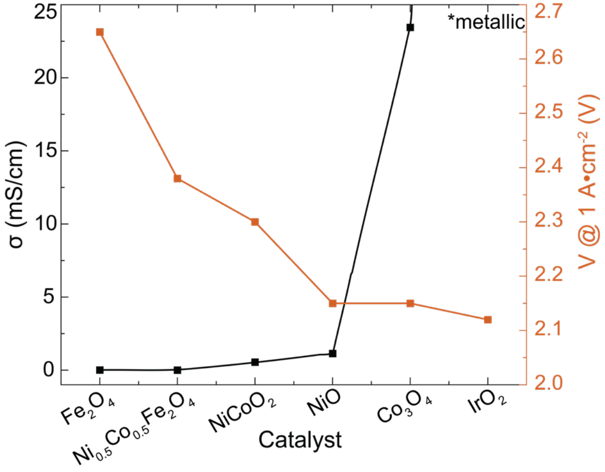




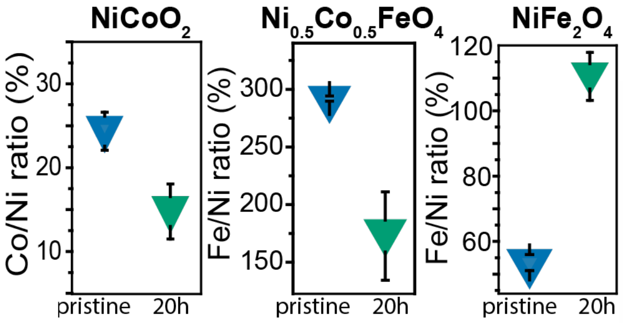
M2.1: Report comprehensive materials and electrochemical characterization of AEM electrolyzer degradation pathways

- Electrical conductivity dictates performance in pure water MEA
- Dynamic structural transformations are detrimental to device stability

Electrical conductivity limits performance

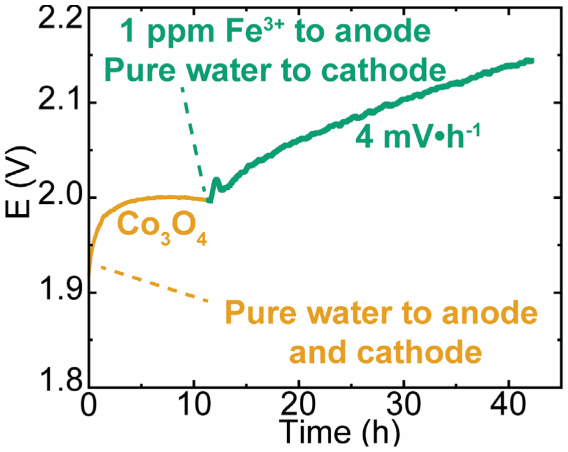


XPS suggests surface instability in mixed-metal catalysts

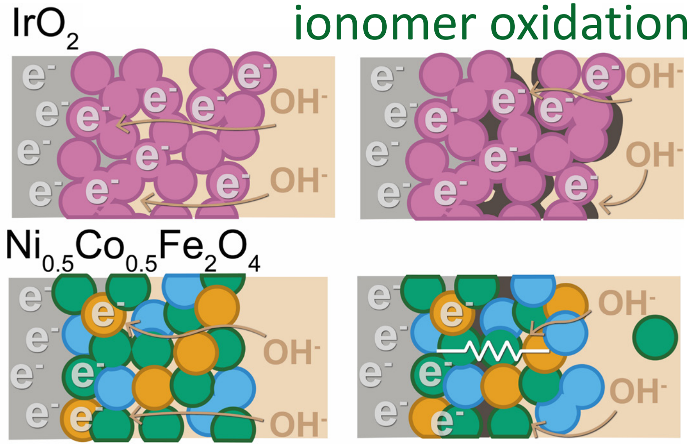


Krivina and Lindquist *et al. Submitted.* **2022.**

Fe increases degradation rate



Conductive catalysts: fast ionomer oxidation

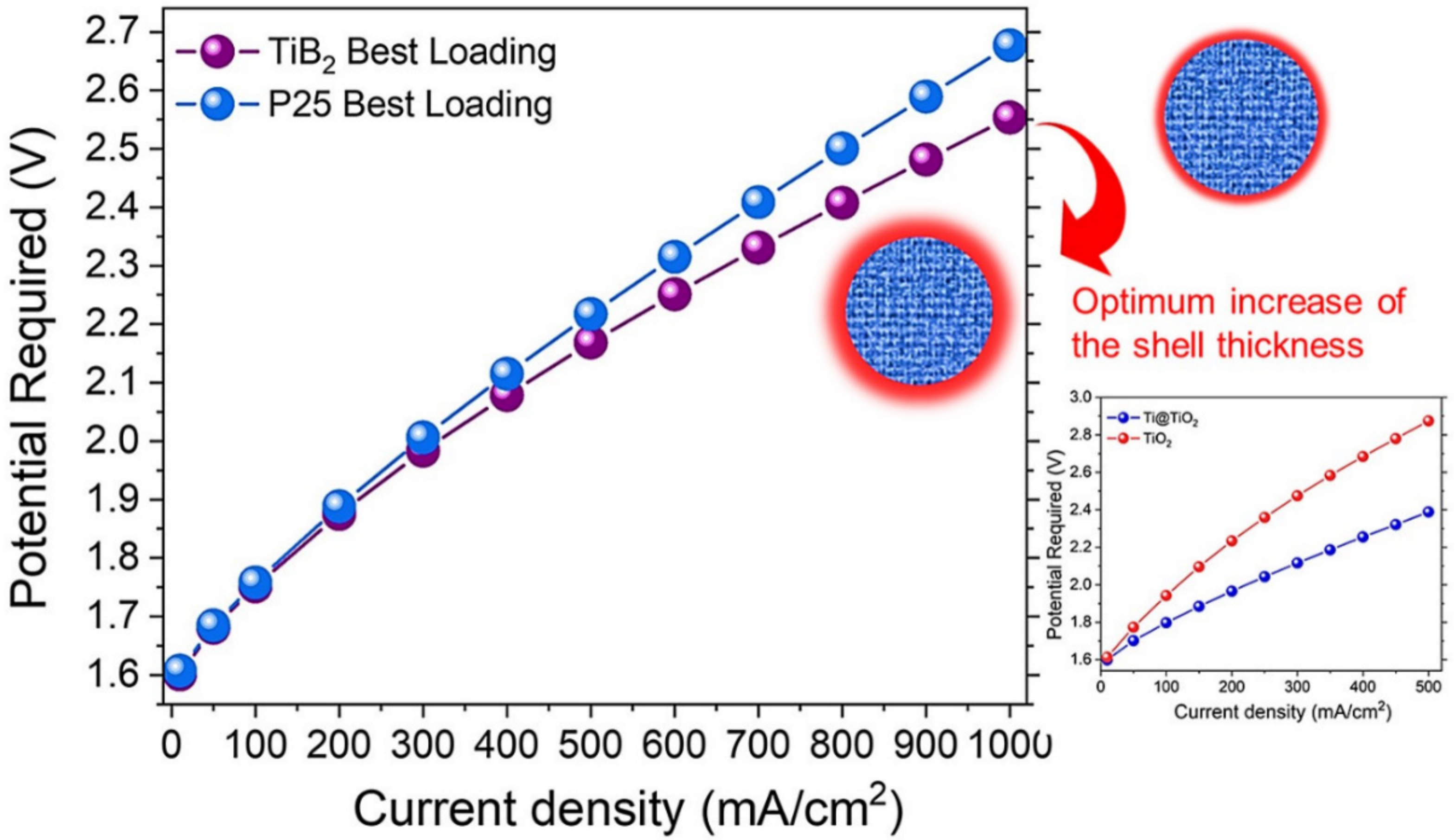


Insulating catalysts: OER cannot occur far from GDL surface; resistance increases

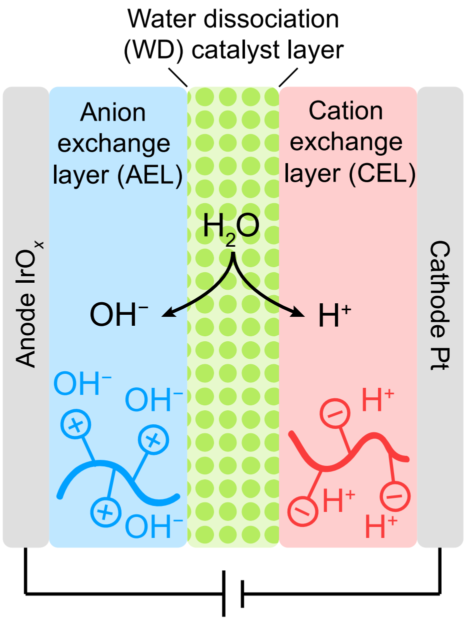
Accomplishments: Improved BPM catalyst design decreases η_{WD}

M 3.1: Demonstrate custom BPM with < 100 mV overpotential for water dissociation at 1 A cm^{-2}

Status: in progress Water dissociation overpotential (η_{WD}) of 200 mV @ 500 mA cm^{-2}



Optimum increase of the shell thickness



Increasing electrical conductivity of TiO2 WD catalyst decreases η_{WD}, **even though no electronic current is carried at the junction**

Collaboration: Effectiveness

- NREL Node
  - Alia – wet/dry cathode operation and scale-up MEA fabrication and testing
- SNL Nodes
  - Fujimoto – novel ionomer and membrane chemistries
- LBNL Nodes
  - Weber: Develop robust numerical simulations (COMSOL) to better understand function in pure and dirty water.
  - Kusoglu: Quantitative measurements of hydration in the membrane and multi-ion partitioning

Proposed Future Work

- Characterize the various degradation modes iteratively tuning membrane, catalyst, and ionomer properties to improve durability and performance. Advanced characterization techniques including cross-sectional and 3D imaging and chemical analysis, electrochemical and impedance analysis, and computer modelling will all be employed to follow/understand the critical processes.
- Systematically feed trace metals to anode side of AEM. Understand *mechanisms to affect membrane and device-fouling rates.* Determine purity limit for various transition metal species.
- Understand ion partitioning in dirty-water-fed BPM and selectivity changes with thin AEL and CEL

Technology Transfer Activities

- Kwak, M.; Lindquist, G. A.; Boettcher, S. W., Passivated Electrodes in Electrolyzers and Fuel Cells. Provisional Patent Application No. 63/291,295 Filed December 17, 2021.
- Obtained new membrane and ionomer from Fujimoto (Sandia)
- Continued knowledge and materials transfer with Alia (NREL) for baseline advancement and scale-up
- Collaboration with Versogen

Project Summary

- **Go/No-Go achieved**: Demonstrated tap-water-fed AEM electrolyzer performance with 1 A cm^{-2} at applied voltages < 2.05 V and with a start-to-end degradation rate of ~2 mV/h
- Characterized anode ionomer oxidation is a significant degradation mode during AEM operation and *demonstrated* HfO_x *protective layer prevents ionomer oxidation*
- High electronic conductivity and stable crystalline structure during operation is essential for pure water AEM operation with non-PGM anode catalysts
- Improved BPM WD catalysts reduce η_{WD}
- 7 academic publications to date:
  - Lindquist and Krivina et al. *Submitted. Adv. Materials* **2022.**
  - Krivina, R. A. *et al. ACS Appl. Mater. Interfaces.* **2022.** ASAP.
  - Krivina, R. A. *et al. Acc. Mater. Res*, **2021**, *2 (7)*, 548-558.
  - Lindquist, G. A. *et al. ACS Appl. Mater. Interfaces*, **2021**, *13, 44*, 51917–51924.
  - Xu, Q. *et al. ACS Energy Lett*. **2021,** *6,* 305-312.
  - Lindquist, G. A.; Xu, Q.; Oener, S. Z.; and Boettcher, S. W. Membrane Electrolyzers for Impure-Water Splitting. Joule, 2020, 4 (12), 2549-2561.
  - Oener, S. Z. *et al*. *ACS Energy Lett.* **2020**, *6 (1*), 1-8.