



Energy Materials Network
U.S. Department of Energy



HydroGEN
Advanced Water Splitting Materials

HydroGEN: Low Temperature Electrolysis

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National Renewable Energy Laboratory

Project ID # P148A

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DOE Hydrogen Program 2023 Annual Merit Review and Peer Evaluation Meeting

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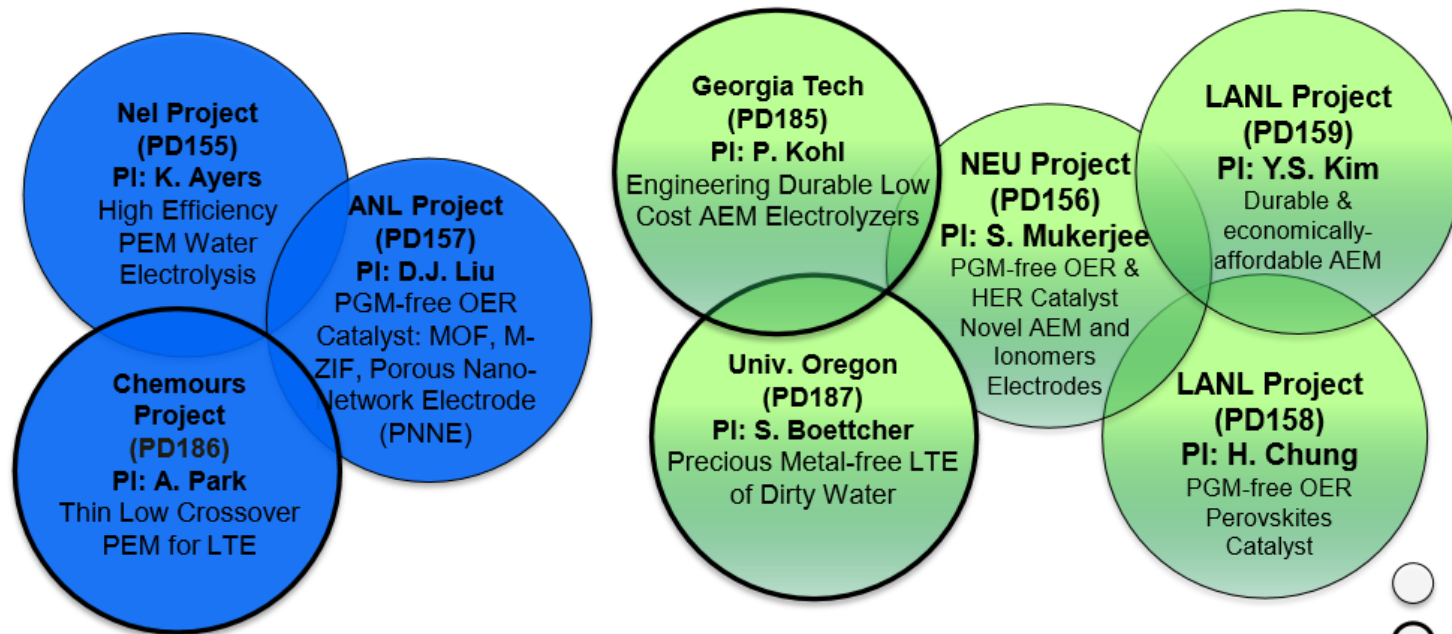




Approach: HydroGEN 2.0 Project Added to LTE Activities

HydroGEN LTE Projects

- 8 FOA projects with 41 nodes
 - 3 currently supported (in Accomplishments)
 - 5 with closeout contributions (in Technical Backup)
- 2 Supernodes with 14 nodes
- LTE 2.0 with 4 nodes



○ Projects added FY'18
● Projects added FY'20

Discussed in PEC, P148A

Discussed here in LTE, P148

LTE Node Labs



Sandia National Laboratories



Support through:



Personnel
Equipment
Expertise
Capability
Materials
Data

LTE FOA Projects



Supernodes

A. Weber	Understanding OER Across pH Ranges
T. Ogitsu	Through Multiscale, Multi-Theory Modeling
H. Dinh	Linking LTE/Hybrid Materials to Electrode
B. Pivovar	Properties to Performance

LTE 2.0

S. Alia	Enabling High Efficiency, Durable AEMWE
B. Pivovar	Performance

PEM: Understanding and improving materials

AEM: Developing and understanding materials

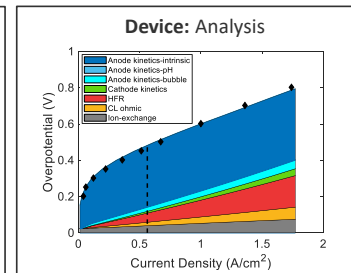
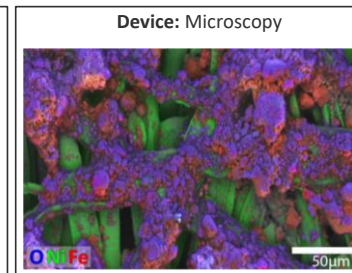
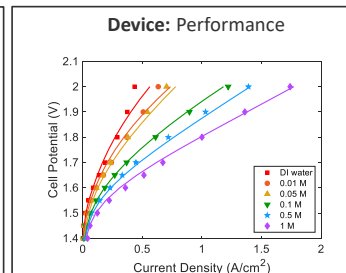
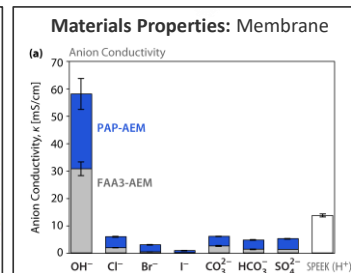
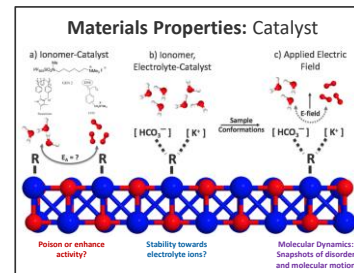
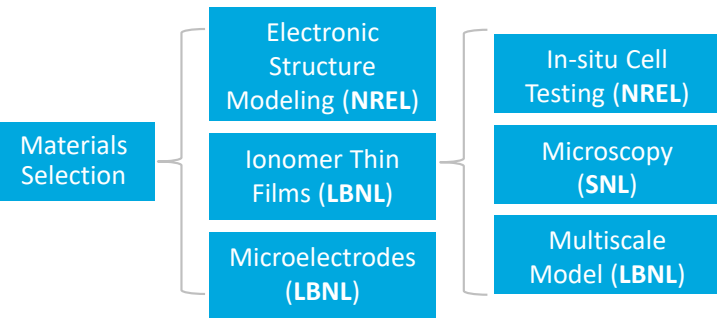


LTE 2.0 Approach:

Enabling High Efficiency, Durable AEM Electrolysis Performance

Goals: Determine the role of the supporting electrolyte and the limiting factors behind water operation in AEM electrolysis

- Evaluate AEM’s ability to approach PEM performance/durability
- Elucidate interactions at the ionomer/catalyst interface to assess ionomer stability and catalyst poisoning
- Understand the impact of catalyst layer composition on performance in a supporting electrolyte
- Delineate the impact of electrolyte conductivity and alkalinity on performance and durability
- Address delamination and longer-term durability due to catalyst layer processing and reordering

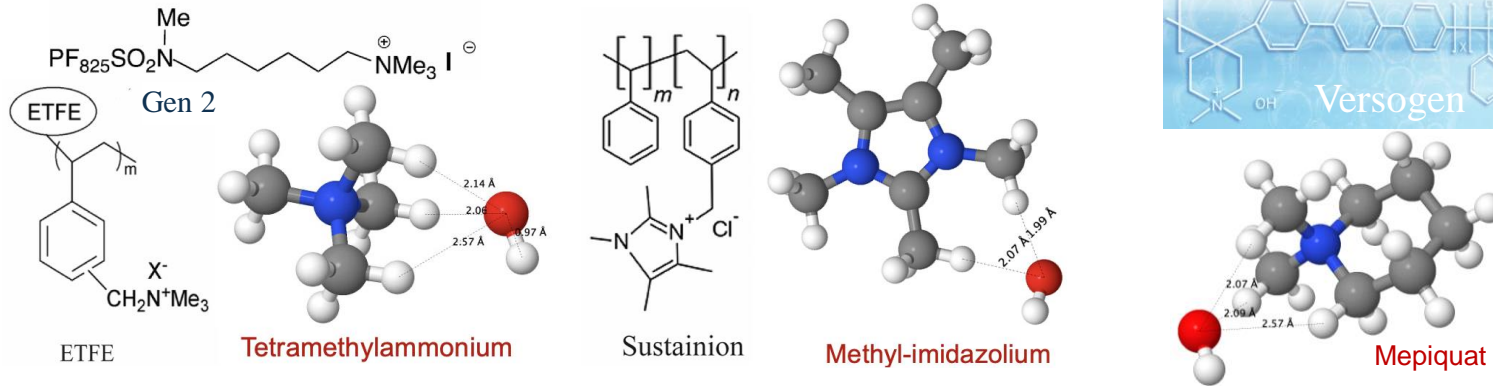




LTE 2.0 Accomplishments:

Understanding Ionomer-Catalyst Effects on OER

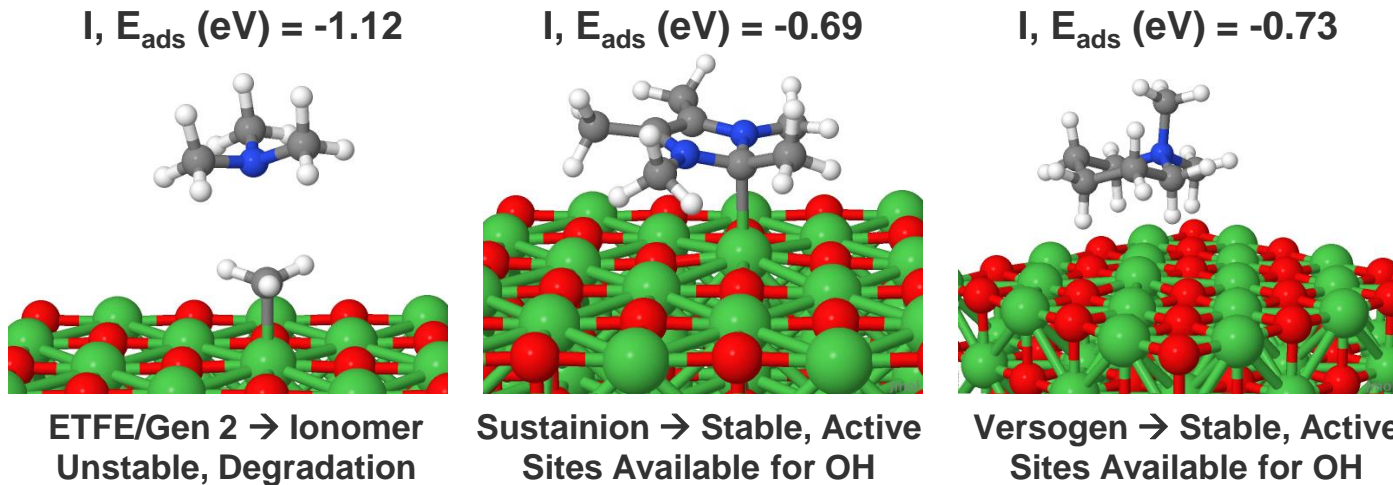
Approximate Ionomer with Smaller Organic Fragments: Theoretical calculations can give critical insights into ionomer-catalyst chemistry



Ionomer/Catalyst Chemistry Can Impact Material Performance and Stability:

- Does the ionomer **poison the catalyst** by introducing competing reactions or covering up active sites?
- Does the ionomer **remain stable** or does it **degrade** into other species?
- Ideal: Ionomer stable, metal active sites available for OH adsorption

Ionomer-Catalyst Interactions: N+R group can poison activity by blocking sites, degrade, or introduce competing reactions to OER



- E_{ads} (eV) of OH^* = -1.49, all ionomers bind weaker than OH^*
- **Sustainion and Versogen Ionomers** are stable and do not block Ni sites
- **ETF, GEN 2 Ionomers** are unstable and poison active sites:
 - Degradation via de-methylation

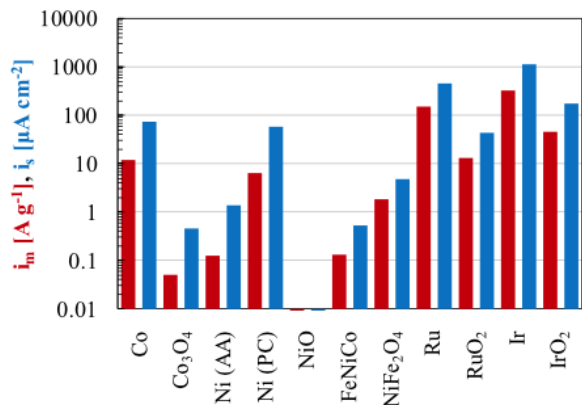
Theory can identify *key limitations or advantages* to specific ionomers, **critical to our understanding of the ionomer/catalyst interface**



LTE 2.0 Accomplishments:

Understanding Ionomer-Catalyst Effects on OER

Interest in mixed materials, due to significantly greater activity than pure NiO



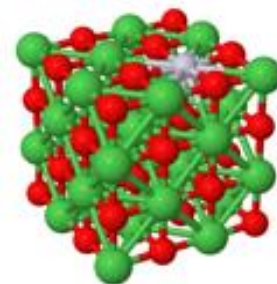
Anderson et al 2020 J. Electrochem. Soc. 167 044503

NiO nearly inactive for OER compared to other commercial baselines of oxide materials:

- $\text{NiFe}_2\text{O}_4 > \text{FeNiCo} \gg \text{NiO}$

Dopant M =

Fe and Co

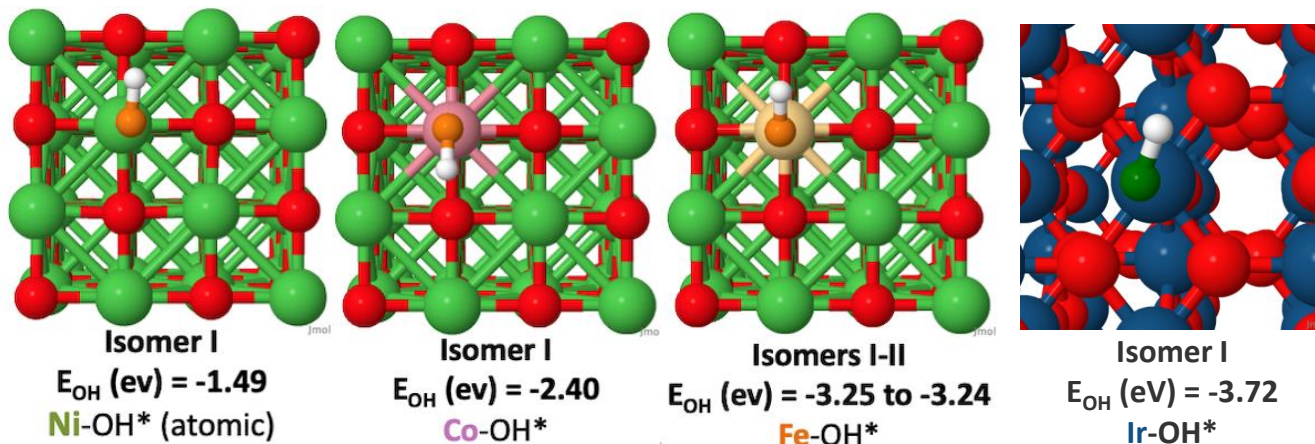


Substitution

Theoretical Model:

- Limit our mixed material model to a single dopant in order to fully examine the geometric and electronic effects of a nearby transition metal e.g. Fe and Co dopants
- Systematically assess adsorption of ionomer vs OH*

OH* Adsorption Strength Increases with Inclusion of Transition Metals, Fe and Co



- Co, Fe considerably increases OH* Binding
- OH* adsorption strength closer to OH* adsorption on IrO₂ with inclusion of Fe
- **Stronger OH* Adsorption Means Ionomer Less Likely to Block Metal Sites**
- **OH* adsorption similar to that of IrO₂ may increase activity**

Theory can showcase that the presence of different transition metals can change the *binding trends* of key reaction intermediates

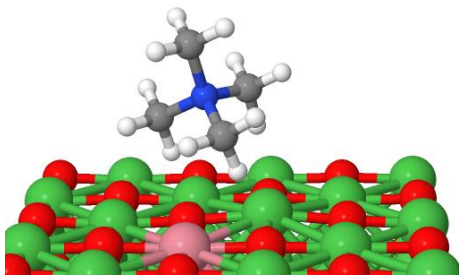


LTE 2.0 Accomplishments:

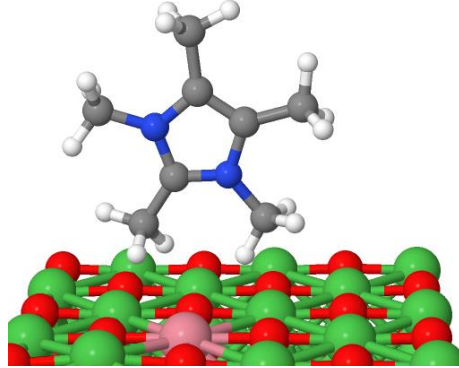
Understanding Ionomer-Catalyst Effects on OER

The Inclusion of Transition Metals, **Fe** and **Co** stabilizes all ionomer fragments, including ETFE/GEN 2's tetramethylammonium

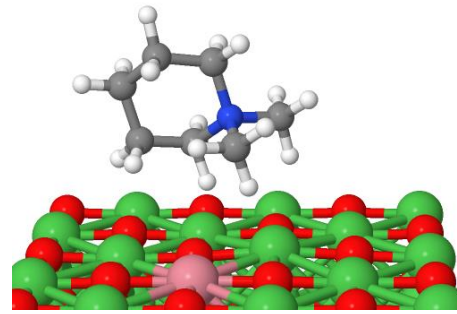
I, E_{ads} (eV) = -1.79



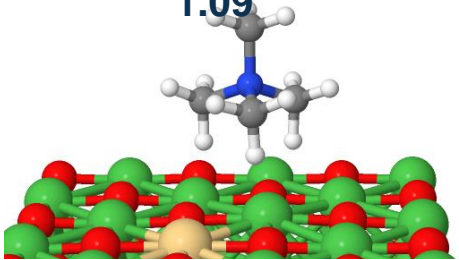
I, E_{ads} (eV) = -1.45



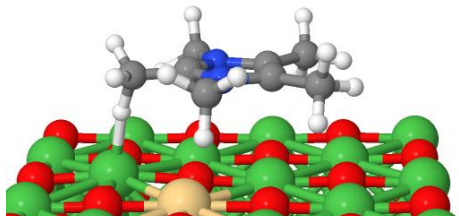
I, E_{ads} (eV) = -1.45



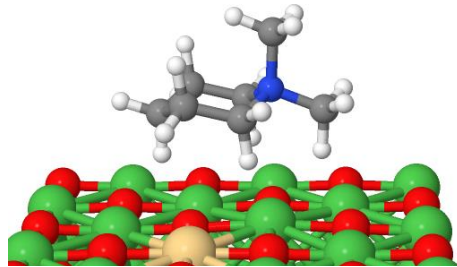
I, E_{ads} (eV) = -1.09



I, E_{ads} (eV) = -0.74



I, E_{ads} (eV) = -0.77



ETFE/Gen 2 → Stable,
Active Sites Available for
OH

Sustainion → Stable,
Active Sites Available for
OH

Versogen → Stable,
Active Sites Available for
OH

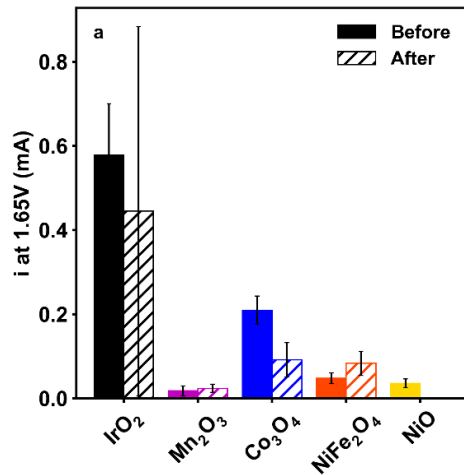
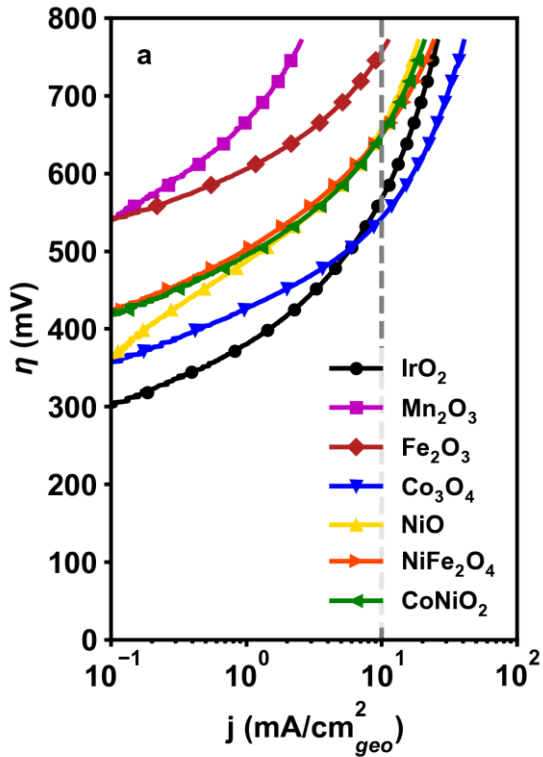
- On NiO, **ETFE, GEN 2 Ionomers** are *unstable* and *poison active sites*:
 - Degradation via de-methylation
- The addition of **Fe** and **Co** *stabilizes the tetramethylammonium fragment*: the de-methylation present in NiO does not occur
- Although OH* is *bound more strongly* on **Fe-** and **Co-**NiO surfaces, the ionomers *remain weakly bound compared to OH**

Theory can potentially predict the relative stability of ionomer fragments on mixed-metal surfaces, critical to our understanding of the ionomer/catalyst interface

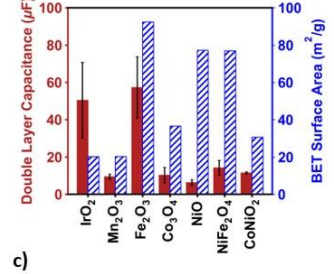
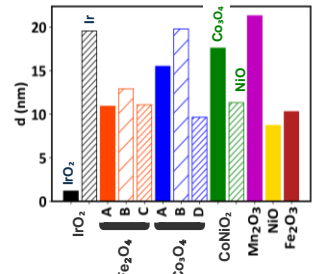
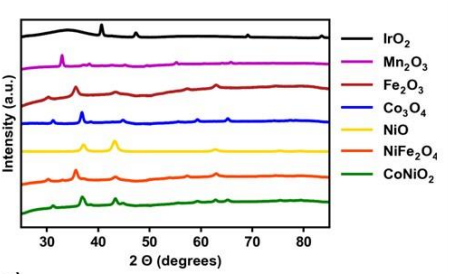
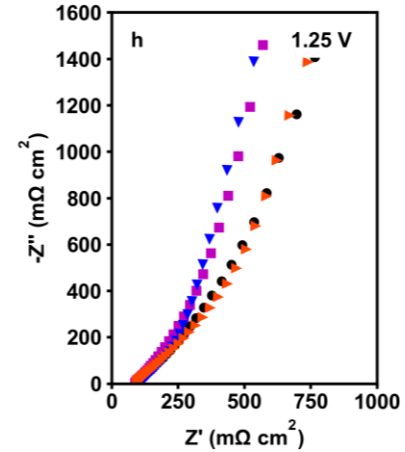
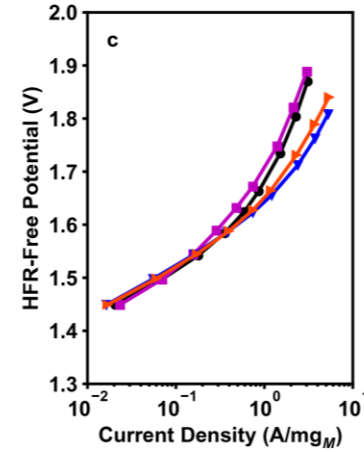
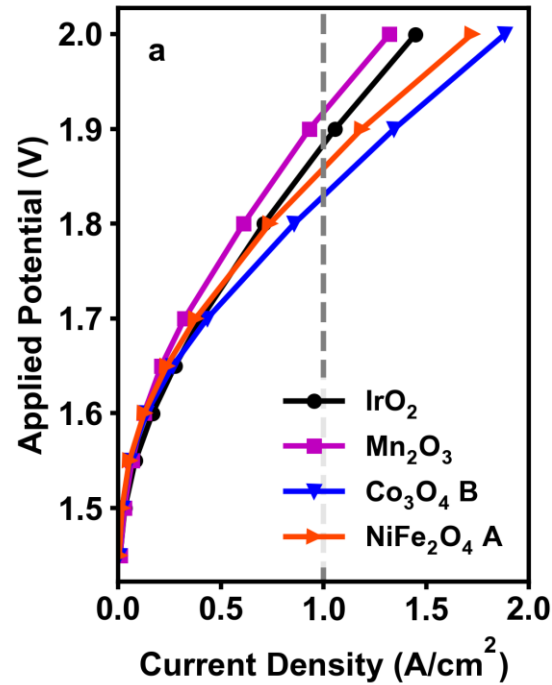


LTE 2.0 Accomplishments: Catalyst Screening for Oxygen Electrode

Ex-situ Materials Characterization



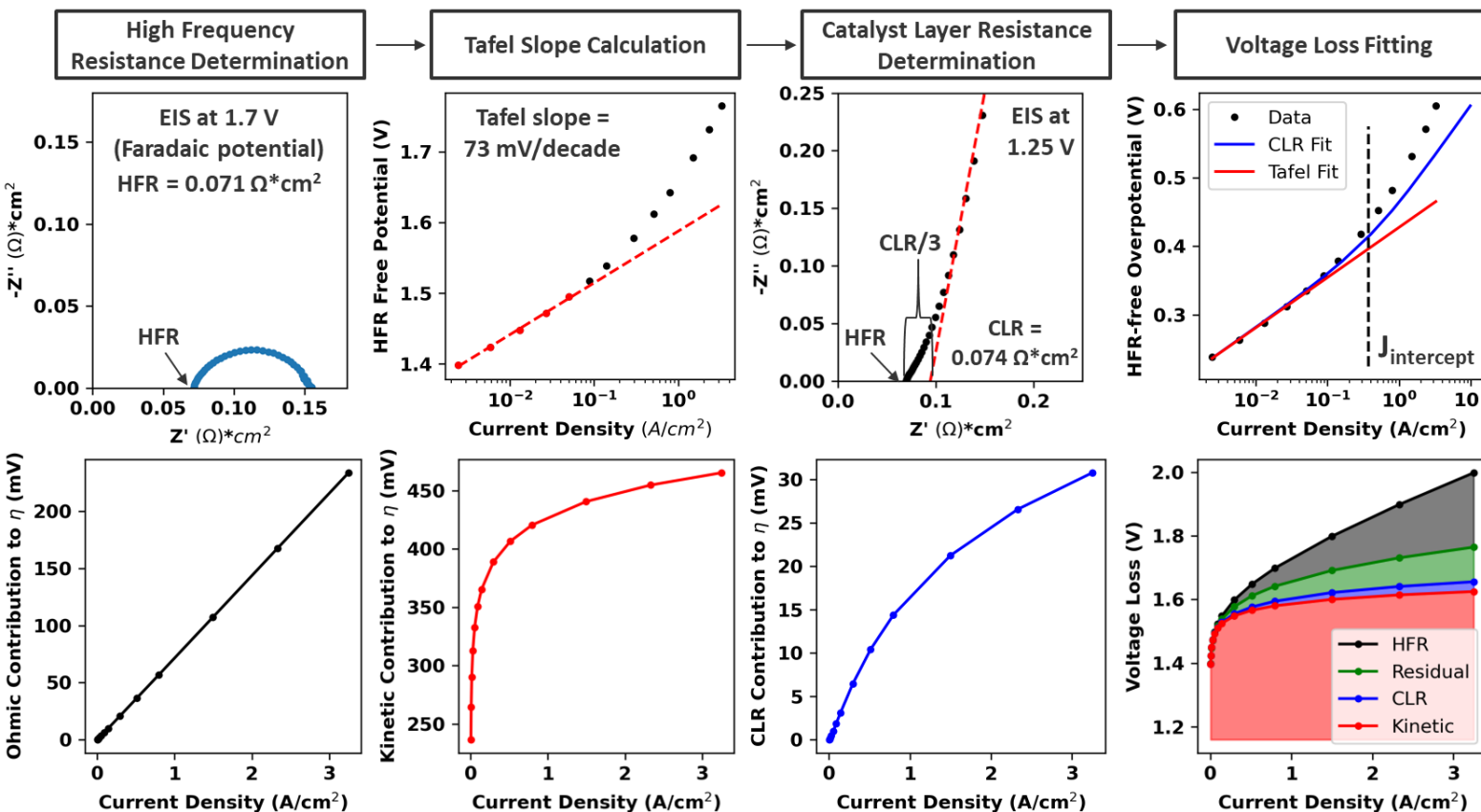
Membrane Electrode Assembly Testing



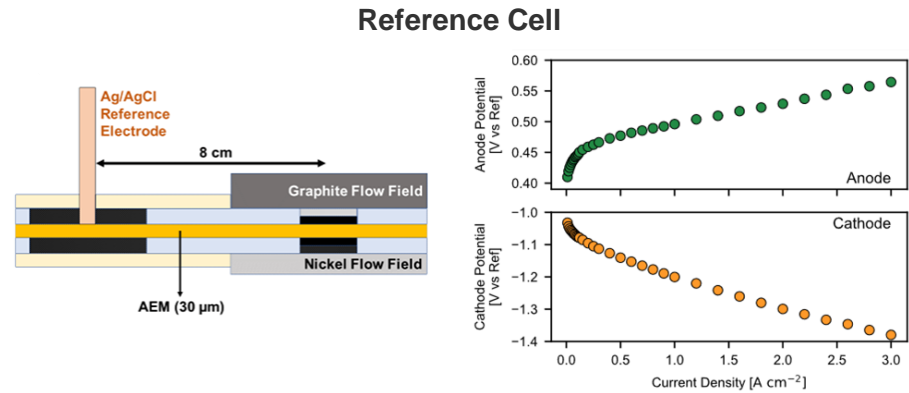
- Baseline activities for commercial materials, goal of improving catalyst kinetics to reach technology target
- Nickel-iron (NiFe₂O₄) and cobalt (Co₃O₄) leveraged as platinum group metal (PGM) -free baselines due to promising performance
- Ni-Fe oxide activity improvement in stability testing due to high initial Fe content



LTE 2.0 Accomplishments: Diagnostics and Resistance Analysis in Continuum Model



- Improved diagnostics to resolve catalyst layer resistance and anode/cathode contributions
- Suggests pathways for performance and durability improvements
- Agreement between diagnostics and continuum model



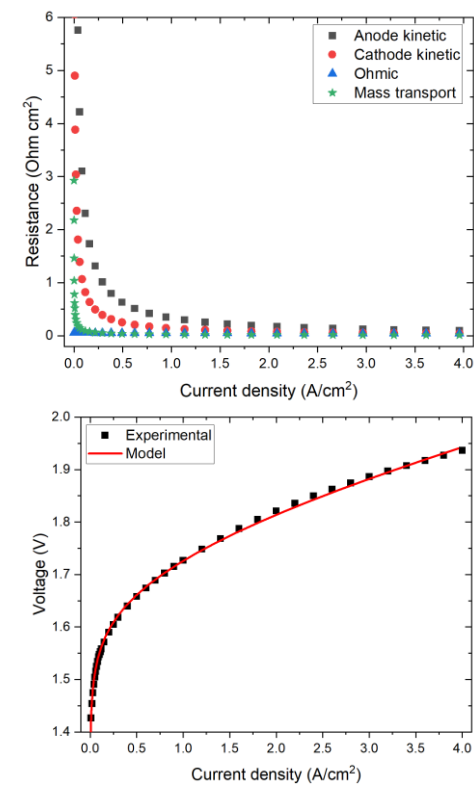
A. W. Tricker, et. al, "Journal of Power Source 567 (2023) 232967"

Resistance analysis utilizes power-loss method

$$P = IV = I^2R \quad \Delta V_k = \frac{\int_{V_k} \nabla \cdot \mathbf{p}_k dv_k}{I_{cell}^2}$$

$$\Delta R_k = \frac{\int_{V_k} \nabla \cdot \mathbf{p}_k dv_k}{I_{cell}^2}$$

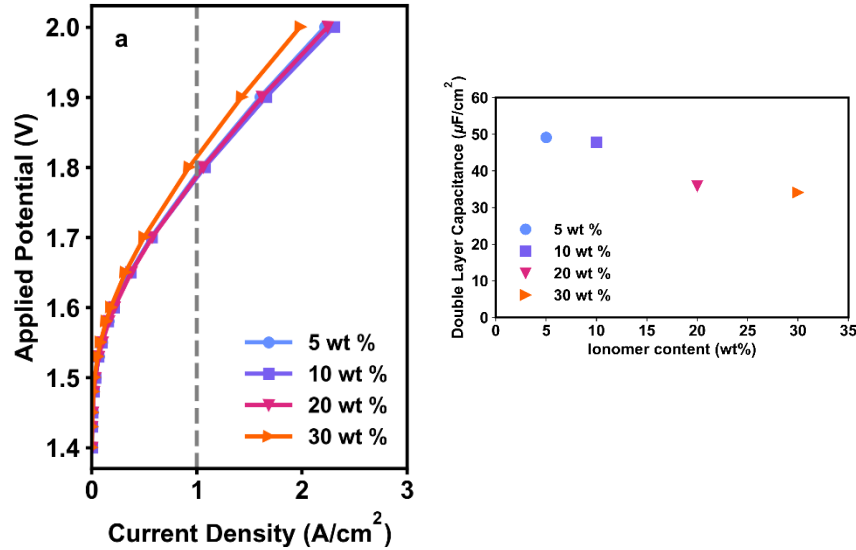
The 1D continuum model successfully predicts experimental polarization curve



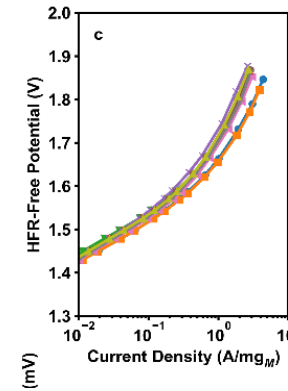
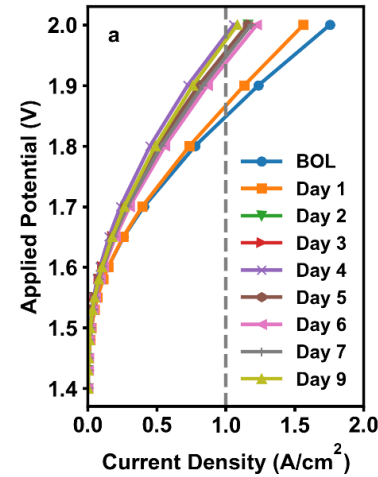


LTE 2.0 Accomplishments: Nickel-Iron Anodes, Ionomer Content

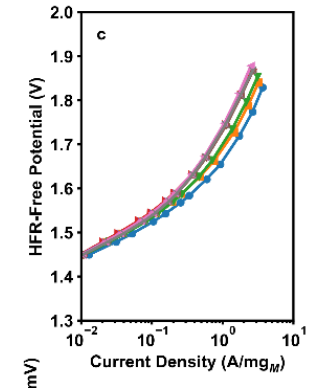
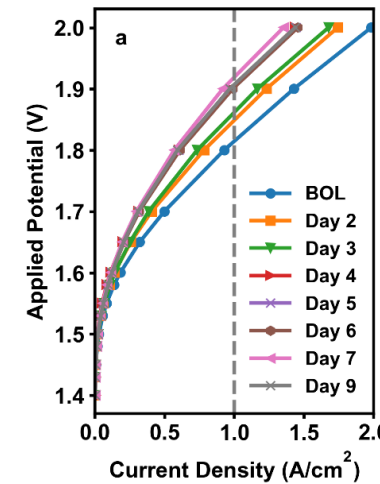
Decrease Ionomer Content



Extended Operation, 5 wt. % (200h)

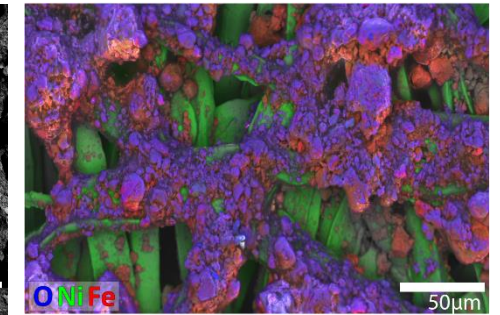
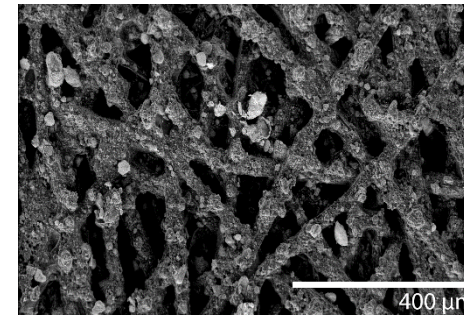


Extended Operation, 30 wt. % (200h)

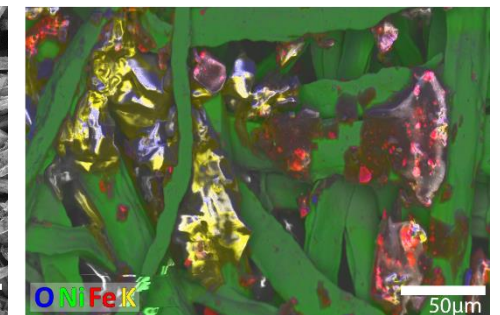
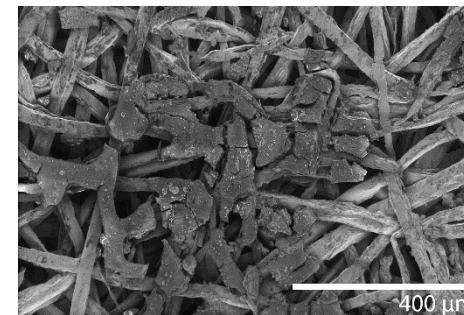


- Higher ionomer content partially blocked active sites, as show in the decrease in double layer capacitance with increased ionomer
- To what degree is ionomer needed in a supporting electrolyte?
 - Role in electrode integrity
 - Hydroxide conduction versus contaminant impact
- Lower ionomer content improved kinetics, similar (to slightly higher) loss in extended operation
- Catalyst layer mobility during extended operation, iron loss

Initial Catalyst Layer



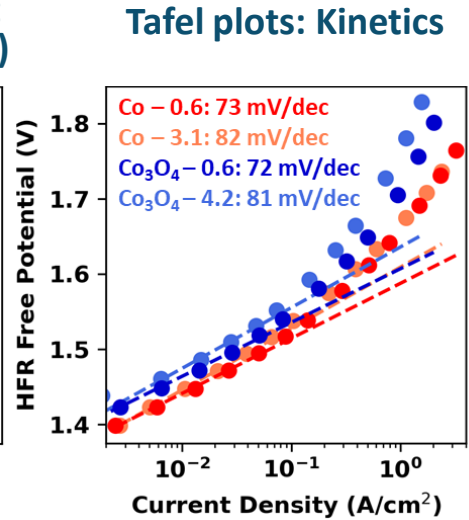
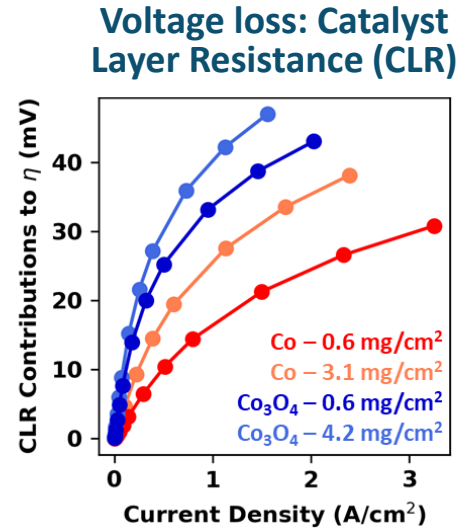
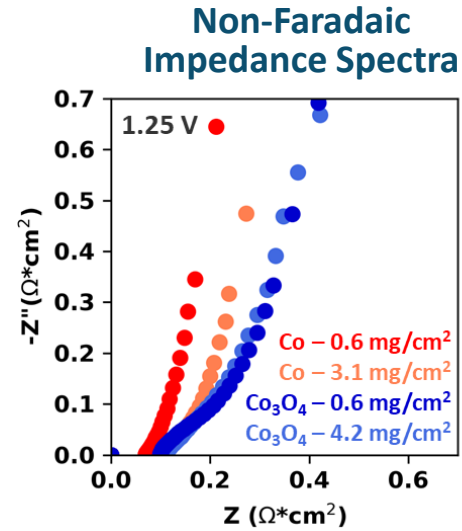
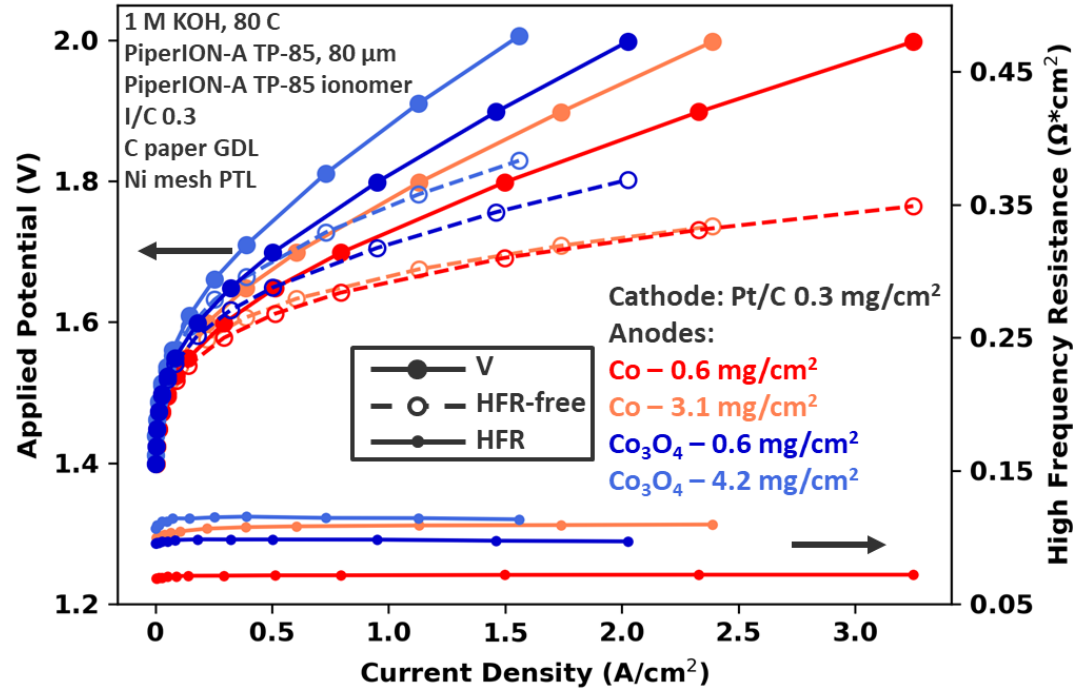
After Durability Testing





LTE 2.0 Accomplishments:

Cobalt Anodes, Effect of Conductivity and Loading

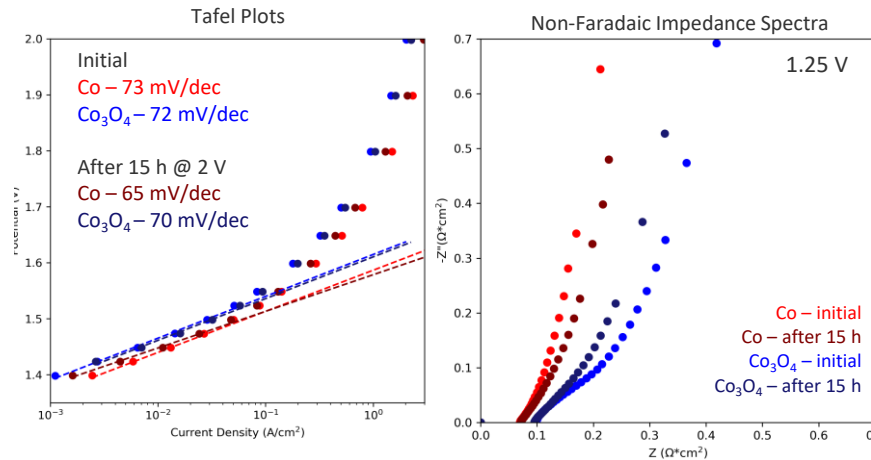
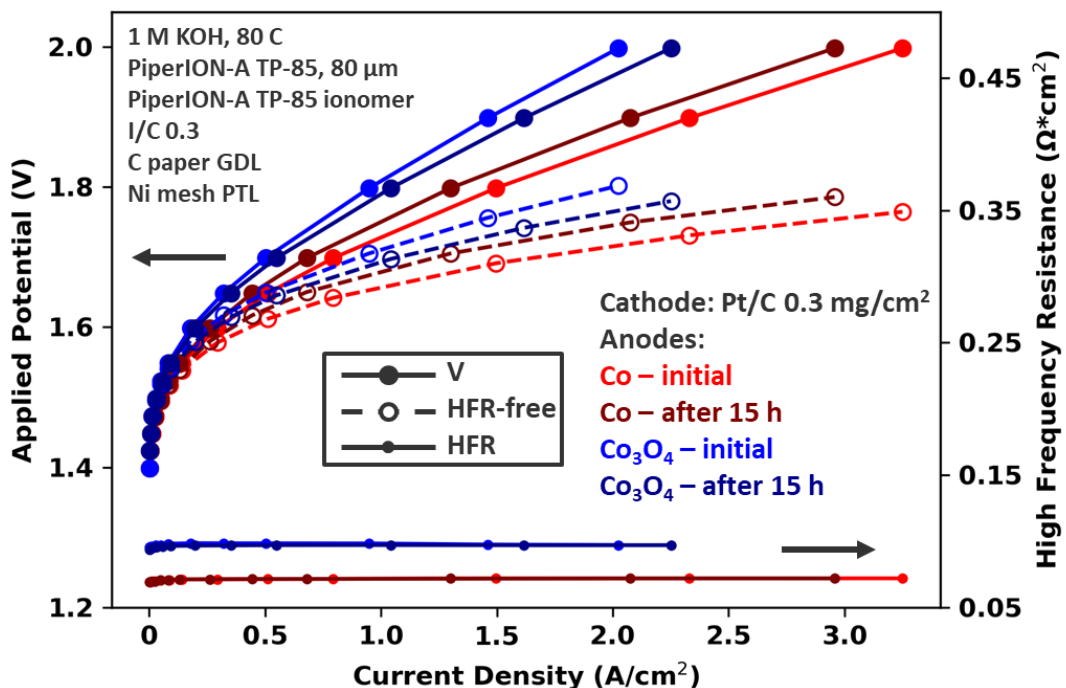


	HFR (Ω*cm ²)	CLR (Ω*cm ²)	Tafel (mV/dec)
Co (0.6 mg/cm ²)	0.071	0.074	73
Co (3.1 mg/cm ²)	0.105	0.147	82
Co ₃ O ₄ (0.6 mg/cm ²)	0.097	0.320	72
Co ₃ O ₄ (4.2 mg/cm ²)	0.112	0.420	81

- Metallic cobalt (Co) has higher performance than Co₃O₄ due to higher kinetics, lower catalyst layer resistance (CLR), compared to Co₃O₄
- Increased anode loading leads to lower performance due to higher HFR, CLR, and Tafel slopes
- Short-term stability tests
 - Co performance decreases slightly due to decrease in number of active sites and exchange current density
 - Co₃O₄ performance improves due to decrease in CLR
- **Low-loaded, metallic Co anode has higher initial performance, retains performance advantage after stability test**



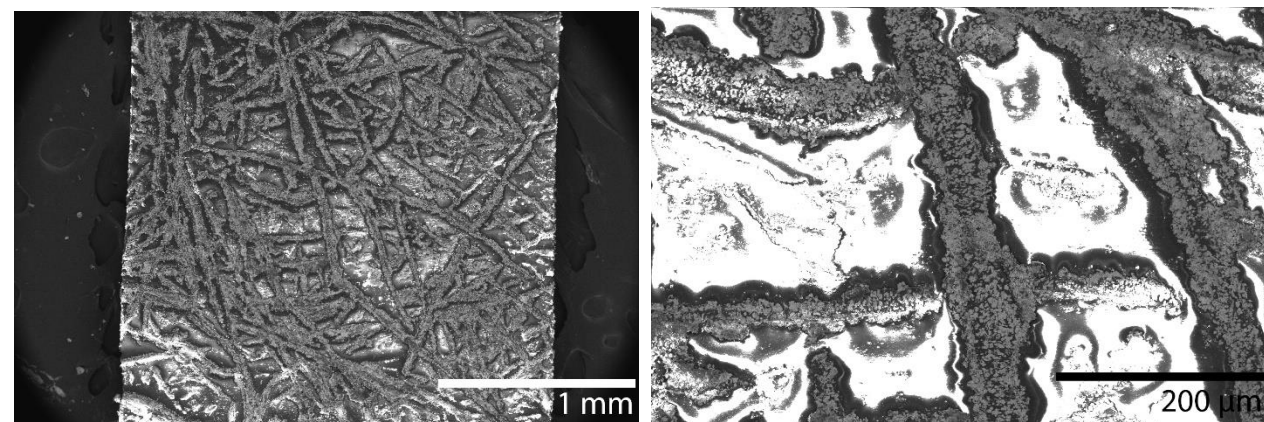
LTE 2.0 Accomplishments: Cobalt Anodes, Extended Operation



	HFR (Ohm*cm ²)	CLR (Ohm*cm ²)	Tafel (mV/dec)
Co pre	0.071	0.074	73
Co after 15 h	0.072	0.072	65
Co ₃ O ₄ pre	0.097	0.320	72
Co ₃ O ₄ after 15 h	0.096	0.239	70

Cobalt oxide (Co₃O₄) Catalyst Layer, After Durability Testing

- Cobalt metal performance decreases slightly → decrease in number of active sites and site-specific activity
- Cobalt oxide (Co₃O₄) performance improves → decrease in catalyst layer resistance
- Minimal catalyst layer compositional change after 400 h testing, catalyst layer transferred and embedded in the membrane



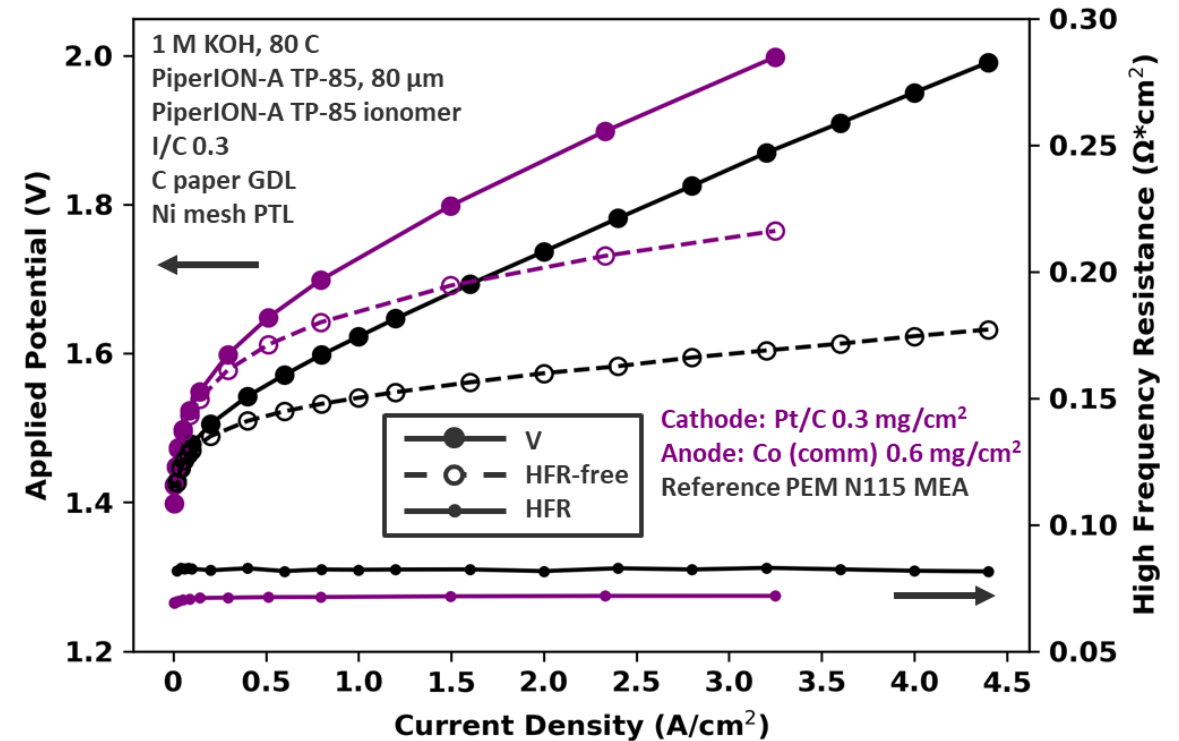


LTE 2.0 Accomplishments:

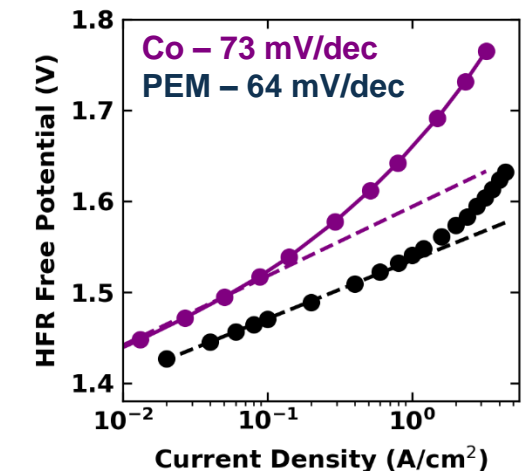
Technology Milestone, Supporting Electrolyte

Name/ Description	Incorporating experiment and modeling, down-select AEM supporting electrolytes (type, concentration) and operating conditions (materials choices, flow configurations, temperature) that demonstrating cell overvoltage within 50 mV (HFR-free) of commercial Nafion at 1 A/cm ² .
Criteria	Demonstrate AEMWE in a supporting with a cell overvoltage within 50 mV (HFR-free) of commercial Nafion at 1 A/cm ² .

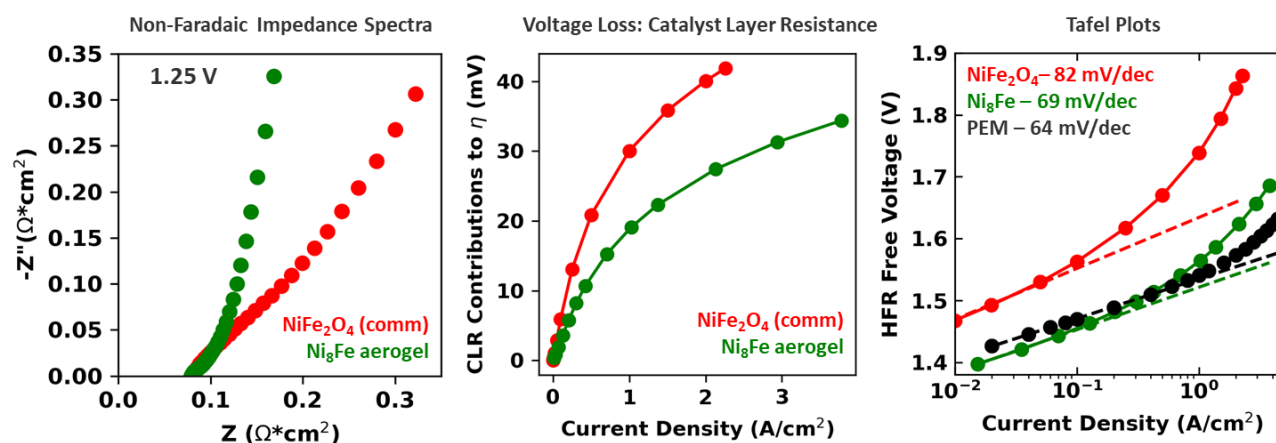
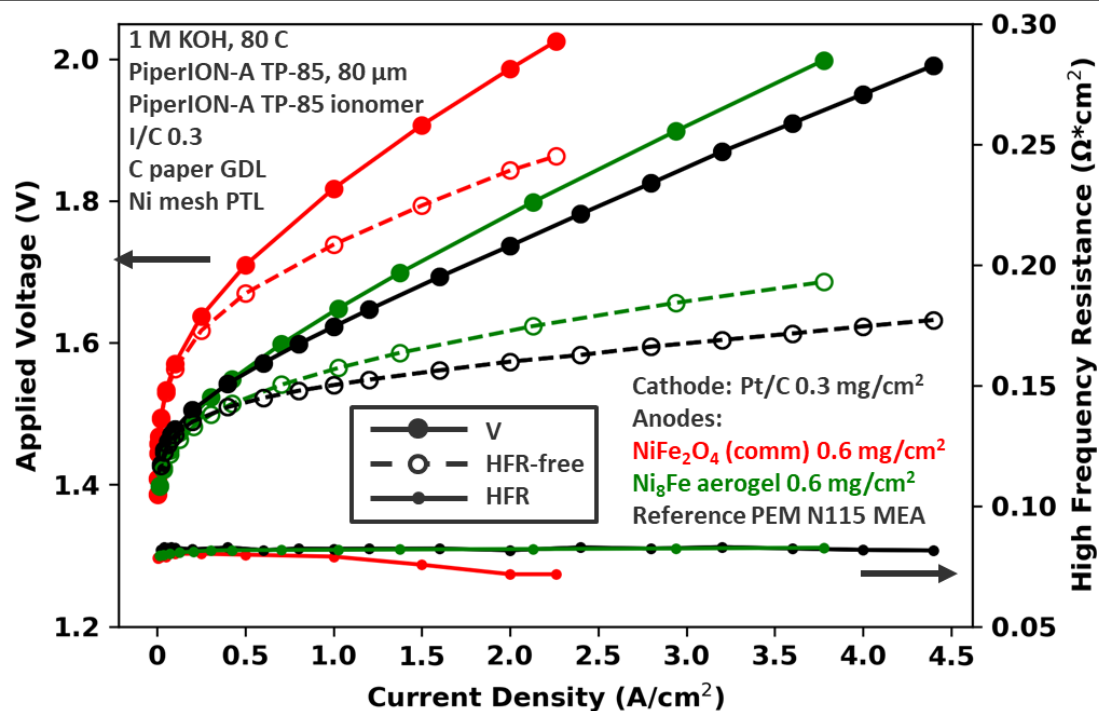
- Milestone related to performance, comparison to Nafion/PEM
- AEM performance challenges, HFR-free:
 - Poor anode catalyst kinetics
 - Large catalyst layer resistance penalty, particularly for low conductivity, commercial non-PGM oxides
 - Catalyst layer challenges of balancing site-access and mechanical integrity, conductivity and passivation, interfacial engineering and materials availability




1.655 (HFR-free) at 1 A/cm ² Q4 milestone: 1.591 V (HFR-free) at 1 A/cm ²				
	HFR	CLR	Tafel	V @ 1
	(Ω*cm ²)	(Ω*cm ²)	(mV/dec)	A/cm ²
				(HFR-free)
Co	0.071	0.074	73	1.728 (1.655)
PEM	0.083	0.008	64	1.623 (1.541)



Milestone (9/30/2023): LTE Catalyst Testing in AEM MEA. **Criteria:** Incorporating ElectroCat-developed catalysts, demonstrate cell overvoltage reduction of more than 50 mV (HFR-free) compared to commercial baseline catalysts (NiFeO_x, established in HydroGEN EMN) at 1 A/cm². Comparisons between novel and commercial catalysts would maintain consistent supporting electrolytes (1 M KOH) and operating conditions, including materials choices, flow configurations (wet/wet), and temperature (80 °C).



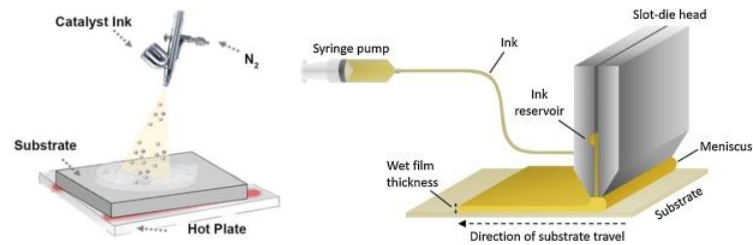
System	HFR (Ω cm ²)	CLR (Ω cm ²)	Tafel (mV/dec)	V _{HFR-free} (V) at 1.0 A cm ⁻²
NiFe ₂ O ₄	0.078	0.197	82	1.739
NiFe 8:1	0.082	0.078	69	1.559
PEM 115 MEA	0.083	0.008	64	1.541

- Highlight:** ElectroCat FY23 annual milestone **exceeded** by **130 mV** with NiFe 8:1 catalyst – 1.559 V vs. 1.739 V baseline established with NiFe₂O₄ catalyst
- Highlight:**  By reaching *iR*-free voltage of 1.559 V NiFe 8:1 catalyst also meeting the **HydroGEN FY23 Q4 milestone:** “Demonstrate AEMWE in a supporting electrolyte with a cell overvoltage within 50 mV (HFR-free) of commercial Nafion at 1 A/cm²”. (Voltage reached with NiFe catalyst within 18 mV of the PEM 115 MEA performance.)

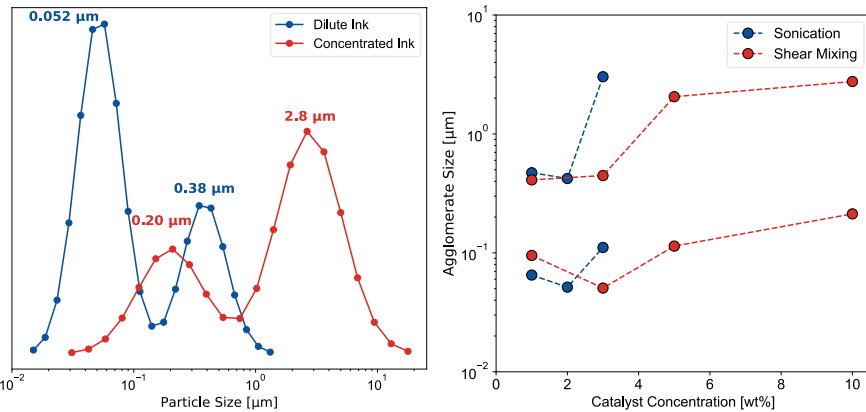


LTE 2.0 Accomplishments: Ink Characterization and Catalyst Layer Fabrication

Compared airbrush (dilute ink, ~1wt% catalyst) to slot die (concentrated ink, ~10 wt% catalyst) electrode fabrication



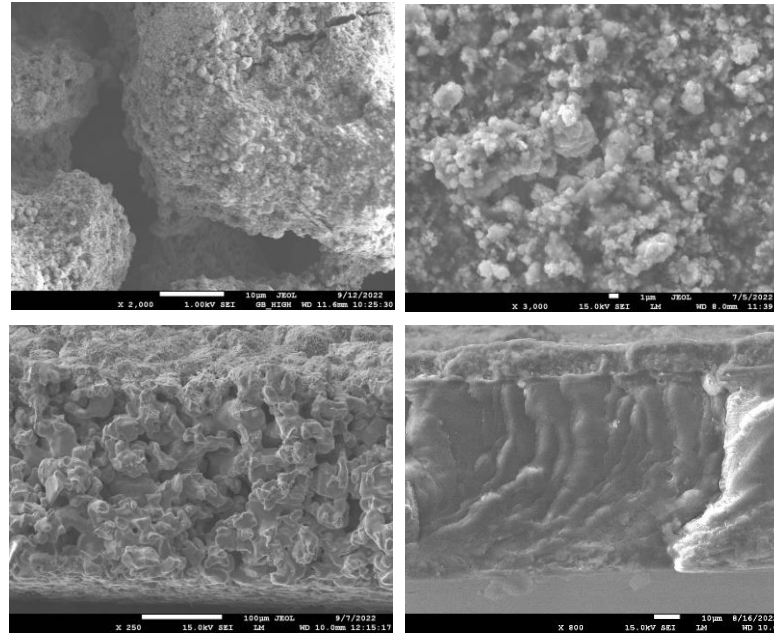
Increasing ink concentration results in larger catalyst/ionomer agglomerates



Larger agglomerates result in larger catalyst particles in the electrode catalyst layer

Airbrush Catalyst Layer

Slot Die Catalyst Layer

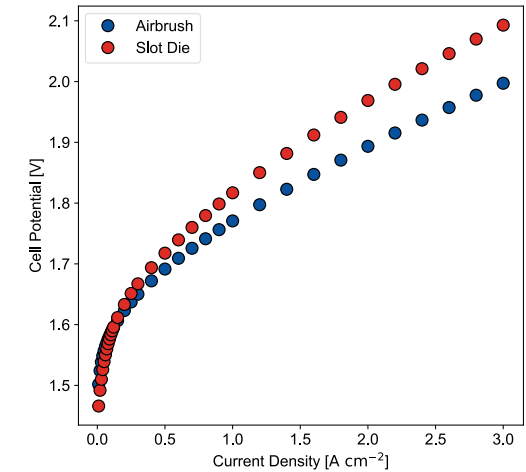


Airbrush PTE Cross Section

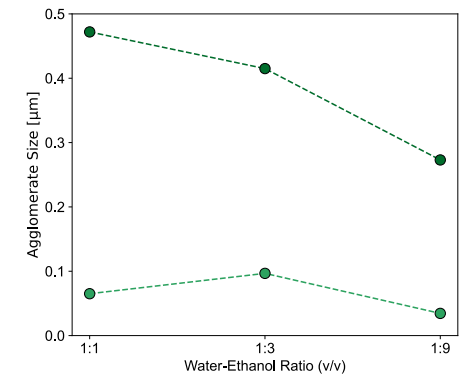
Slot Die CCM Cross Section

- Catalyst ink concentration influences agglomerate size, catalyst layer properties, and ultimately cell performance
- Controlling ink properties will require tuning of concentrated ink formulations

Significant difference in cell performance based on fabrication method



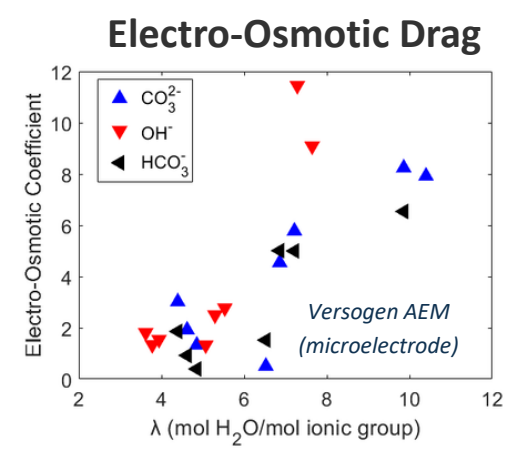
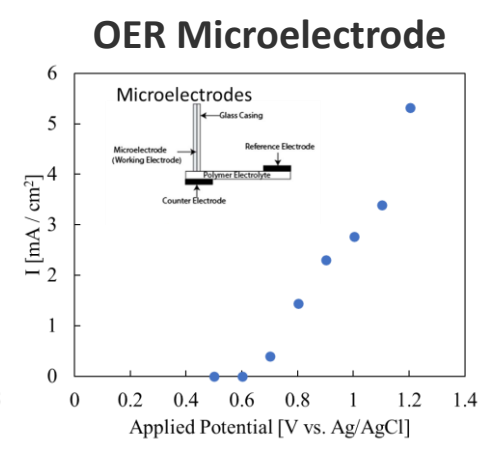
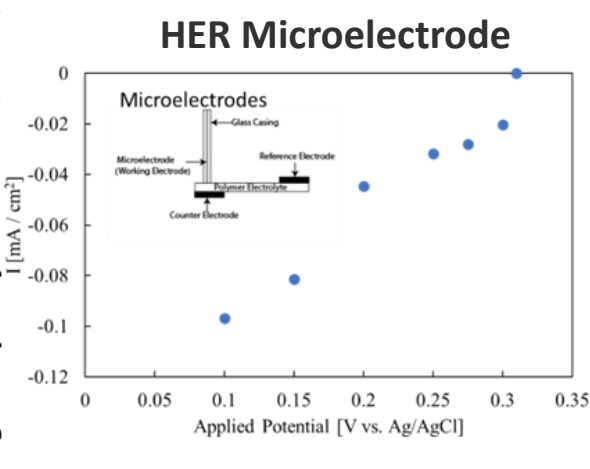
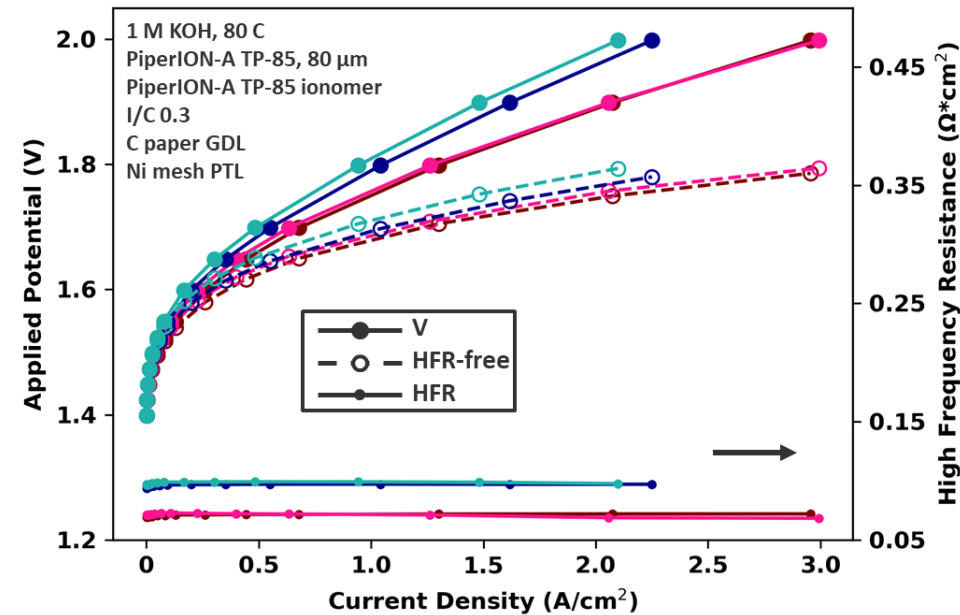
Ink formulation can be used to control agglomerate size



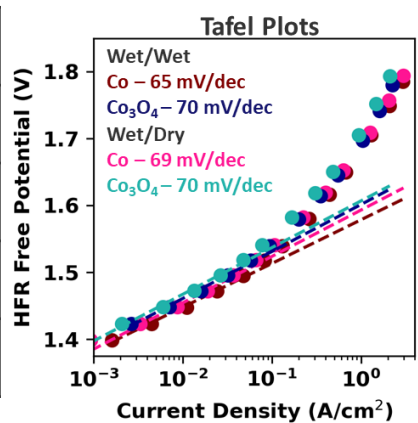


LTE 2.0 Accomplishments:

Cathode Water Consumption and Effects of Dry Operation



	HFR (Ohm*cm²)	CLR (Ohm*cm²)	Tafel (mV/dec)
Co wet/wet	0.072	0.072	65
Co wet/dry	0.071	0.073	69
Co ₃ O ₄ wet/wet	0.096	0.239	70
Co ₃ O ₄ wet/dry	0.096	0.345	70

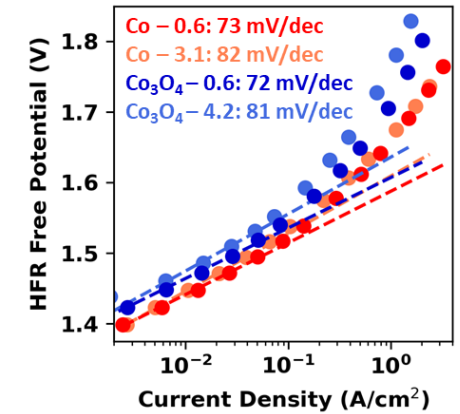


- Cathode a larger concern in anion exchange membrane (AEM) electrolysis
 - Kinetics and transport are factors
 - Poor catalyst-ionomer interaction at the hydrogen electrode (microelectrode)
- Feeding electrolyte to the anode simulates backpressure and requires transport across the membrane to the cathode (electro-osmotic drag)
- **Anode only feed has minimal effect on initial performance for Co and Co₃O₄ catalysts**

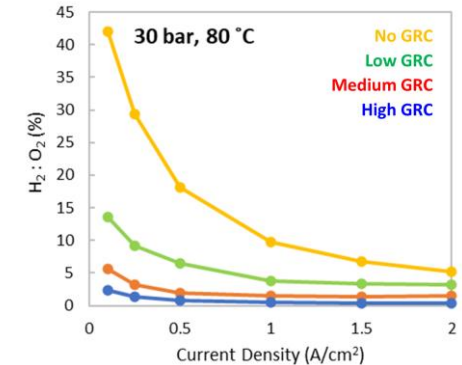


Summary of Accomplishments

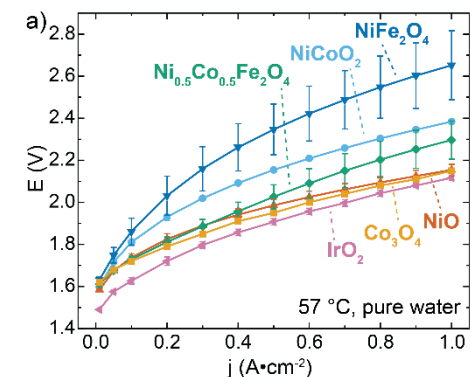
- LTE 2.0
 - Doping nickel oxide (NiO) with cobalt, iron can both stabilize ionomers and enhance OH* adsorption, comparable to iridium oxide (IrO₂), potentially increasing catalyst durability and oxygen evolution activity
 - Screening of commercial materials improved membrane electrode assembly kinetics to approach technology target
 - Incorporated diagnostics that improved resolution of loss type and cause. Materials challenges including balancing site-access and mechanical integrity, catalyst/transport layer conductivity and passivation, and nonideal interfacial contact, all affect performance of the technology.
- (P185) P. Kohl. Minimized durability losses (30 μ V/1000 hr at 1.77 V for 270 hr at 1 A/cm²) and distinguish between degraded materials (catalyst, ionomer, PTL, AEM) and harmless conditioning of nickel, stainless steel, or other components.
- (P186) A. Park. Quantified effect of GRC loading and identified membrane protrusion into the PTL as potential risk factor for hydrogen crossover stability. Making GRC membranes more resistant to topographical changes has been a priority.
- (P187) S. Boettcher. Identified and characterized key degradation modes of AEM electrolysis in pure and contaminated water associated with ionomer oxidation at the anode and develop new catalyst and mitigation strategies for high performance and durability.



P186 A. Park



P187 S. Boettcher





Future Work

- LTE 2.0
 - Optimize catalyst layer composition and processing technique to improve site-access, catalyst layer resistances, and device performance
 - Understand the impact of catalyst layer composition on performance in a supporting electrolyte
 - Delineate the impact of electrolyte conductivity and alkalinity on performance and durability
 - Address delamination and longer-term durability due to catalyst layer processing and reordering
- Leverage HydroGEN nodes to enable successful completion and continuation of the seedling projects, depending on which budget period they are in

Any proposed future work is subject to change based on funding levels



Responses to Reviewers

The demarcation of HydroGEN 2.0 and Hydrogen from Next-generation Electrolyzers of Water (H2NEW) based on current technology readiness levels (TRLs) is smart and practical to move the two consortiums forward. It is a good idea to focus HydroGEN 2.0 on low-TRL areas of AWS R&D, since low-temperature polymer electrolyte membrane (PEM) electrolyzers are far more advanced compared to other AWS routes. Although the HydroGEN 2.0 scope seems to specifically exclude PEM-based LTE technologies, it is not clear why PEM electrolysis projects are still in the portfolio.

- The Chemours seedling (P146, A. Park) is the only HydroGEN EMN effort in PEM-based LTE technologies. This seedling began in 2019, prior to the demarcation of HydroGEN/H2NEW and has met milestone and GNG decisions.



Collaboration, Effectiveness

- Interfacing between HydroGEN and IEA Annex 30 in benchmarking
- Interfacing between HydroGEN and ElectroCat in catalyst benchmarks
- Contributions to the Meta Data development for the HydroGEN Data Center

Seedling Leads

Shannon Boettcher
Paul Kohl
Andrew Park

Seedling Teams



LTE 2.0 Team



Shaun Alia
Ai-Lin Chang
Huyen Dinh
Mai-Anh Ha
Melissa Kreider
Ross Larsen
Doug Marsh
Bryan Pivovar
Meital Shviro
Emily Volk



Grace Anderson
Tugrul Ertugrul
Xiong Peng
Johnny Petrovick
Andrew Tricker
Adam Weber



Josh Sugar
Jamie Trindell
Arielle Clauser



Presentations and Publications

Publications

- E.K. Volk, S. Kwon, S.M. Alia, “Catalytic activity and stability of non-platinum group metal oxides for the oxygen evolution reaction in anion exchange membrane electrolyzers,” *Journal of the Electrochemical Society* (2023) [Under Review]
- A. W. Tricker, J. L. Lee, J. R. Shin, N. Danilovic, A. Z. Weber, X. Peng, “Design and operating principles for high-performing anion exchange membrane water electrolyzers,” *Journal of Power Source* 567 (2023) 232967, <https://doi.org/10.1016/j.jpowsour.2023.232967>

Presentations

- S. Intikhab, E.K. Volk, R.R. Beswick, H. Yu, D.A. Cullen, S. Kwon, S.M. Alia, “Materials Integration, Catalyst-Ionomer Interfaces, and Durability Implications in Anion Exchange Membrane-Based Low Temperature Electrolysis” 243rd ECS Meeting (May 28 – June 2, 2023)
- E.K. Volk, R.R. Beswick, S. Kwon, S.M. Alia, “Electrochemical Activation of NiFe₂O₄ for the Oxygen Evolution Reaction in Alkaline Media” 243rd ECS Meeting (May 28 – June 2, 2023)
- S.M. Alia, S. Intikhab, M.-A. Ha, S. Ghosal, “(Invited) Materials Integration, Durability, and Perspectives in Anion Exchange Membrane-Based Low Temperature Electrolysis” 241st ECS meeting (May 29 – June 2, 2022)
- E.K. Volk, “Establishing half- and single- cell baselines for the oxygen evolution reaction (OER) on non- platinum group metal (PGM) oxide electrocatalysts in alkaline media”, Poster Presentation, International Conference on Electrolysis, (July 2022)
- E.K. Volk, “Establishing half- and single- cell baselines for the oxygen evolution reaction (OER) on non- platinum group metal (PGM) oxide electrocatalysts in alkaline media”, Oral Presentation, ACS Colloids and Surface Science Symposium, (July 2022)
- X. Peng, “The Cutting-edge in Clean Electrolysis for Green Hydrogen Production”, Invited talk, U.S. Frontiers of Engineering Symposium (September 22, 2022)
- X. Peng, “Pathways to Terawatt Scale Electrolysis— Importance of Interfaces and Underexplored Opportunities”, Fuel Cell Gordon Research Conference (July 27, 2022)
- A. W. Tricker, “Tuning Catalyst-Ink Formulations for Blade Coating of Hydroxide-Exchange-Membrane Water Electrolyzers”, 242nd ECS meeting (October 9-13,2022)