DOE Hydrogen Program
2024 Annual Merit Review and Peer Evaluation Meeting
May 6 – 9, 2024, Arlington, Virginia

ElectroCat 2.0
(Electrocatalysis Consortium)

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Project ID: FC160

This presentation does not contain any proprietary, confidential, or otherwise restricted information

Overview

Timeline

- **Start date**: Oct 1, 2020
- **End date**: Sep 30, 2025

Budget

- **FY23 DOE Funding:** $4M
- **FY24 Planned DOE Funding:** $4M
- **Total DOE Funds Received to Date:** $14.5M

Barriers

- **A. Cost** (catalyst)
- **D. Activity** (catalyst; MEA)
- **B. Durability** (catalyst; MEA)
- **C. Power density** (MEA)

Laboratory – PI

Los Alamos National Laboratory

Los Alamos NATIONAL LABORATORY – Piotr Zelenay

Argonne National Laboratory

Argonne NATIONAL LABORATORY – Deborah Myers

National Renewable Energy Laboratory

NREL NATIONAL RENEWABLE ENERGY LABORATORY – Derek Vigil-Fowler
Shaun Alia

Oak Ridge National Laboratory

OAK RIDGE National Laboratory – David Cullen

Relevance and Goals

Heavy-Duty Transportation Fuel Cell Targets (2025)

- Durability: 25,000-hour lifetime
- 68% peak efficiency
- $80/kW fuel cell system cost
- **Overall Target:** 2.5 kW/g_{PGM} power (1.07 A cm^{-2} current density at 0.7 V after 25,000 hour-equivalent accelerated durability test)

Liquid Alkaline Electrolyzer Stack Goals (2026)

- Durability: 80,000-hour lifetime
- 69% efficiency at 1 A cm^{-2}
- $50/kW
- **Overall Target:** $2/kg H_2 over 80,000-hour lifetime

End-of-consortium Goals:

Fuel Cell: H_2-air performance of ≥ 100 mA/cm^2 at 0.8 V and ≥ 500 mA/cm^2 at 0.675 V at beginning of test (BOT) and ≥ 80 mA/cm^2 and ≥ 400 mA/cm^2 after 30,000 AST cycles (0.6 V to OCV, 3 s each, H_2-air), respectively, under integral conditions for a PEMFC with a PGM-free oxygen reduction catalyst

Electrolyzer: 2.5-fold increase, from 0.2 A/cm^2 to 0.5 A/cm^2 at 1.8 V and reduction in the voltage loss at a reference current density of 0.2 A/cm^2 from 0.2 mV/h to 0.1 mV/h with anion-exchange membrane electrolyzer using PGM-free oxygen and hydrogen evolution catalysts*

*Goal currently being updated based on progress of ElectroCat to date

FY23 Q3 Fuel Cell Quarterly Progress Measures and Annual Milestones

Milestone Name/Description	Criteria	End Date	Type	Status
ORR activity surrogate models	Demonstrate (develop and integrate) first surrogate models of ORR activity into Pareto optimization scheme using DFT model input to identify (atomic and electronic) structural descriptors of activity. **(LANL)**	6/30/2023	Quarterly Progress Measure (Regular)	**Complete** See slide #16
PEFC H_2-air fuel cell performance improvement through cathode catalyst layer composition optimization	Evaluate 25 variations of ionomer to catalyst ratio and solvent composition of ink for best-in-class ANL PGM-free electrode. Characterize structure of electrode layers using electron microscopy. (**ANL, ORNL**)	6/30/2023	Quarterly Progress Measure (Regular)	**Complete** See slide #15
Effect of Nafion polymer fragments on binding at Fe-N-C active site	Compute adsorption energies for O_2, NO, and OH on the Fe bulk under applied potential and in the presence of Nafion fragments at 3 different locations. (**NREL**)	6/30/2023	Quarterly Progress Measure (Regular)	**Complete** See slide #18
ORR catalyst performance in H_2-air fuel cell	Current density of ≥ 85 mA cm^{-2} at 0.80 V and ≤ 40 mV voltage loss at 0.80 A cm^{-2} after 30,000 catalyst AST cycles. (**LANL, ANL, ORNL**)	9/30/2023	Annual Milestone (Regular)	**Complete** See slide #9
Upgrade of ElectroCat Data Hub	Complete release of the update to the ElectroCat Data Hub, with all data migrated. (**NREL**)	9/30/2023	Annual Milestone (Regular)	**Partially Complete***

*The core data hub plugins have been updated to a newer version that meet new DOE standards. Additional work was performed to prepare and test an upcoming release as well as upgrade long term architecture and deployment infrastructure. Staffing issues prevented the full release of these developments.

FY24 Fuel Cell Quarterly Progress Measures and Annual Milestones

Milestone Name/Description	Criteria	End Date	Type	Status
Data Hub	Upload cell data, electron microscopy images, and DFT results to ElectroCat datahub for future ML efforts. Download and utilize these data in ML activities. **(All Labs)**	12/31/2023	Quarterly Progress Measure (Regular)	**Complete**
Machine learning-guided synthesis and characterization of ORR catalysts	Develop a new iteration of the adaptive learning loop based on most current experimental data and identify the four most promising samples for synthesis conditions to further decrease the ML model uncertainty and/or discover new catalysts with improved activity or stability. Perform advanced characterization (e.g., by microscopy, XAS) of select samples, focusing on the nature of ORR active site. **(LANL, ANL)**	3/31/2024	Quarterly Progress Measure (Regular)	**Complete** See slides #12,13
ORR modeling methodology	Develop agreed upon modeling methodology for DFT-derived activity, stability, and spectroscopy descriptors including utilized code, treatment of potential, and solvation. Finalized methodology will be quantitatively compared against a standard computational hydrogen electrode (CHE) approach to identify relative importance of additional modeling steps. **(LANL)**	6/30/2024	Quarterly Progress Measure (Regular)	**On track**
ORR catalyst performance in H_2-air fuel cell	Current density of >=90 mA cm^{-2} at 0.80 V and ≤ 35 mV voltage loss at 0.80 A cm^{-2} after 30,000 catalyst AST cycles. **(LANL, ANL)**	9/30/2024	Annual Milestone	**Complete** See slide #9

Safety

- ElectroCat is NOT required to submit a safety plan for review by the Hydrogen Safety Panel
- Every National Lab has a rigorous DOE-approved Safety Procedure which is regularly reviewed and monitored by cognizant DOE Field Offices
  - **LANL:** Integrated Safety Management (ISM) by an Integrated Work Management (IWM) process
  - **ANL:** Work Planning and Control (WPC) which uses ISM
  - **NREL:** WPC with ISM
  - **ORNL:** Research Hazard Analysis and Control (RHAC) System

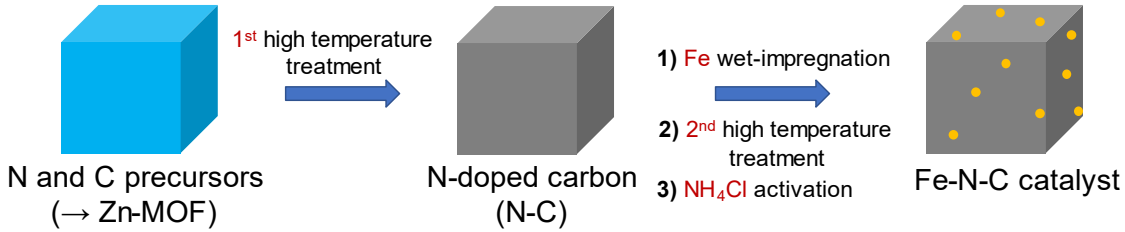
- **Integrated Safety Management Process can be described:**
  - **Define the scope of work**
    - What are you going to do?
    - Do I know how to perform this work and if not, what training do I need
  - **Analyze hazards associated with the work**
    - What are the hazards to people, environment, and equipment?
    - What can go wrong?
  - **Develop and implement hazard controls**
    - How can the hazards be eliminated/mitigated?
    - Are the necessary controls in place?
  - **Perform work within controls**
    - Follow the plan that incorporates the controls and be aware of any new hazards
  - **Provide feedback and continuous improvement**
    - Make sure people who need to know are aware of successes and issues



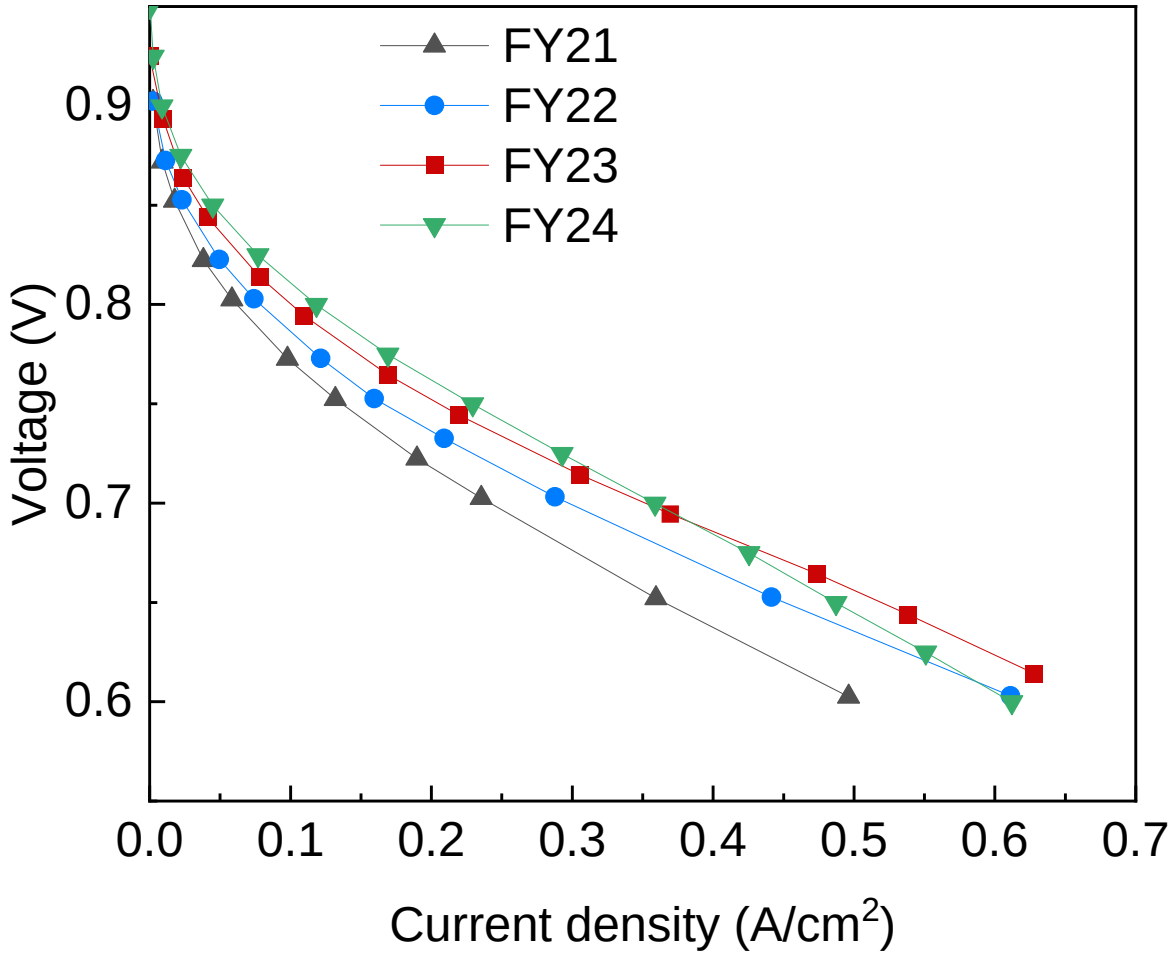
Improved Initial MEA Performance of Fe-N-C Catalysts

Cathode: *ca. 4*.0 mg cm^{-2}, Fe-N-C catalysts, 1700 sccm, 1.0 bar air partial pressure, 100% RH; **Anode:** 0.3 mg_{Pt} cm^{-2} Pt/C, H_2, 700 sccm, 1.0 bar H_2 partial pressure, 100% RH; **Membrane:** Nafion® 211; **Cell:** differential, 5 cm^2, **Temperature:** 80 °C.

Two-step, ammonia chloride activation synthesis of Fe-N-C catalyst (FY24):



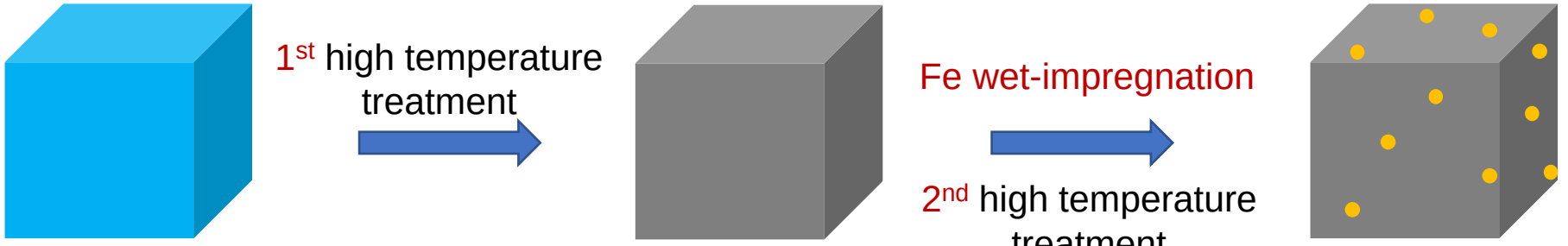
Current density at 0.80 V (mA cm^{-2})			
FY21	**FY22**	**FY23**	**FY24**
61	79	97	117



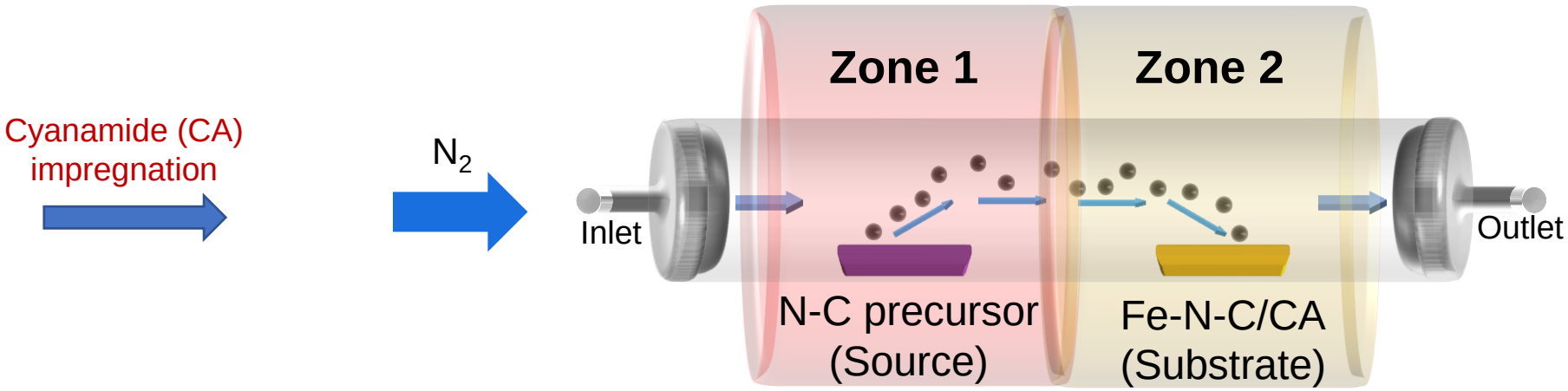
Highlight: Fe-N-C catalyst developed via a two-step, ammonia chloride (NH_4Cl) activation approach showing ~21% (at 0.80 V) performance improvement over FY23

Combining Two-step Synthesis with Dual-Zone Approach; Additional Nitrogen Precursors

Two-step synthesis

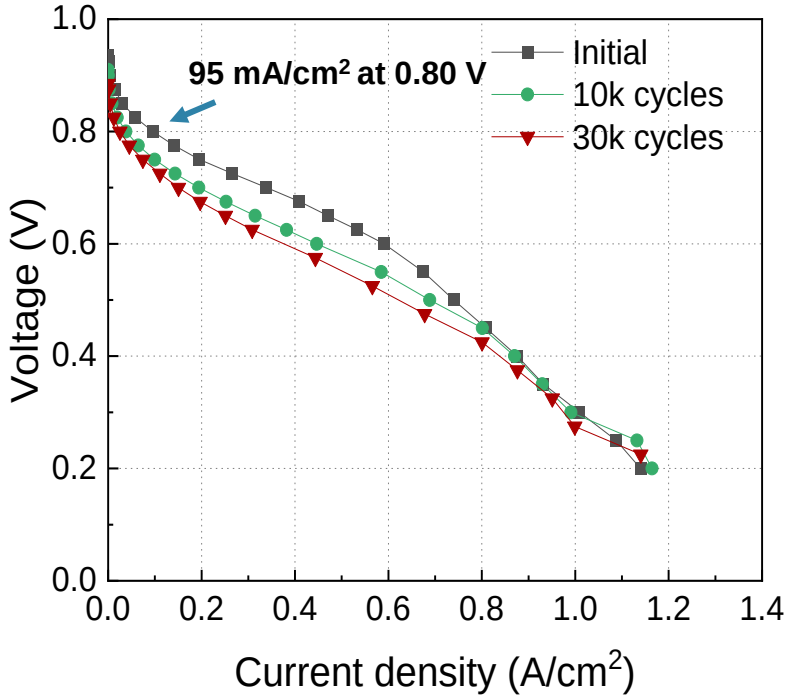


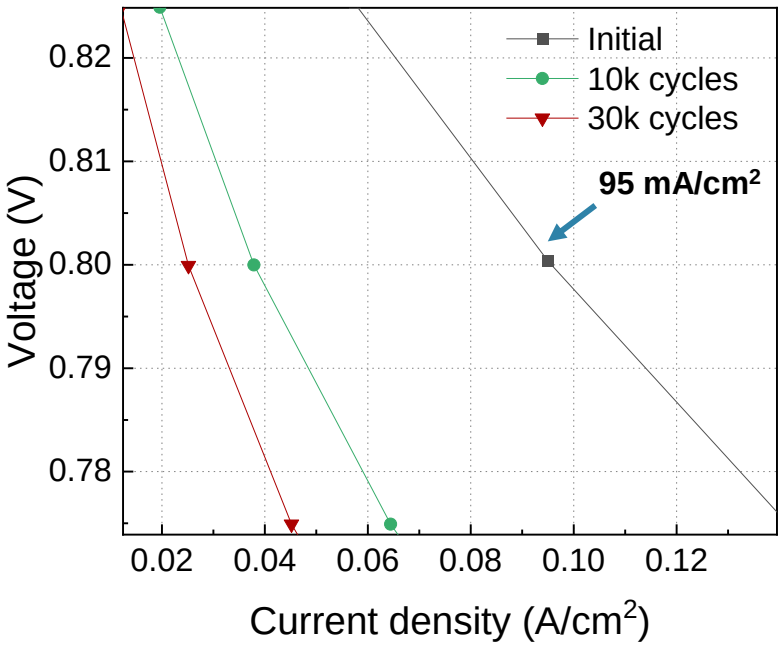
'Dual-zone' synthesis

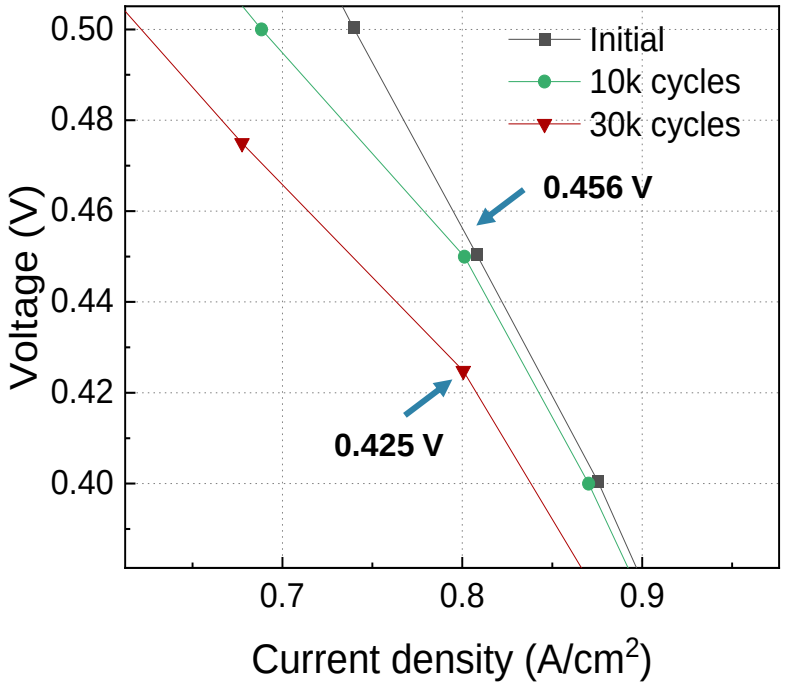


FY23 and FY24 Annual Milestones Exceeded with N-C/Fe-CA-DZ Catalyst

Cathode: *ca.* 5.8 mg cm^{-2}, N-C/Fe$_{1.5}$-CA-DZ catalyst, 1700 sccm, 1.0 bar air partial pressure, 100% RH; **Anode:** 0.3 mg$_{Pt}$ cm^{-2} Pt/C, H_2, 700 sccm, 1.0 bar H_2 partial pressure, 100% RH; **Membrane:** Nafion® 211; **Cell:** differential, 5 cm^2, **Temperature:** 80 °C. **AST:** square-wave cycle from (OCV-0.01) V to 0.60 V



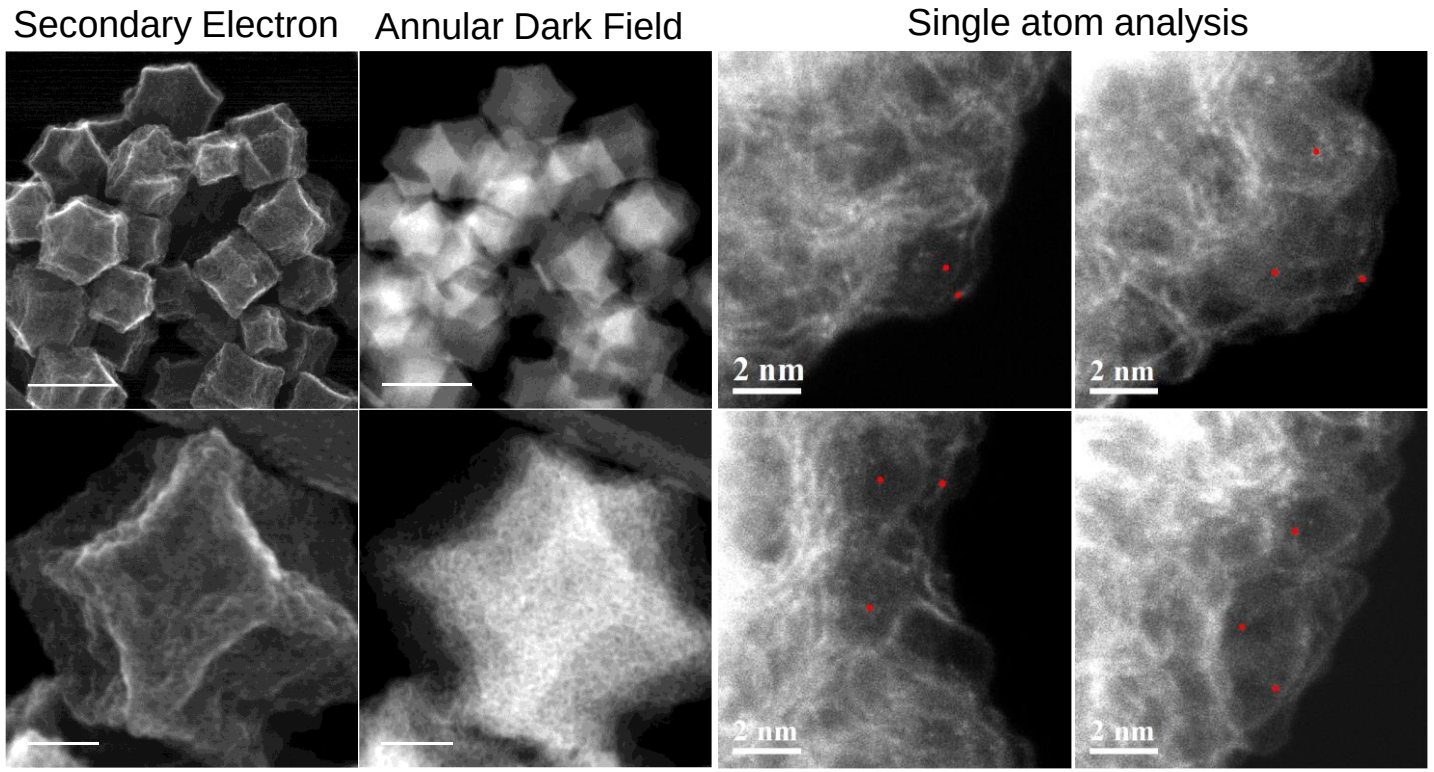




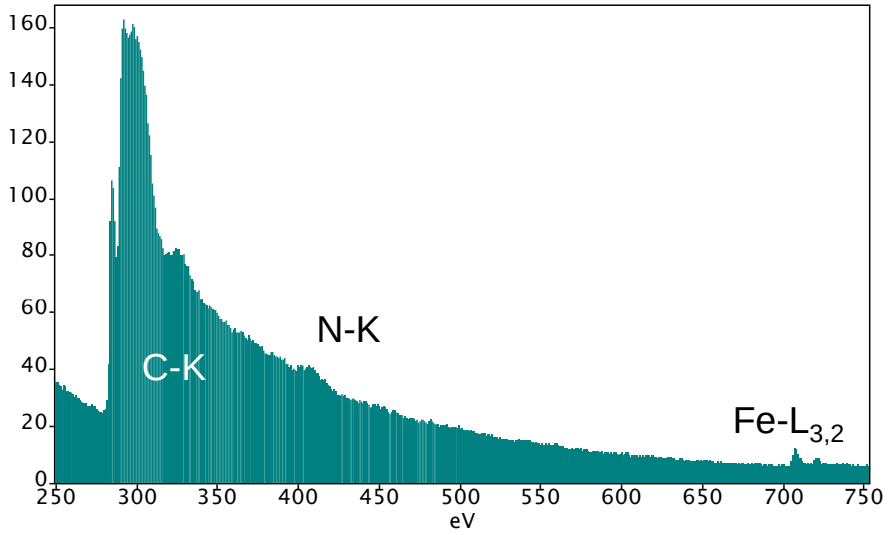
Metrics	FY23 annual milestone	FY24 annual milestone	N-C/Fe$_{1.5}$-CA-DZ
Current density at 0.80 V (initial)	≥ 85 mA/cm^2	≥ 90 mA/cm^2	95 mA/cm^2
Voltage loss at 0.80 A/cm^2 (30k cycles)	≤ 40 mV	≤ 35 mV	31 mV

- **FY24 Annual Milestone:** ≥ *90 mA/cm^2 at 0.80 V for initial and ≤ 35 mV loss at 0.80 A/cm^2 after 30k AST cycles*
- **Highlight: 95 mA/cm^2** at 0.80 V for initial and **31 mV** loss at 0.80 A/cm^2 after 30k AST cycles, **exceeding FY24 Annual Milestone**

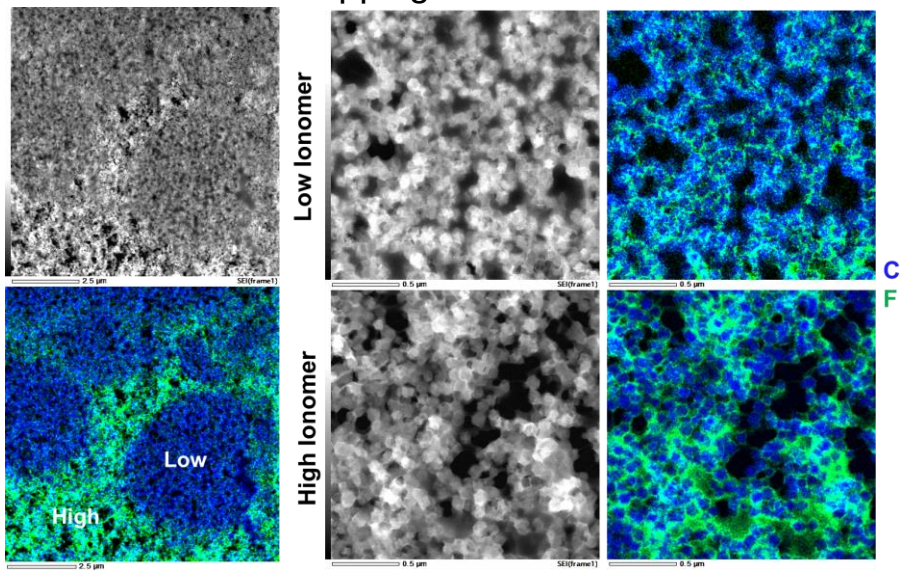
Electron Microscopy Characterization of N-C/Fe-CA-DZ Catalyst



Summed EELS point spectra from ten sites



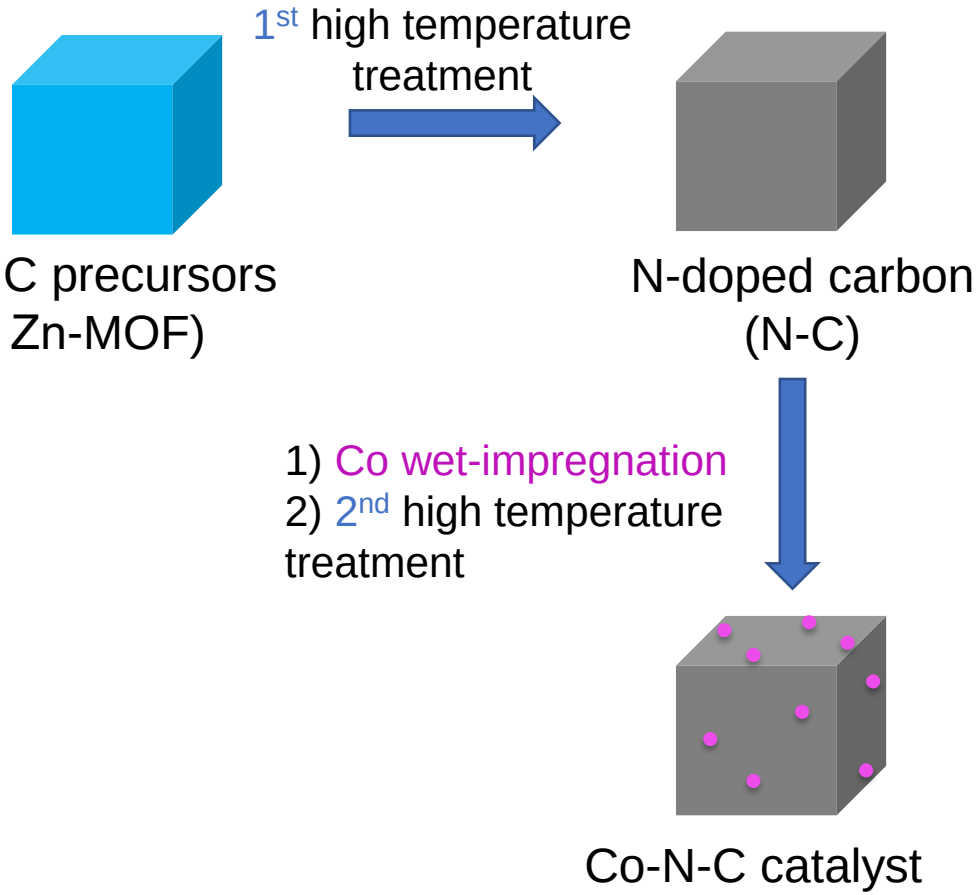
STEM-EDS Mapping of Ionomer Distribution



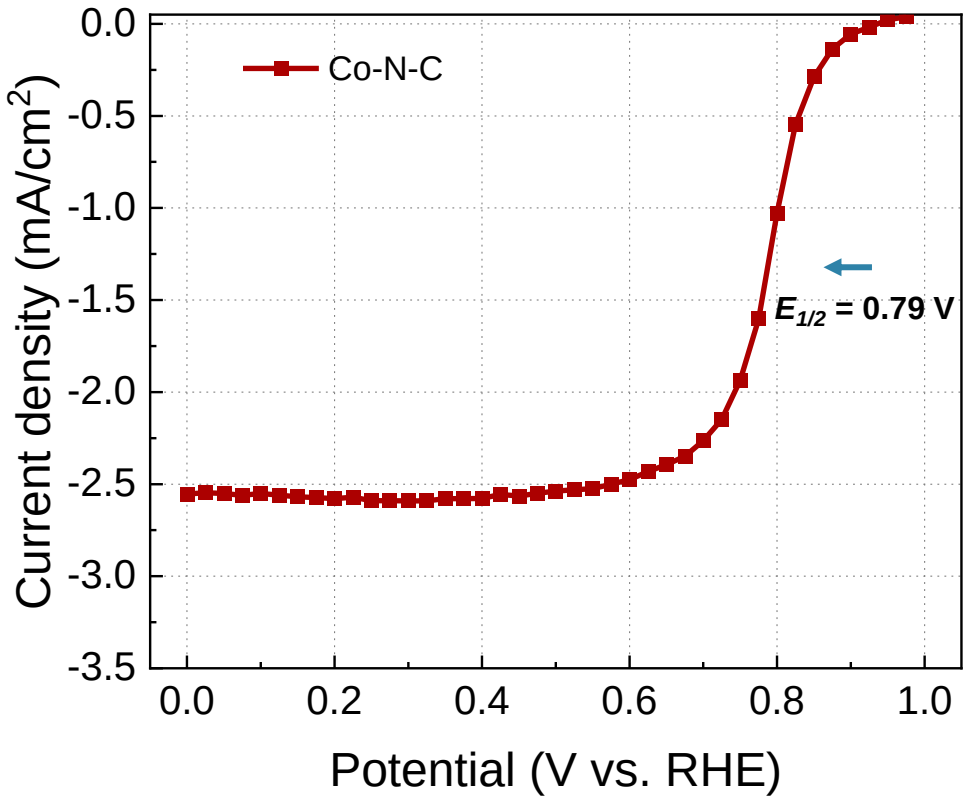
- Nitrogen content is lower than in previous generations of atomically-dispersed ORR catalysts
- Catalyst particles maintain rhombic dodecahedron shape and exhibit high microporosity and mesoporosity
- Fe atoms are much more stable under beam than previous generations
- Non-homogeneous ionomer distribution indicates room for further electrode optimization
- XAS, XPS, Raman, BET, and Mössbauer characterization is ongoing

Progress Towards Fe-free ORR Catalysts: Co-N-C Catalyst

Two-step synthesis of Co-N-C catalysts



Rotating ring electrode (RDE) measurement: catalyst loading: 0.6 mg/cm^2; O_2 saturated 0.5 M H_2SO_4; 900 rpm; 25 ºC; staircase voltammetry: 25 mV step, 45 s



- Two-step synthesis for Fe-free PGM-free ORR catalysts
- Promising RDE performance of a Co-N-C catalyst with a half-wave potential of **0.79 V**

High-Throughput Synthesis of ORR Catalysts Guided by Machine Learning

Accomplishment

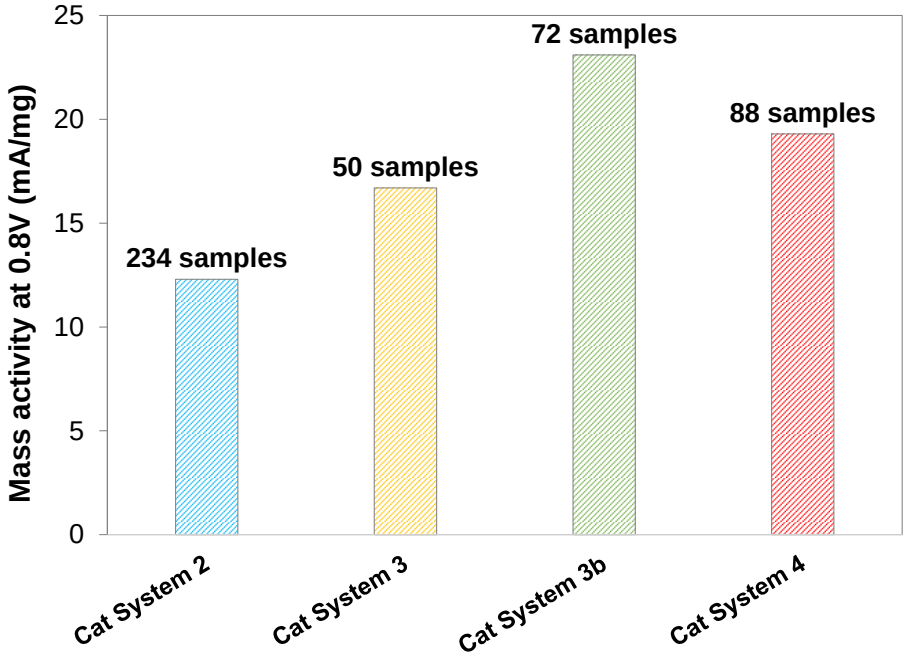
2: Ball milling of Fe salt + ZIF-8 and/or C; pyrolysis in horizontal furnace with NH_3 treatment
- BP vs ZIF-8
- Fe precursor identity
- Fe loading
- Cooling rate/mode
- Pyrolysis time, heating rate
- Pyrolysis temp.

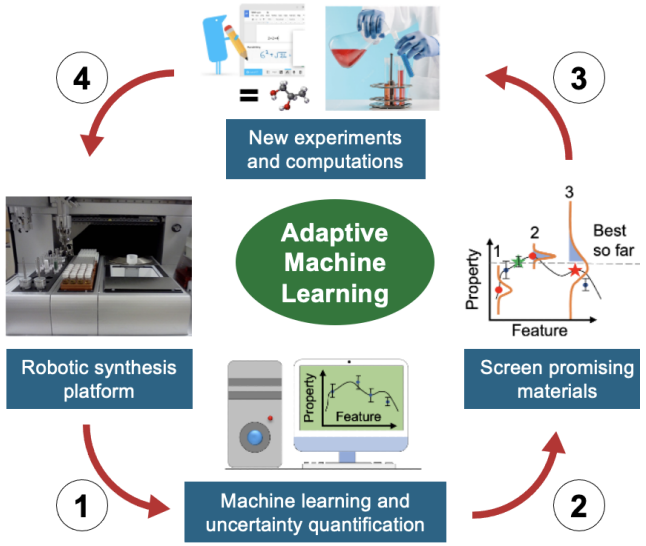
3: Ball milling of Fe + N-C; pyrolysis in horizontal furnace with NH_3 treatment
- N-C synthesis methods
- Fe precursor identity
- Fe loading
- Pyrolysis time, heating rate
- Pyrolysis temp.

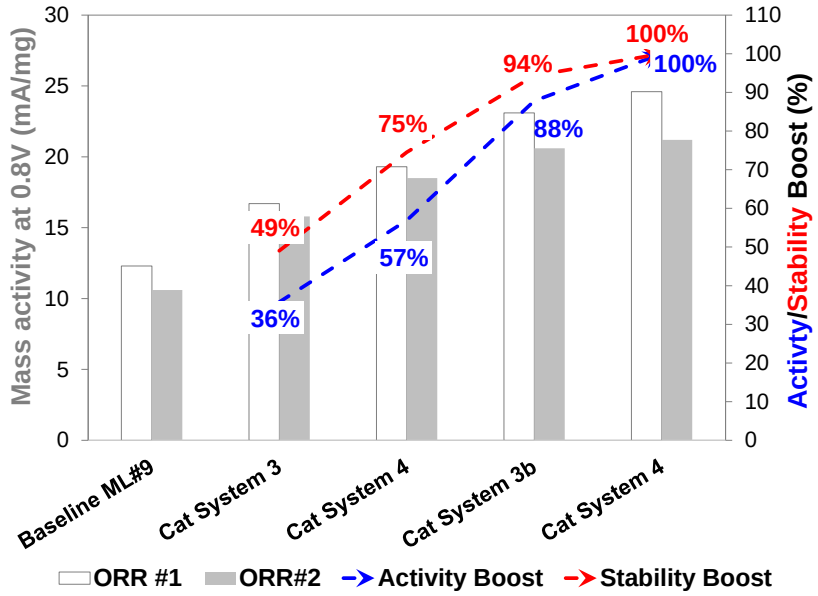
3b: Chemical vapor deposition of $FeCl_3$ into N-C in parallel vertical reactors
- N-C vs ZIF-8
- $FeCl_3$:N-C
- Additives (e.g., Sn, Co)
- Carbon coating
- CVD temp.
- Ball milling time

4: Ball milling of Fe_2O_3 NPs + ZIF-8; pyrolysis in vertical fixed-bed reactor
- Fe loading
- Phen:ZIF
- Fe_2O_3 particle size
- Pyrolysis temp./time
- Pyrolysis heating rate

- Exploring the efficacy of different ML optimization functions
- First iteration completed of ML model trained on initial 27 system #4 samples – 4 new synthesis conditions recommended to refine model
- **FY24 Q2 QPM:** 4 additional synthesis conditions recommended; synthesis underway **(QPM met)**







Highlight: Continuous improvement in mass activity within catalyst systems and faster optimization enabled by machine-learning guided high-throughput synthesis. 100% improvement in ORR activity and stability vs baseline.

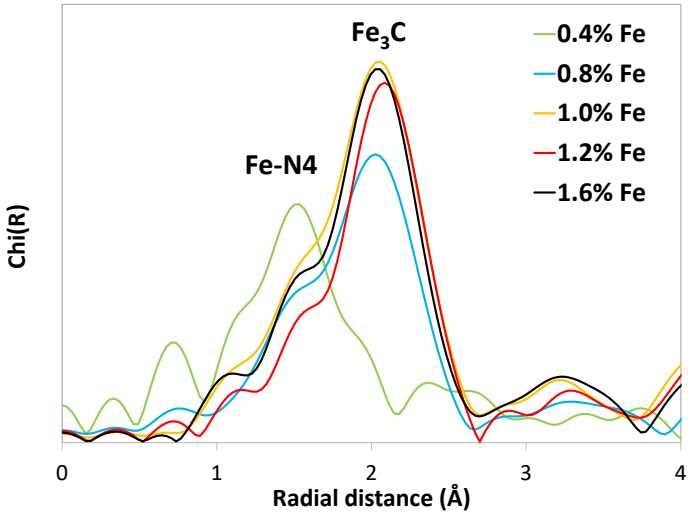
Publications: M. R. Karim *et al.*, *ACS Appl. Energy Mater.* 3, 9083 (2020).; W. J. M. Kort-Kamp *et al.*, *J. Power Sources* 559, 232583 (2023).; M.S. Ferrandon, et al., *Electrochim. Acta* 441, 141850, 2023.

System #4: Adaptive Learning Loop and High-throughput Data

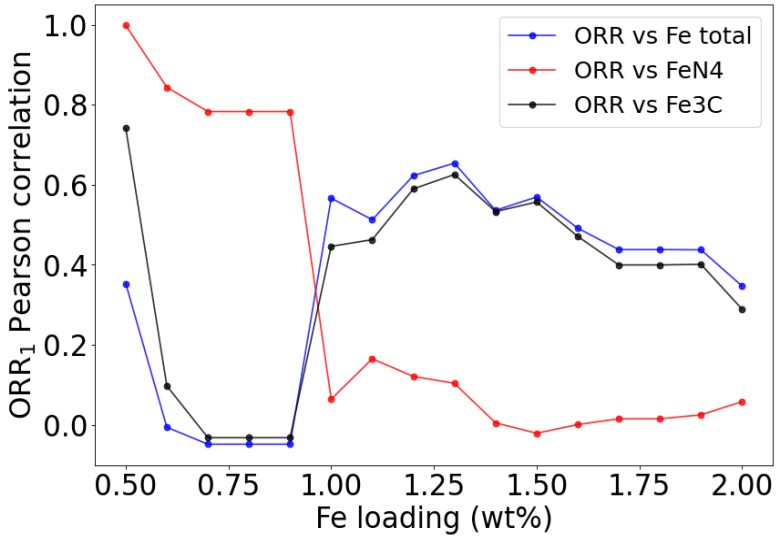
FY24 Q2 QPM: *Perform advanced characterization (e.g., by microscopy, XAS) of select samples, focusing on the nature of ORR active site.*

QPM complete: 26 samples analyzed by ex-situ XAFS at both Fe and Zn K edges (Cat system #4) and 13 samples by in-situ pyrolysis (effect of Fe precursors and ZIF-8 vs N-C). ML model included mass activity, stability, and composition of 26 samples.

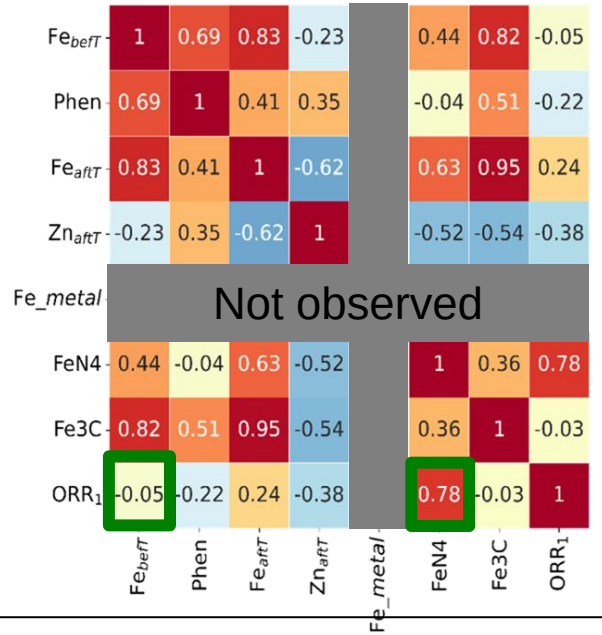
Catalyst composition by X-ray absorption spectroscopy



ML correlation of RDE-determined ORR activity and catalyst composition



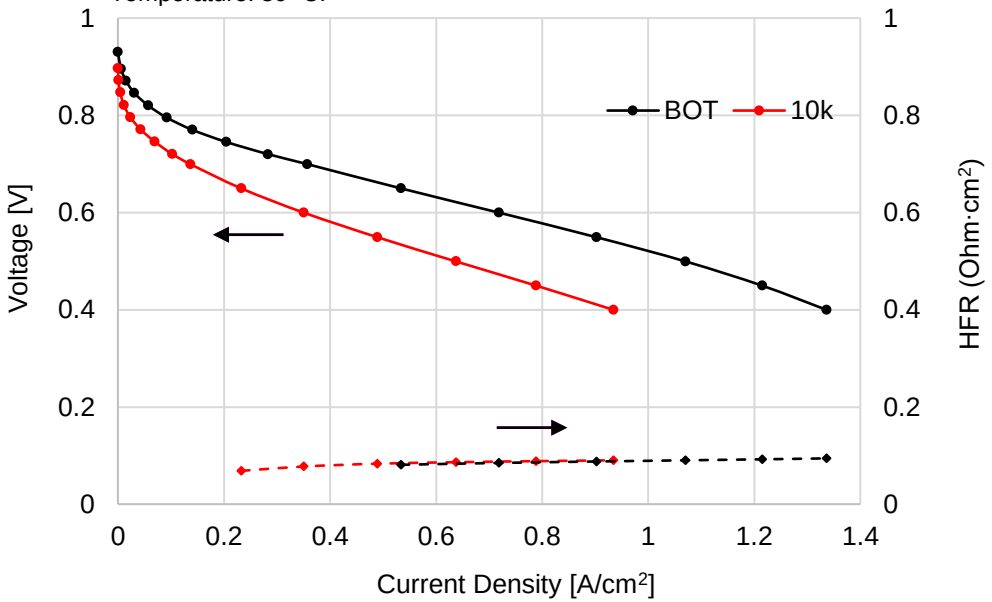
Pearson correlation: filtered data with Fe <1%

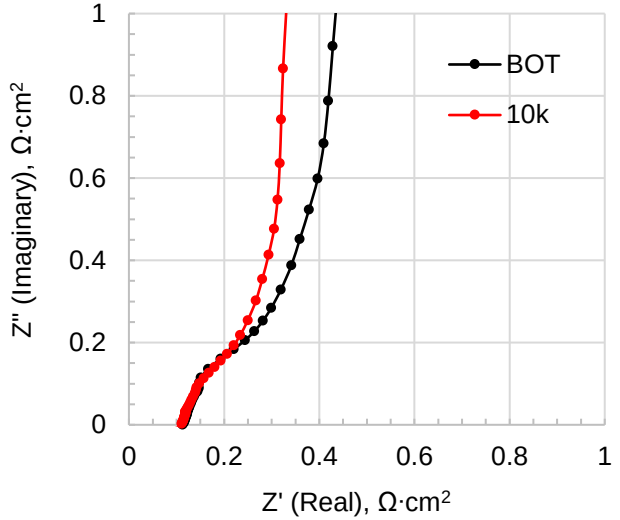


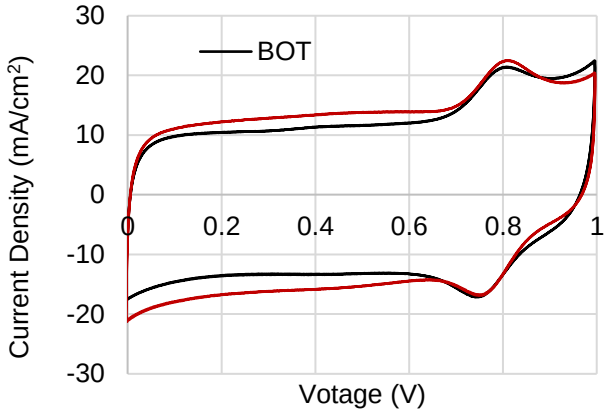
Highlight: Employed statistical data science analysis to **reveal that the nature of Fe sites is the most relevant factor governing high ORR activity** at low iron concentrations (< 1%)

Status of MEA H_2-Air Performance and Durability of High-Throughput Fe-N-C

Cathode catalyst: FeAc_ML9, 5.5mg cm^{-2}, I/C=0.8, 1700 sccm, 1.0 bar air partial pressure, 100 %RH; Anode: 0.3 mg_{Pt} cm^{-2} Pt/C, 700 sccm, 1.0 bar H_2 partial pressure, 100% RH; Membrane: Nafion 212; Cell: differential, 5 cm^2, Temperature: 80 °C.







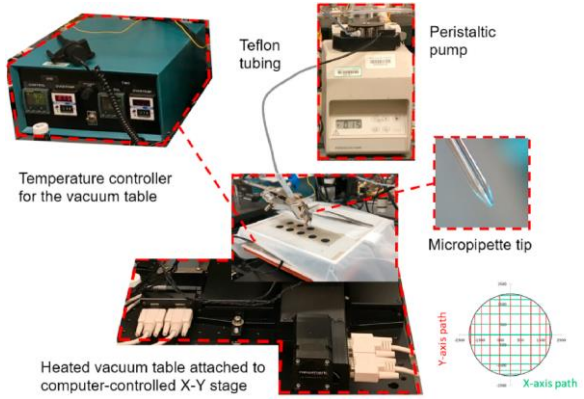
	mA/cm²		V
	0.8 V	**0.675 V**	**0.8 A/cm²**
BOT	**92**	445	0.57
10k AST cycles	23	185	0.43
2022 Status	88	354	

- Sheet resistance decreased with AST cycling
- Charge of Fe^{3+}/Fe^{2+} couple decreased, capacitive current increased
- Diagnostics results consistent with carbon corrosion and Fe loss degradation mechanisms

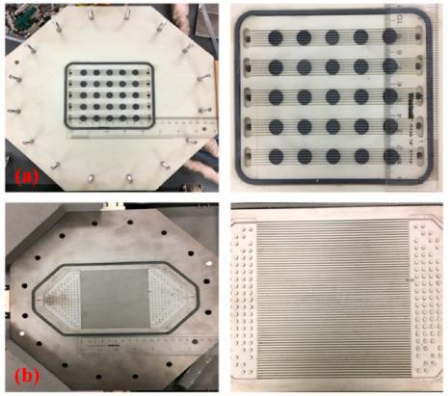
Progress: Exceeded FY24 performance milestone with 92 mA/cm² at 0.8 V (≥ 90 mA cm^{-2}); durability lower than target

Next Steps: Incorporate boron in structure to prevent carbon corrosion. Utilize computer-controlled deposition system to improve quality of electrode layer using best-in-class ElectroCat catalyst

Combinatorial Exploration of Fe-N-C Cathode Catalyst Ink Composition

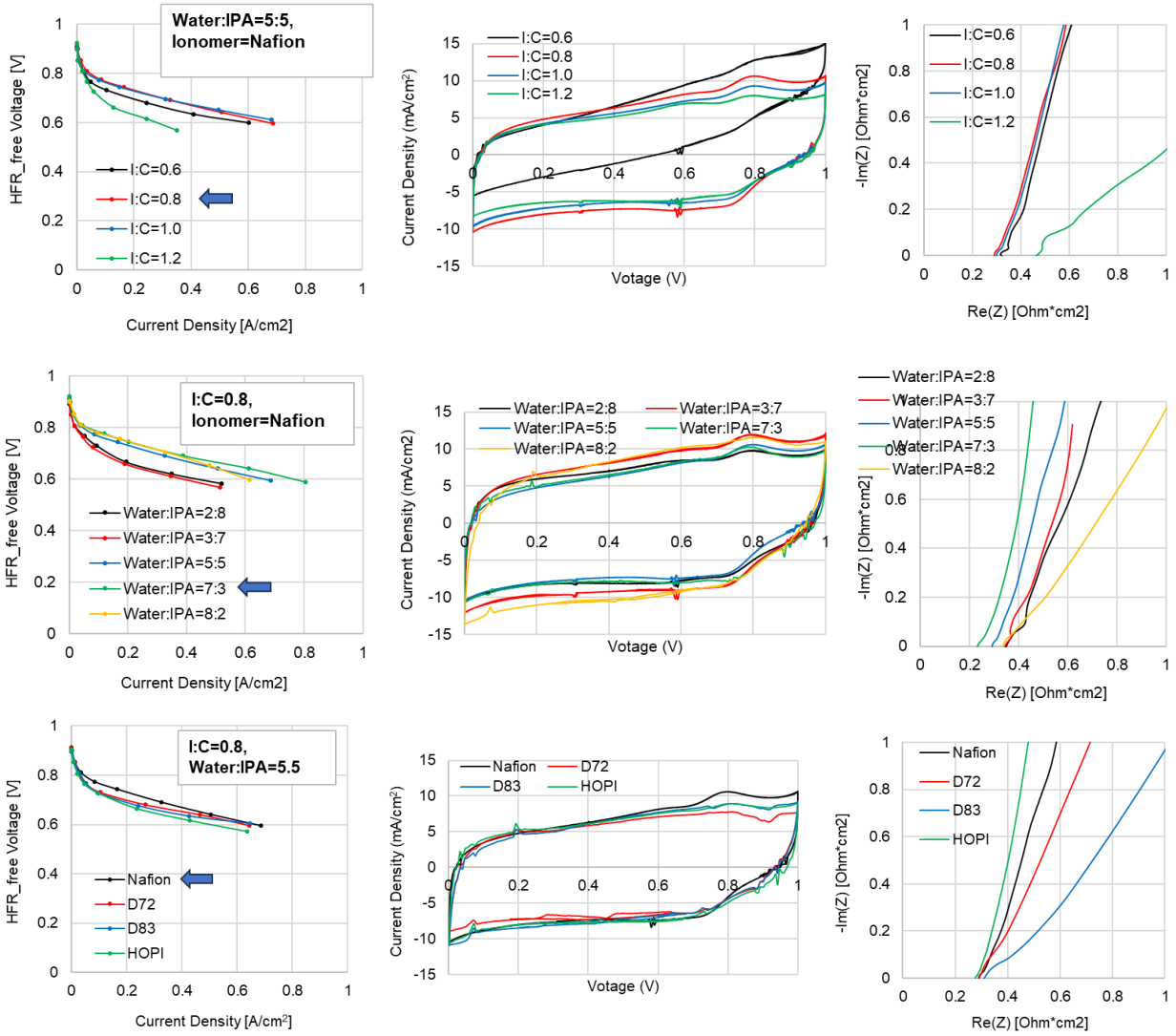


Automated ink deposition system to make multiple 1 cm diameter circular electrodes along the X–Y linear paths.



Combinatorial fuel cell hardware: (a) cathode and (b) anode

- Ink composition of I/C of 0.8, water:IPA ratio of 7:3, and Nafion ionomer gives the highest H_2-air cell performance
- I/C over 1.2 shows extremely high resistance and mass transport issues are likely due to higher water accumulation and associated cathode flooding
- Higher ORR overpotential losses are observed for electrodes made from IPA-rich solvents due to lower catalyst utilization

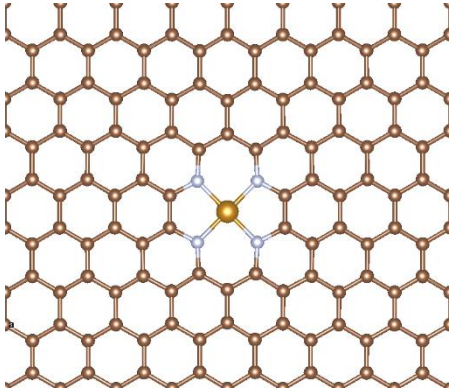


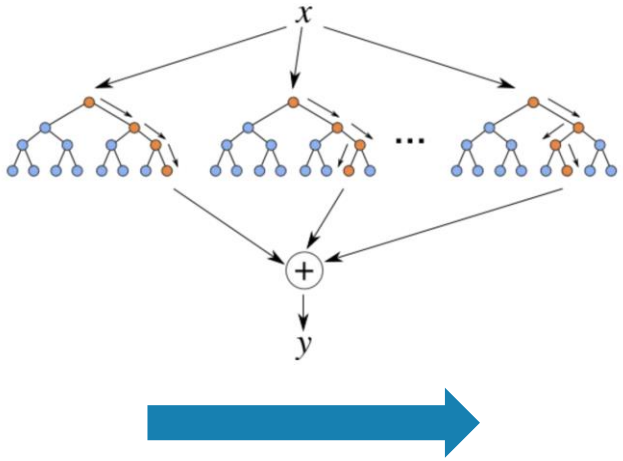
Highlight: Evaluated variations of ink ionomer to catalyst ratio and solvent composition for best-in-class high-throughput PGM-free electrode (ML#9) using twenty-five electrode array cell hardware **(FY23 Q3 QPM complete)**

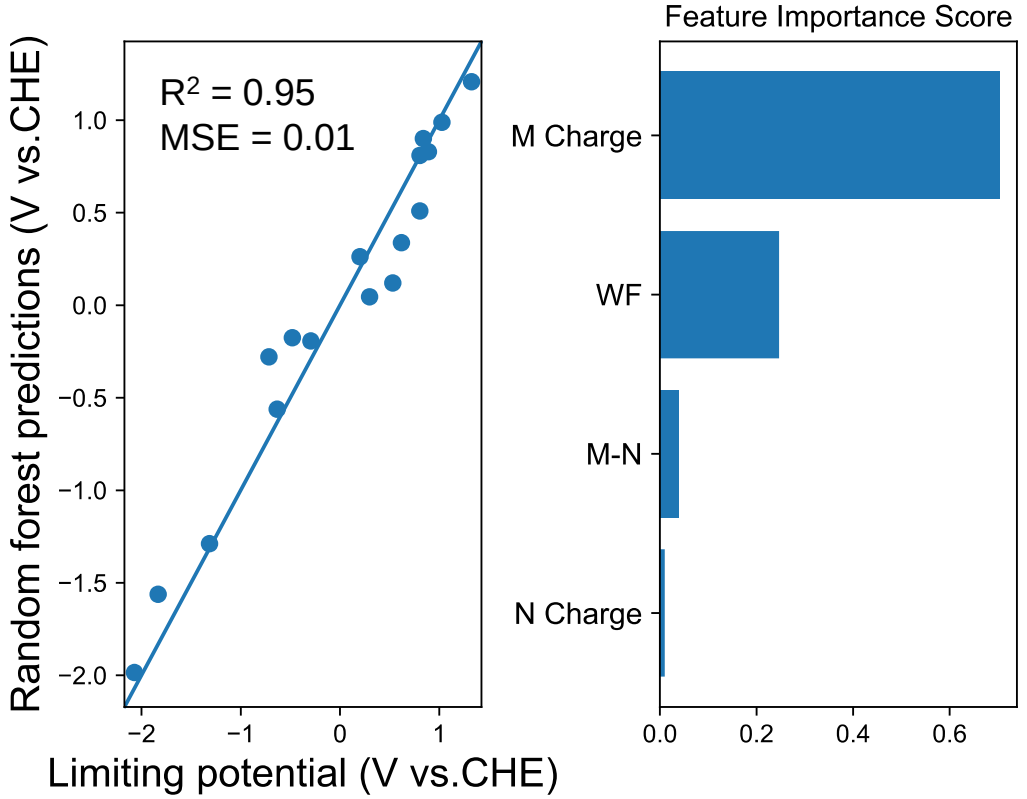
Multi-Objective Optimization and Machine Learning of DFT Descriptors

FY23 Q3 QPM: *Demonstrate (develop and integrate) first surrogate models of ORR activity into Pareto optimization scheme using DFT model input to identify (atomic and electronic) structural descriptors of activity*

QPM complete: Model identified metal Bader charge (i.e., metal species) as most important feature with random forest regression approach yielding highest performance





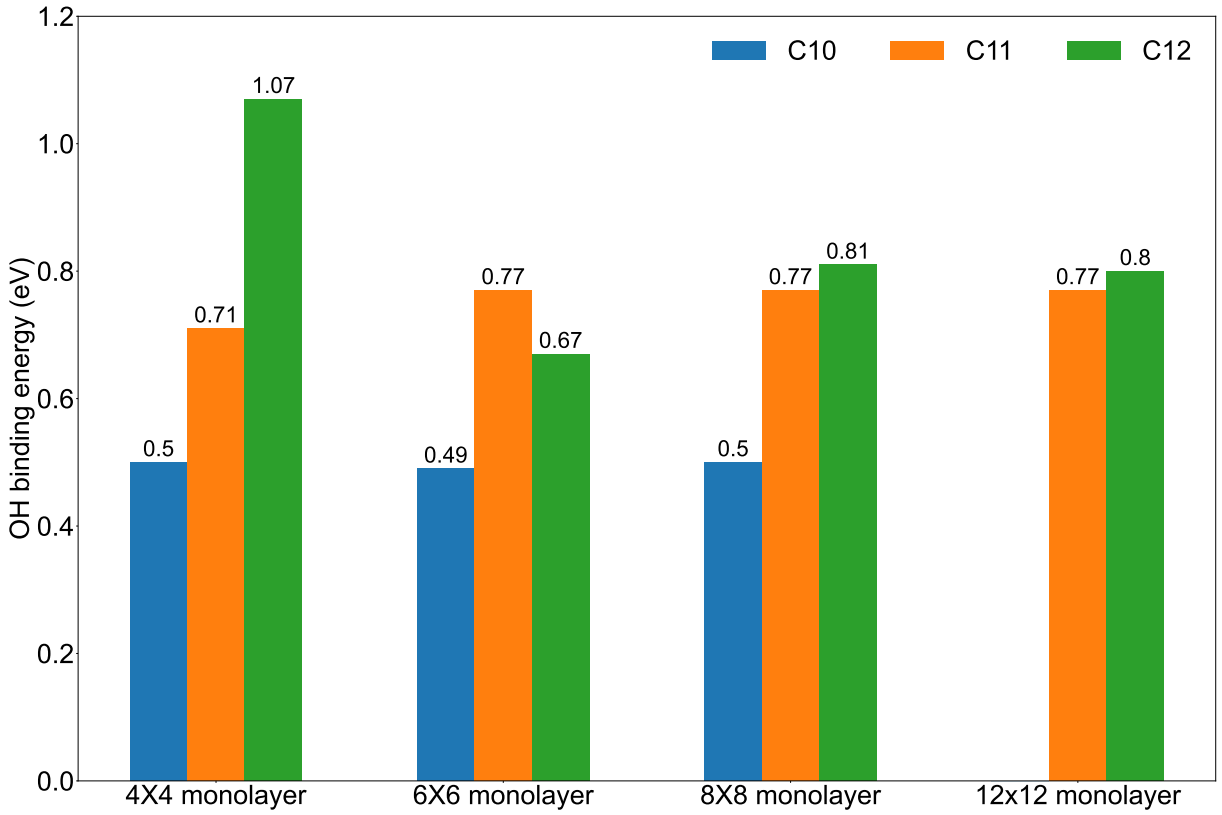


- M Charge: Bader charge on metal
- WF: catalyst work function
- M-N: average bond length amongst metal and nitrogen
- N charge: average Bader charge amongst nitrogen

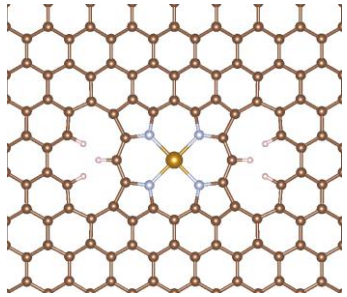
Multi-Objective Optimization and Machine Learning of DFT Descriptors

- Relatively small dataset (~20 structures) → High-throughput DFT needed to augment structure-to-function library (underway)
- Library will aid ML efforts and ML model will help identify next structure to add to library
- Need to test general convergence of DFT parameters/cell size and methods, particularly to accommodate extended defects
- **Highlight**: Self-interaction strain found to impact ORR intermediate binding energetics significantly for C-defected systems

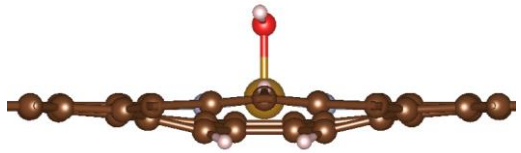
OH binding energy convergence test with respect to graphene size representations



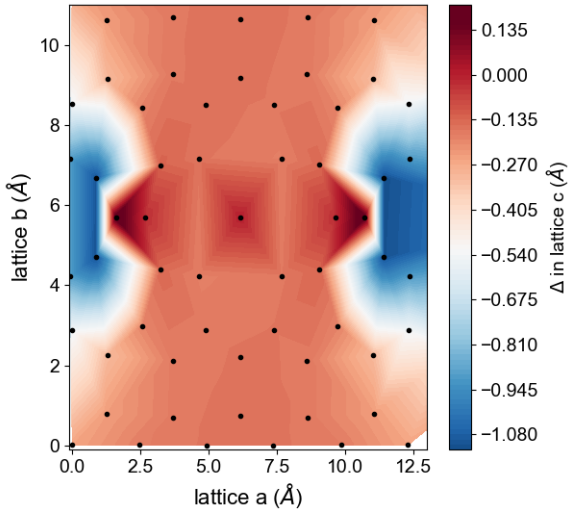
Top view – surface prior to adsorption



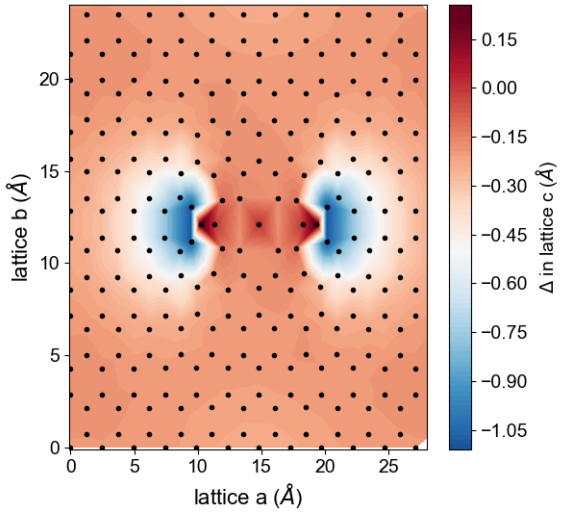
Side view – finite thickness ~ 1.2 Å



6X6 FeN_4C_{12} strain field in Z direction



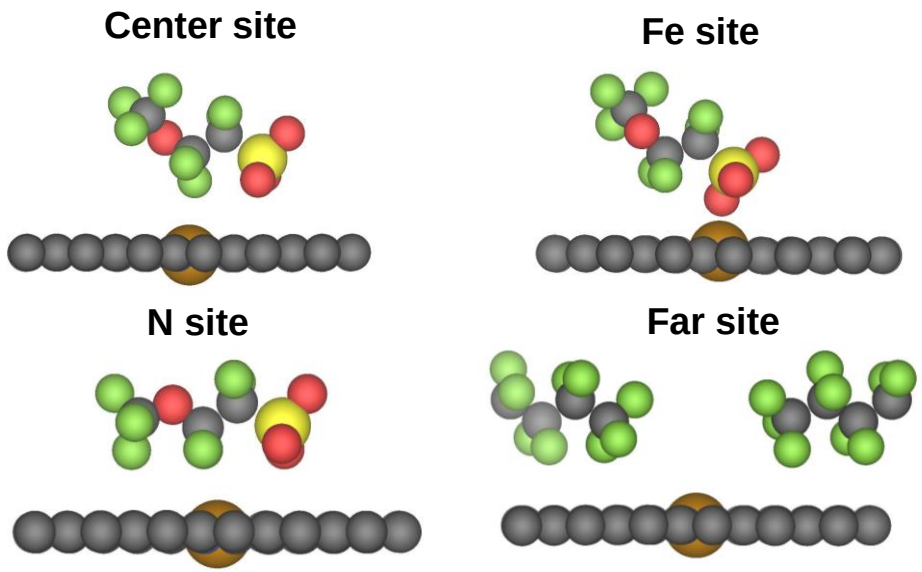
12X12 FeN_4C_{12} strain field in Z direction



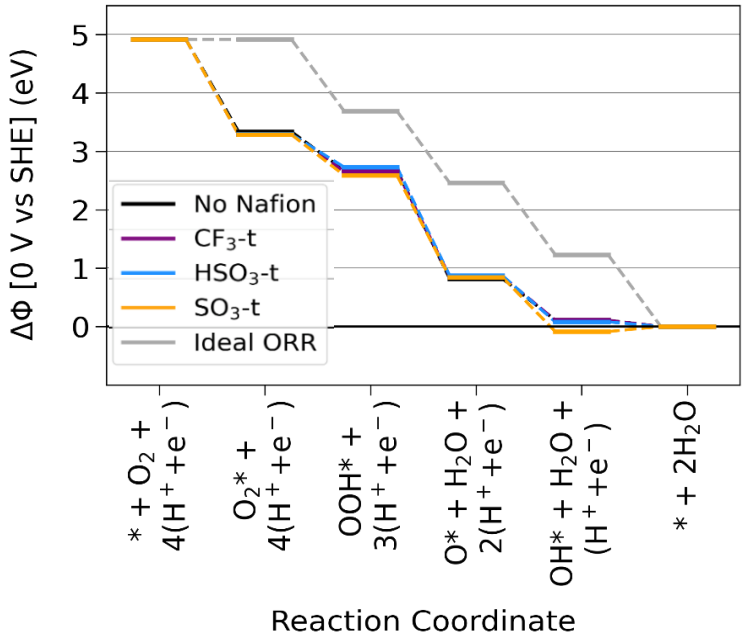
DFT to Understand Effect of Nafion on ORR

FY23 Q3 QPM complete: *Compute adsorption energies for O_2, NO, and OH on the Fe bulk under applied potential and in the presence of Nafion fragments at 3 different locations*

The effect of ionomer on binding energy, ORR thermodynamics for FeN_4@graphene were studied



ORR pathway for different fragments adsorbed on Fe site, 1 V vs SHE



Adsorption energies with SO_3-terminated fragment, 1 V vs SHE

	Center	Fe	N	Far	None
O_2	-0.5 eV	-0.7 eV	-0.7 eV	-0.6 eV	-0.6 eV
NO	-2.1 eV	-1.9 eV	-2.3 eV	-2.2 eV	-2.2 eV

- Grand Canonical (GC) DFT predicts small effects of Nafion fragments on adsorption energies, ORR thermodynamics
- SO_3 functional group binds to Fe active site, competing with ORR intermediates
- GC DFT predicts NO to bind more strongly than O_2, aligning well with experimental NO probe molecule studies.*

*See ElectroCat 2.0 2022 AMR, slide #27

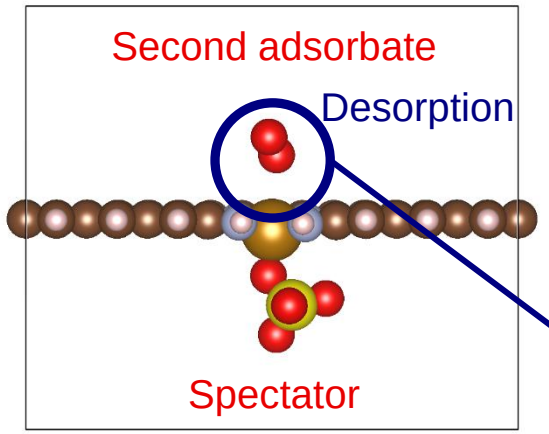
Effect of Axial Spectator Ligands on ORR Active Sites

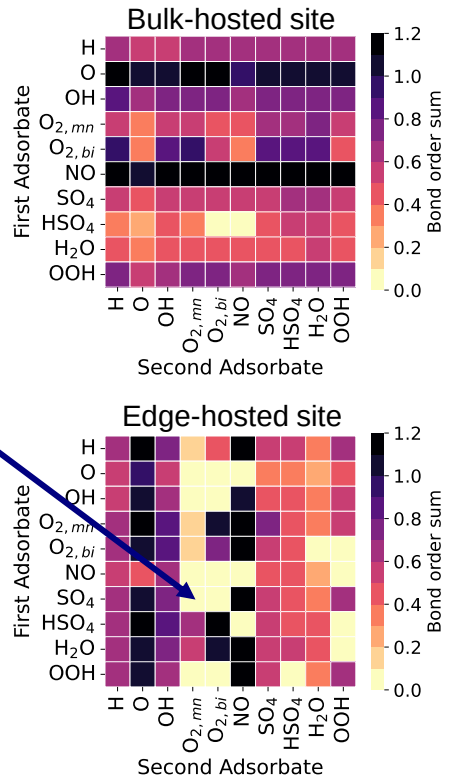
- Synthetic methods have been shown to create bulk and edge Fe-N-C sites
- Goal: understand effect of Fe-N-C site coordination, spectators, and potential on ORR thermodynamics

Effect of axial spectator ligands on adsorption on active site

DFT simulations performed combinatorically for 10 selected adsorbate/spectator species.

Presence of counterions are destabilizing with physical desorption correlated to bond orders of ≤ 0.1.

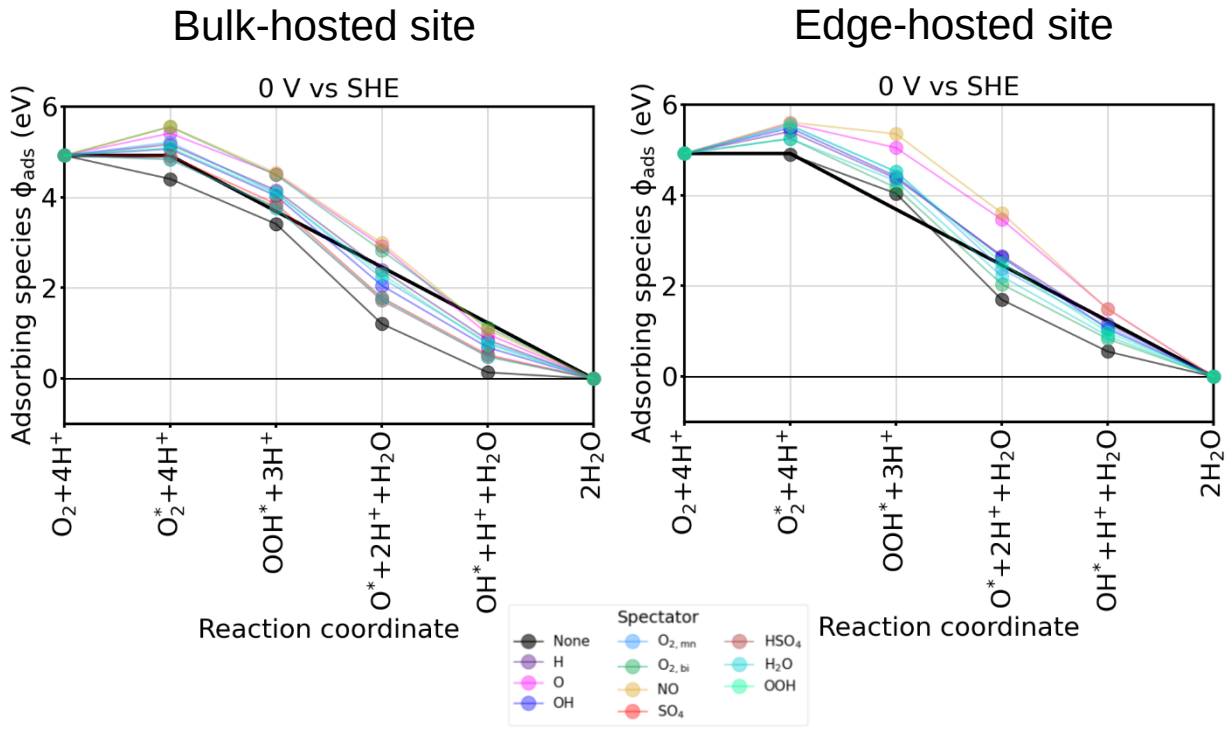




Edge-hosted active site causes more desorption

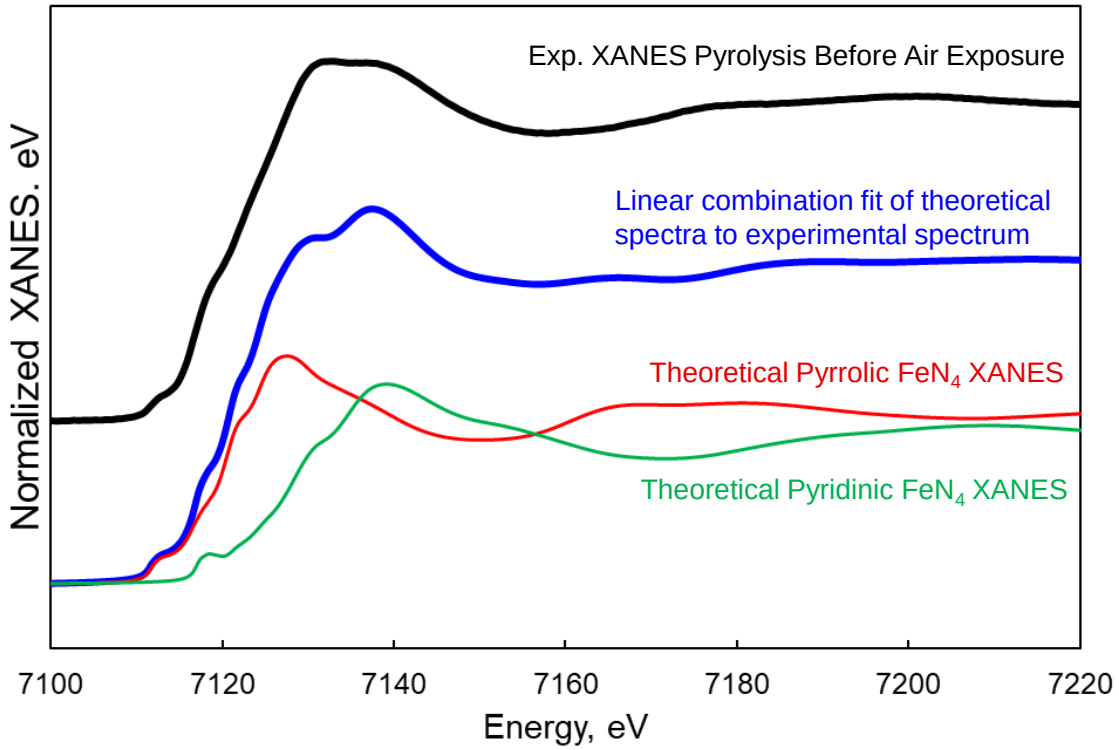
ORR at FeN_4@G bulk vs. edge sites in presence of spectator

ORR thermodynamics are more destabilized at edge-hosted site

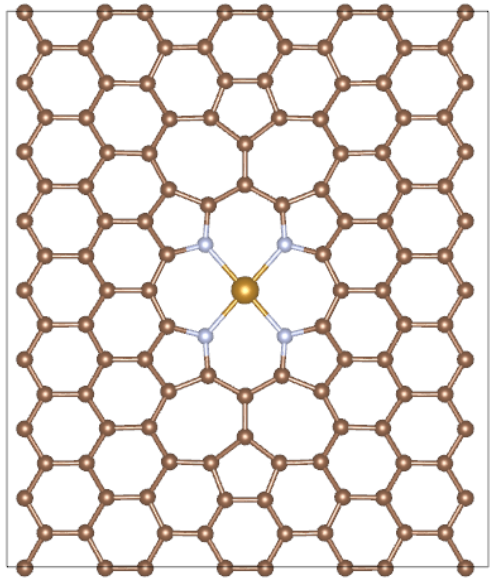


Edge-rich catalyst is less promising based on this active site model

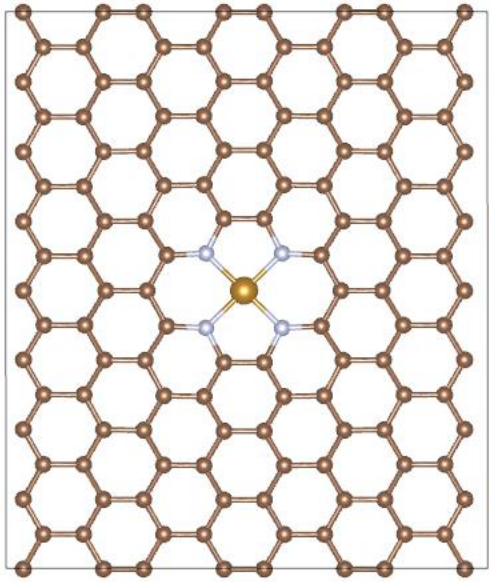
Simulation of XANES: Linear Combination Fitting (LCF) of FeN_4 Sites



Pyrrolic FeN_4 sites



Pyridinic FeN_4 sites



8x8 graphene-nitrogen matrix
No effect of matrix size observed between 4x4 and 8x8

Motivation: Employ X-ray absorption near edge spectroscopy (XANES) simulation to understand XANES features and active site structure evolution under various conditions, further elucidating the active site properties

Highlight: Comparison of DFT-calculated XANES spectra and experimental XANES spectrum immediately after pyrolysis and before air exposure indicates that the near-edge features can be attributed to a mixture of pyridinic and pyrrolic FeN_4 sites.

Next steps: Refine models, including vacancy sites and edge sites, to improve LCF quality. Determine effect of adsorbates on theoretical XANES

PGM-free OER and HER Electrocatalysts for AEMWE

FY23 Electrolysis Quarterly Progress Measures (QPMs)

Milestone Name/Description	Criteria	End Date	Type	Status
Adaptive learning strategy for oxygen evolution catalysts	Based on available experimental data, develop new artificial neural network models for OER activity dependence on synthesis conditions. Use uncertainty quantification and global optimization to identify the next two most promising experiments targeting improved OER (**LANL, ANL**).	6/30/2023	QPM (Regular)	**Completed** See slide #37
High-throughput synthesis of OER catalysts for adaptive learning	Provide LANL machine learning activity with aqueous electrolyte OER polarization curve data for 20 unique materials (**ANL, LANL**).	6/30/2023	QPM (Regular)	**Completed**
IL-STEM visualization of catalyst transformation during conditioning	Quantify change in LANL NiFe aerogel catalyst composition, morphology, and crystal structure before and after cycling in three electrode cell and correlate with Mossbauer, XRD, and XAFS characterization (**ORNL**).	6/30/2023	QPM (Regular)	**Completed** See slide #69
Water domain structure of AEM polymer	Calculate the water domain width in poly(aryl piperidinium)-based polymers as a function of hydration. Compare computed scattering functions to existing x-ray scattering data (**NREL**).	9/30/2023	QPM (Regular)	**Completed** See slide #39

FY23 Electrolysis Annual Milestones

Milestone Name/Description	Criteria	End Date	Type	Status
OER performance in liquid electrolyte	OER current density in an aqueous alkaline electrolyte of 10 mA cm^{-2} at a potential of ≤ 1.54 V vs. RHE (iR-free) at beginning of test after activation and no more than 0.5 mV/h potential loss during ≥ 72 h durability test at 10 mA cm^{-2} (**LANL**, **ANL**, **ORNL**).	9/30/2023	Annual Milestone (Regular)	**Completed** See slides #32,33 in 2023 AMR
HER performance in liquid electrolyte	HER current density in an aqueous alkaline electrolyte of 10 mA cm^{-2} at a potential of ≥ -0.30 V vs. RHE (iR-free) at the beginning of test and no more than 0.8 mV/h potential loss during ≥ 48 h durability test at 10 mA cm^{-2} (**LANL**, **ANL**).	9/30/2023	Annual Milestone (Regular)	**Completed** See slide #76
LTE Catalyst Testing in AEM MEA	Incorporating ElectroCat-developed catalysts, demonstrate cell overvoltage reduction of more than 50 mV (HFR-free) compared to commercial baseline catalysts (NiFeOx, established in HydroGEN EMN) at 1 A/cm^2. 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) (**NREL**).	9/30/2023	Annual Milestone (Regular)	**Completed** See slide #62 (also slide #35 in 2023 ElectroCat presentation)

FY24 Electrolysis Quarterly Progress Measures (QPMs)

Milestone Name/Description	Criteria	End Date	Type	Status
NiFe OER catalyst characterization	Correlate the potential dependence of the Ni and Fe oxidation states as determined using in situ X-ray absorption spectroscopy with Fe speciation determined using in situ Mössbauer spectroscopy for high-performing NiFe aerogel OER catalyst and correlate findings with OER activity. **(LANL, ORNL, ANL)**	12/31/2023	QPM (Regular)	**Completed** See slide #27
HER performance in liquid electrolyte	HER current density in an aqueous alkaline electrolyte of 10 mA cm^{-2} at a potential of ≥ -0.26 V *vs.* RHE (*iR*-free) at the beginning of test and no more than 0.4 mV/h potential loss (calculated after the break-in period) during ≥ 100 h durability test at a current density of at least 10 mA cm^{-2} **(LANL, ANL)**	3/31/2024	QPM (Regular)	**Completed** See slides #41,42
Figure of merit	In coordination with HFTO, prepare a “figure of merit” slide for the HFTO AMR OER and HER performance/durability benchmarking in 3-electrode and MEA to show current status and historical consortium progress. **(LANL, ANL)**	3/31/2024	QPM (Regular)	**Completed** See slide #45
Machine learning surrogated models for OER catalysts	Develop surrogated regression models of the activity of mesoporous self-healing OER catalysts and implement uncertainty quantification and global optimization strategies to identify the next four most promising samples to be tested. Implement new iteration of adaptive learning for improving the activity and stability of Ni-Fe-Co aerogel-based OER catalysts, achieving an improvement in the model's accuracy by 10%. **(LANL)**	6/30/2024	QPM (Regular)	**On track**

FY24 Electrolysis Quarterly Progress Measure (QPM) and Annual Milestones

Milestone Name/Description	Criteria	End Date	Type	Status
OER performance in liquid electrolyte	OER current density in an aqueous alkaline electrolyte of 10 mA cm^{-2} at a potential of ≤ 1.52 V *vs.* RHE (*iR*-free) at beginning of test (after break-in) and no more than 0.45 mV/h potential loss during ≥ 100 h durability test at a current density of ≥ 10 mA cm^{-2}.	9/30/2024	QPM (Regular)	**Complete** See slides #29,30
OER milestone involving all labs	Achieve 1.65 V *iR*-free at 1.0 A cm^{-2} for an AEMWE electrolyzer having ElectroCat PGM-free catalysts at both anode and cathode, operating with supporting electrolyte feed (1.0 M KOH) and run ≥ 100 h durability test.	9/30/2024	Annual Milestone (Regular)	**On Track** See slide #44
Outreach to MSIs/HBCUs/TCUs/ Underrepresented Communities	Engage in at least 4 activities that support recruitment of students and alumni of MSIs/HBCUs/TCUs (e.g., national lab staff going to MSIs/HBCUs/TCUs, hosting visits from professors and/or students from those institutions at the national lab, attending conferences such as NOBCChE and SACNAS). Attempt to recruit interns, graduate students, postdocs, or research scientists to work on ElectroCat tasks that are either alumni from an HBCU/MSI or are from a population that is underrepresented in STEM.	9/30/2024	Annual Milestone (Stretch)	**On Track** See slide #50

OER and HER Catalyst Development Paths

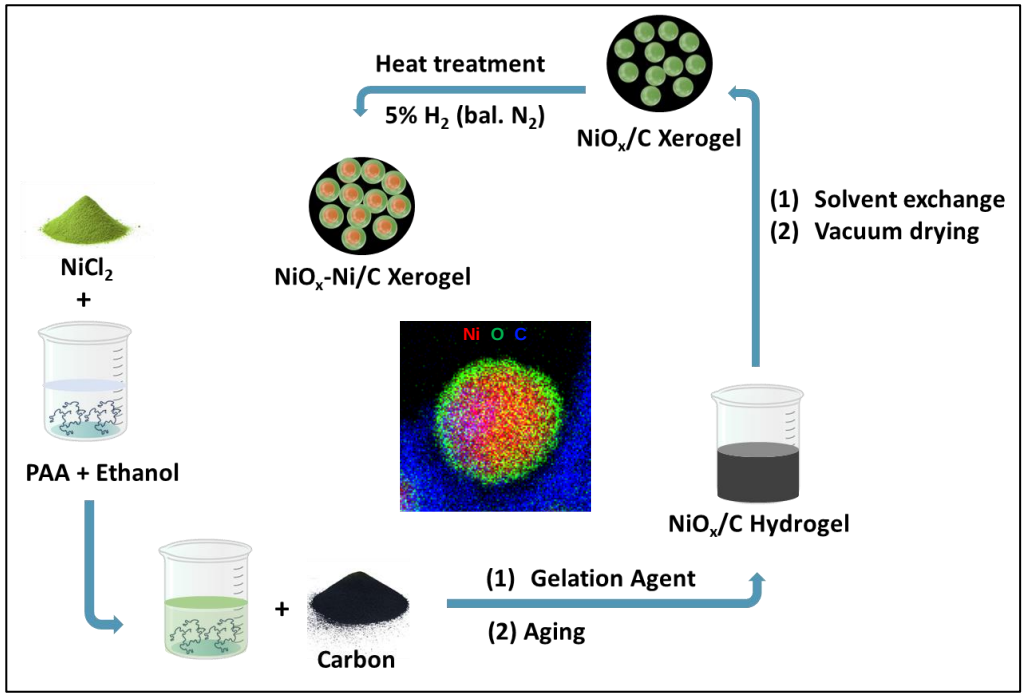
Oxygen Evolution Reaction (OER) Catalysts

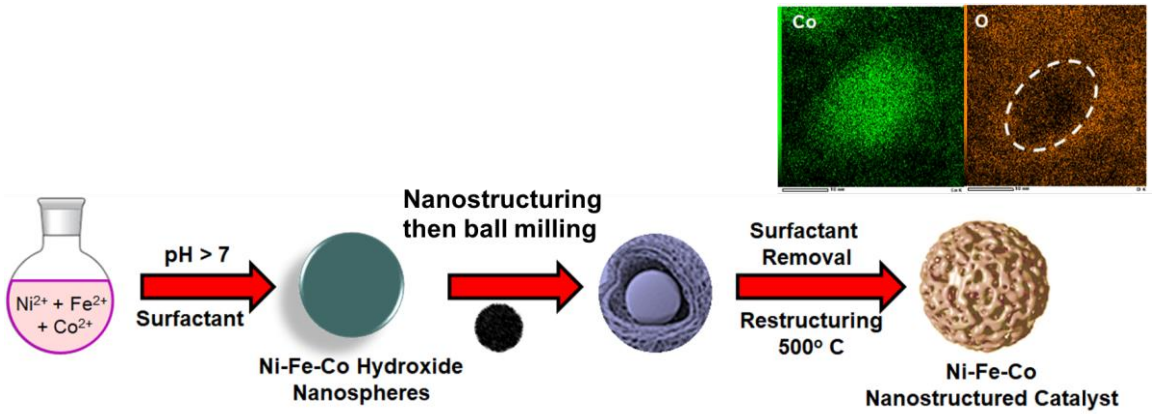
- ✓ Binary and ternary Ni-based aerogel catalysts, using different metals (*e.g.*, Fe, Mn, Cr, Co) and synthesis conditions
- ✓ PTL-supported NiFe catalysts
- ✓ ZnCoMOF-derived catalysts
- ✓ Monometallic, bimetallic, and trimetallic nanostructures
- ✓ $NiFeMO_x$ (M = Re or Mo)

Hydrogen Evolution Reaction (HER) Catalysts

- ✓ Carbon-supported, xerogel-derived Ni using different heat-treatment temperature and time, Ni-to-carbon/ionomer ratio, carbon support type, etc.
- ✓ Binary and ternary Ni-based catalysts, carbon- and PTL-supported
- ✓ Bimetallic nanostructured oxyphosphide nanocomposites

Adaptive-learning and high throughput methods extensively used

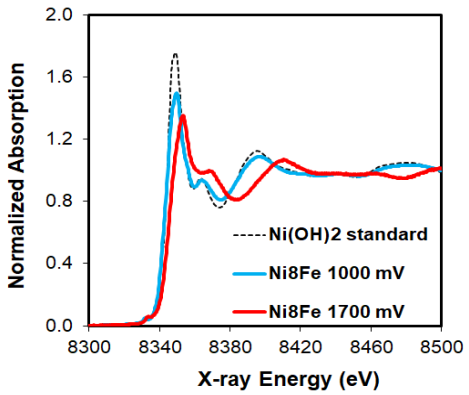




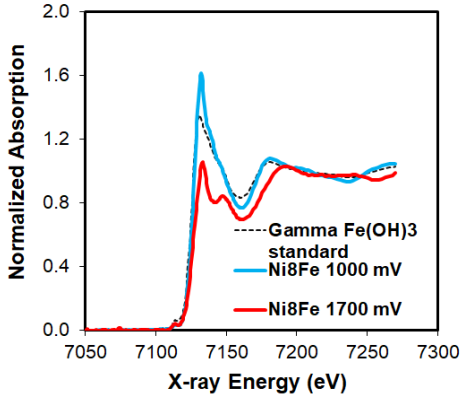
OER Catalysis: Correlation of Mössbauer and XAS for Aerogel NiFe 8:1 OER Catalyst*

Accomplishment

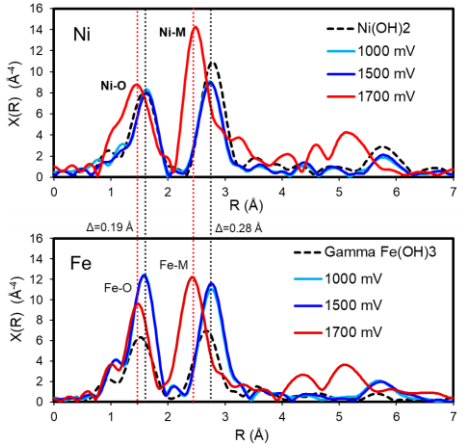
In situ Ni K-edge X-ray spectra at 1.0 V and 1.7 V (vs. RHE) in 0.1 M KOH

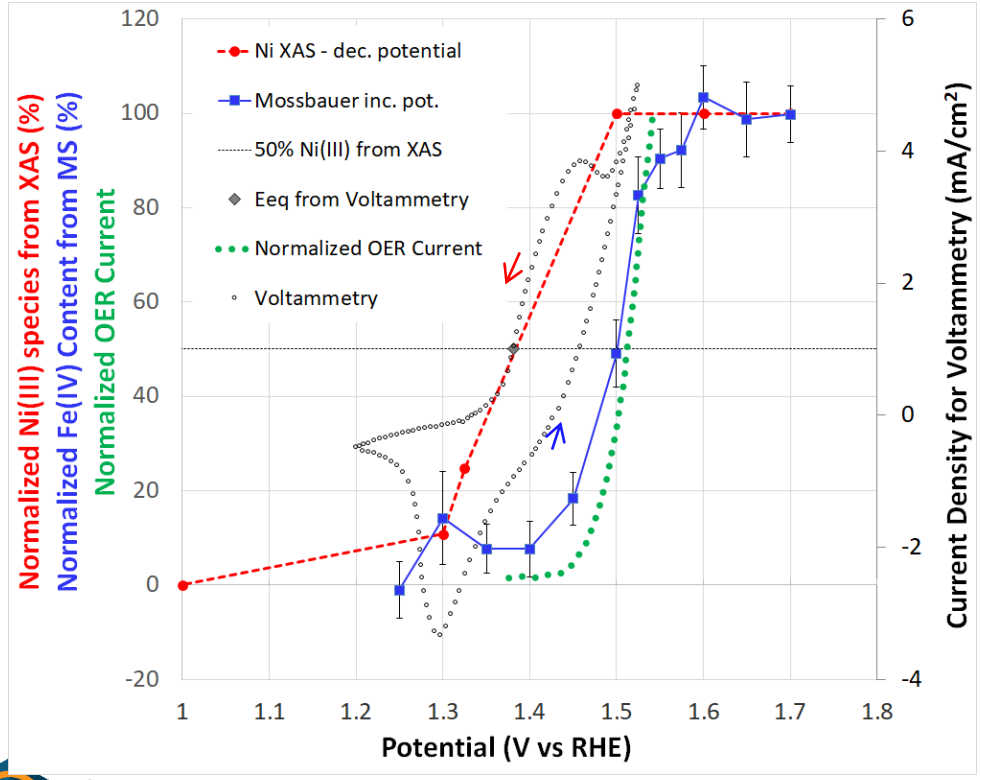


In situ Fe K-edge X-ray spectra at 1.0 V and 1.7 V (vs. RHE) in 0.1 M KOH

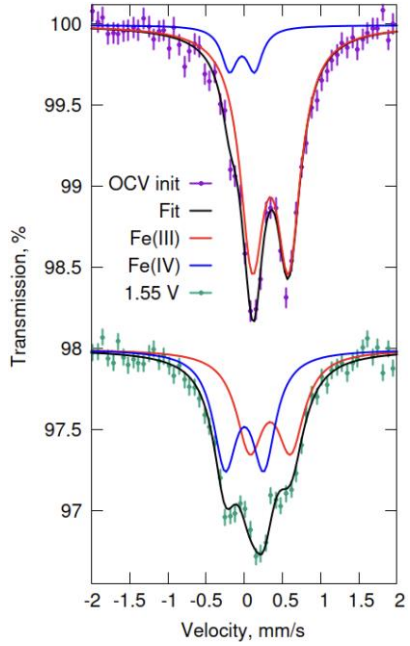


Fourier Transforms of Ni and Fe K-edge EXAFS





In situ ^{57}Fe Mössbauer spectra: open circuit and 1.55 V (vs. RHE)

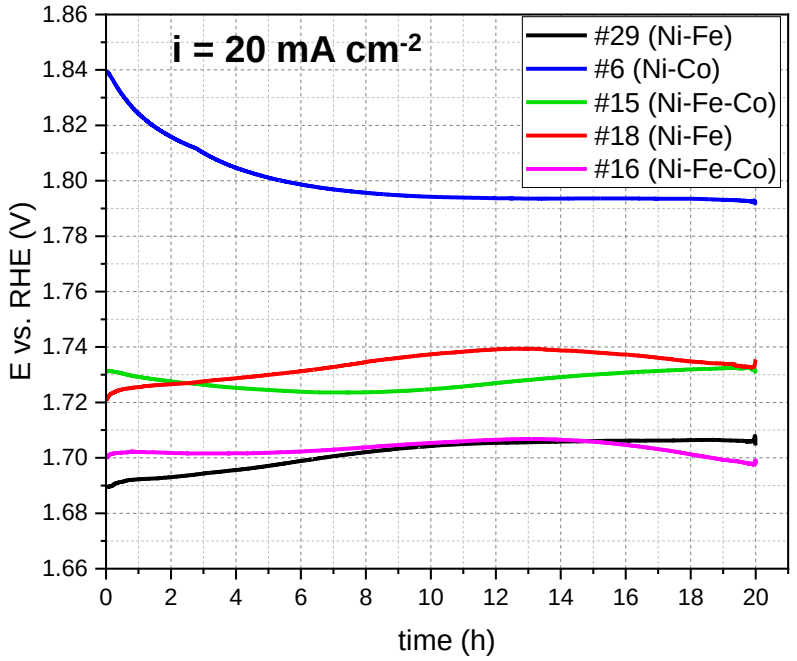


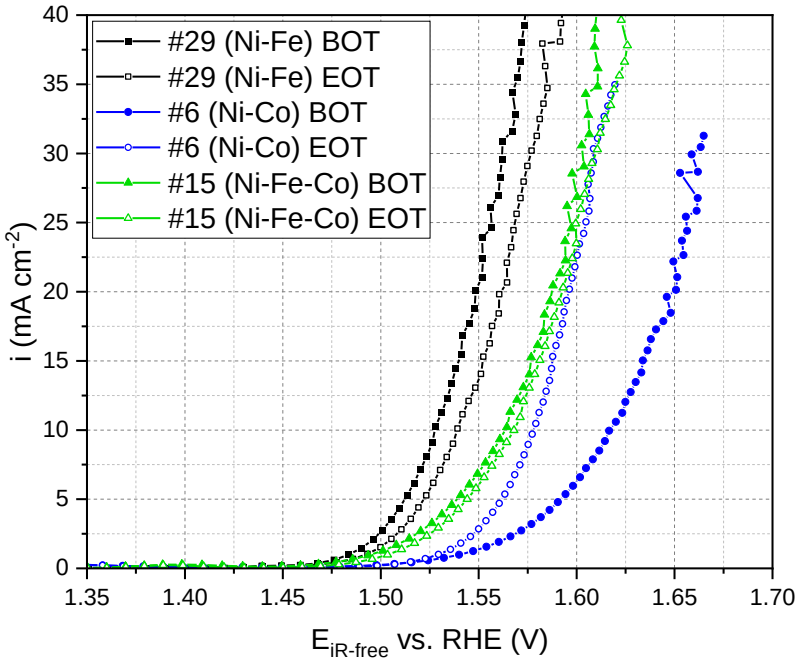
FY24 Q1 QPM: *"Correlate potential dependence of Ni and Fe oxidation states, using in situ X-ray absorption spectroscopy and Mössbauer spectroscopy, for NiFe aerogel OER catalyst; correlate findings with OER activity"*

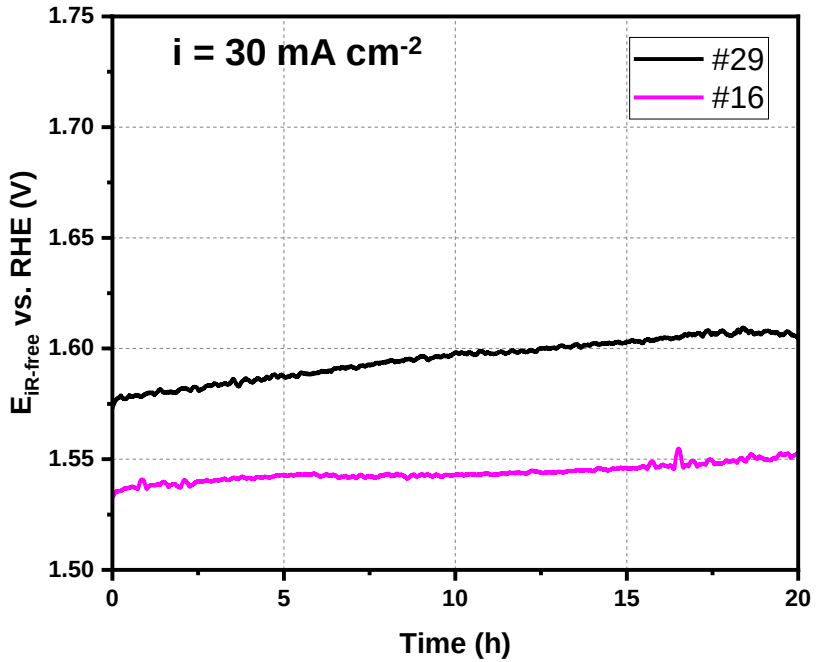
- **Results:**
  - ✓ Ni oxidation state and structure changes correlate well with reversible redox couple and quantitative conversion of α-$Ni(OH)_2$ to γ-NiOOH between 1.2 and 1.5 V
  - ✓ Fe incorporated in NiO_xH_y structure; Fe(III) oxidized to Fe(IV) at ≥ 1.45 V (OER onset); Fe(IV) saturates at ~1.55 V
  - ✓ Fe(IV) species are metastable, conversion back to Fe(III) takes several hours at <1.3 V (observed by both XAS and Mössbauer)
  - ✓ OER current not correlated with bulk concentration of Fe(IV)
- **Highlight:** No correlation between bulk Ni oxidation state and Fe oxidation state after initial oxidation; onset potentials for OER and Fe(IV) formation are correlated (**FY24 Q1 QPM completed**)

*Described in 2023 AMR slides #31, 54 and slide #64 in this AMR presentation

OER Catalysis: Activity and Durability Patterns for Ni-based Aerogel Catalysts





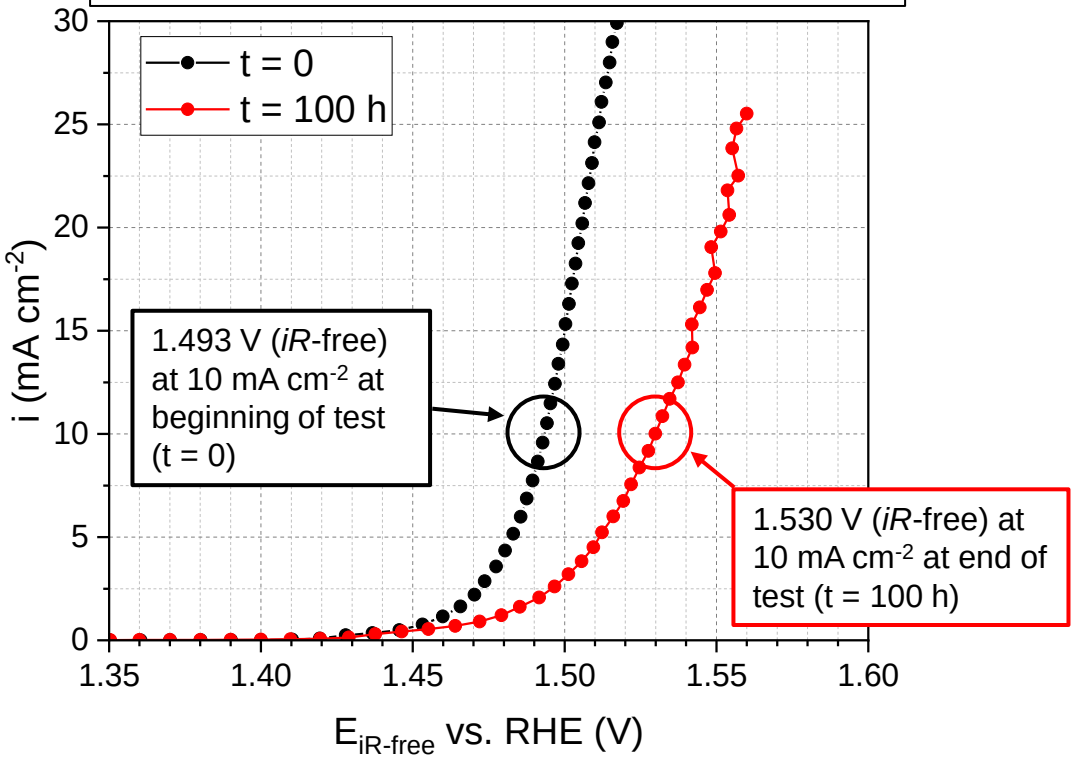


- **Highlight:** 30 binary and ternary aerogel catalysts synthesized with different compositions for input into machine learning algorithms
- Break-in at 20 mA cm^{-2} for these catalysts (plots for five selected catalysts shown on the left) results in **very different voltage-time behavior**
- Increasing break-in current density to 30 mA cm^{-2} assures monotonic *E-t* behavior of all catalysts (plots for two selected catalysts shown on the right)
- **Highlight:** Appropriate break-in protocol depends on the catalyst type

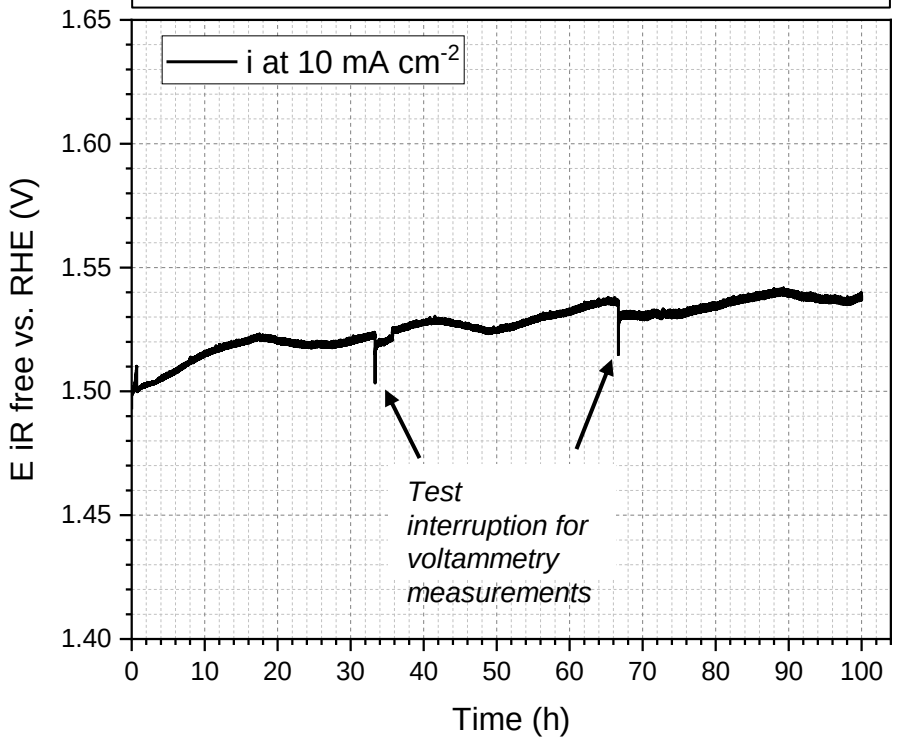
OER Catalysis: NiFeCo Catalyst; FY24 Q4 QPM

FY24 Q4 QPM: *"OER current density in an aqueous alkaline electrolyte of 10 mA cm^{-2} at a potential of ≤ 1.52 V vs. RHE (iR-free) at beginning of test (after break-in) and no more than 0.45 mV/h potential loss during ≥ 100 h durability test at a current density of ≥ 10 mA cm^{-2}."*

Staircase Voltammetry: 10 mV step, 10 s hold; 1600 rpm; Ar-saturated 0.1 M KOH; 0.25 mg/cm^2 catalyst loading



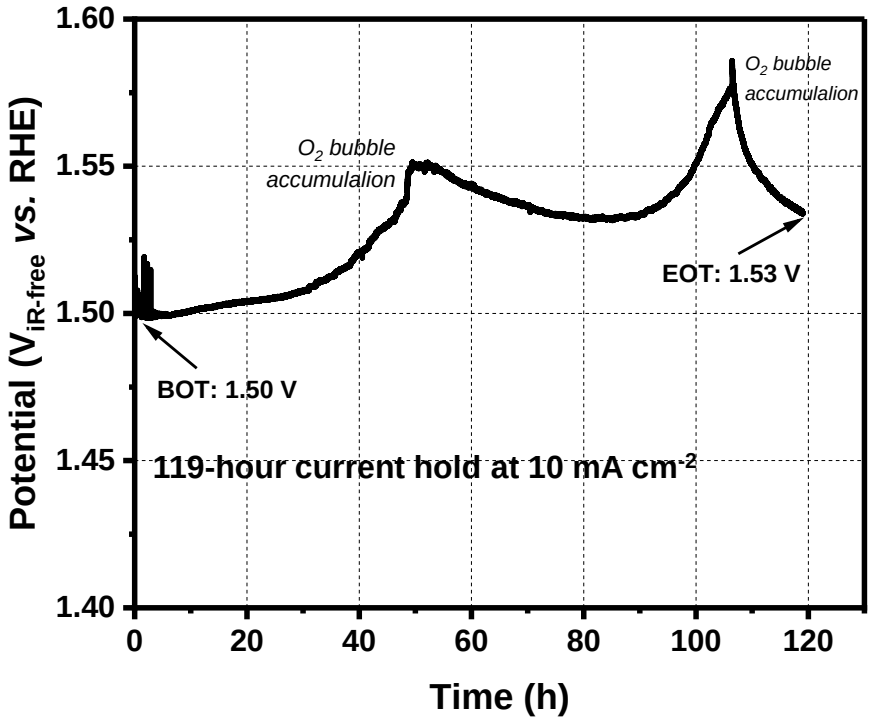
Chronopotentiometry: NiFe 3:2 aerogel catalyst; Ar-saturated 0.1 M KOH, 1600 rpm; 0.25 mg/cm^2 catalyst loading; 100 h test at 10 mA cm^{-2}.



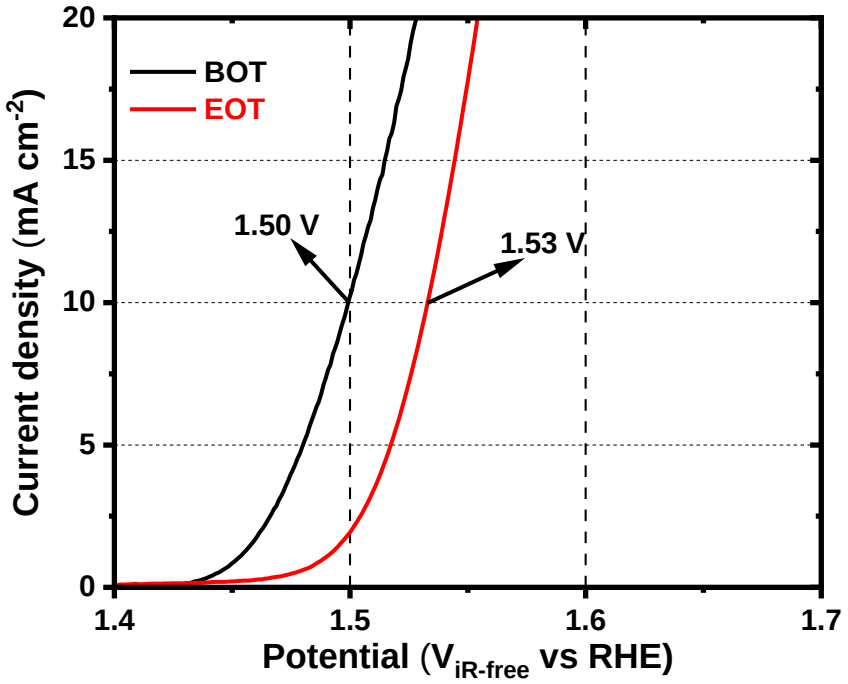
- NiFe 3:2 aerogel catalyst synthesized with a higher PAA content and higher solvent volume
- **Highlight: Exceeded FY24 Q4 QPM** with 10 mA/cm^2 measured at **1.49 V** at BOT (*vs.* QPM target of ≤ 1.52 V) and **0.37 mV/h** in a 100-hour test (*vs.* QPM target of 0.45 mV/h)

Activity and durability of nanostructured Ni_4FeCo_2 catalyst synthesized using a high temperature approach

Chronopotentiometry: Ni_4FeCo_2 catalyst; O_2-saturated 1.0 M KOH, 1600 rpm; 0.25 mg/cm^2 catalyst loading; 119 h test



LSV before and after 119-hour chronopotentiometry: 1600 rpm; O_2-saturated 1.0 M KOH; 0.25 mg/cm^2 catalyst loading, BOT (t = 0 h) and EOT (t = 119 h)

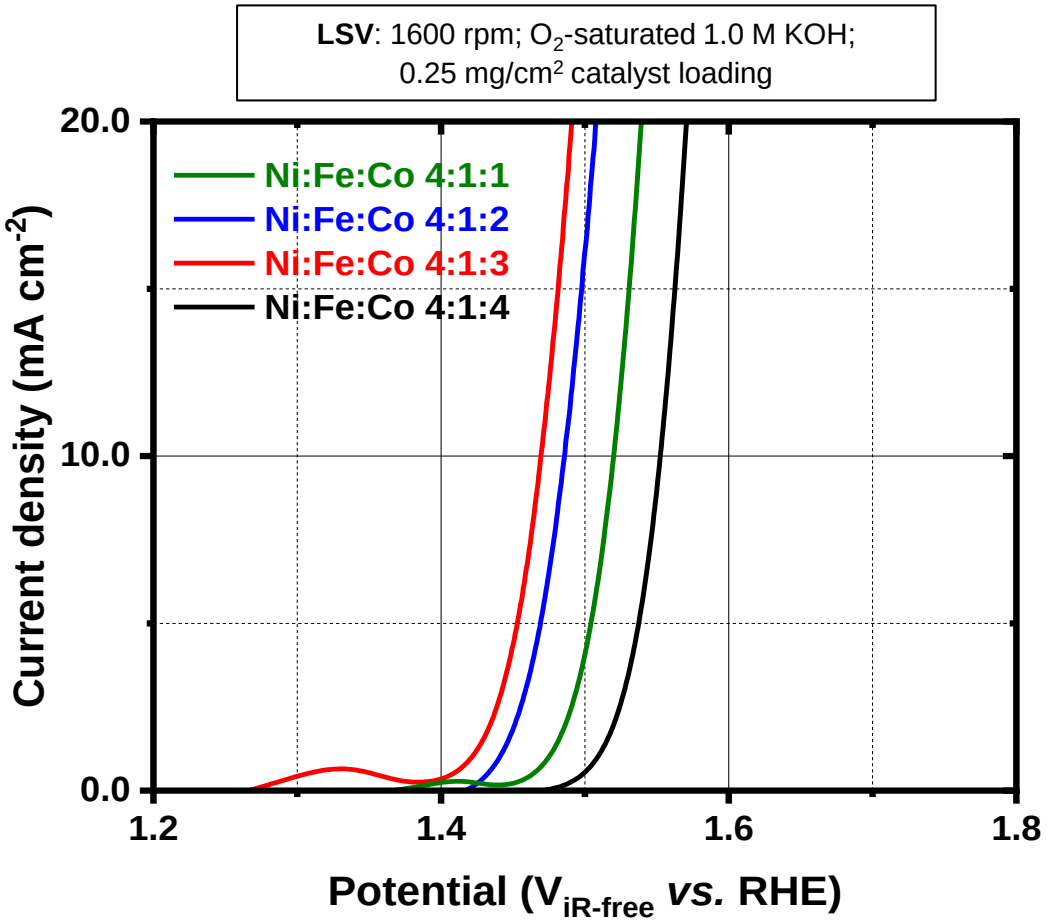


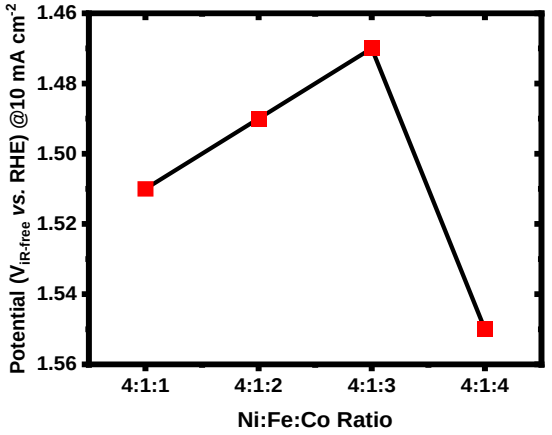
Degradation rate from LSV before and after 119 h at 10 mA cm^{-2}: (1.53 V - 1.50 V) / 119 h = 0.25 mV/h

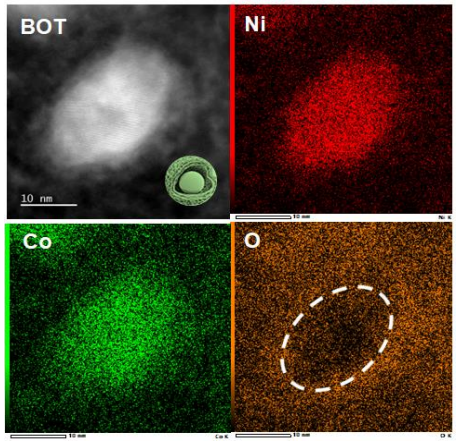
- **Highlight: Exceeded FY24 Q4 QPM** with 10 mA/cm^2 measured at **1.50 V** at BOT (*vs.* QPM target of ≤ 1.52 V) and **0.25 mV/h** in a 119-hour test (*vs.* QPM target of 0.45 mV/h after 100-hour test)

OER Catalysis: Optimization of Trimetallic Nanostructured Catalysts

- Enhanced performance of trimetallic nanostructured catalysts via colloidal *vs.* high-temperature synthesis approach
- Enhancement in performance attributed to the incorporation of sulfur into the catalyst structure during the colloidal synthesis process
- Explored the effect of Ni:Fe:Co ratio on OER activity of colloidal catalysts: catalyst with nominal ratio of 4:1:3 showed lowest OER overpotential at 10 mA cm^{-2}

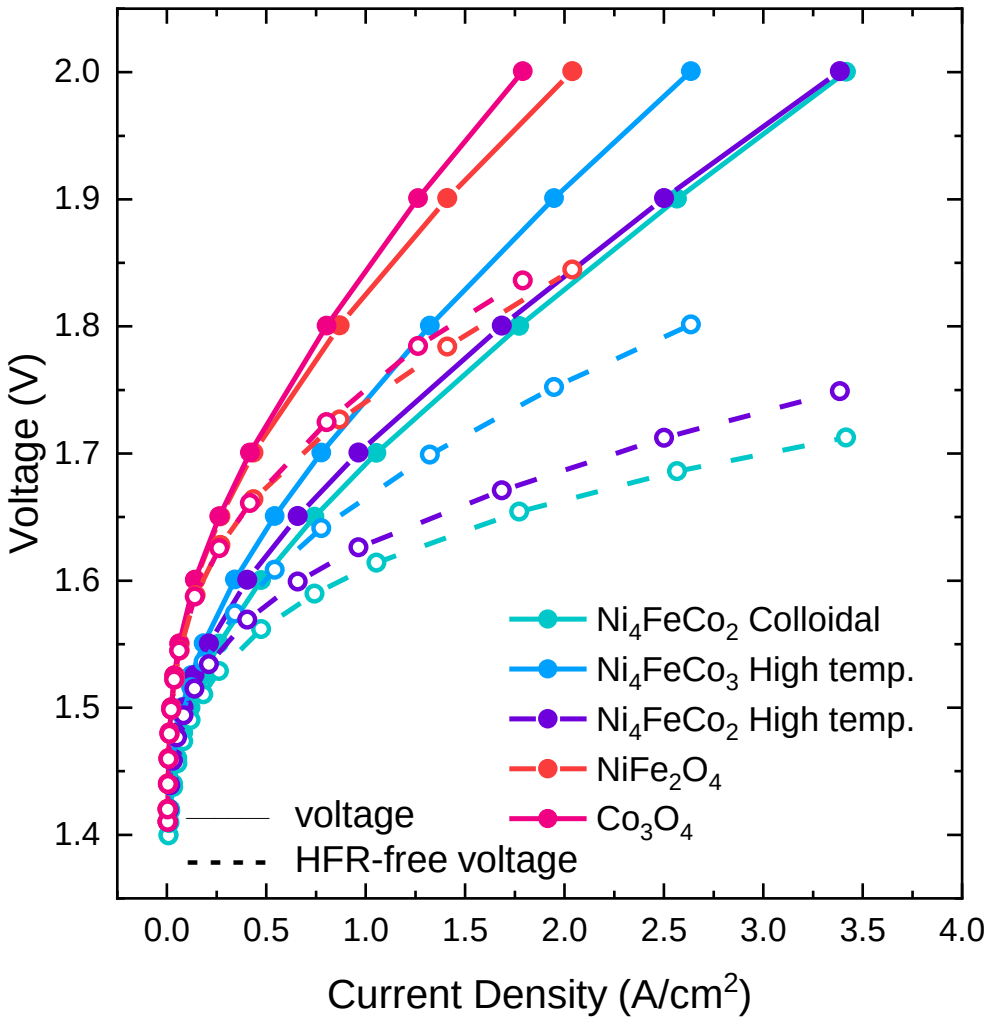




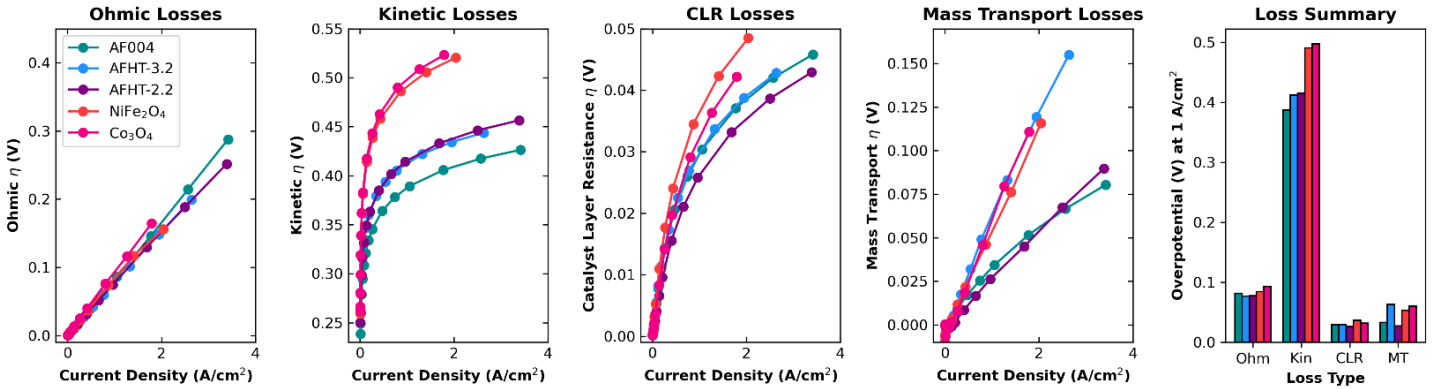


Catalyst ID	mol %					
	Ni	Fe	Co	O	P	S
Ni_4FeCo_2 High Temp.	3.4	1.1	2.0	91.4	2.1	0
Ni_4FeCo_3 High Temp.	3.0	0.9	2.6	90.7	2.8	0
Ni_4FeCo_2 Colloidal	5.6	1.9	2.8	88.8	0.6	0.3
Ni_4FeCo_3 Colloidal	4.6	1.5	3.0	89.3	0.8	0.8

OER Catalysis: Performance of Multi-Metal Catalysts in AEMWE



- **Highlight:** Consortium anode catalysts outperform commercial $NiFe_2O_4$ and Co_3O_4 catalysts
- Similar performance between colloidal and high-temperature syntheses
- Achieved 75 – 130 mV improvement at 1 A/cm² (HFR-free)
- Improved performance primarily due to decreased kinetic and transport losses



Anode Catalyst Composition	Ni_4FeCo_2 Colloidal	Ni_4FeCo_3 High temp.	Ni_4FeCo_2 High temp.	Commercial $NiFe_2O_4$	Commercial Co_3O_4
HFR-free Potential at 1.0 A/cm² (V)	1.610	1.665	1.629	1.741	1.750
Current Density at 2.0 V (A/cm²)	3.417	2.636	3.386	2.039	1.791

Anode: 0.5 mg/cm² ElectroCat catalysts or commercial $NiFe_2O_4$, Co_3O_4 (USRM); **Cathode:** 0.3 mg_{Pt}/cm² Pt/C (TKK); **Electrolyte:** 1 M KOH; **Temperature:** 80 °C; **Membrane:** PiperION TP-85 (80 µm); **Ionomer:** PiperION TP-85 (30 wt%); **Anode PTL:** Ni 18-025 (Bekaert); **Cathode GDL:** MGL280 C paper

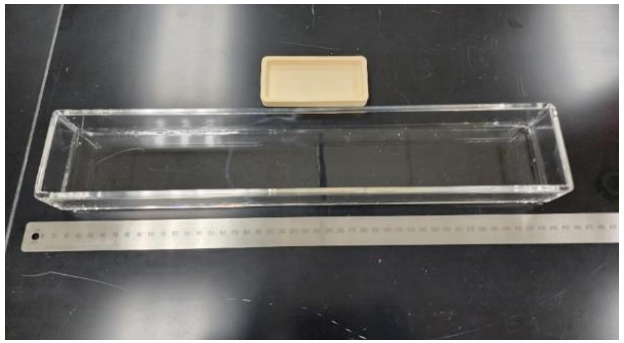
OER Catalysis: $NiFeMO_x$ Catalysts

Synthesis and Materials:

- Fe, Ni, and M (M = Re or Mo) precursors
- Sodium borohydride reduction at 25 °C
- Filtration; heat treatment at 250, 300, 350 °C for 1 h

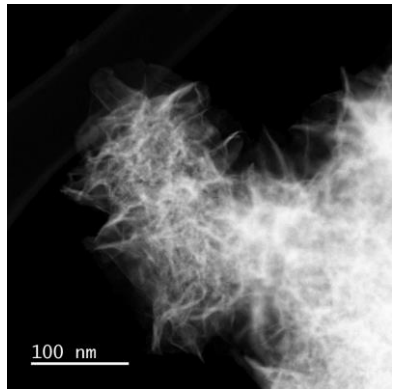


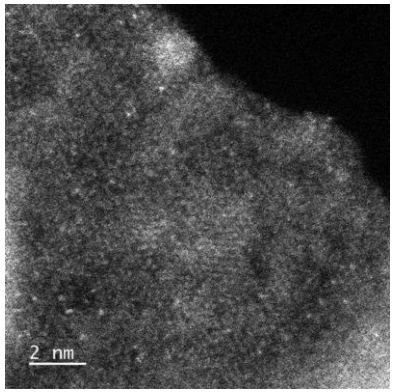




- Re atomically dispersed in the catalyst
- Highest activity obtained following heat treatment at 350 °C
- Re-containing ternary catalyst outperforming Mo-containing one
- Synthesis up to 20 g/batch

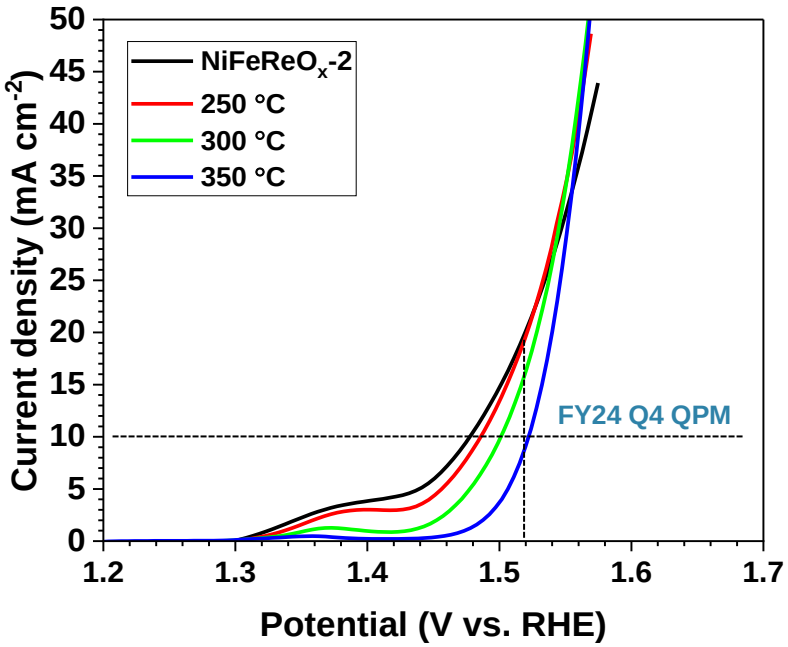
TEM images of $NiFeReO_x$ catalyst *





** Bright dots are Re atoms*

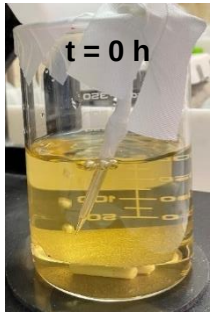
LSV: O_2-saturated 1.0 M KOH; 25 °C

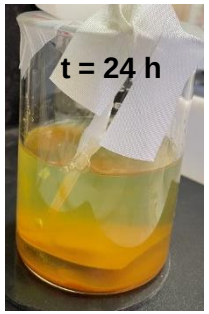


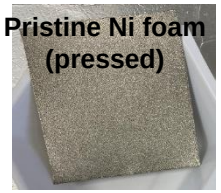
OER Catalysis: PTL-supported NiFe Catalysts – Synthesis, Characterization & Testing

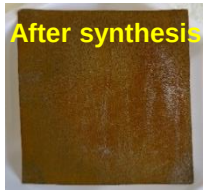
Accomplishment

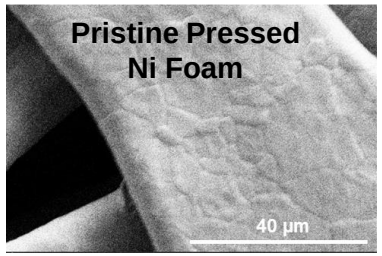
Synthesis: Pressed commercial Ni foam, ~280 µm thick, immersed into O_2-saturated solution of $Fe(NO_3)_3$ or $FeCl_2$ for 24 h













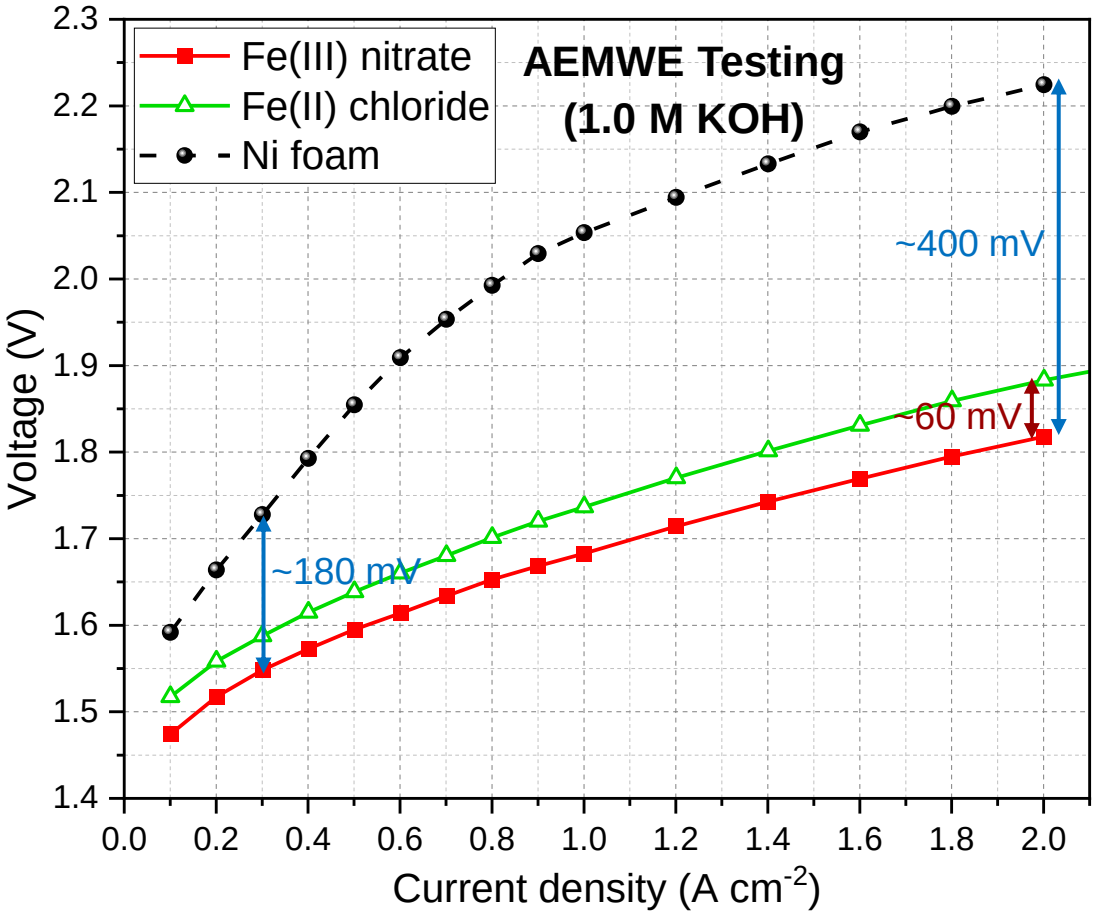
Advantages of PTL-supported catalysts:

- *Synthesized directly on Ni foam; entire PTL surface catalytically active*
- *No need for ink preparation/deposition or for ionomer likely blocking active sites*

Drawbacks

- *Catalyst loading difficult to control precisely*
- *AEMWE operation requiring electrolyte (no DI water operation)*

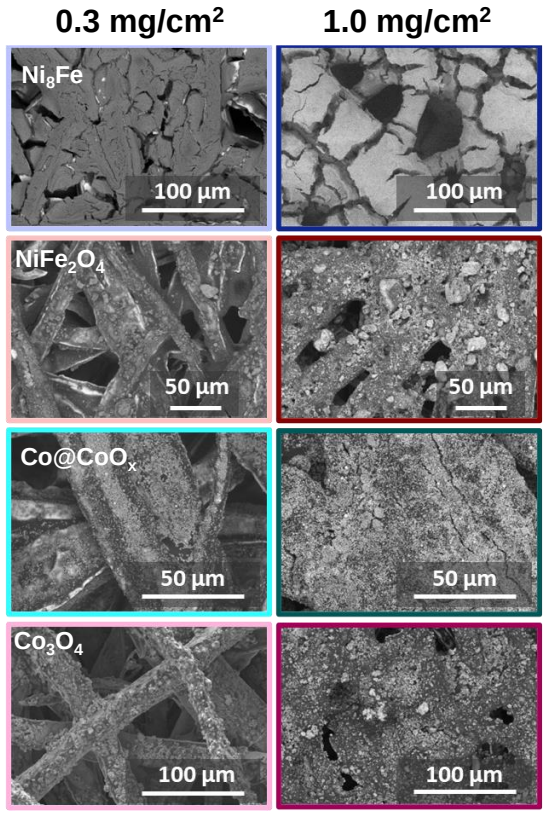
Anode: Fe-functionalized Ni foam; **Cathode**: Pt 20% Ru 10% on C ~0.5 mg_{Pt}/cm^2, spray-coated MGL370 GDL; **Cell:** 5 cm^2, 1.0 M KOH, 10 mL min^{-1} flow on anode only; **Membrane:** Versogen PiperION (40 µm); **Temperature:** 70 °C



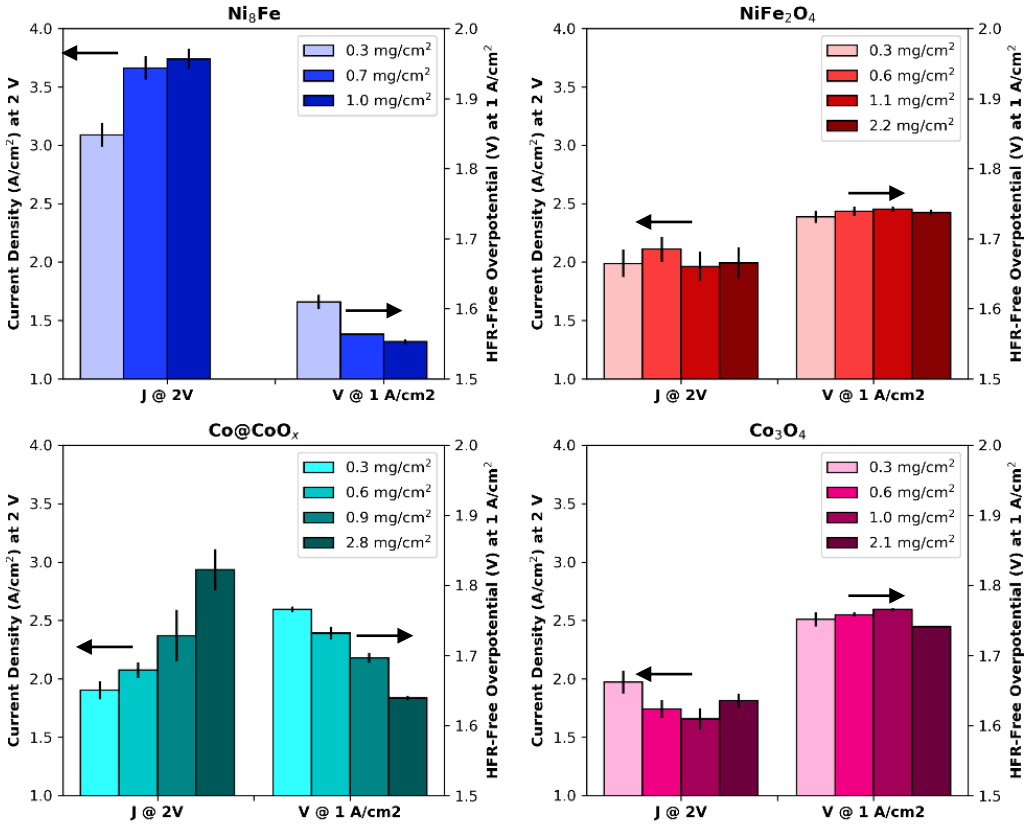
- Large performance improvement due to surface functionalization of Ni foam with Fe
- Better performance at BOT with NiFe catalyst synthesized using $Fe(NO_3)_3$ *vs.* $FeCl_2$ (*ca.* 60 mV at 2 A cm^{-2})
- **Highlight: 1.82 V at 2.0 A cm^{-2}** achieved in 1.0 M AEMWE with PTL-supported NiFe catalyst

OER Catalysis: Impact of Catalyst Properties on Optimal Anode Loading

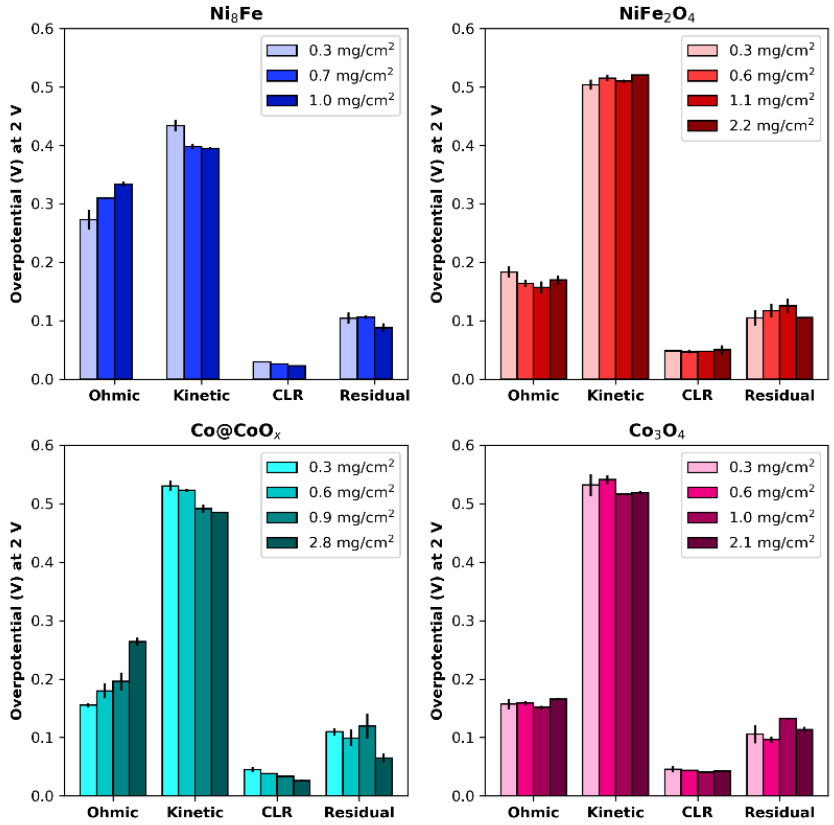
Anode: 0.3-2.8 mg_{TM} cm^{-2} Ni_8Fe (ElectroCat), commercial $NiFe_2O_4$, Co_3O_4 (USRM), Co (Alfa Aesar); **Cathode:** 0.3 mg_{Pt}/cm^2 Pt/C (TKK); **Electrolyte:** 1 M KOH; **Temperature:** 80 °C; **Membrane:** PiperION TP-85 (80 µm); **Ionomer:** PiperION TP-85 (30 wt%); **Anode PTL:** Ni 18-025 (Bekaert); **Cathode GDL:** MGL280 C paper



Performance Summary



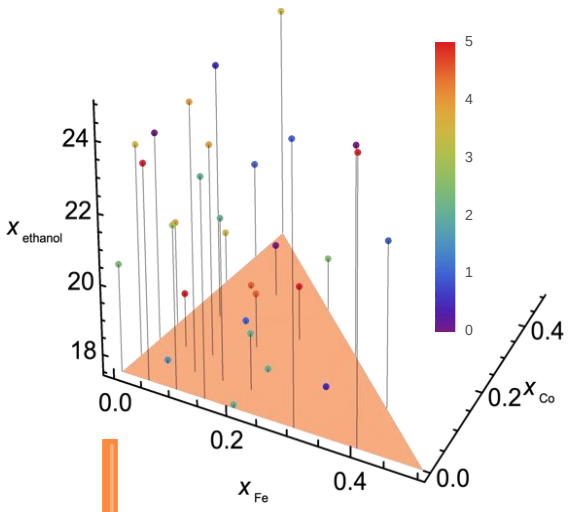
Voltage Breakdown Analysis



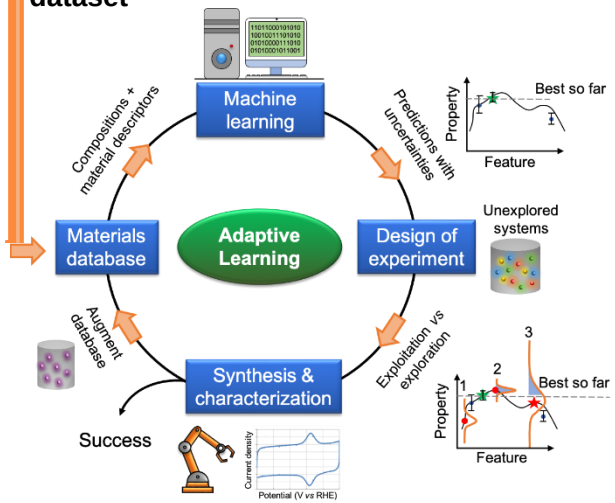
Highlight: Optimal anode catalyst loading depends on catalyst properties:

- Increased loading improving performance of Ni_8Fe and Co → Enhanced kinetics and decreased catalyst layer resistance
- Increased loading having minimal effect on $NiFe_2O_4$ and Co_3O_4 performance → Decreased mass activity

Composition space



Initial dataset

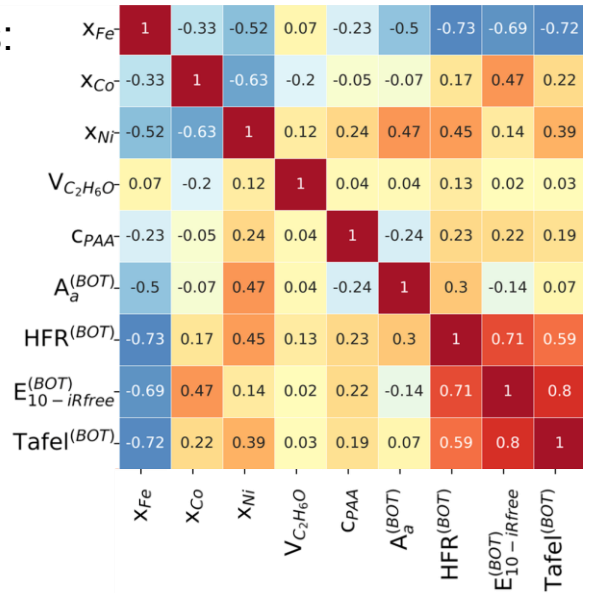


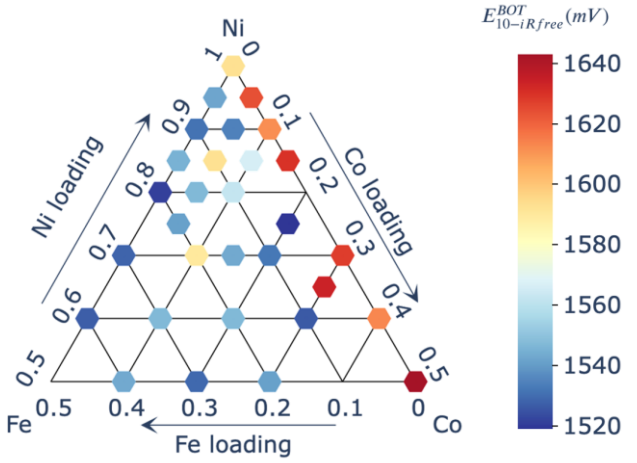
- Adaptive learning used for the design of aerogel-derived, Ni-based OER catalysts
- Four synthesis variables as OER catalyst descriptors:
  - ✓ Ni:Fe molar ratio
  - ✓ Ni:Co molar ratio
  - ✓ ethanol volume
  - ✓ polyacrylic acid (PAA) concentration
- 30 catalysts synthesized and characterized; performance data of **20 catalysts** used to form the initial database (remaining 10 data sets not selected due to nonmonotonic response during durability testing, see slide #28 for details)
- **Relative importance of synthesis variables**

(OER activity inversely correlated to $E_{10-iRfree}^{(BOT)}$):

  - ✓ Little impact of ethanol content; PAA decreasing activity
  - ✓ Key role of chemical composition (not surprisingly)
  - ✓ Low initial activity of binary CoNi catalyst samples
  - ✓ Activity of all binary FeNi higher than that of pure Ni
  - ✓ **Some ternary FeCoNi samples worth further studies**

Pearson correlations





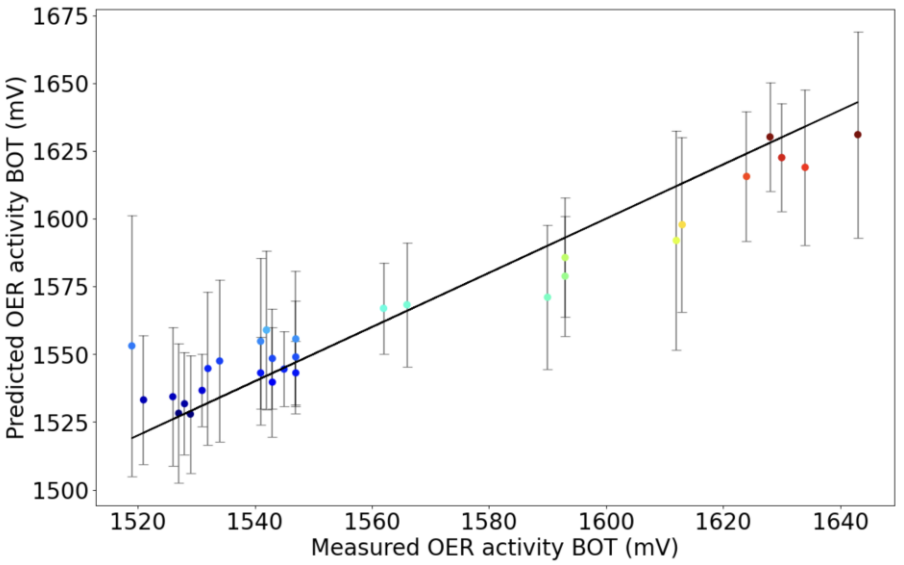
OER Catalysis: Machine Learning of FeNiCo Catalyst Activity

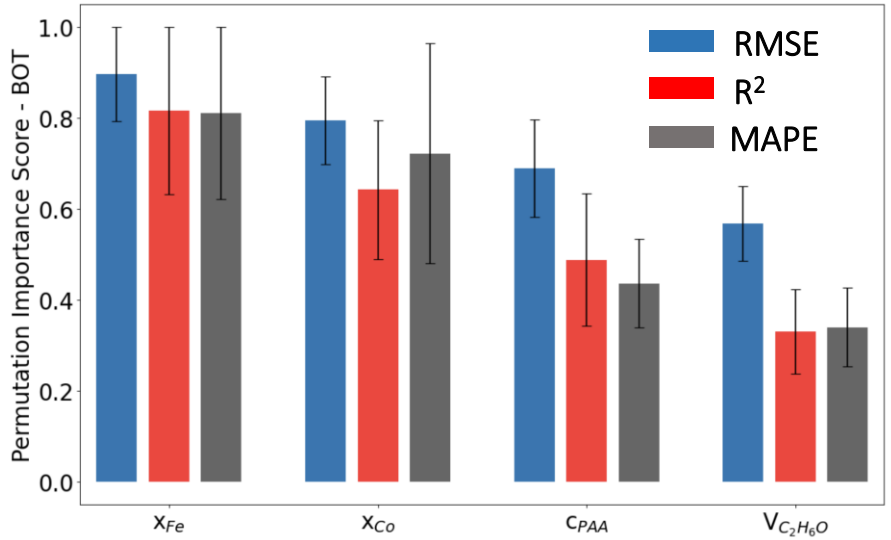
- ✓ Optimized and trained an artificial neural network models (ANN) for OER activity
- ✓ Performed uncertainty quantification using bootstrap sampling
- ✓ Model predicting **further OER activity improvement** by at least 30 mV
- ✓ **Five new samples** selected for synthesis following adaptive learning

Sample	x_{Fe}	x_{Co}	V_{C2H5OH} (mL)	C_{PAA} (mg/mL)	E_{BOT} (V)
1	0.15	0.00	21	3.9	1.51 ± 0.02
2	0.25	0.24	24	0.0	1.52 ± 0.03
3	0.00	0.35	21	3.3	1.63 ± 0.03
4	0.19	0.00	22	4.3	1.50 ± 0.03
5	0.20	0.00	21	4.7	1.50 ± 0.01

- ✓ ***Catalyst samples about to be synthesized!***

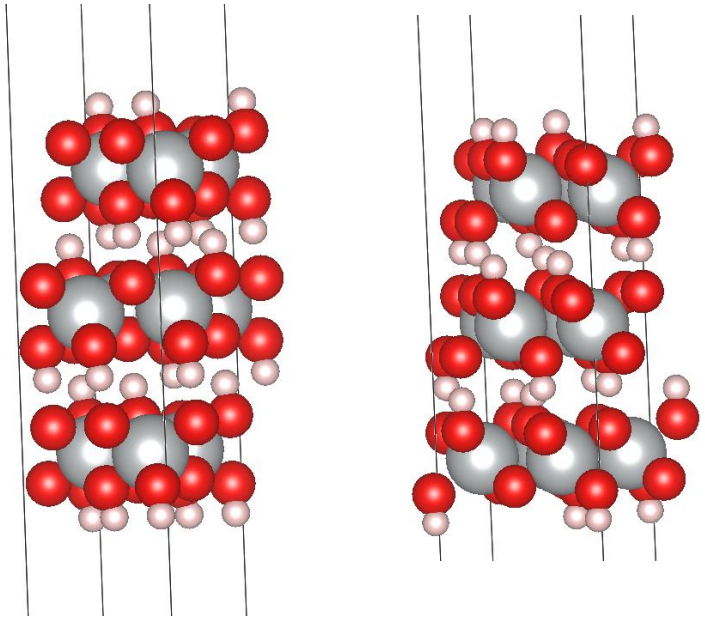
Highlight: Developed **new adaptive learning framework** applied to OER FeNiCo catalysts, successfully using uncertainty quantification and Bayesian optimization to **select the best next 5 samples for synthesis and testing**





OER Catalysis: Effect of Methodology and Model on Calculated Band Gap

- Materials with a band gap predicted to have charged defects, *e.g.*, oxygen vacancies (lattice oxygen OER mechanisms) and cation vacancies (dissolution/stability), impacting formation energetics
- Band gap calculated with three levels of theory and varied NiOOH structural representation, showing that
  - ✓ *Structure matters (H occupation position in 3-layer structure gives a change of 0.62 eV between two structures)*
  - ✓ *Number of layer matters*
  - ✓ *DFT methodology has biggest impact*

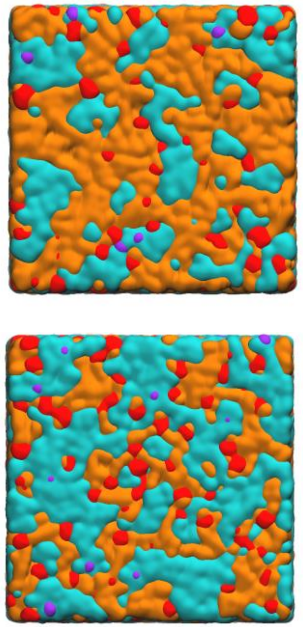


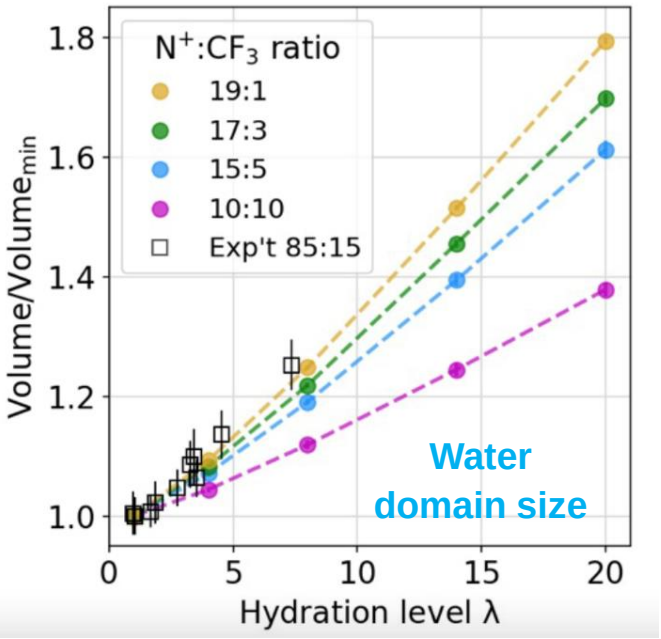
Structure and Method	Calculated Band Gap (eV)
2-layer GGA+U	0.62
2-layer r2SCAN	0.57
2-layer HSE06	2.03
2x2 2-layer GGA+U	0.62
3-layer structure 1 GGA+U	0.00
3-layer structure 2 GGA+U (lower energy)	0.47

Highlight: Calculated band gap found to be a function of methodology and model; position of H and O determined to be fluid, especially for the active surface, impacting the band gap and likely the formation energy of oxygen vacancies

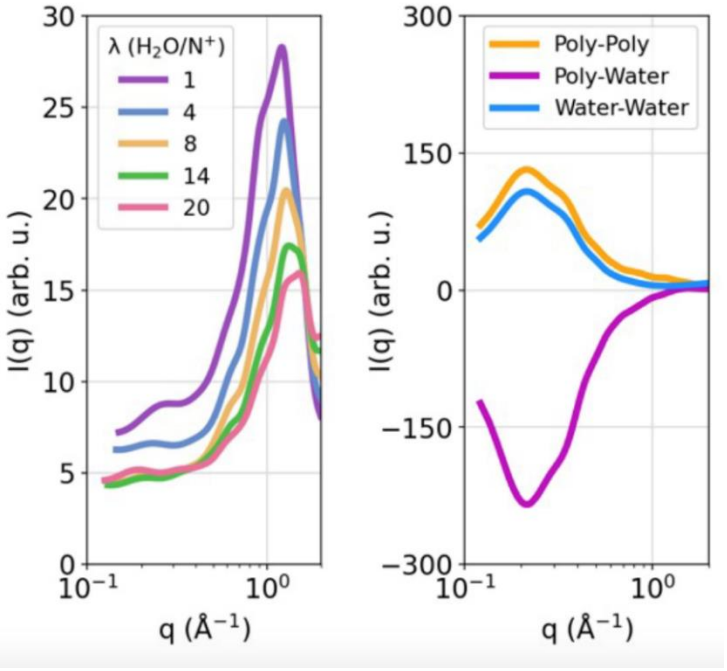
- *Understanding water domain structure in polymer membranes key for realistic device performance*
- *Water domain structure changes with polymer stoichiometry and hydration, significantly effecting transport*

Bulk Polymer Modeling: PiperION





Simulated X-ray Scattering

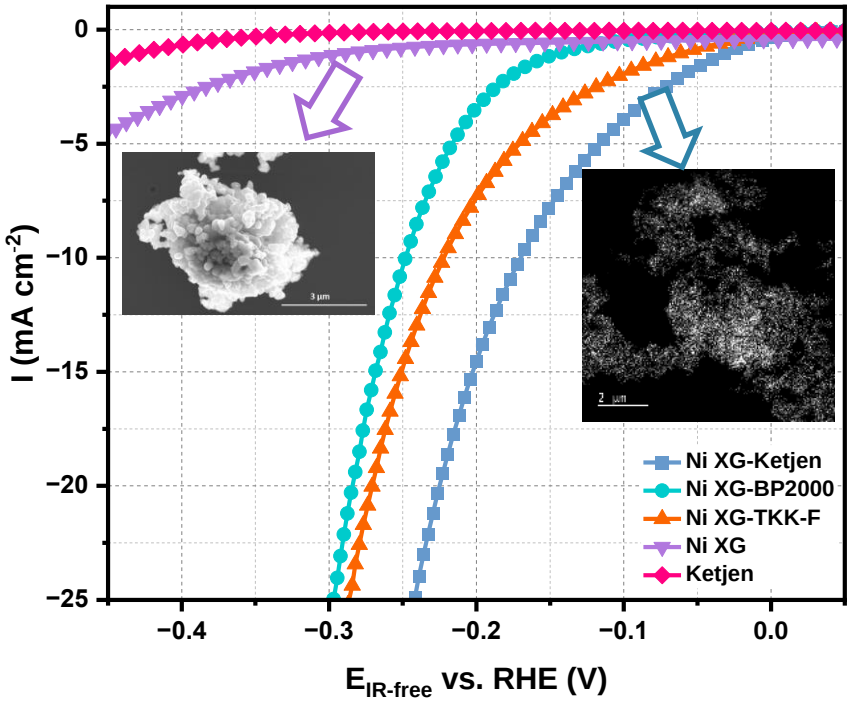


- **Computed swelling** of poly(aryl piperidinium) polymers in good agreement with experiment (Y. Yan data)
- **Computed simulated X-ray scattering**: (1) small scattering peak for poly(aryl piperidinium) polymers in good agreement with experiment (Y. Yan and A. Kusoglu data); (2) different components of scattering resolved
- **Highlight: Completed FY23 Q4 QPM** (*"Calculate the water domain width in poly(aryl piperidinium)-based polymers as a function of hydration. Compare computed scattering functions to existing x-ray scattering data."*)

HER Catalysis: Carbon Supported Ni/C Catalysts

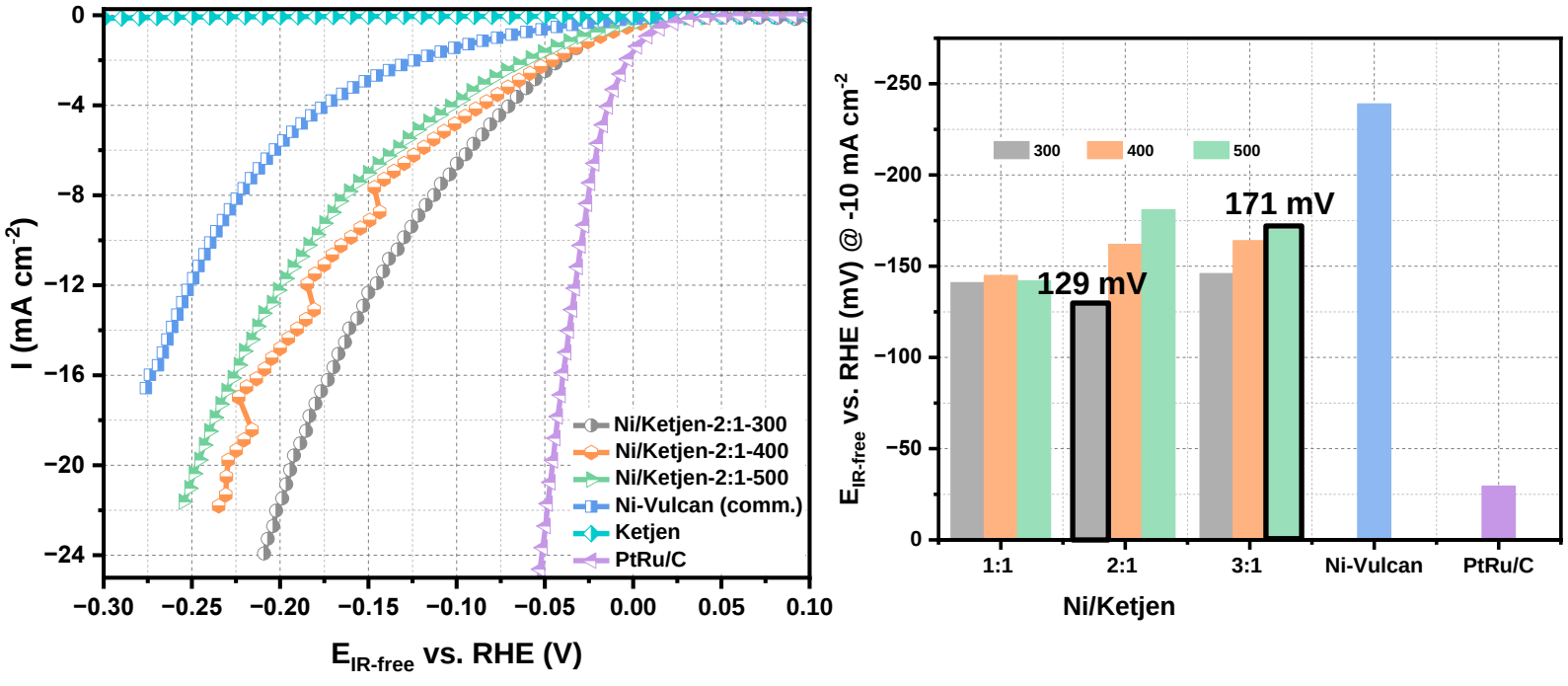
Effect of Carbon Support

Heat treatment at 500 °C for 2 h; Ni-to-C ratio 3:1; 0.1 M KOH



Effect of heat treatment temperature and Ni:C ratio

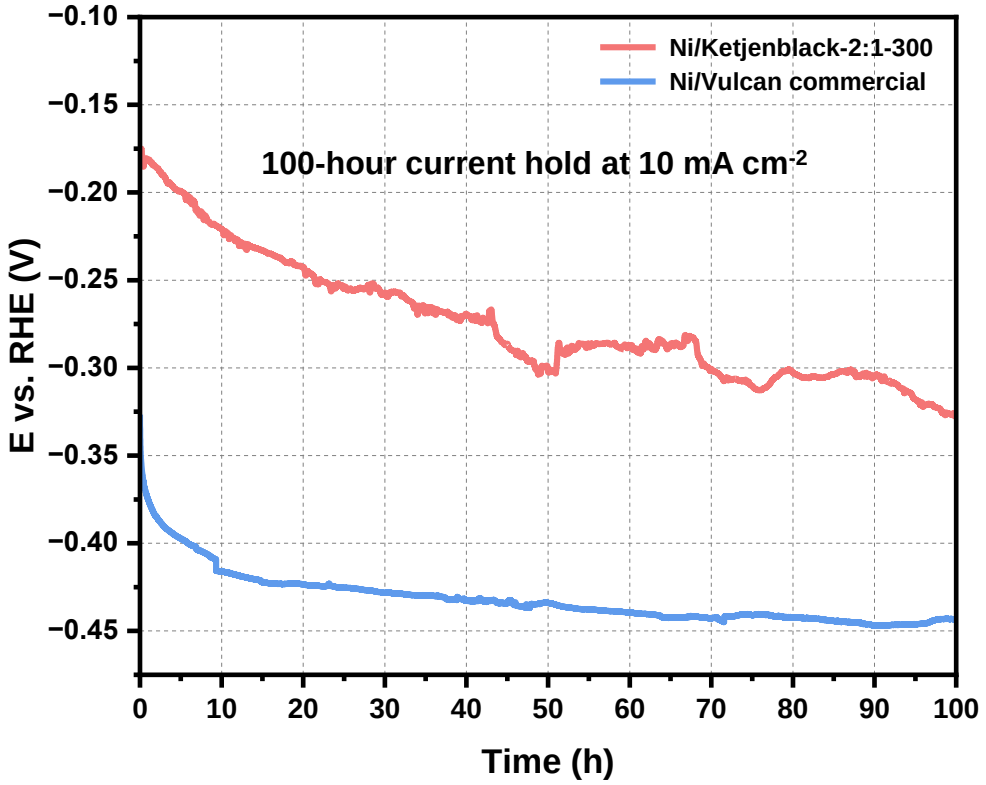
Catalysts heat-treated at 300, 400, and 500 °C for 2 h; 0.1 M KOH



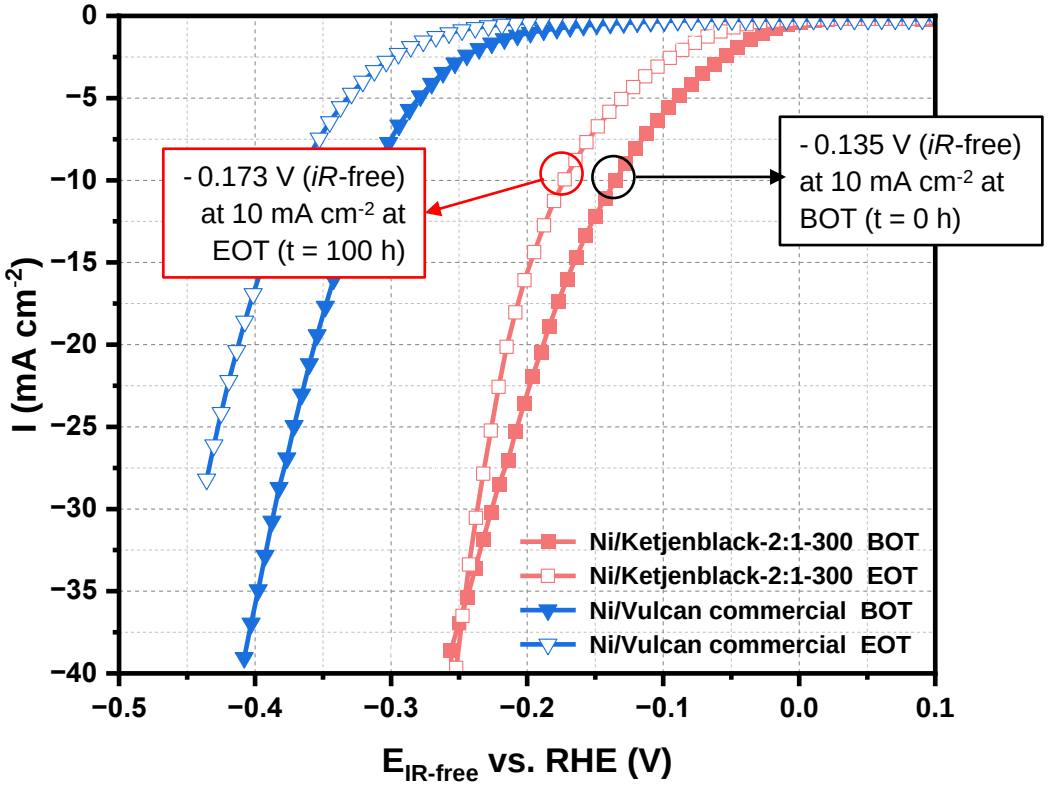
- Performance enhancement with Ketjenblack substrate by *ca.* 350 mV relative to the unsupported catalyst
- **Highlight:** All Ni/C samples outperforming commercial 40% Ni/Vulcan XC-72 by at least 100 mV at 10 mA cm^{-2}
- HER activity at 10 mA cm^{-2} recently improved by approximately **40 mV**

HER Catalysis: FY24 Q2 Quarterly Progress Measure (QPM, Ni Catalyst)

FY24 Q2 QPM: *"HER current density in an aqueous alkaline electrolyte of 10 mA cm^{-2} at a potential of ≥ - 0.26 V vs. RHE (iR-free) at the beginning of test and no more than 0.4 mV/h potential loss (calculated after the first ≥ 10 h break-in period) during ≥ 100 h durability test at a current density of at least 10 mA cm^{-2}."*



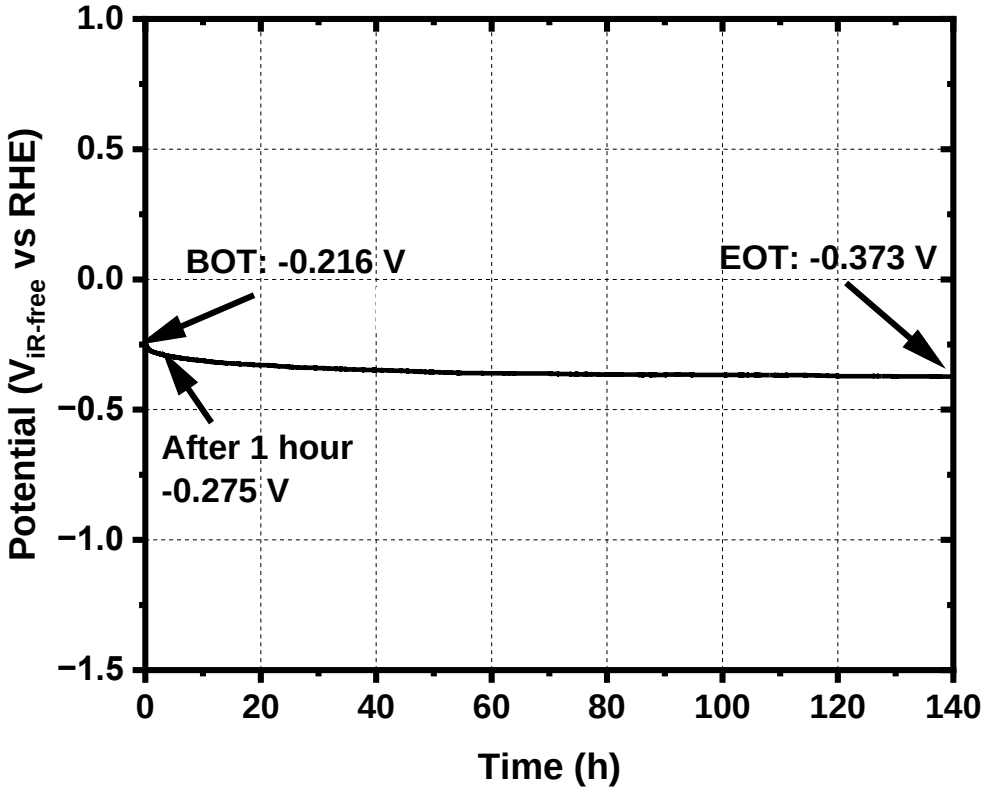
Staircase voltammetry: 10 mV step, 10 s duration; 2500 rpm; N_2-saturated 0.1 M KOH, I/C = 0.6; 0.75 mg/cm^2 catalyst loading



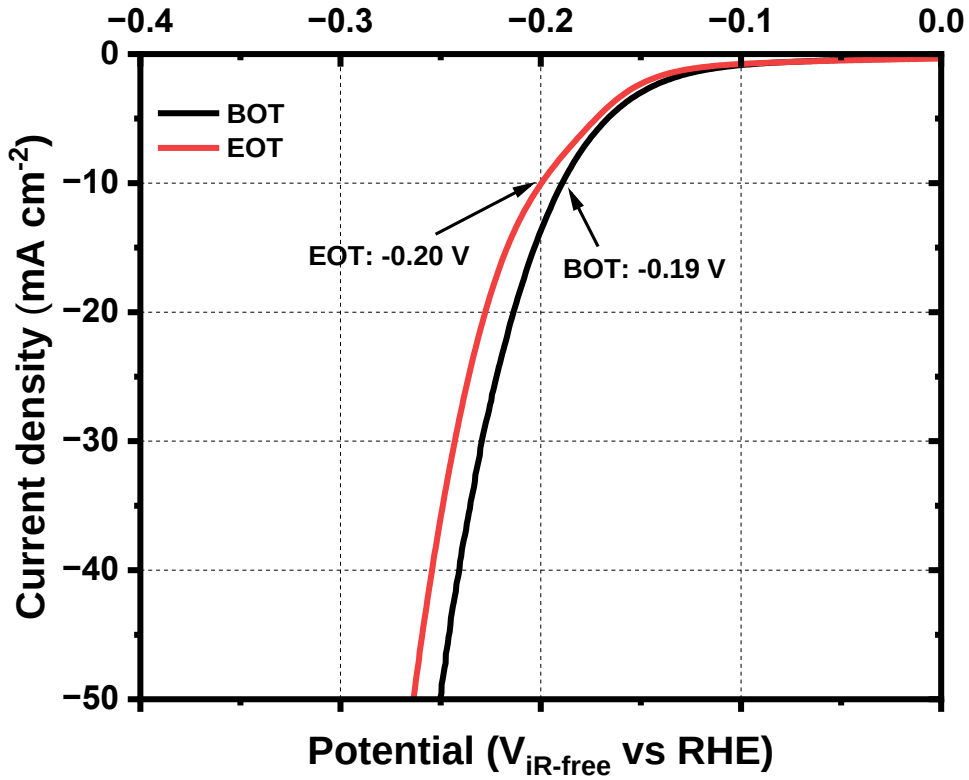
Highlight: Exceeded FY24 Q2 QPM with 10 mA/cm^2 measured at **- 0.15 V** at BOT (*vs.* QPM target ≥ - 0.26 V) and **0.38 mV/h** (0.55 mV/h without any interruption) in a 100-hour test (*vs.* QPM target of 0.4 mV/h)

HER Catalysis: FY24 Q2 QPM (NiCo 1:1 Catalyst)

Chronopotentiometry: 10 mA/cm^2; Ar-saturated 1.0 M KOH; 0.25 mg/cm^2 catalyst loading



Staircase voltammetry: 3600 rpm; Ar-saturated 1.0 M KOH; 0.25 mg/cm^2 catalyst loading



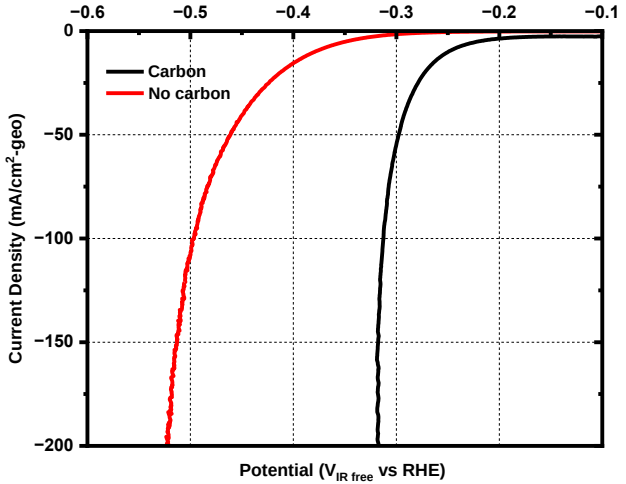
Degradation rate: = (0.20 V - 0.19 V)/140 h = 0.071 mV/h

Highlight: Exceeded FY24 Q2 QPM with 10 mA/cm^2 measured at **- 0.22 V** at BOT (*vs.* QPM target ≥ - 0.26 V) and **0.07 mV/h** (1.1 mV/h without any interruption) in a 140-hour test (*vs.* QPM target of 0.4 mV/h)

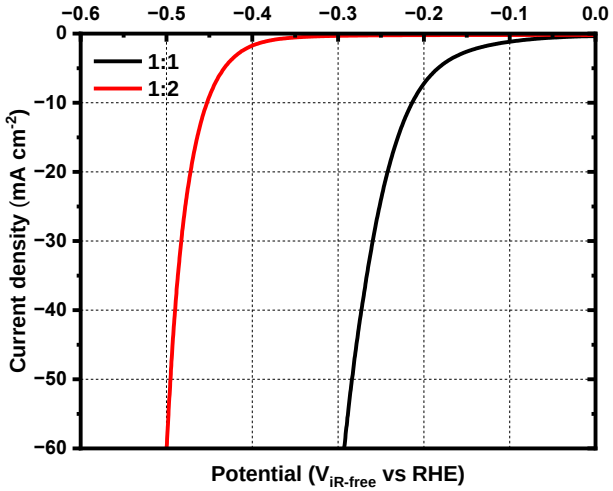
HER Catalysis: Multi-metallic Nanocomposites

LSV: 5 mV/s, 3600 rpm; Ar-saturated 1.0 M KOH; 0.25 mg/cm^2 catalyst loading

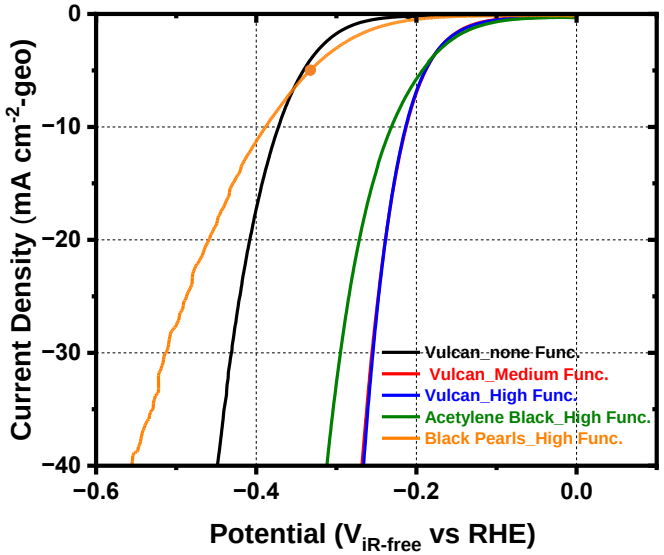
NiFeCo: Effect of carbon addition



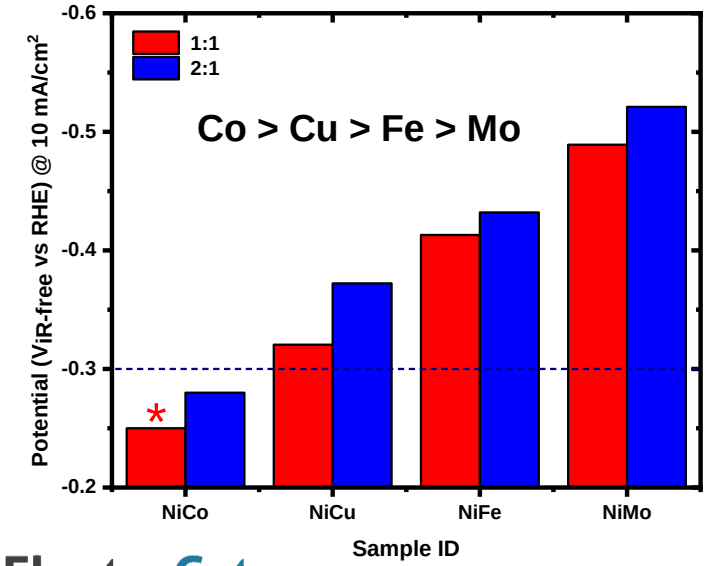
Effect of Ni-to-Co ratio



Effect of carbon type



Effect of second metal

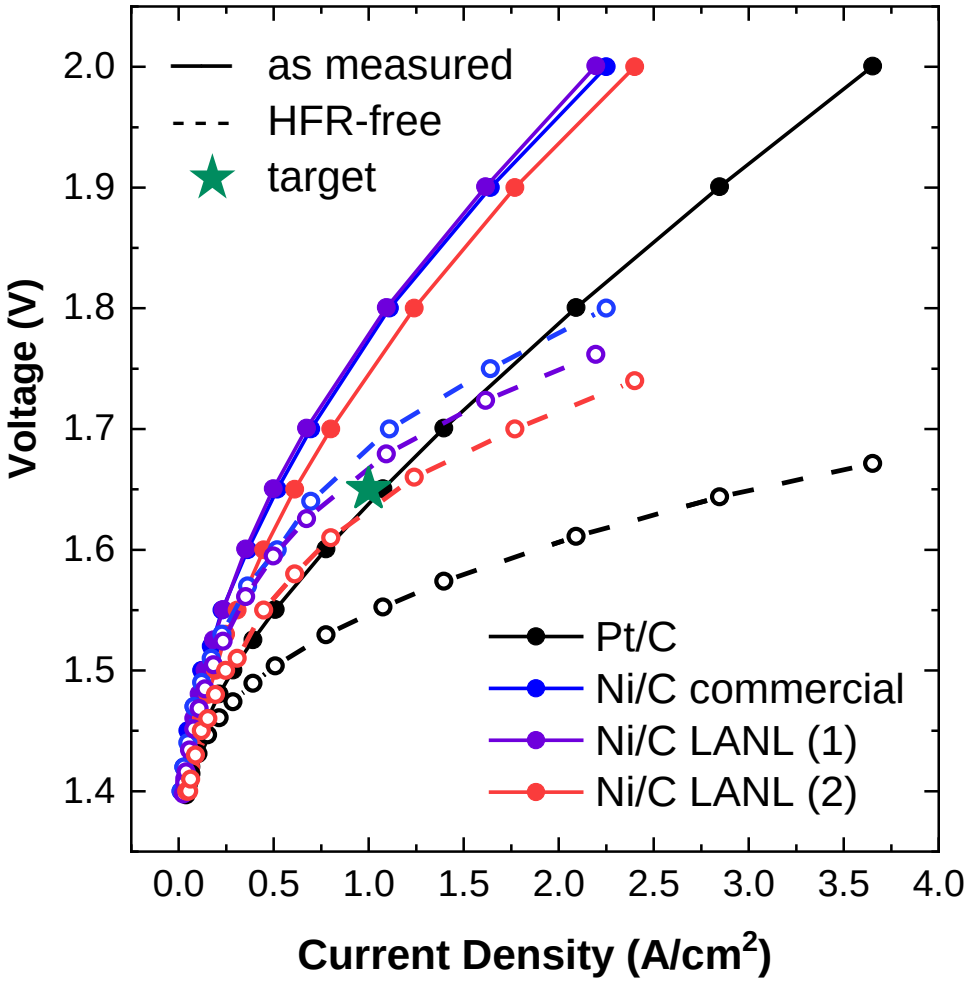


- Carbon addition, especially during, rather than post, synthesis significantly enhancing HER activity of the ternary NiFeCo nanocomposite catalyst
- Highest activity achieved with functionalized Vulcan carbon
- 1:1 NiM catalysts consistently outperforming their 1:2 counterparts, with 1:1 NiCo showing the highest activity
- Low performance of NiMo nanocomposite attributed to low Mo loading on carbon requiring further optimization
- Type of solvent and separation method found to impact performance of the catalysts – highest performance measured following synthesis in water

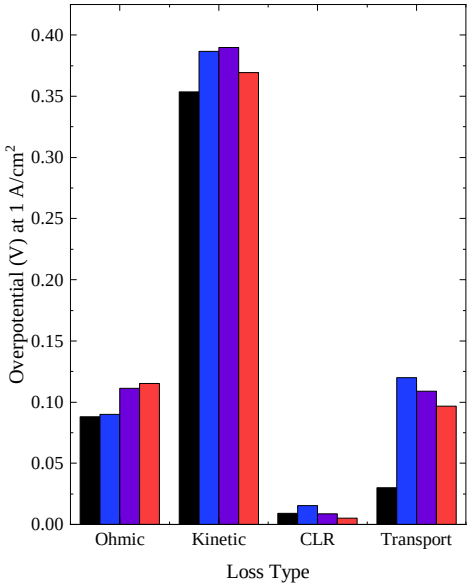
HER & OER Catalysis: Towards Fully PGM-Free AEM Electrolyzer System

FY24 Q4 QPM: *"Achieve **1.65 V** iR-free at 1.0 A cm^{-2} for an AEMWE electrolyzer having ElectroCat PGM-free catalysts at both anode and cathode, operating with supporting electrolyte feed (1.0 M KOH) and run > 100 h durability test."*

Anode: 0.7-1.1 mg_{TM} cm^{-2} Ni_8Fe (ElectroCat); **Cathode:** 0.3 mg_{Pt}/cm^2 Pt/C (TKK) or 4.8 mg_{Ni}/cm^2 Ni/C (Fuel Cell Store) or 4.0 mg_{Ni}/cm^2 Ni/C (ElectroCat); **Electrolyte:** 1 M KOH; **Temperature:** 80 °C; **Membrane:** PiperION TP-85 (80 µm); **Ionomer:** PiperION TP-85 (30 wt%); **Anode PTL:** Ni 18-025 or HR alloy (Bekaert); **Cathode GDL:** MGL280 C paper



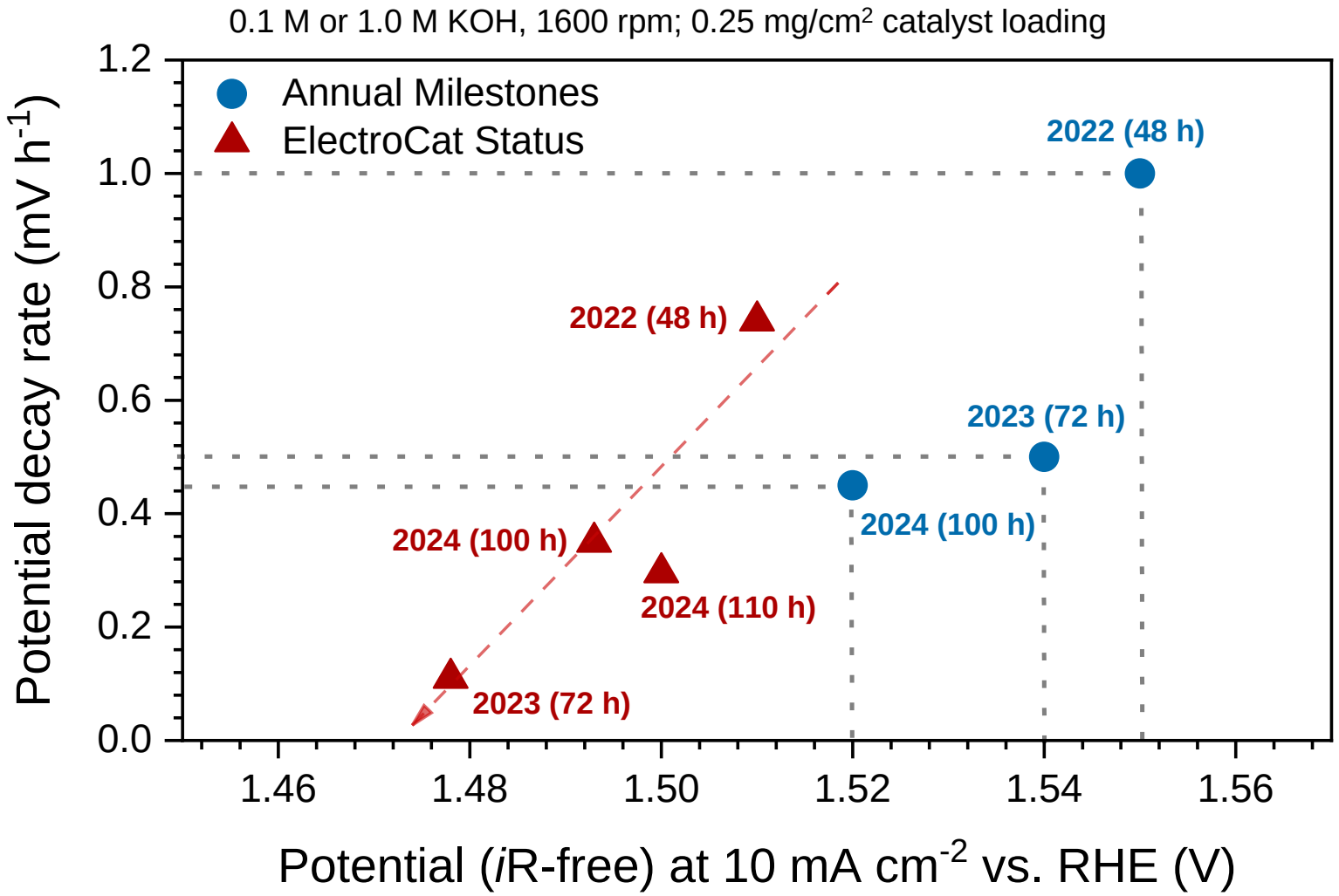
Performance Loss Summary



- Overall performance loss dominated by kinetic losses for all systems
- **Highlight: Target PGM-free AEMWE performance reached** with ElectroCat Ni_8Fe catalyst on NiCrMoFe PTL (anode) and ElectroCat Ni/C catalyst (cathode)
- Possible catalytic effect of NiCrMoFe PTL in need of assessment

Cathode Catalyst	Pt/C	Ni/C commercial	Ni/C LANL (1)	Ni/C LANL (2)
Anode PTL	Ni	Ni	Ni	NiCrMoFe
HFR-free Voltage at 1.0 A/cm² (V)	1.56	1.68	1.67	**1.63**
Current Density at 2.0 V (A/cm²)	3.78	2.25	2.19	2.40

Progress in OER Activity and Durability in Aqueous Electrolyte



Collaboration and Coordination

ElectroCat core national laboratories:

- Los Alamos National Laboratory – ElectroCat co-Lead
- Argonne National Laboratory – ElectroCat co-Lead
- National Renewable Energy Laboratory
- Oak Ridge National Laboratory

Collaborators not directly participating in ElectroCat (no-cost)**:**

- Cornell High Energy Synchrotron Source, Ithaca, New York – X-ray catalyst characterization
- Bar-Ilan University, Israel – aerogel-based catalysts with high active-site density
- Giner Labs – independent catalyst evaluation
- Israeli Fuel Cell Consortium (IFCC) – PGM-free activity indicators and durability
- Pajarito Powder, Albuquerque, New Mexico – catalyst commercialization
- Rensselaer Polytechnic Institute (RPI), Troy, New York – alkaline membranes and ionomers
- University at Buffalo, Buffalo, New York – novel PGM-free catalyst characterization
- University of Warsaw, Warsaw, Poland – PGM-free catalyst development

Response to Reviewers' Comments from 2023 Annual Merit Review

- *Hitting the project's activity "target" has little impact if it [the catalyst] is not durable.*

  As shown in slide #9, ElectroCat's Annual Milestones include both performance and durability metrics and has for several years (e.g., FY23: ≥ 85 mA cm^{-2} at 0.8 V and ≤ 40 mV loss at 0.8 A cm^{-2} after 30k AST cycles; FY24: ≥ 90 mA/cm^2 and ≤ 35 mV. While, in general, higher beginning of life performance can be achieved with less stable catalysts, we have succeeded in continually improving both the performance and durability of PGM-free ORR catalysts.

- *[…] there is virtually no interest from industry or the international community.*

  ElectroCat 2.0 is a lower TRL consortium focused on higher risk, higher reward materials development consortium. We have received requests from industry for ElectroCat-developed materials for evaluation. There is interest from the international community, as evidenced by the number of invited presentation requests to ElectroCat 2.0 researchers from this community

- *[…] one can argue about the direct applicability of modeling outcomes toward technical targets and deliverables.*

  The simultaneous improvements in activity and stability required for PGM-free electrocatalyst systems requires a more fundamental understanding of experimental findings, a role in which modeling has excelled within the consortium. For instance, the likely presence of an axial fifth ligand predicted by modeling has both aided interpretation of *in situ* XAS results and influenced the design process of materials (e.g., increasing access to the M-N-C on both "sides" of the graphitic support). In FY24, synthesis targeting bilayer μ-nitrido structures was motivated by modeling calculations of activity and stability that are only possible due to previous modeling development within the consortium. Furthermore, the underlying chemistry of the activity-stability tradeoff often reported in these materials is being directly explored through DFT models, something which is difficult, if not impossible, to do with present experimental methods. An argument that modeling efforts do not apply toward technical targets, which include fundamental understanding to guide the simultaneous improvements in both activity and stability, has not been the reality within ElectroCat where modelers and experimentalists have worked together to achieve the consortium goals.

Response to Reviewers' Comments from 2023 Annual Merit Review

- *[…] [The electrolyzer] current density at 1.8 V is not state-of-the-art.*

  The best ElectroCat 2.0 performance achieved to date is 2.17 A cm^{-2} at 1.8 V with 0.3 mg_{Pt} cm^{-2} cathode, an ElectroCat 2.0 Ni_8Fe anode, and a PiperION 80 µm thick membrane in 1.0 M KOH. This is comparable to the highest performance reported in the literature using an activated SS PTL anode (A. W. Tricker *et al.*, 10.1002/aenm.202303629). ElectroCat 2.0's status for a completely PGM-free MEA is 1.25 A cm^{-2} at 1.8 V, also using 1.0 M KOH and the same membrane. Electrolyzer performance is highly dependent, among many factors, on the type of anion-exchange membrane, its thickness, the concentration of electrolyte. While much higher current densities can be achieved with thinner membranes (e.g., 15 µm thick), thin membranes are prone to shorting and crossover. ElectroCat 2.0 is a catalyst development and implementation consortium, therefore, we chose a thick robust membrane that would allow us to measure catalyst durability. We also typically compare and report HFR-free voltage values to allow comparison of catalyst performance even when using different membranes.

- *National lab responsibilities are clear from the milestone tables, but in the accomplishment slides, it is not always clear where the work is being done. A note (or logo) in proximity to key technical results would help the viewer understand the roles of each of the national labs and the other collaborators.*

  It has been a common practice for the last several years for the DOE HFTO consortia to not attribute research results to a particular national laboratory to illustrate and reinforce the collaborative nature of the consortia.

Selected Accomplishments and Progress

ElectroCat Development and Communication

- Consortium-wide in-person meetings held at ANL September 14-15, 2023, and at NREL February 13-14, 2024
- Initiated integration of two minority-serving institution (UC Riverside and UT El Paso FOA projects into ElectroCat)
- 15 papers/book chapters published and 20 presentations, including 14 invited
- Further developed and validated *in situ* Mössbauer capabilities for OER catalyst activation and degradation studies
- Implemented new, cooperative game theory-based ML methods to enhance understanding of the effect of synthesis conditions on catalysts performance

Progress in Performance of PGM-free ORR Catalysts since 2023 AMR

- Achieved initial MEA H_2-air current density of 117 mA cm^{-2} at 0.80 V for an Fe-N-C catalyst, a ~21% improvement
- Achieved combined H_2-air performance of 95 mA cm^{-2} at 0.80 V and durability of 31 mV loss at 0.80 A cm^{-2} after 30k AST cycles (compared to 49 mV after 10k AST, 2023 status)
- Achieved 100% enhancement in ORR activity and 100% enhancement in stability versus FY22 best-in-class high-throughput synthesized Fe-N-C catalysts (*vs.* 88% and 78% reported in 2023 AMR)

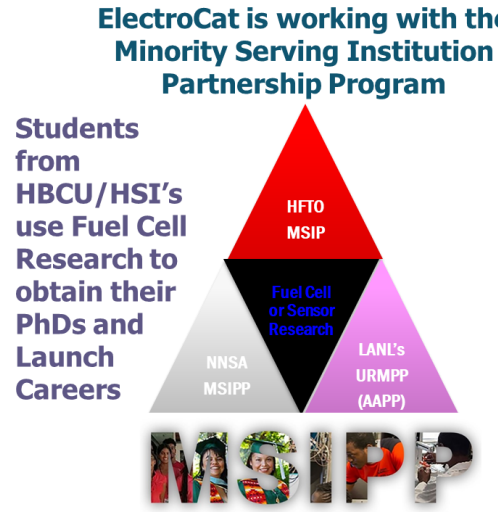
Progress in PGM-free OER and HER Catalysts since 2023 AMR

- Accomplished major progress in realizing entirely PGM-free AEMWE water electrolyzer by reaching 1.0 A/cm^2 at 1.67 V
- With two catalyst systems exceeded FY24 OER catalyst performance target (10 mA/cm^2 at 1.52 V and 0.45 mV/h)
- Developed PTL-supported NiFe OER catalyst with very high AEMWE initial performance (2.0 A/cm^2 at 1.82 V)
- Applied machine learning to 20 OER catalyst samples identifying five new samples for next synthesis round (*ongoing*)
- Performed voltage breakdown analysis for OER catalysts, identifying kinetic losses as impacting performance the most
- Used molecular dynamics to compute swelling of AEM polymers and simulate X-ray scattering data
- Exceeded FY23 annual milestone and FY24 Q2 QPM for two classes of HER catalysts, demonstrating 10 mA/cm^2 at -0.15 V and 0.38 mV/h and -0.19 V and 0.07 mV/h, respectively

Diversity, Equity, Inclusion, and Accessibility

Outreach and Workforce Development

- ElectroCat has recruited a diverse workforce, including several from communities that have been historically underrepresented in science and technology. ElectroCat has Steering Committee member from this community
- ElectroCat is hosting graduate students from the University of Chicago
- ElectroCat is hosting several DOE Science Undergraduate Laboratory Interns (SULI) students from underrepresented communities each summer
- University of Texas-El Paso (UTEP) and LANL initiated collaboration through the university graduate program
- NREL hosting a student from New Mexico State University through the minority-serving institution internship program, which is part of MSIPP
- ElectroCat is supporting two HFTO/FECM-sponsored DE-FOA-0002598 projects, led by UC Riverside and UTEP, with expertise and capabilities



MSI Visits and Recruitment

- ANL has established a joint appointment for a professor from the University of Illinois – Chicago (UIC), a minority-serving institution
- ANL ElectroCat researchers are participating in a seminar series hosted by UIC

Remaining Challenges and Barriers

Fuel Cells

- Increasing the density of stable ORR active sites and ORR turnover frequency (TOF) to meet DOE H_2-air performance targets
- Increasing accessibility of stable active sites in Fe-N-C catalysts, protection and/or stabilization of active sites, and alternative non-Fe M-N-C catalysts
- Gaining fundamental knowledge in electrocatalysis as a prerequisite for further catalyst development
- Developing atomic-level surface techniques for *in situ* and *operando* studies of surface reactions

Low-Temperature Electrolysis

- Increasing further the performance and durability of electrolyzer operating with PGM-free anode and cathode catalysts
- Improving durability of alkaline membrane electrolyzer operating with liquid KOH and on pure water, also at temperatures higher than 60 °C
- Minimizing degradation of anion-exchange ionomers without a loss in conductivity (outside ElectroCat's scope)
- Understanding key factors determining performance and durability of PGM-free OER and HER catalysts in AEM electrolyzers
- Developing atomic-level surface techniques for *in situ* and *operando* studies of surface reactions

Proposed Future Work

Fuel Cell Catalysts and Electrodes

- Advance performance and durability of cathode catalysts by maximizing volumetric density and accessibility of active sites through alternative synthesis methods and synthesizing catalysts based on insights from theory
- Optimize fuel cell performance of the best-in-class high-throughput catalysts and N-C/Fe-CA-DZ using high-throughput ink optimization and computer-controlled ink deposition
- Incorporate boron, shown to inhibit carbon corrosion in *ex situ* tests, into Fe-N-C catalyst structure
- Further characterize N-C/Fe-CA-DZ catalyst (which met FY24 Annual Milestone) to understand source of stability
- Refine active site and reaction mechanism modeling by:
  - ✓ Accommodating extended defects with modified DFT parameters/cell size and methods
  - ✓ Improving XANES LCF quality by including vacancy sites and edge sites; determine effect of adsorbates on theoretical XANES

Electrolyzer Catalysts and Electrodes

- Enhance activity and improve durability of PTL-supported OER catalysts
- Apply adaptive machine learning and high-throughput synthesis to development of nanostructured OER catalysts
- Include phosphide, sulfide, and selenide free-standing catalysts in HER catalyst development
- Include second metal in the synthesis of Ni-based xerogels for HER
- Calculate charged M and O vacancies on NiOOH with and without Fe- and Co-doping with surface corrections
- Connect molecular dynamics to atomic scale towards understanding the polymer-NiOOH catalyst interface
- Assess viability of AEMWE operating on pure water

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

Summary

Status of Performance and Durability of PGM-free ORR Catalysts for PEMFCs

- Achieved initial MEA H_2-air current density of 117 mA cm^{-2} at 0.80 V, a ~21% improvement vs. 2023 status
- Achieved BOT MEA H_2-air performance of **95 mA cm^{-2} at 0.8 V** and **31 mV loss at 0.80 A cm^{-2}** after 30k AST cycles, exceeding FY23 and FY24 Annual Milestones
- Completed seven out of nine FY23 and FY24 QPMs and Annual Milestones; remaining technical QPM is on-track for completion by FY24 Q4

Status of PGM-free OER and HER Catalysts for Alkaline Exchange Membrane Water Electrolyzers

- Exceeded FY24 HER catalyst performance target in aqueous electrolyte ("10 mA cm^{-2} at a potential of ≥ -0.26 V *vs.* RHE (*iR*-free) at the beginning of test and no more than 0.4 mV/h potential loss […] during ≥ 100 h durability test") with two catalysts: one reaching **10 mA/cm^2 at -0.15 V** and performance loss of **0.38 mV/h** and the other reaching **10 mA/cm^2 at -0.22 V** and losing performance at a rate of only **0.07 mV/h**
- Exceeded FY24 OER catalyst performance target in aqueous electrolyte of 10 mA/cm^2 at 1.52 V and performance loss of ≤ 0.45 mV/h with two catalysts
- Demonstrated **2.17 A cm^{-2} at 1.8 V** (as-measured) with ElectroCat Ni_8Fe anode catalyst, PGM cathode catalyst, and a 80 µm thick PiperION membrane (in 1.0 M KOH)
- Demonstrated **1.0 A/cm^2 at 1.67 V** (*iR*-free) in an AEM water electrolyzer operating with ElectroCat-developed PGM-free catalysts at the anode and the cathode (zero PGM content)

Co-Authors

PGM-free catalyst development, electrochemical, electrolyzer, and fuel cell testing, atomic-scale modeling, machine learning

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