FC171

Advanced PGM-free Cathode Engineering for High Power Density and Durability

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Project Goal

- Enable high, durable power density with new cathode designs specifically for PGM-free catalysts
- Increase PGM-free catalyst activity and stability through synthesis using a simplified, low-cost method
- Improve PGM-free mass activity through optimization of the ionomer integration
- Mitigate PGM-free cathode flooding for fast oxygen transport across thick electrodes

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Overview

Timeline and Budget

- Project Start Date: 09/01/2017
- Project End Date: 08/31/2020
- Total Project Budget: $2,292,324
  - Total Recipient Share: $292,324
  - Total Federal Share: $2,000,000
  - Total DOE Funds Spent*: $1,778,198
    *As of 1/30/2021

Barriers

B. Cost

➢Reduce PEM fuel cell costs by replacing precious metal catalysts with PGM-free catalysts

C. Performance

➢Increase catalyst activity, utilization, and effectiveness to enable high fuel cell power density operation

A. Durability

➢Increase stability of PGM-free catalysts at relevant fuel cell voltages

Project Lead

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- PI: Shawn Litster
- Co-PI: Venkat Viswanathan
- Co-PI: Reeja Jayan

Partners

University at Buffalo, SUNY

- PI: Gang Wu

Giner, Inc.

- PI: Hui Xu

3M Company

- PI: Andrew Haug

Electrocatalysis Consortium Members

Technical Targets and Status

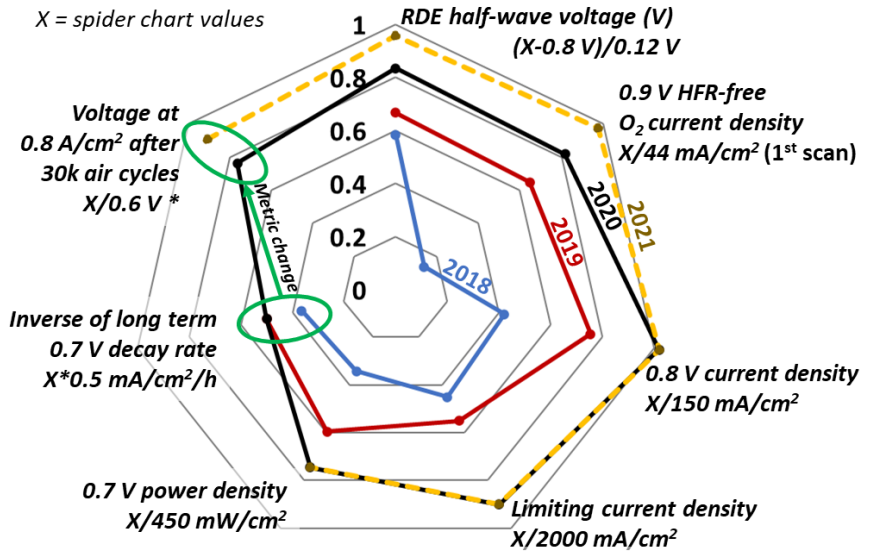
Property	DOE 2020 target	Present project status	Project end goal
PGM free catalyst activity (voltage at 0.044 A/cm²)	0.9 $V_{IR\text{-}free}$ (**2025**)	**0.90 $V_{IR\text{-}free}$, 43 mA/cm²** Ave. of 3 consecutive scans: 0.89 $V_{IR\text{-}free}$, 35 mA/cm²	>0.9 $V_{IR\text{-}free}$
Loss in initial catalyst mass activity	PGM: <40 %	**71%**	<50%
Loss in performance at 0.8 A/cm²	PGM: <30 mV	**30 mV**	<50 mV
MEA air performance @ 0.8 V	PGM: 300 mA/cm²	**153 mA/cm²**	>150 mA/cm²
MEA performance @ rated voltage	PGM: 1000 mW/cm²	**410 mW/cm² at 0.67 V (94°C)**	Stretch goal: >450 mW/cm²

Highlights

- Achieved 0.915 V vs. RHE RDE half-wave voltage
- Met 2025 PGM-free activity target on first scan IV curve
- Demonstrated an active catalyst that meets project power density durability targets
- Established innovative catalyst synthesis and electrode fabrication methods
- Demonstrated stable self-life of scaled-up PGM-free catalyst

Best metrics achieved up to each AMR year.

Normalization factors given. MEA at 80°C, 1.5 atm, 4 mg/cm²



**2020 0.8 A/cm² durability value is 2020 gen catalyst tested in 2021*

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Approach

Year 2 & 3 Milestones and Go/No-Go Points

Milestone or GNG No.	Description	% complete	Notes
Q6 M2.2	CMU model results for synthesis targets and electrode optimization based on imaging and characterization of SOA catalysts. Provide **target active site density and cathode thickness** to meet project end goal.	100%	Model updated with detailed validation against O_2 transport resistance experiments
Q7 M2.3	Demonstrate **30% increase in MEA limiting current density** through improved water management by hydrophobic support layers or iCVD treatment while **current density is >100 mA/cm² at 0.8 V** (150 kPa abs backpressure, 100% RH H2/air at a cell temperature of 80˚C)	100%	Increased limiting current density achieved through enhanced hydrophobicity by ink solvent control and 3D structured cathode/MPL
Q8 G2	Demonstrate **≥25 mA/cm² at 0.90 V** (iR-corrected) in an H_2-O_2 fuel cell with an O_2 partial pressure of 1.0 bar (cell temperature 80 °C). Voltage loss at 0.044 A/cm² less than 100 mV after 30,000 voltage cycles (0.6 to 1.0 V) under H_2-N2 condition.	100%	Achieved **28.5 mA/cm² at 0.9 $V_{HFR\text{-}free}$** MEA durability testing underway.
Q9 M3.2	50% reduction in cathode ohmic losses with advanced ionomers as estimated by N2/H2 electrochemical impedance spectroscopy (EIS).	100%	Achieved with I/C of 0.6 with 725 EW 3M PFSA
Q10 M2.4	MEA with integrated water management components and advanced ionomers meeting performance targets of 150 mA/cm² at 0.8 V and 450 mW/cm² at 0.7 V at beginning of life when operating with 150 kPa abs backpressure 100% RH H2/air at cell temperature of 80 ˚C.	80%	>150 mA/cm² at 0.8 V achieved
Q11 M1.3	Demonstrate catalysts with a half-wave potential comparable to a Pt catalyst (60 µgPt/cm2): E½ > 0.87 V vs. RHE in acidic electrolyte (RDE test); generate a current density of 1.0 mA/cm2 at 0.90 $V_{IR\text{-}free}$ (RDE test); demonstrate MEA performance of 44 mA/cm_2 at >0.90 $V_{IR\text{-}free}$	90%	RDE half-wave potential target achieved with E½ > 0.9 V vs. RHE. Kinetic current density of 6.3 mA cm^{-2} at 0.9 V MEA target nearly met with 43 mA/cm² at 0.9 $V_{HFR\text{-}free}$ on first scan (>44 mA/cm2 with H_2 crossover)
Q12 (Q16) Final deliverable	50 cm² MEAs with ≥30 mA/cm2 at 0.90V (iR-corrected) (with a stretch goal of 0.044 A/cm² at >0.9 VIR-free) in a H2-O2 fuel cell, voltage loss ΔV at 0.044 A/cm2 less than 100 mV after 30,000 voltage cycles (0.6 to 1.0 V) under H2-N2 conditions, <50 mV performance loss at 0.8 A/cm², and performance at 0.8 V of >150 mA/cm2 (with stretch performance goal at rated voltage of >450 mW/cm2) in H2-air fuel cell (measured) while maintaining partial pressure of O2 + N2 at 1.0 bar (cell temperature 80 °C).	75%	**Except for stretch goal for power density at rated voltage, all targets have been met in 5 cm² cells but with different catalysts. Remaining efforts focus increasing activity and power density of stable catalysts and 50 cm² scaling**

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Project Team & Collaborations

Carnegie Mellon University (University prime)

Prof. Shawn Litster (PI), Dr. Bahareh Tavokoli, Dr. Aman Uddin, Lisa Dunsmore, Diana Beltran, Shohei Ogawa, Leiming Hu, Yuqi Guo, Chaofan Yu, Jon Braaten, Jiawei Liu, Prof. Venkat Viswanathan (co-PI), Hasnain Hafiz, Prof. Reeja Jayan (co-PI), Laisuo Su

Electrode design, hydrophobicity treatments, electrode fabrication, fuel cell testing, X-ray imaging, multi-scale modeling, DFT, project management.

University at Buffalo-SUNY (University sub)

Prof. Gang Wu (UB PI), Shengwen Liu, Hanguang Zhang, Yanghua He, Xiaolin Zhao, Mengjie Chen, Hao Zhang

Catalyst development, synthesis, and experimental characterization.

Giner, Inc. (Industry sub)

Dr. Hui Xu (Giner PI), Shuo Ding, Sadia Kabir

Catalyst and MEA fabrication scale-up analysis and demonstration, fuel cell testing, support of hydrophobic cathode development.

3M Company (Industry sub)

Dr. Andrew Haug (3M PI)

Ionomer supply and optimization support.

Electrocatalysis (ElectroCat) EMN Consortium Members (National Laboratories)

X-ray abs. spectroscopy, high-throughput electrodes (ANL), electron microscopy (ORNL), electrode development (NREL), fuel cell durability testing (LANL).

Unfunded Collaborations

Indiana University–Purdue University Indianapolis (IUPUI)

Jian Xie, Chenzhao Li – MEA fabrication and testing

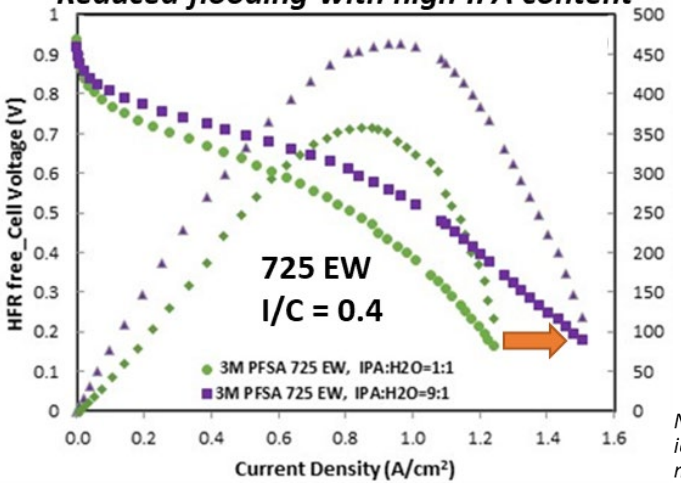
University of Pittsburgh

Guofeng Wang – DFT

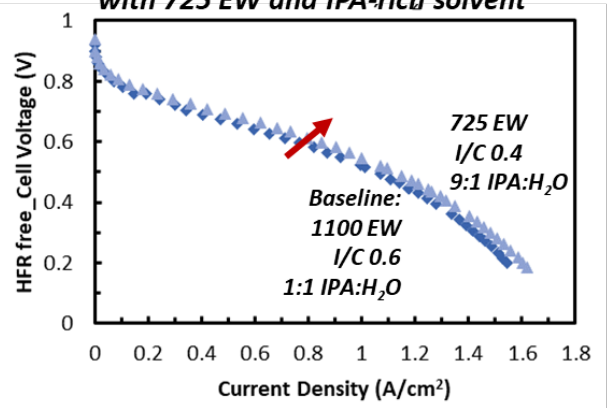
Meeting the 450 mW/cm^2 at 0.7 V Stretch Goal

- Model-based evaluation of mass activity (MA) increase to achieve 450 mW/cm^2 at 0.7 V with air at 80°C and 1.5 atm gas pressure.
- Baseline 2020 Nafion 1100 EW electrode reaches target with **4X** increase of mass activity with a loading of 2 mg/cm^2.
- **2.5X** MA increase required with 725 EW ionomer with hydrophobic pores through solvents tuned for hydrophobicity equivalent to 1100 EW
- MA increase reasonable within current range of reported PGM-free RDE mass activity[1]
- Increased mass activity in concert with high ionomer conductivity and hydrophobic cathode pores are critical to achieving power density target

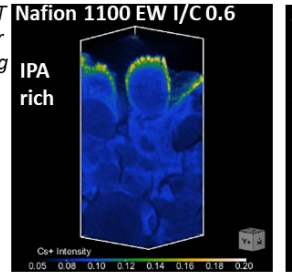
Reduced flooding with high IPA content

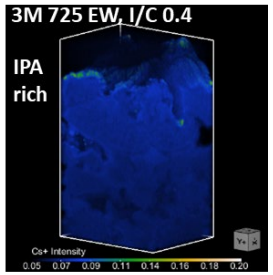


Improved performance with 2/3 ionomer with 725 EW and IPA-rich solvent

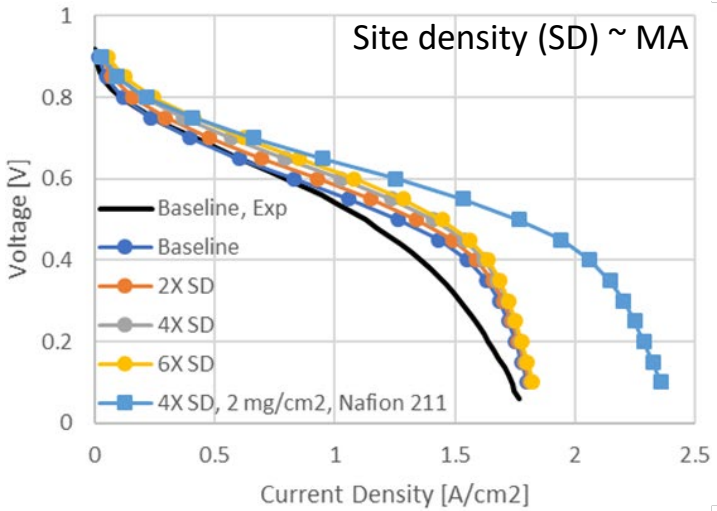


Nano-CT ionomer mapping

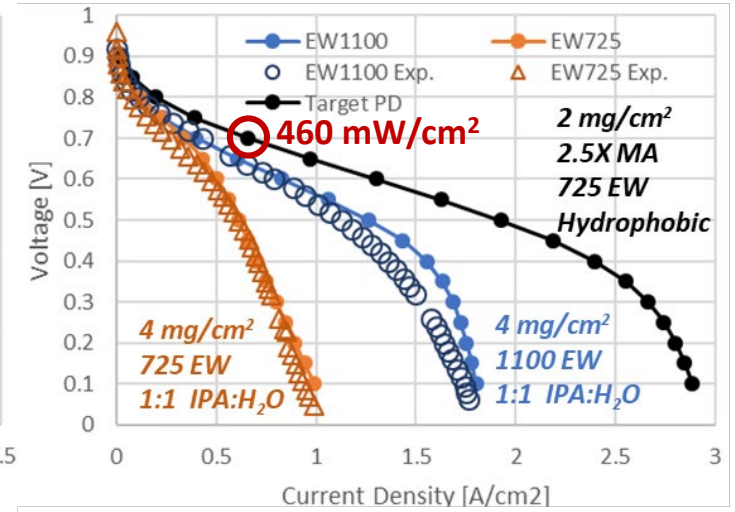




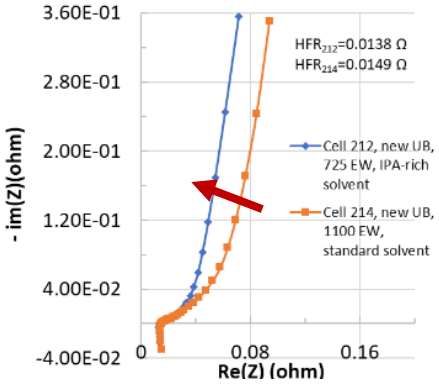
Model evaluation of baseline MA effect



Model evaluation of ionomer & MA effect



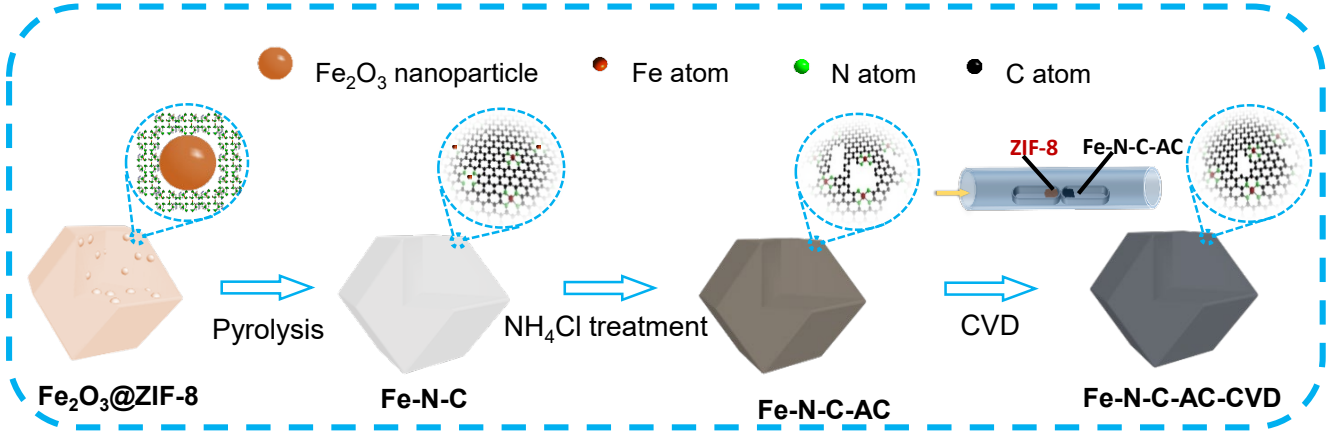
Reduced electrode resistance



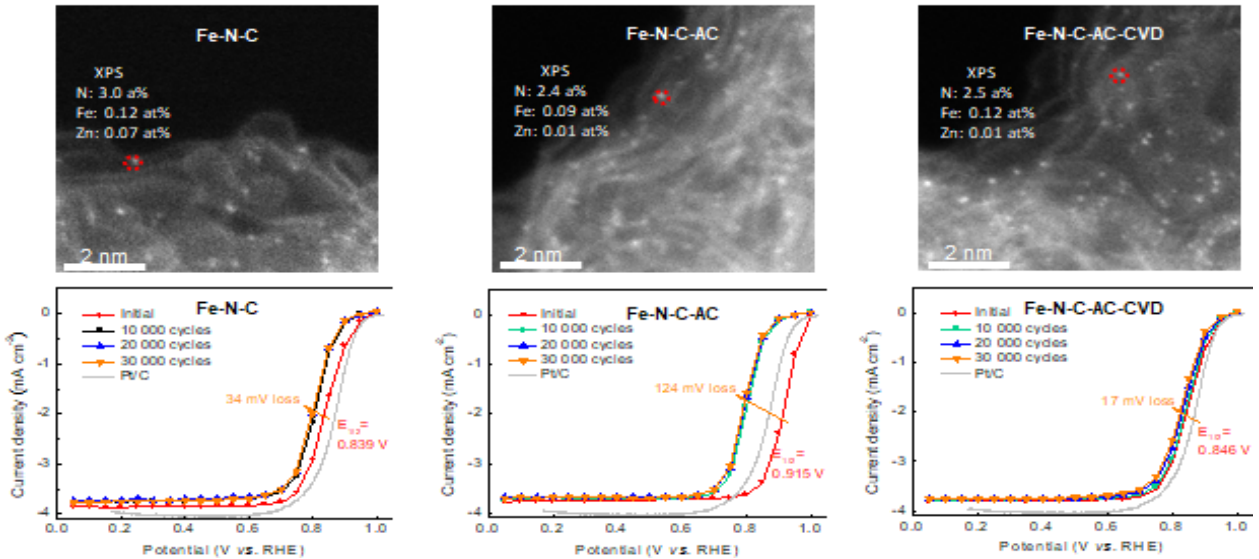
Baseline: I/C = 0.6, 100 nm Fe-N-C primary particles, Nafion 211 membrane

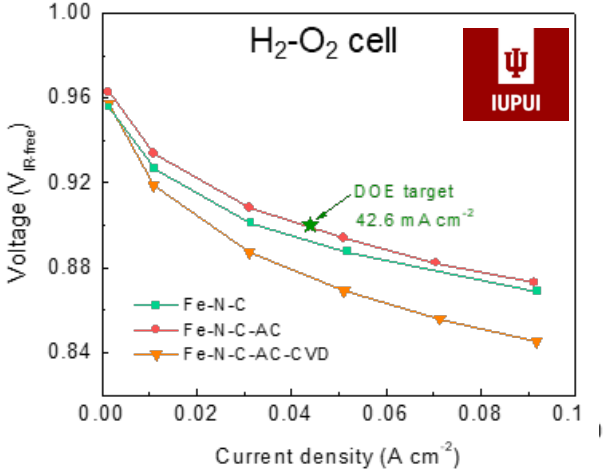
1. Beltrán & Litster, ACS Energy Letters, 2019

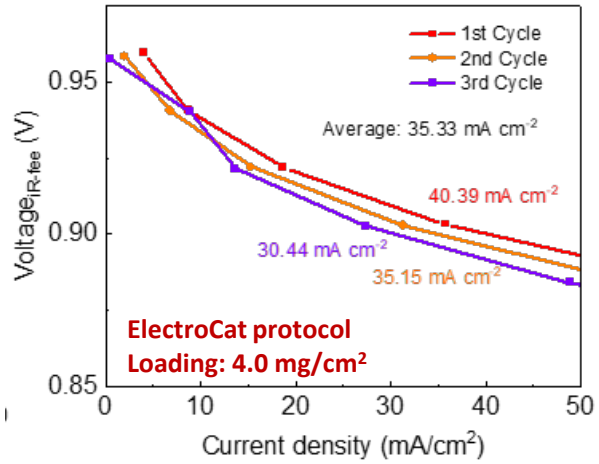
Innovative Fe_2O_3 Precursor Synthesis and CVD Approach



- Active site density can be increased by directly transforming solid-state Fe_2O_3 nanoparticles into FeN_4 sites.
- FeN_4 active site's intrinsic activity is significantly enhanced by regulating local carbon structures with a salt treatment.
- Resulting Fe-N-C-AC catalyst achieved a record half-wave potential of **$E_{1/2}$ = 0.915 V vs. RHE** and a kinetic current density of 6.3 mA/cm² at 0.9 V in RDE tests.
- Depositing nitrogen-carbon species on the catalyst surface *via* chemical vapor deposition (CVD) enhances stability.
- High MEA activity with Fe-N-C-AC catalyst: 43 mA/cm² at 0.9 $V_{IR\text{-}free}$ (O_2) on first scan. Average of 35 mA cm^{-2} based on average of 3 IV scans per ElectroCat protocol.
- **>44 mA/cm² achieved on first scan (exceeding 2025 target) when accounting H_2 crossover (see Technical Backup slides for H_2 crossover analysis).**





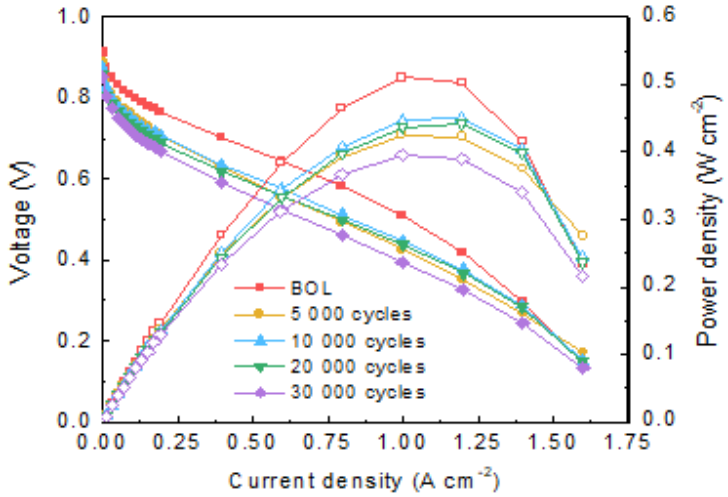


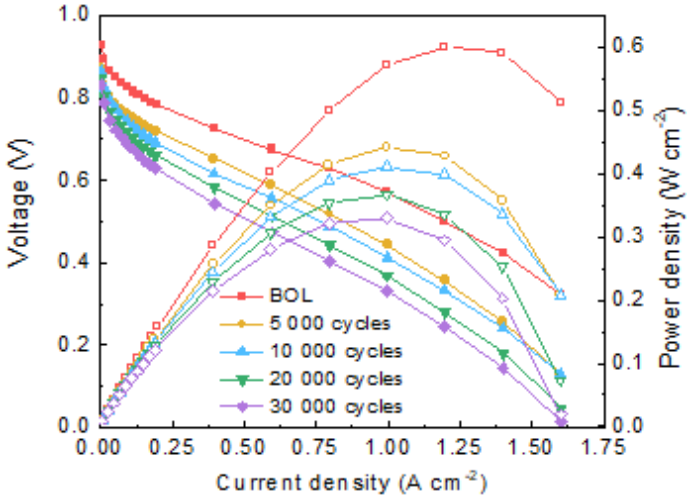
IUPUI testing: 5 cm² serpentine; anode: 30% Pt/C, 0.2mg$_{Pt}$/cm², cathode: 4 mg/cm², Ionomer: Aquivion, Membrane: N212, 80°C, 100% RH, Flow: 300:500 sccm (H_2/O_2 or Air) 1.0 bar partial pressures.

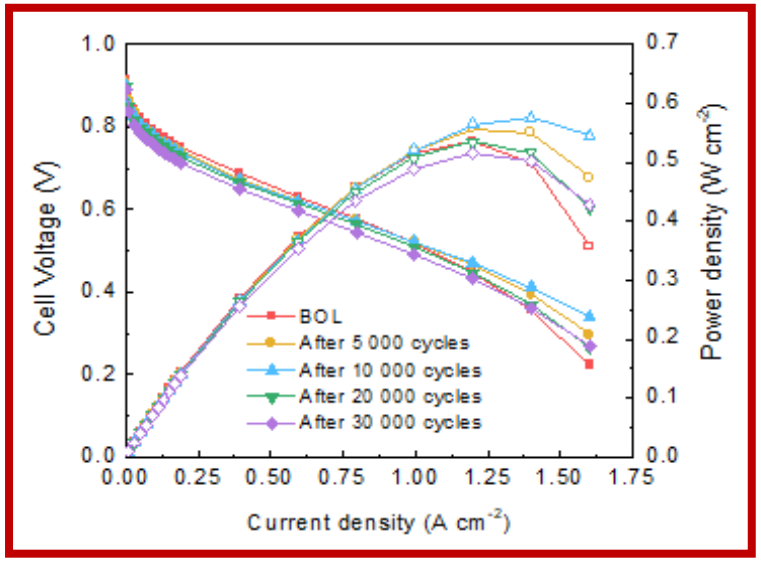
Technical Accomplishments

MEA Performance & Durability

- The CVD treated Fe-N-C catalyst demonstrated significantly enhanced durability only **losing 30 mV at 1.0 A/cm²** after 30,000 cycles under H_2/air.
- **CVD-treated maximum power density after air cycling: >0.5 W/cm²** vs. 0.34 W/cm² (Fe-N-C) and 0.4 W/cm² (Fe-N-C-AC).
- The 0.8 V current density of 90 mA/cm² of Fe-N-C-AC-CVD indicates additional improvement in activity needed.
- Nano-CT and HAADF-STEM indicate morphological changes and activity loss occurs below the primary-particle scale.

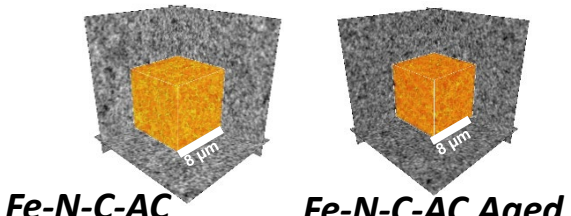






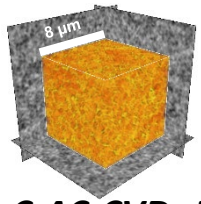
Voltage cycling with square-wave cycle in air with 0.60 V (3 s) and OCV (3 s) and rise time of 0.5 s.

Anode: H_2, 200 sccm; Cathode: air, 400 sccm, 1.0 bar partial pressures

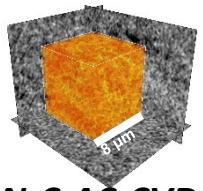


Fe-N-C-AC

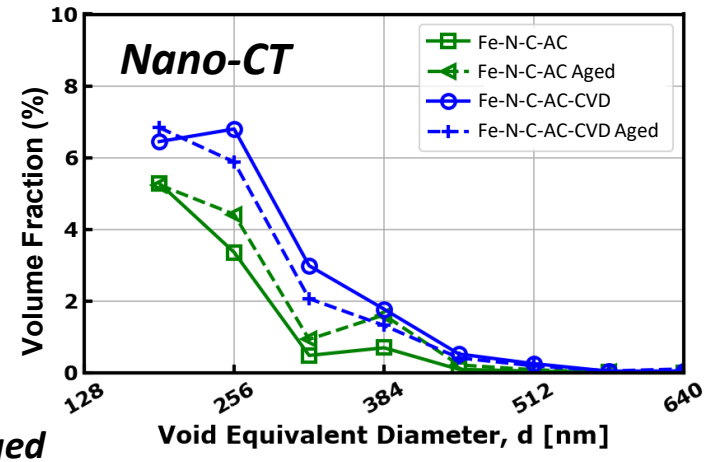
Fe-N-C-AC Aged



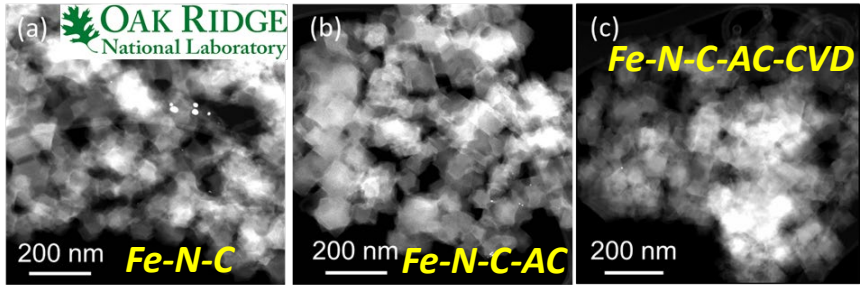
Fe-N-C-AC-CVD



Fe-N-C-AC-CVD Aged



HAADF-STEM of aged Fe-N-C catalysts



Elemental Composition (at. %)

MEAs	C	N	O	Fe	Zn
Fresh CVD MEA	96.92	1.54	1.34	0.20	0.00
Aged CVD MEA	91.82	2.12	5.94	0.11	0.00

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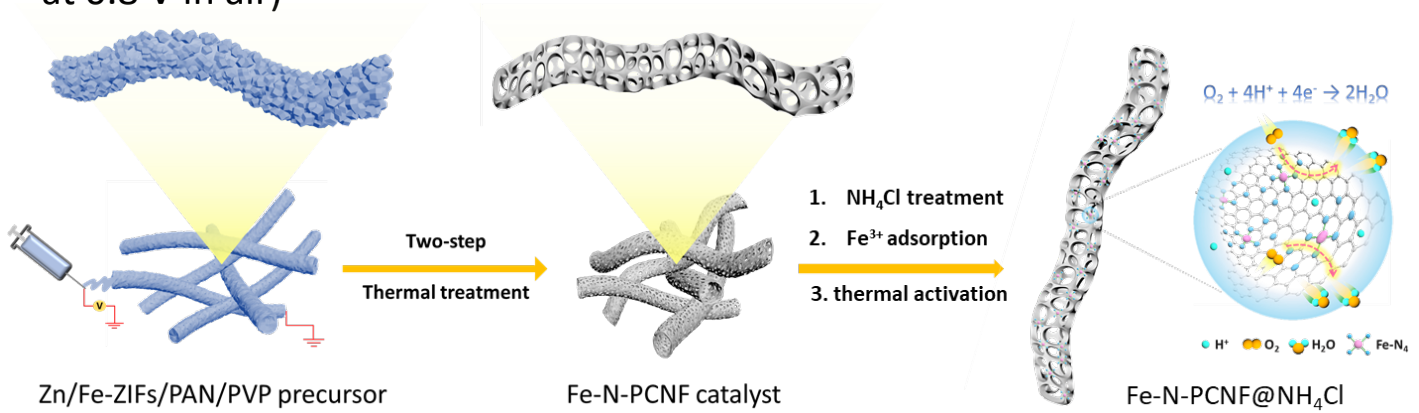
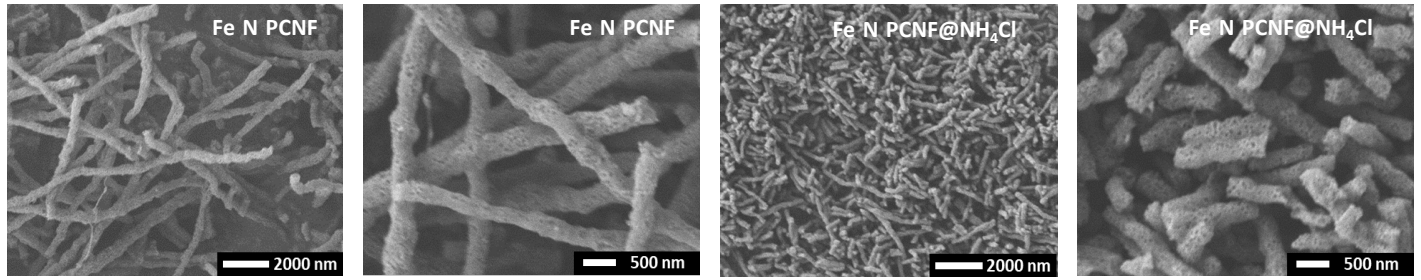
Improved Catalyst Morphology - Electrospun Fe-N-C

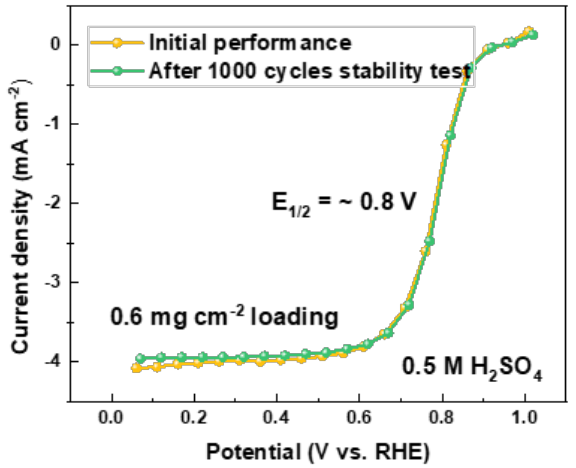
- Typical large aggregate Fe-N-C catalysts (>5 µm) result in poor ionomer infiltration and challenge coating processes, especially at low loading (<25 µm) thickness
- Electrospinning precursors controls catalyst size and morphology
- Previous reported results with Co-N-C extended to Fe-N-C
- Encouraging preliminary results with good mass transport properties
- RDE and MEA ORR activity below that of standard Fe-MOF processing (75 mA/cm^2 at 0.8 V in air)



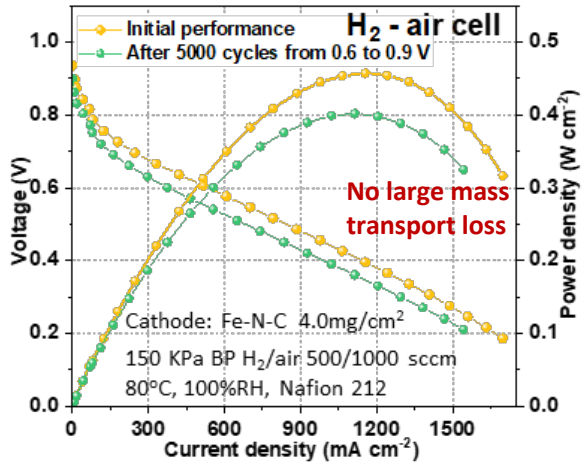
Zn/Fe-ZIFs/PAN/PVP precursor | Fe-N-PCNF catalyst | Fe-N-PCNF@NH_4Cl



RDE Tests



MEA Tests



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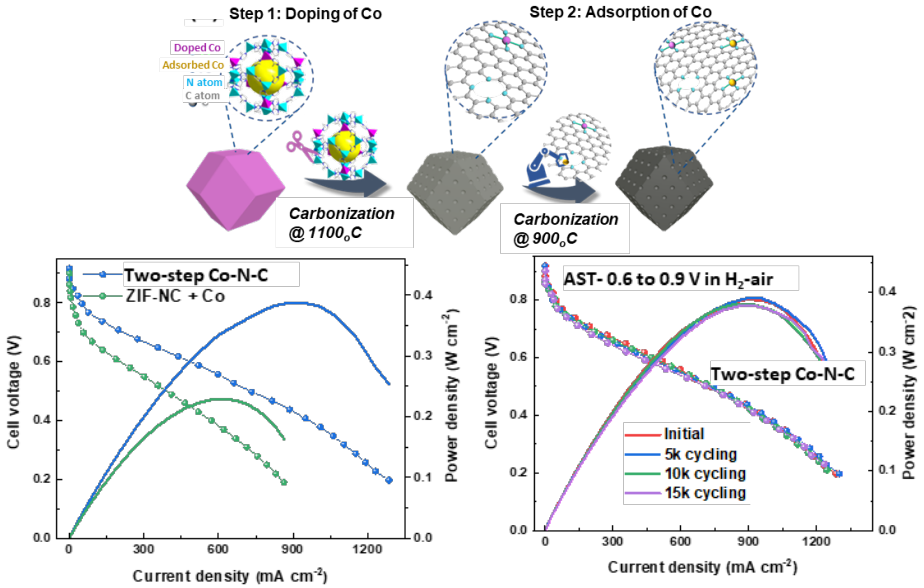
Fe-free Catalysts and Additives

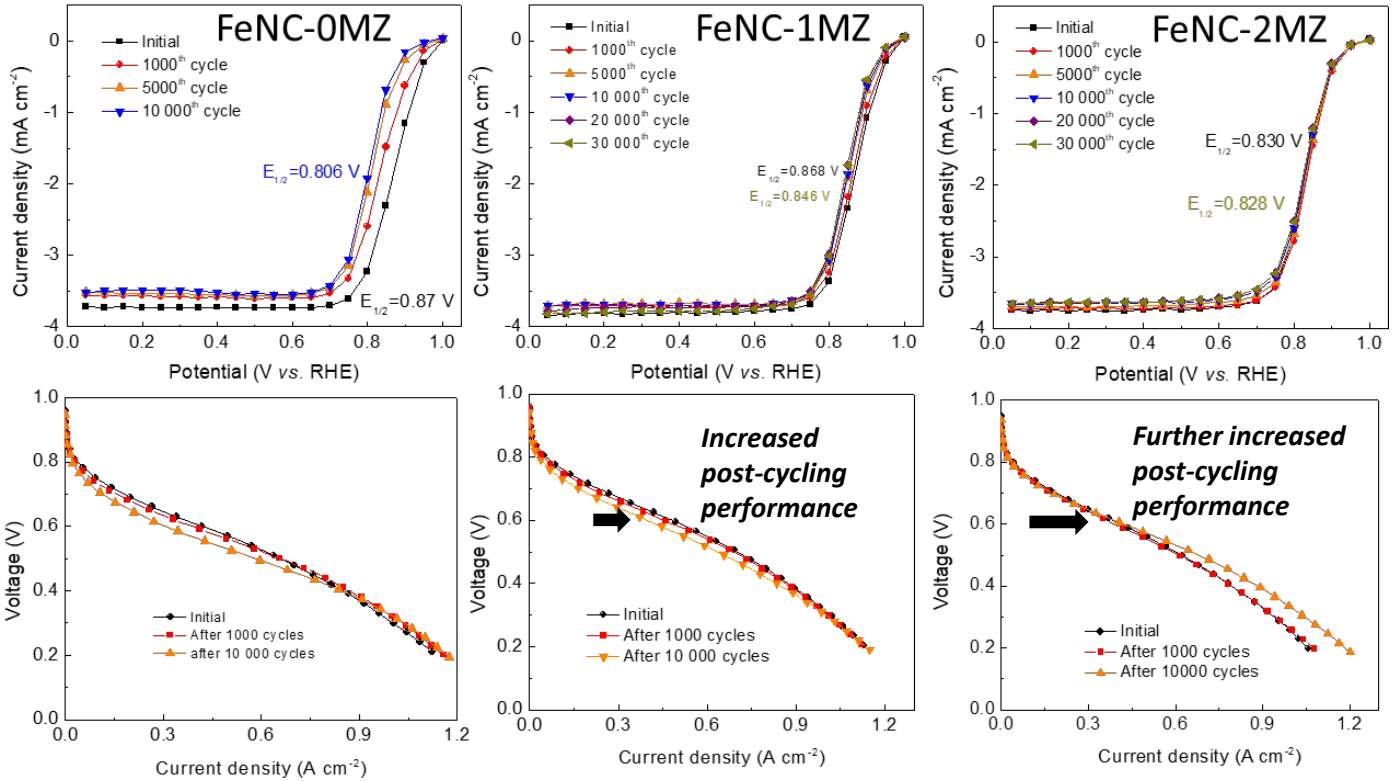
Co-N-C Active Site Catalyst

- 2-step formation of Co active site. Co based catalysts are more stable than Fe catalysts with enhanced MEA durability. Co has less concern than Fe for Fenton reactions and membrane degradation.
- Model system analysis (see Technical Backup Slides) indicates relatively low temperature of 700°C is sufficient for substantial ORR activity; 900°C is the optimal for the highest activity and 4e$^-$ selectivity.
- Displayed encouraging H_2-air cell performance with a peak power density of 0.39 W/cm^2, together with excellent stability under H_2-air voltage cycling tests.



Magnesium additive for enhanced durability

- Optimal Mg doping into Fe-N-C catalysts can enhance catalyst stability
- Lower initial activity in RDE and MEA
- Mg doping leads to higher MEA performance after cycling



Cathode: Fe-N-C catalyst loading: 4.0 mg/cm^2; anode: 20% Pt/C catalyst loading: 0.2 mg$_{pt}$/cm^2; membrane: Nafion 212 ; I/C=0.6; RH: 100 %; 0.5 L/min for H_2 anode and 1.0 L/min for air cathode.

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Kinetics Analysis for Fe Catalyst Stability

- Evaluation of degradation rate during constant voltage holds at varying loading.
- Two proposed models evaluated:
  - Logistic decay model based on autocatalytic degradation.[1]
  - Double exponential decay model with two populations of active sites based on first-order degradation mechanism.[1]
- Double exponential decay model offer better fit andidentifies two types of active sites (T1 and T2), the remaining fraction of their initial site density, and kinetic rates (k_1 and k_2).
- Consistent with recent results using ^{57}Fe Mössbaur spectroscopy[2] that has identified two active sites of distinct stability.

Double Exponential Decay Model

$$j_{k\,normal} = ce^{k_1 t} + (1-c)e^{k_2 t}$$

$T_1 = ce^{k_1 t}$

$T_2 = (1-c)e^{k_2 t}$

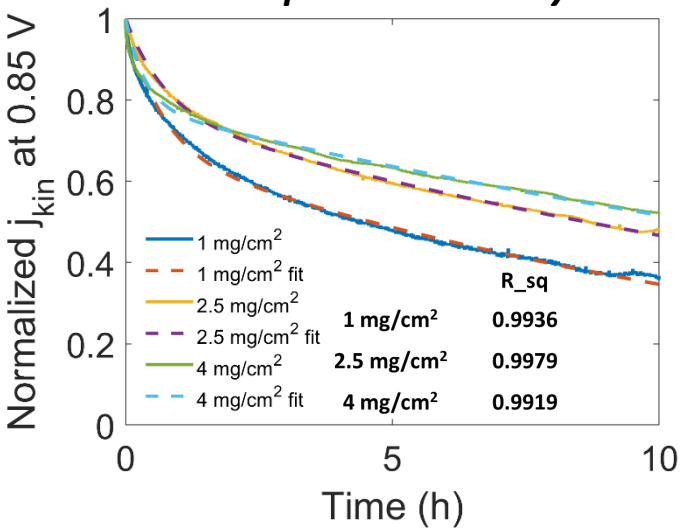
Site fraction relative to initial

Initial T_1 site fraction

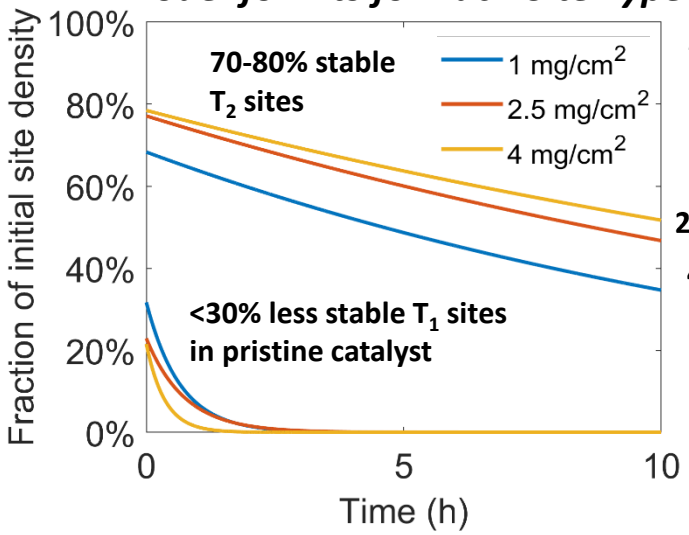
Logistic Decay Model

$$j_{k,normal} = 1/(1 + \frac{kt}{C})$$

Double Exponential Decay Model



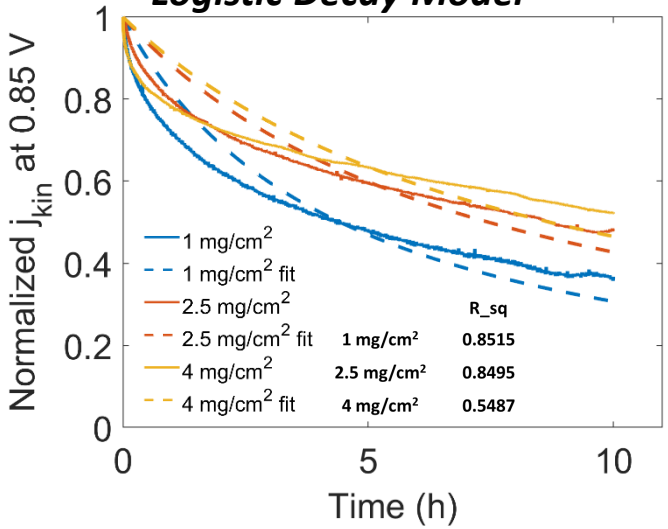
Model for Fits for Each Site Type



Distinct time-scales (k^{-1}) for two types of active sites

	k_1^{-1} [h]	k_2^{-1} [h]
1 mg/cm²	0.66	15
2.5 mg/cm²	0.75	20
4 mg/cm²	0.36	24

Logistic Decay Model



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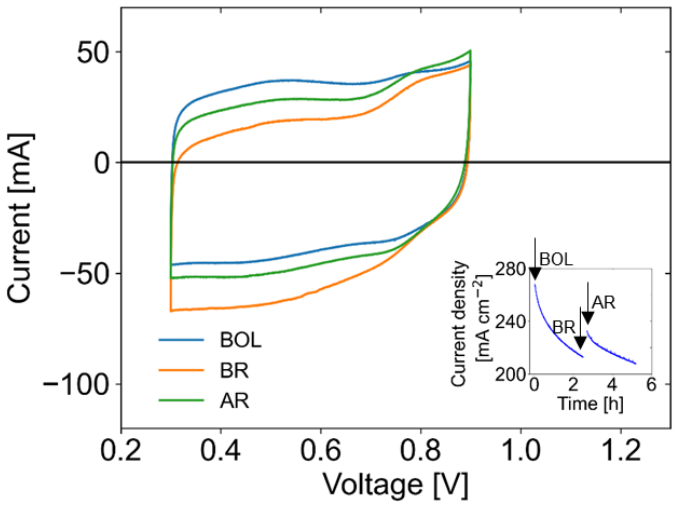
[1]*Yin and Zelenay 2018. ECS Transactions.*

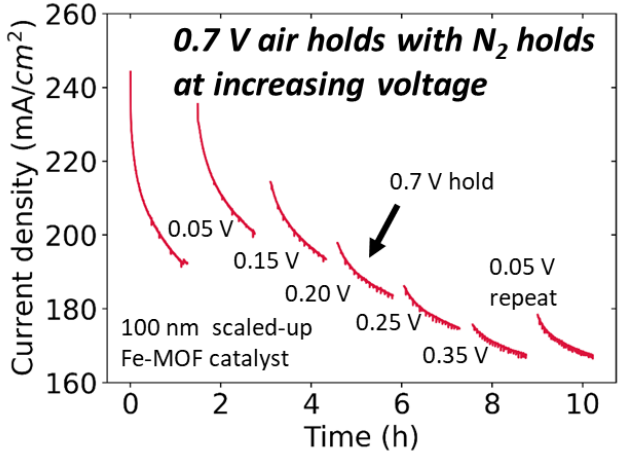
[2]*Li et al., Nature Catalysis, 2021.*

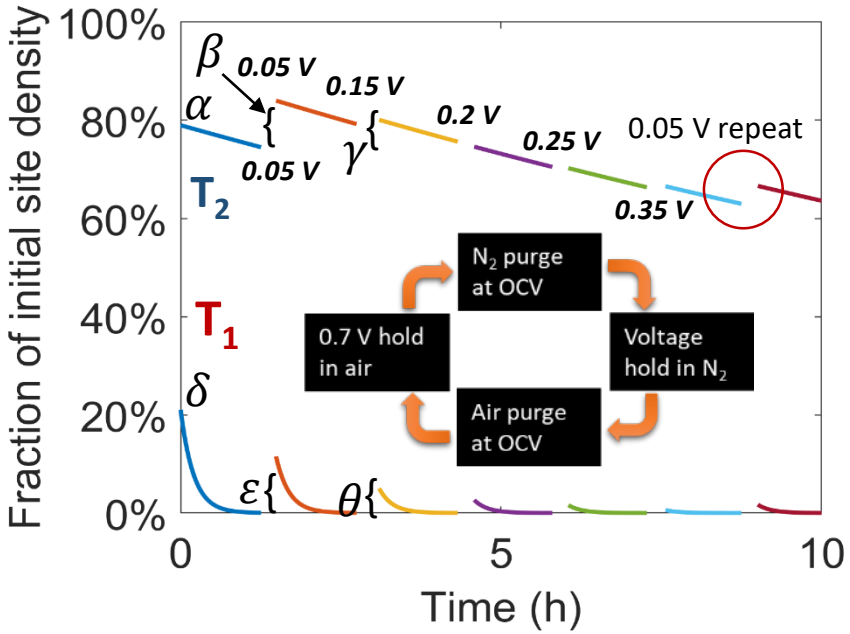
Kinetics Analysis of Activity Recovery

- Partial recovery of initial activity using low voltage holds in O_2-free environments
- Initially fit each 0.7 V hold with its own *c* and *k* values, then used average *k* values in modeling T_1 and T_2 recovery.
- The more stable T2 sites are mainly responsive to the lowest N_2 voltage hold at 0.05 V, increasing stable T2 site density above the initial BOL value during the first recovery.
- CV analysis indicates a loss of Fe during 0.7 V air hold and significant increase of redox active Fe following 0.05 V N_2

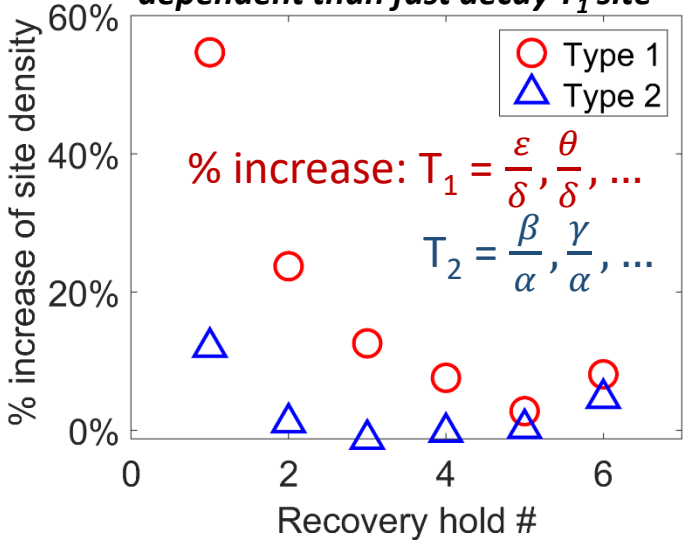
CVs at beginning of life (BOL), before recovery (BR), and after recovery (AR)



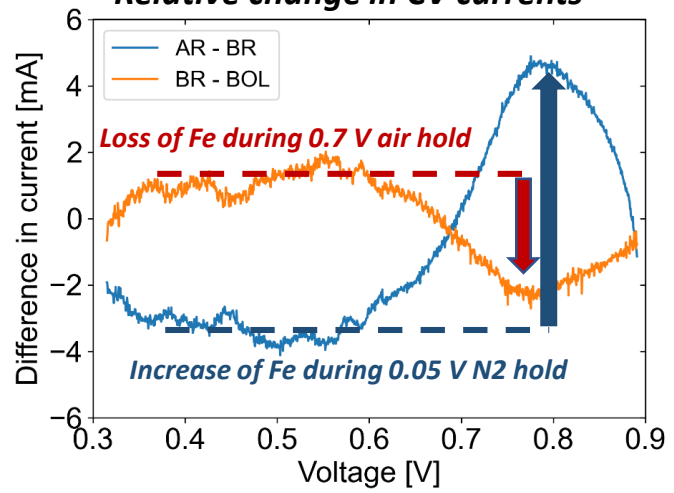




Stable T_2 site recovery more voltage dependent than fast decay T_1 site



Relative change in CV currents



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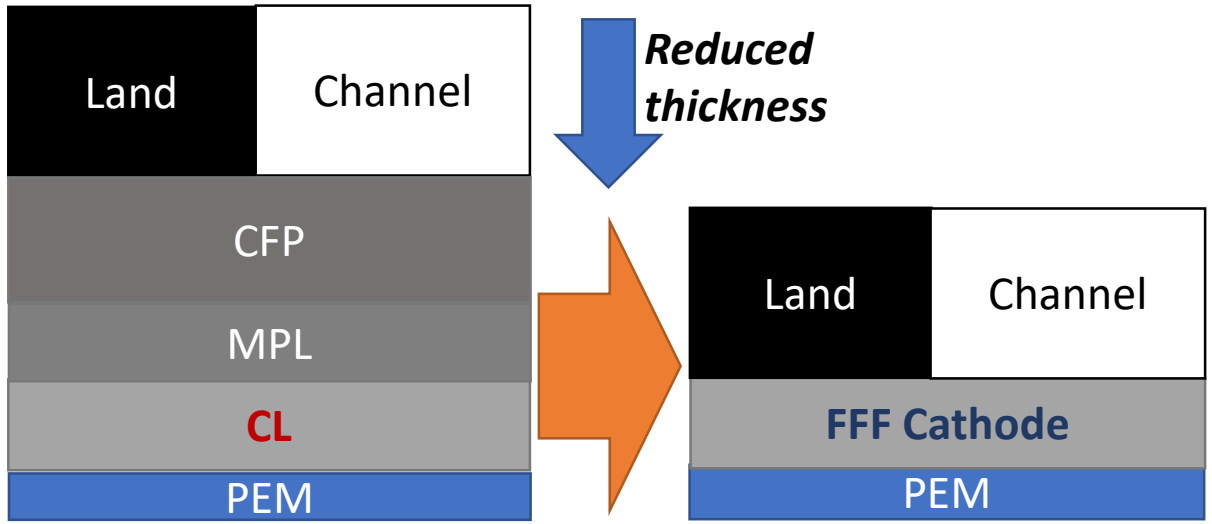
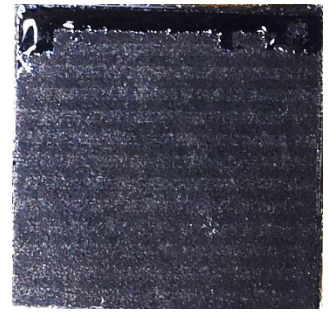
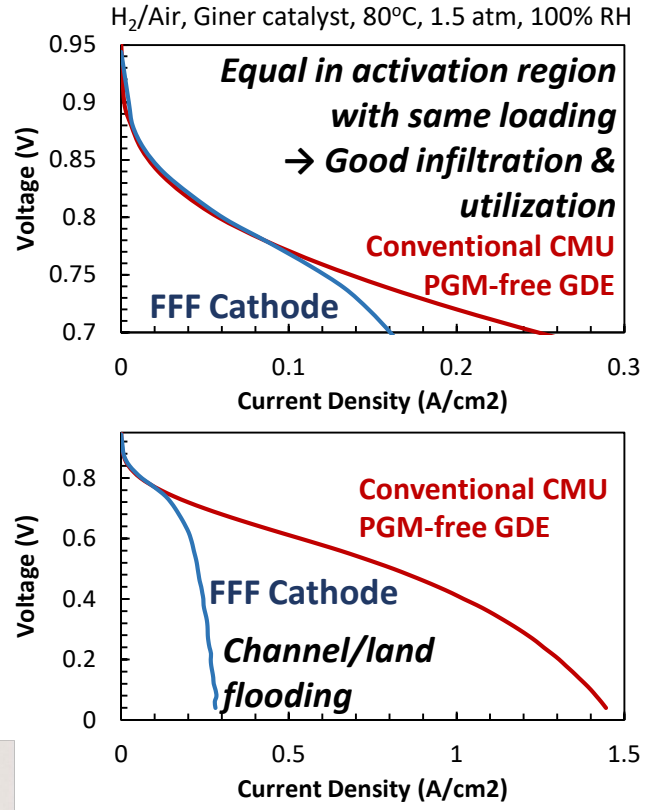
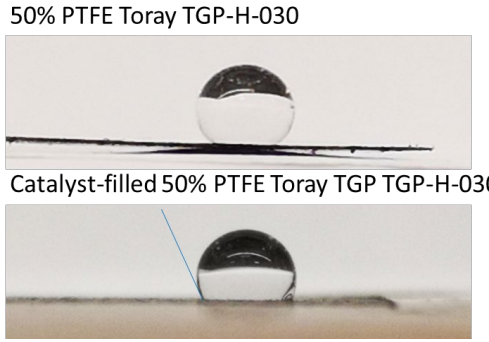
Free-standing GDL-free PGM-free (FFF) Cathodes



- Replace entire cathode (CL+DM) with single semi-rigid layer
  - Simplified, single component with 200 µm less thickness
  - Embedded high conductivity, hydrophobic substrate
  - Direct contact of catalyst with high O_2 in the channel
- Catalyst ink fully imbibed into high PTFE-loading TGP-H-030 carbon fiber paper (CFP) (100 µm thick)
  - Development of ink and infiltration for high loading
- Equal or better performance to conventional GDE at > 0.75 V
- Significant channel/land interface flooding at moderate currents
  - Different flow field or interface treatment required







Surface of catalyst-filled TGP more hydrophilic

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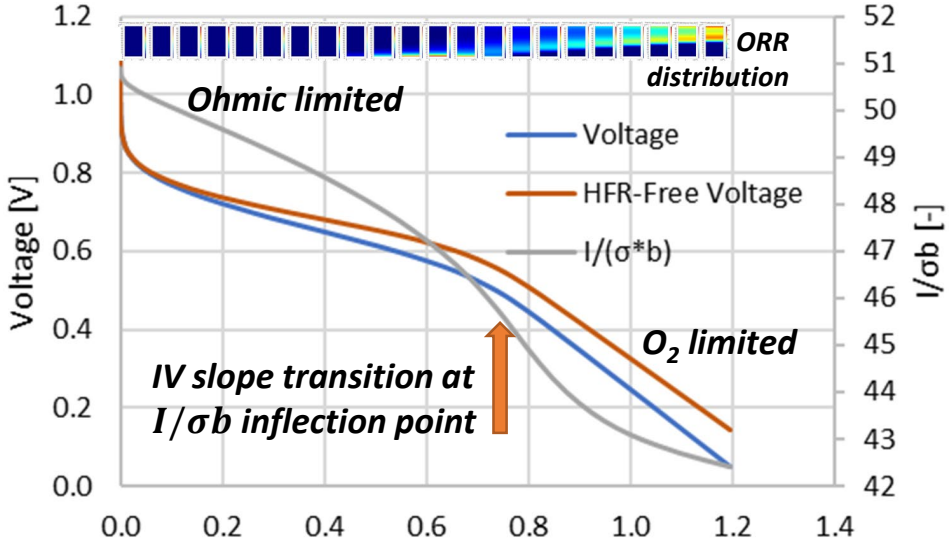
Origin of 2nd Ohmic Slope Onset & ORR Distribution

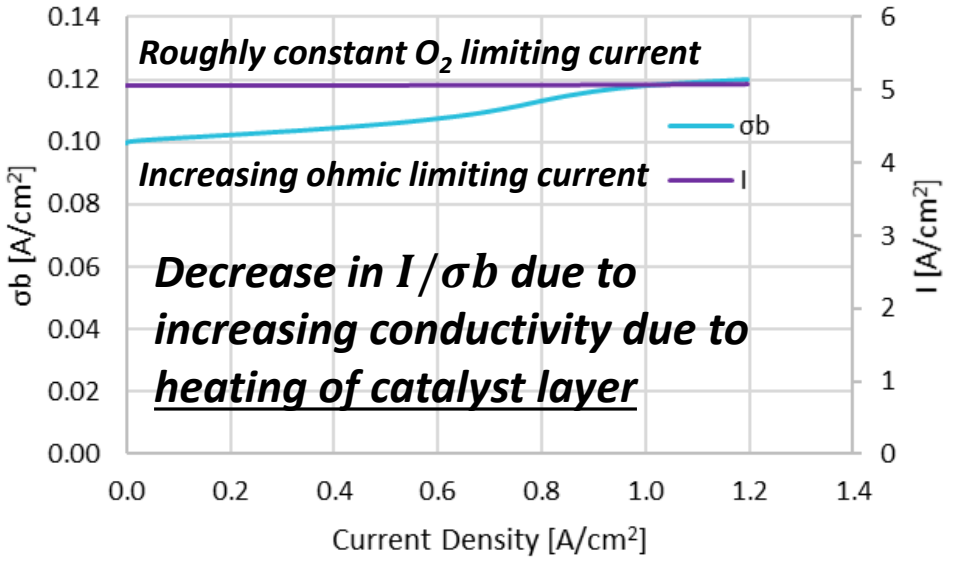
- $I/\sigma b$ is a dimensionless number that describes the ratio of I a characteristic parameter of oxygen diffusion and σb a proton conductivity parameter

$$\frac{O_2\ limiting\ current}{Ohmic\ current\ per\ b} = \frac{I}{\sigma b} = \frac{4FP_TD}{RT\sigma b}$$

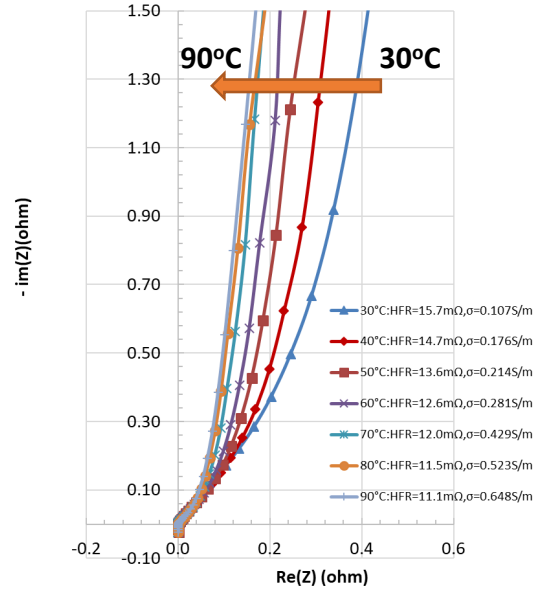
  I is the O_2 limiting current density across the cathode, σ is the conductance, & b is the Tafel slope

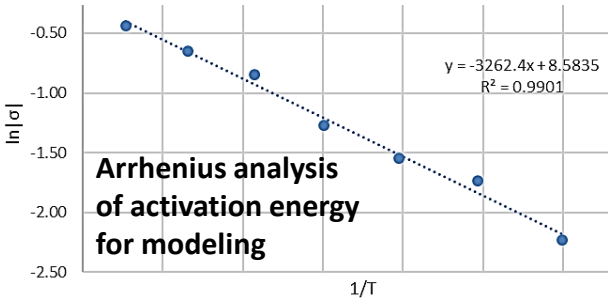
- **Large** $I/\sigma b$: proton transport is rate limiting - ORR occurs near the PEM where ohmic resistance is lowest
- **Small** $I/\sigma b$: O_2 transport is rate limiting - ORR pushed toward GDL
- $I/\sigma b$ **e**valuated based on simulation properties as function of current with measured temperature dependence of electrode proton conductivity and implemented as activation energy in model
- The simple $I/\sigma b$ parameter shows good correlation with the change in IV curves and reaction distribution
- Inflection point of $I/\sigma b$ indicates the transition to the O_2 limited, 2nd Ohmic slope portion of the IV curve.
- **2nd slope arises due to increased conductivity, which makes the O_2 transport more limiting, moving ORR closer to GDL.**





Temperature dependence of electrode proton conductivity





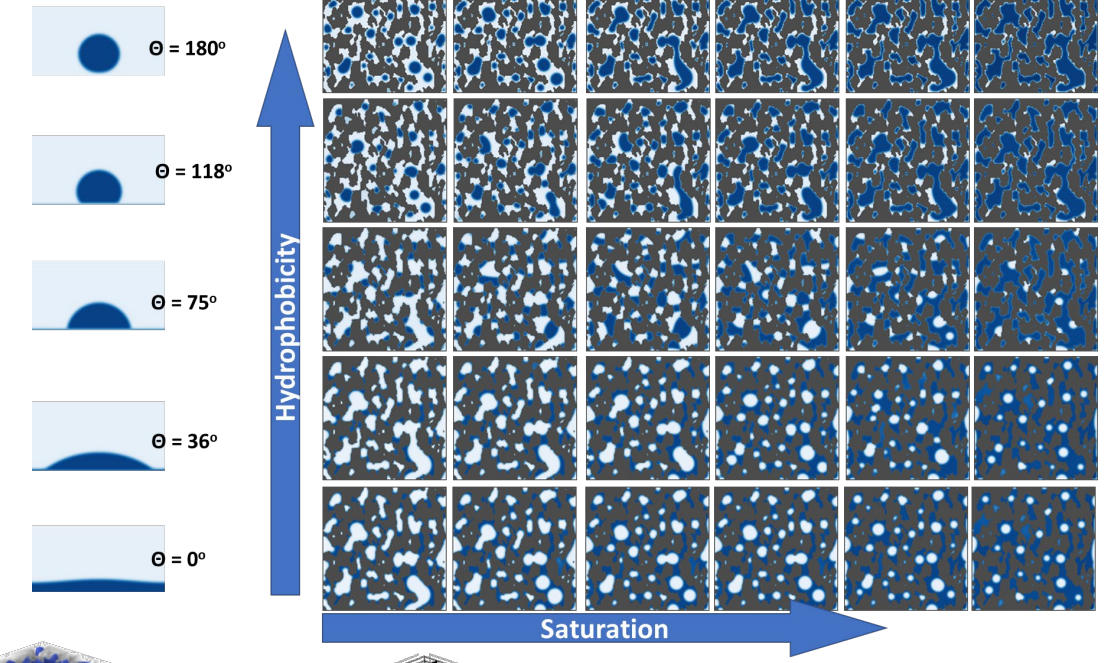
[1]Eikerling & Kornyshev, J. Electroanal. Chem., 453, 89-106, 1996.

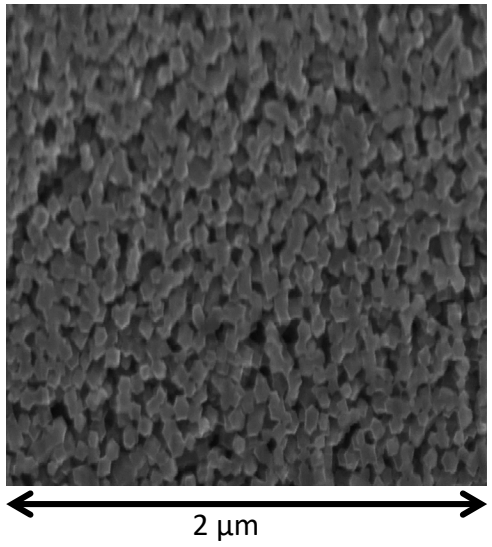
Modeling Hydrophobicity Effect on Gas Diffusivity

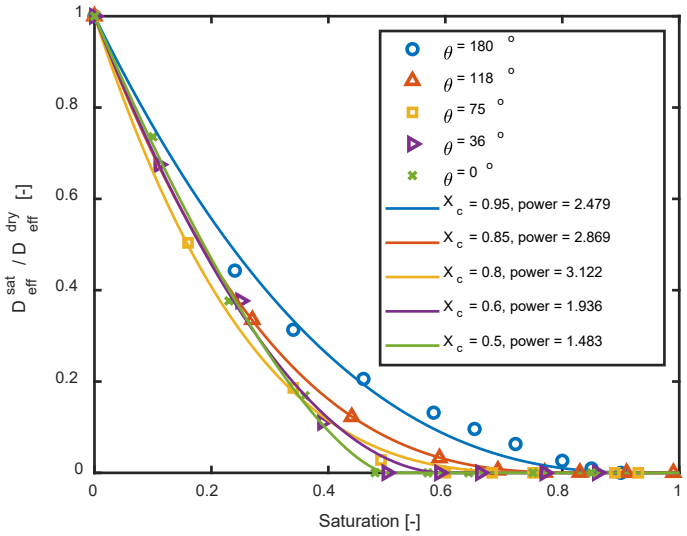
- Impact of cathode hydrophobicity on effective gas diffusivity as a function of saturation.
- Modeled using 2 nm resolution pFIB-SEM 3D images of Fe MOF-derived cathode
- Two-phase Lattice-Boltzmann simulations to determine water distribution as a function of contact angle and average saturation
- Finite element simulation of O_2 diffusion through two-phase mixture (including water)
- Effective diffusivity fitted to porous media percolation-threshold correlation
- Strong effect of contact angle on percolation threshold
- Diffusivity becomes negligible at saturations above 60%

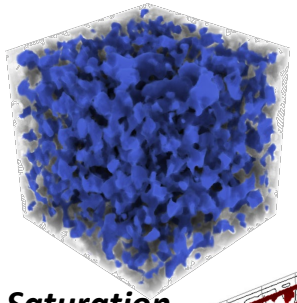
$$\frac{D_{effect}^{sat}}{D_{effect}^{dry}} = \left(\frac{(1-s)-(1-s_c)}{1-(1-s_c)}\right)^t \Theta\big((1-s)-(1-s_c)\big)$$

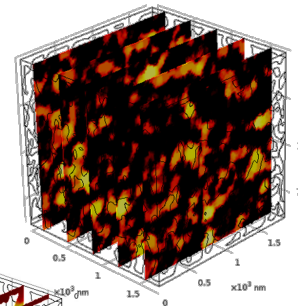
S is the saturation level
S_C is the critical saturation level (i.e., percolation threshold)

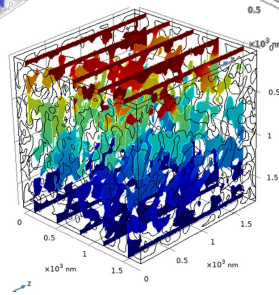


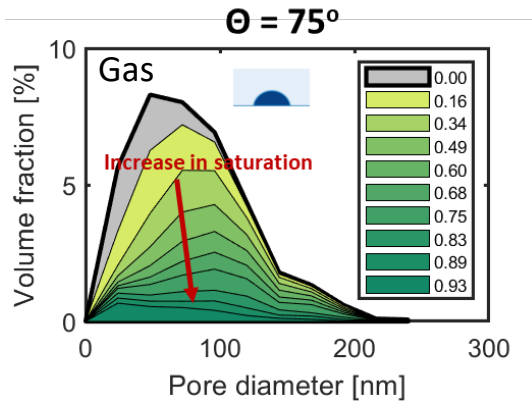












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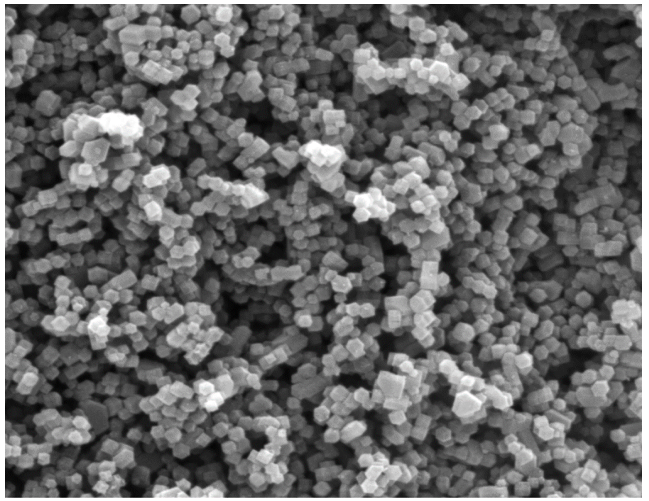
Catalyst Synthesis Scale up

20 L Reactor and Chiller

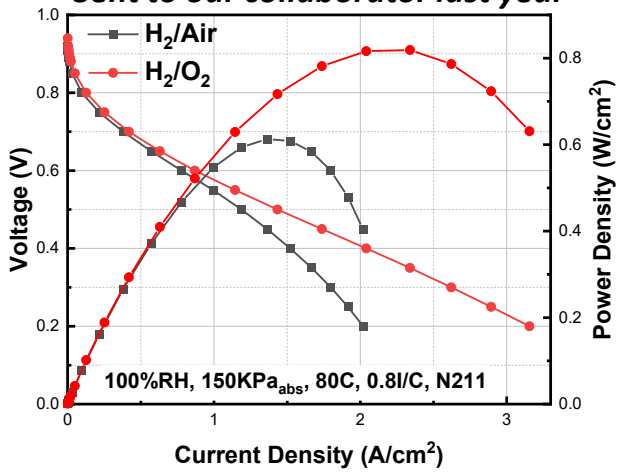
Al Foam in Furnace Tubes

- Alumina foam block is used to preheat Ar and create a relatively closed situation for the precursor at the center of the tube.

SEM images of 6L catalyst (~100nm)



MEA result from one batch catalyst Sent to our collaborator last year



- 3 grams of Fe-MOF-based catalyst synthesized per batch
- Alumina foam block is used to maintain a consistent pyrolysis environment in different furnaces and heating boats to yield material with reproducible performance.
- Promising initial performance obtained by our collaborators using the catalyst synthesized at Giner.
- Catalyst could be provided to more protentional collaborators for further analysis and lab-to-lab performance evaluation.

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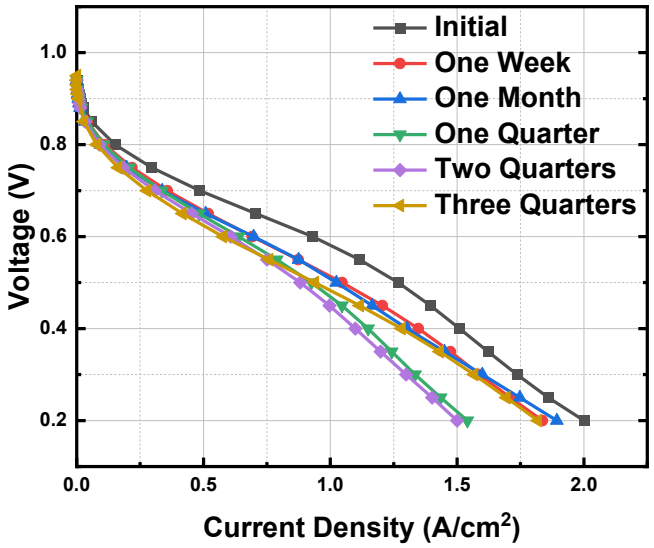
Shelf-Life Performance and Durability

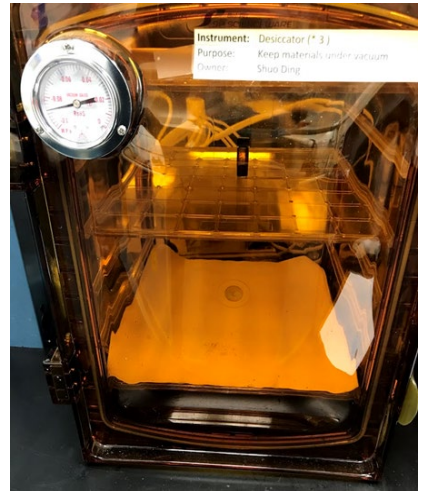
MEA results from the same batch catalyst for shelf-life investigation



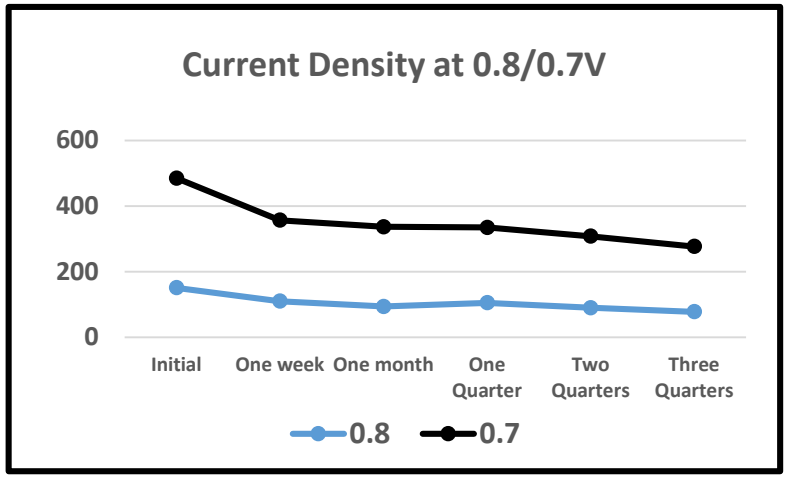
Current density at 0.8/0.7V(Percentage lost)
(Set One Week as Initial Performance)

	Initial	One Week	One Month	Two Quarters	Three Quarters
0.8V	150	110	95(15%)	90(18%)	78(30%)
0.7V	485	357	337(6%)	308(14%)	277(22%)
				Less than 20%	**Less than 30%**

Desiccator used for catalyst storage under Ar



Degradation Trend at 0.8/0.7V



- Shelf-life of the large-scale catalyst investigated (June-2020 to March-2021) by storing about 500mg catalyst in a vial, under ultra-high purity Ar in a vacuum chamber.
- Initial catalyst degradation is significant, while performance becomes stabile after a week storage. Initial high activity is also typically lost in first few hours of PGM-free PEFC operation.
- Current density at 0.7/0.8V is higher than 270/70 mA/cm^2 even after nine months storage in Ar.
- A 25% performance loss is observed at 0.7V. (from 485 to 357mA/cm^2) **in the first week.**
- Catalyst degradation from one week to **nine months** is less significant
- If the performance from the **first week** is used as initial performance, more than 80%/70% performance is retained after storage in Ar for **six/nine months,** respectively.

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Response to 2019 AMR Comments (not reviewed in 2020)

PGM vs PGM-free

"not clear yet that non-PGM fuel cells will be significantly less costly", "PGM cost is no longer the major obstacle that it once was"

Agreed that current PGM-free catalysts and MEAs are still behind the low-PGM counter-parts, but the BOL performance is becoming comparable, but improvements in durability are still crucial. The dramatic rate of progress is PGM-free merits further development. In the past year, this project's best 0.8 V current density on air alone increased 35%.

Catalyst

"suggested that the team look at Mössbauer spectroscopy", "project should include … Mössbauer spectroscopy"

The UB team is actively looking for Mössbauer facilities in the US to meet their needs, but the currently only difficult to access facilities outside of the US are available.

"reliance on Fe-based materials and an unclear catalyst focus", "Fe-doped MOFs …improvements are required"

The catalyst focus is on increasing the activity and stability of highly active Fe catalysts. But, the project includes new Co and FeCo catalysts for enhanced stability.

"It would be good to see less emphasis placed on catalyst activity and more placed on understanding material issues and transport limitations in the electrode"

The electrode is a key focus area of this project, but increased catalyst activity is vital to improvement in PGM-free cathode development. Recent modeling has investigated transport losses and material requirements for meeting targets. Catalyst activity increases are needed to reach goals. Modeling shows electrode improvements alone are not sufficient.

MEA and Power Density

"re-investigate the older, well-known, non-ionomer-based (polytetrafluoroethylene [PTFE]) electrode"

The CMU group spent significant effort on PTFE-bound PGM-free gas diffusion electrodes and did not see compelling performance, likely due to poor ionomer infiltration into the sintered electrodes.

"MEA performance is poor, and stability at the MEA level is very poor", "High high-frequency resistance (HFR), very high accumulated water-induced mass transport losses, and 30% performance loss in less than 40 hours will each require significant effort to resolve", "power produced is well behind that shown by other developers"

We agree there is room for improvement in PGM-free MEAs in general, but we disagree with these comments. The project reported record-level PGM-free MEA performance at the 2019 AMR. HFR and water-flooding issues are highly mitigated in our current MEAs. The HFR and water flooding are consistent with validated modeling of a high performance MEA.

"good to see the team expand beyond the current conventional wisdom regarding electrode composition and structure","develop a hybrid hydrophobic–hydrophilic electrode composition", "should concentrate the ionomer at the membrane–catalyst interface", "should look at the PTFE content of the microlayer"

We actively working on novel structures, such as free-standing cathodes with infiltrated support layers, PTFE-bound electrodes, hydrophobic additives, hydrophobic iCVD coating reported at the 2018 AMR and the 3D structure MPL/cathode reported at the 2019 AMR. So far the microstructured MPL/cathode and the tuning of solvents for more hydrophobicity have shown the most promise.

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MEA and Power Density cont'd

"increased focus be put on the high-current-density, transport-limited regime and less focus be put on catalyst activity"

Catalyst activity should remain a key area of focus. The oxygen transport limited regime is less crucial than finding methods to dramatically enhance proton conductivity without increasing wettability and flooding.

Durability

"Limited durability at this point does raise the question of whether these materials are serious contenders", "There should be more focus on durability"

Significant recent improvements in durability and understanding have been achieved by tuning the level of graphitization and the CVD treatment. We have also developed a method to recover a substantial fraction of activity loss.

"authors report reversible and irreversible losses. However, their data show the decay rate after recovering the recoverable losses is much higher than the earlier decay rates, so the reversible losses are not really reversible"

Recent tests show that the early decay can be partially recovered in a repeatable manner

"This is probably the most promising PGM-free project, with exception of the Fe effect on membranes."

There is no clear evidence that atomically dispersed Fe accelerates membrane degradation and is an upcoming area of experiments.

Modeling

"Model-driven design should be more emphasized", "maintain a model-based design approach by continuing modeling activities", "A reduced role of modeling is detected in the near future, which reduces the potential for impact"

Modeling remains a key component of the project in reestablishing targets and interpreting the impacts of material and design changes in experiments. Recent results include a large number of model study comparisons to experiments. Modeling was a critical part of the oxygen transport resistance analysis

Project focus, tasks, targets, and logistics

"description of future efforts is general and could be more precise." More details are provided this year.

"Roughly 40% of the project has been completed, but only about 25% of the budget was used.", "needs to add resources to accelerate"

Spending was initially slow due to ramp up at beginning of project.

"The team could maybe use a spider chart to track progress and include the primary metrics"

This is a good suggestion and we have included such a chart in summary slide.

"It is unclear how much progress is occurring in catalysts, with the overlap with other projects."

Distinct catalyst advancements include the high activity Fe-adsorption catalyst, the electrospun precursor, and the high stability of the graphitized catalyst.

"It is not clear that Giner, Inc., is the right partner for synthesis scale-up. This should involve a chemical company."

Giner has focused on demonstrating larger catalyst batches and preparing those the project's MEA studies, collaborators, and other ElectroCat projects.

"need to reach out to teams that are further along in the development of this type of catalyst, such as ElectroCat, EMN, and consortium members, including national laboratories…"

This comment is confusing as the UB catalyst has demonstrated best-in-class PGM-free catalyst performance

"It is not clear how fuel cell initiative changes at 3M will impact the company's involvement in the project."

This had not affected 3M's role in the project given the smaller percent effort of 3M in the project, primarily supplying ionomer

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Future Work

- Project ends on August 31, 2021
- Project's Planned Final Deliverable:

  50 cm^2 MEAs with ≥30 mA/cm^2 at 0.90V (iR-corrected) (with a stretch goal of 44 A/cm^2 at >0.9 VIR-free) in a H_2-O_2 fuel cell, voltage loss ΔV at 44 mA/cm^2 less than 100 mV after 30,000 voltage cycles (0.6 to 1.0 V) under H_2-N_2 conditions, <50 mV performance loss at 0.8 A/cm^2, and performance at 0.8 V of >150 mA/cm^2 (with stretch performance goal at rated voltage of >450 mW/cm^2) in H_2-air fuel cell (measured) while maintaining partial pressure of O2 + N2 at 1.0 bar (cell temperature 80 °C).

- Performance goals have been achieved with high activity Fe-N-C-AC catalysts.
- Durability goals have been far exceeded with Fe-N-C-AC-CVD using more aggressive cycling in H_2-air conditions with promising first scan ORR activity of 23 mA/cm2 0.9 $V_{IR\text{-}free}$ in H_2-O_2 fuel cell
- Scale-up of new durable, high activity catalyst
- Fabrication and testing of 50 cm^2 PGM-free MEAs

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Summary

Accomplishments and Progress

- Significant increases in activity and stability of catalysts
- New synthesis for Fe-N-C catalyst yielding exceptionally high BOL ORR activity, meeting 2025 targets on first scan. Within 10 mV of 2025 voltage target at 44 mA/cm^2 from average of 3 consecutive scans.
- CVD catalyst treatment for power density durability exceeding project target (30 mV loss at 0.8 A/cm^2 after 30k cycles in air)
- Electrospinning of precursors to eliminate large dense aggregates and demonstrate high performance with Co catalyst
- Co-N-C catalyst and Mg additives to potentially enhance stability
- Evaluation of 2-site stability and analysis of activity recovery mechanisms
- Modeling analysis identifying temperature dependence of electrode conductivity as origin of transition to second ohmic slope in thick PGM-free cathodes.
- Free-standing, GDL-free, PGM-free cathode development of improved integration of PGM-free cathodes into fuel cll systems.
- Scale-up of high-performance catalyst and delivery outside of the project.
- Scaled-up catalysts present reasonable stable shelf-life up to 9 months after initial week.

Collaboration and Coordination with Other Institutions

- Rapid iteration cycle with catalyst development at UB and MEA fabrication and testing at CMU and IUPUI.
- Catalyst scale-up at Giner using UB developed process
- Ionomer integration at CMU using 3M ionomer
- ElectroCat consortium actively collaborating on XAS, XRF, electron microscopy, and electrode fabrication

Relevance/Potential Impact

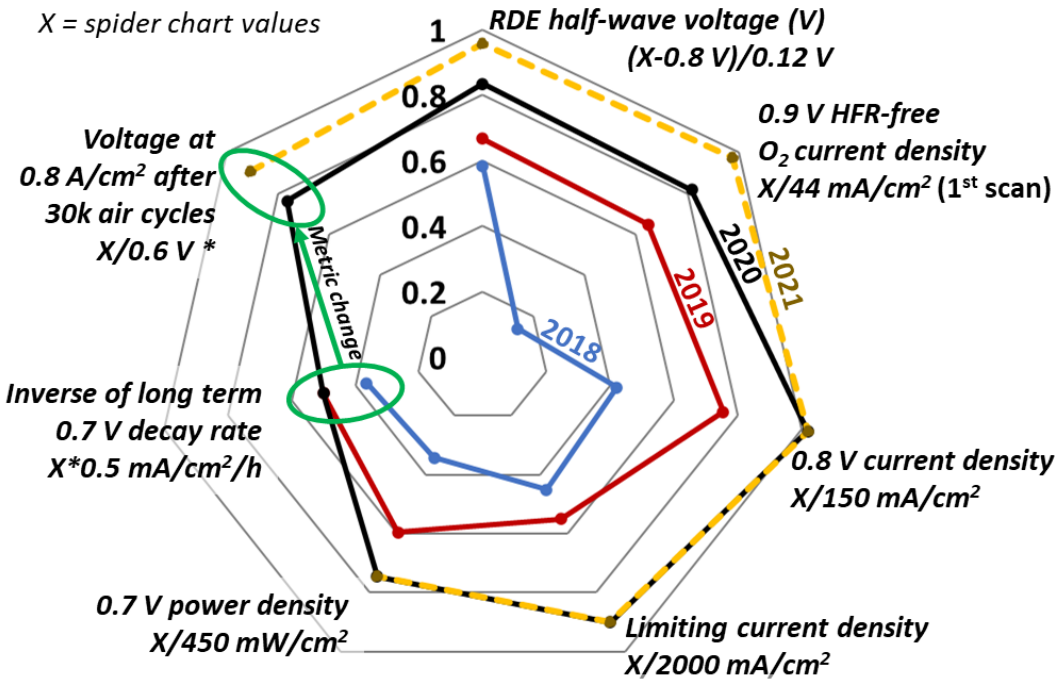
- Advancing synthesis of atomically dispersed active sites at high density with a simplified, low-cost approach in order to meet activity and stability targets.
- Establishing new cathode designs specifically for PGM-free catalysts such that active sites are efficiently utilized to enable high power densities with durable performance.

Proposed Future Work

- Increasing activity of stable Fe-N-C-AC-CVD catalyst
- Increasing power density of MEAs
- Scaling to 50 cm^2 for end of project goals and deliverables

Best metrics achieved up to each AMR year.

Normalization factors given. MEA at 80°C, 1.5 atm, 4 mg/cm^2



**2020 0.8 A/cm^2 durability value is 2020 gen catalyst tested in 2021*

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Acknowledgements

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Yanghua He
Mengjie Chen
Hao Zhang

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Hui Xu (Giner PI)
Shuo Ding
Sadia Kabir
Fan Yang

3M Company

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Eric Coleman
Jae Park

Los Alamos National Laboratory

Piotr Zelenay
Hoon Chung
Siddharth Komini Babu

National Renewable Energy Laboratory

KC Neyerlin
Luigi Osmieri
Sunilkumar Khandavalli
Scott Mauger

Oak Ridge National Laboratory

Karren More
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Technical Backup Slides

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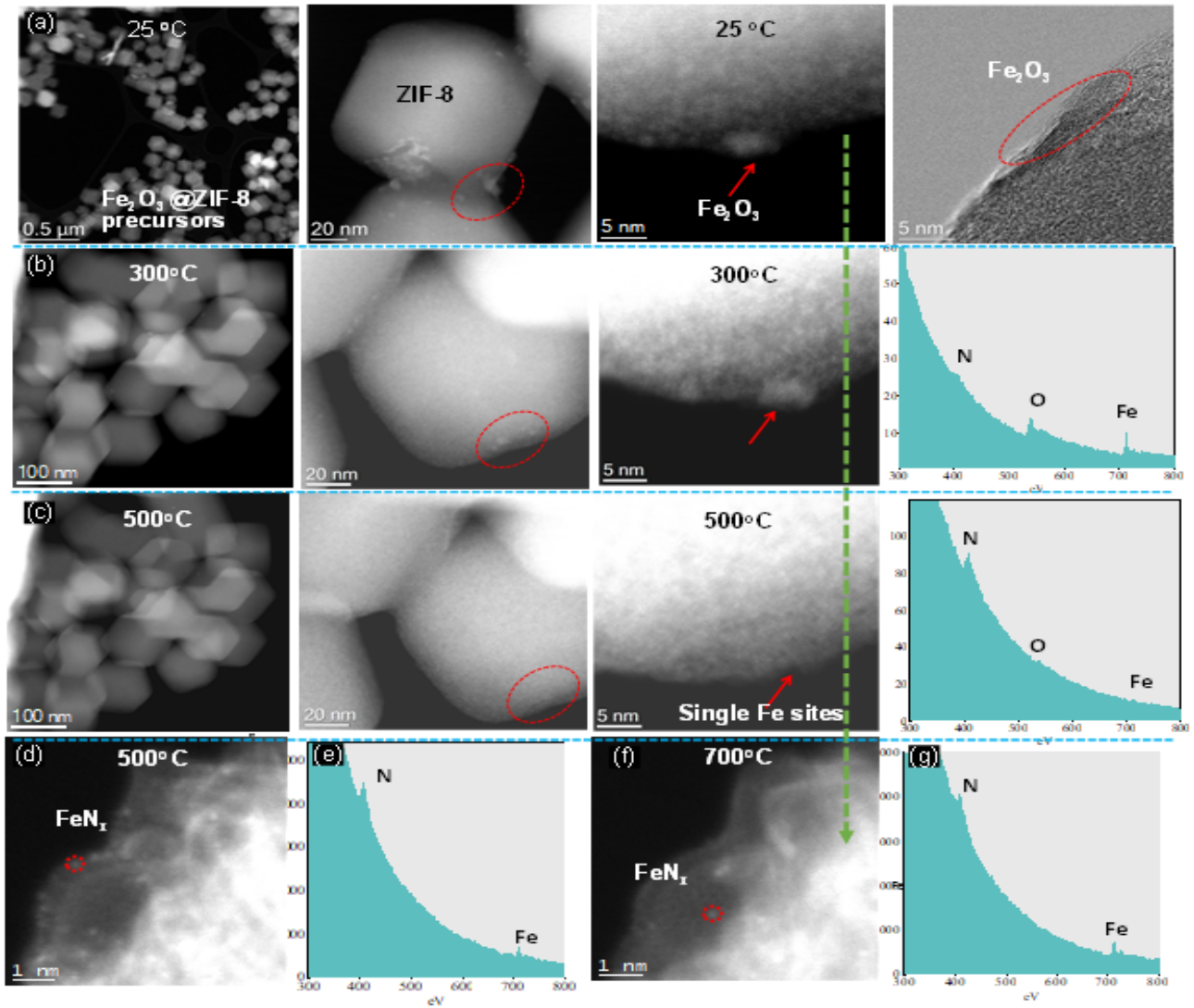
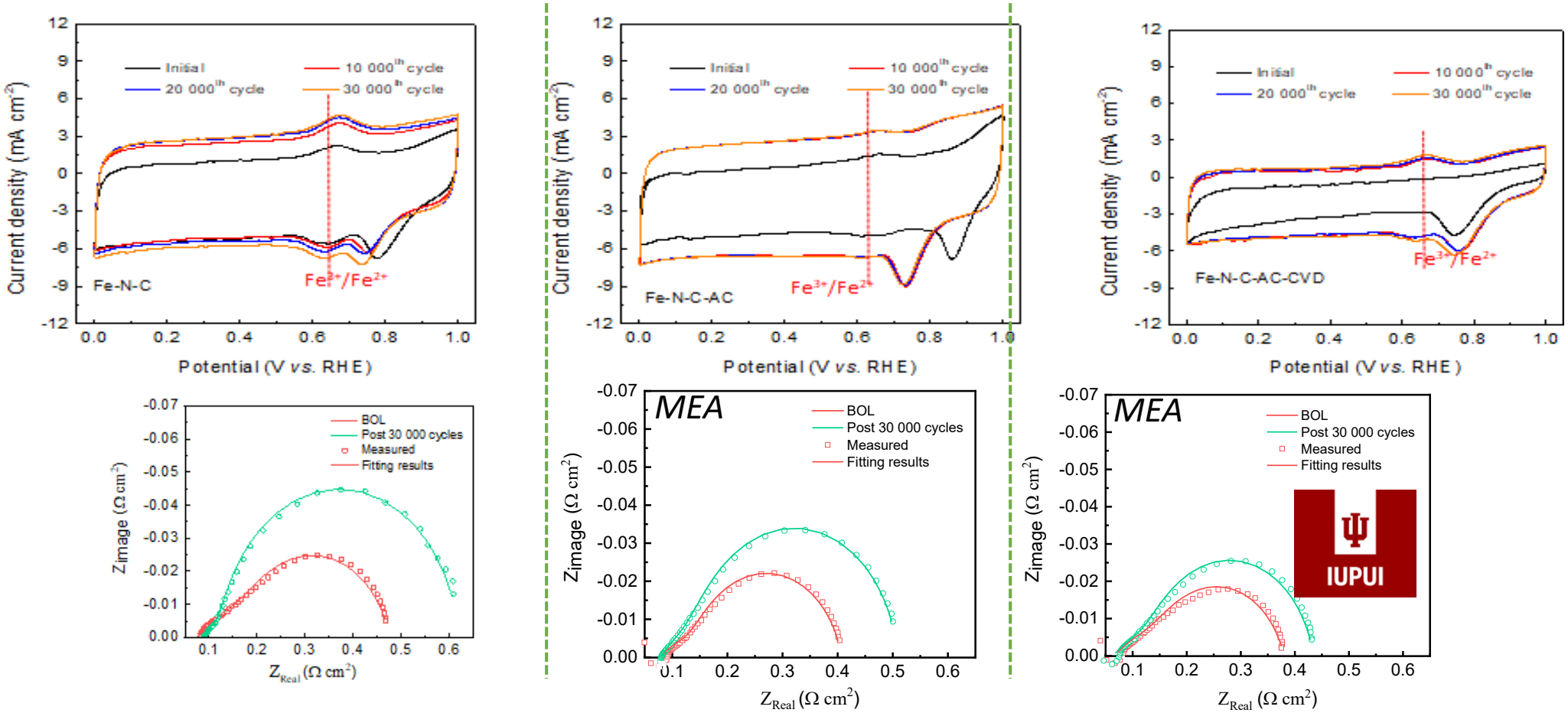
Transition of Fe_2O_3 nanoparticles to atomic FeN_4 active site



- *In situ* high-temperature STEM observe the evolution process of Fe_2O_3 nanoparticles to atomically dispersed FeN_4 sites in real-time from 25 to 700 °C under vacuum, involving Fe_2O_3 decomposition and Fe-N bond formation.
- Temperatures at 300-500°C are critical to form active FeN_4 sites for the ORR; 700°C is the optimal to realize completely atomic dispersion

Primary Degradation Mechanism- Demetallation



- The decrease of FeN_4 site densities for each catalyst is consistent with their $E_{1/2}$ loss.
- The most active Fe-N-C catalyst suffered a faster FeN_4 site loss (10 %) after 10 000 cycles relative to the most stable Fe-N-C catalyst only with 1.9 % loss.
- EIS analysis suggested the performance loss is due to increased charge transfer resistance

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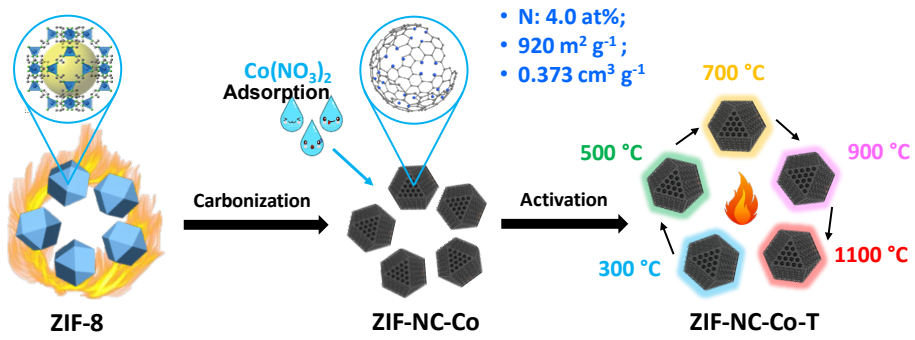
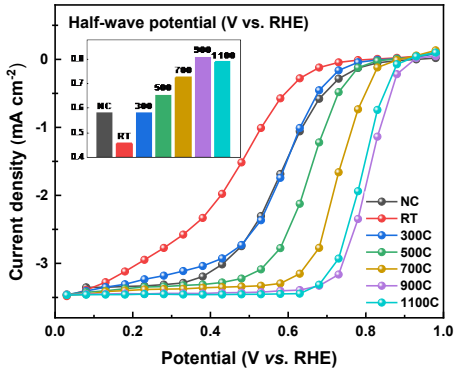
Dynamically Unveiling CoN_4 Active Site Formation Mechanisms

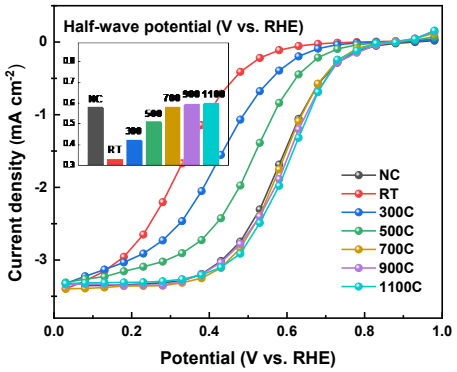
- **Co based catalysts are more stable than Fe catalysts with enhanced MEA durability**
- **Co has less concern the Fe on Fenton reactions**

Defined Model Systems

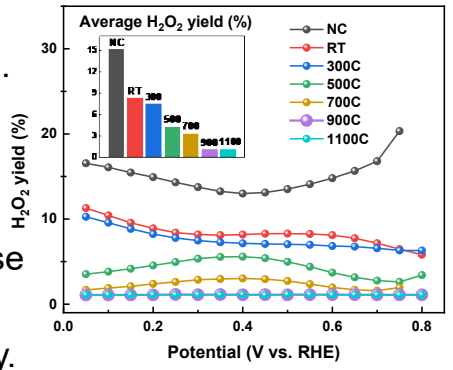


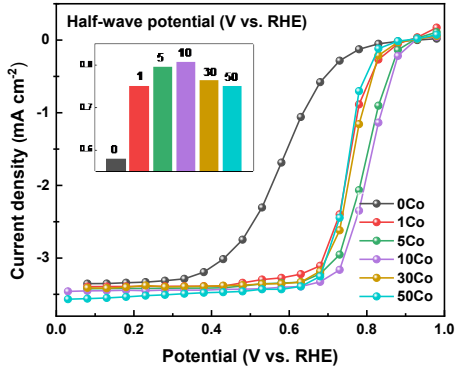
Temperature dependent ORR Activity





- **Model systems** with defined nitrogen dopants, carbon structures, and porosity were developed by using ZIF-8-derived nanocarbon **(ZIF-NC)** treated at 1100°C.
- Controlled **Co^{2+} ion adsorption into the ZIF-NC** host allows to exclusively monitor Co-N coordination evolution during **thermal activation** at different temperatures .
- A relatively low temperature of **700°C** is sufficient to trigger a substantial increase in ORR activity; **900°C** is the optimal for the highest activity and $4e^-$ selectivity
- Heating treatments **without** Co ion adsorption **do not** promote any ORR activity.





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Structural Evolution at the Atomic Level

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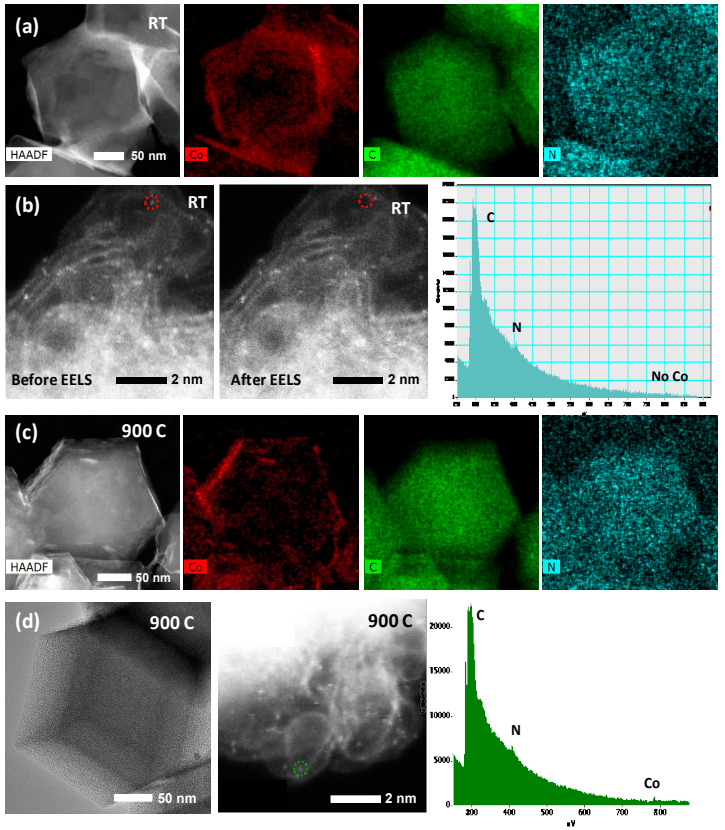
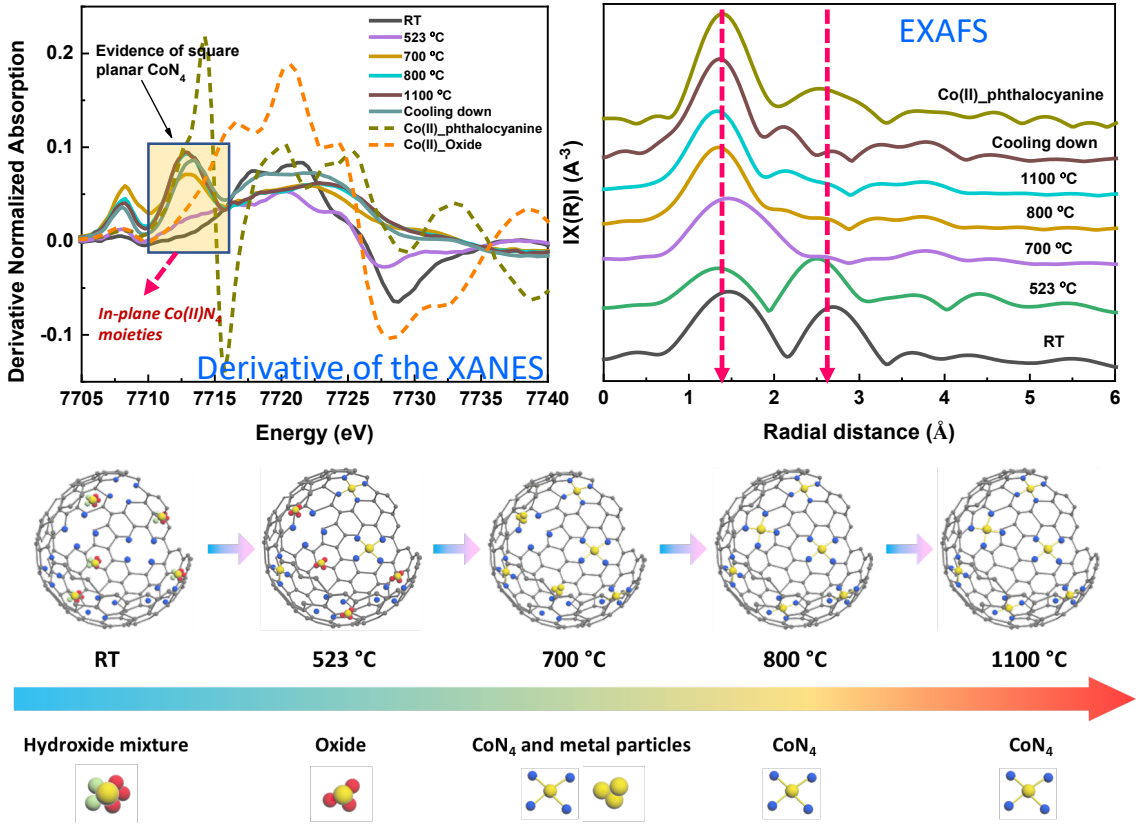
Ex-situ Electron Microscopy



In-situ High-Temperature XAS

Argonne NATIONAL LABORATORY



- Co hydroxide after Co^{2+} adsorption at **RT** undergoes decomposition to an oxide-rich mixture up to **523 °C**, to CoN_4 with a minor Co metal contribution at **~700 °C**, and entirely to atomically dispersed CoN_4 active sites at **>800 °C**.
- The formation of CoN_4 sites requires larger thermal energy (700 °C) *vs.* FeN_4 site (400°C)

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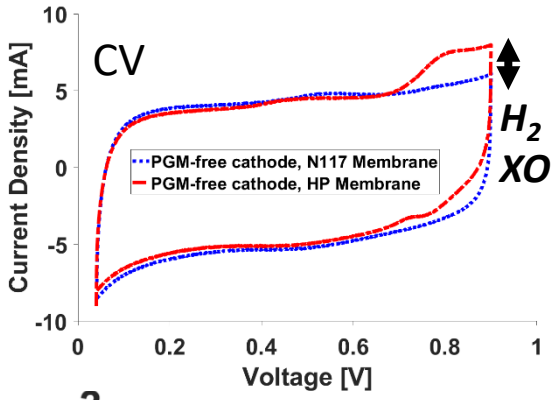
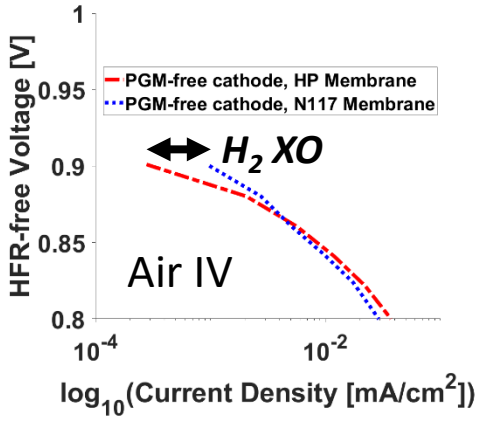
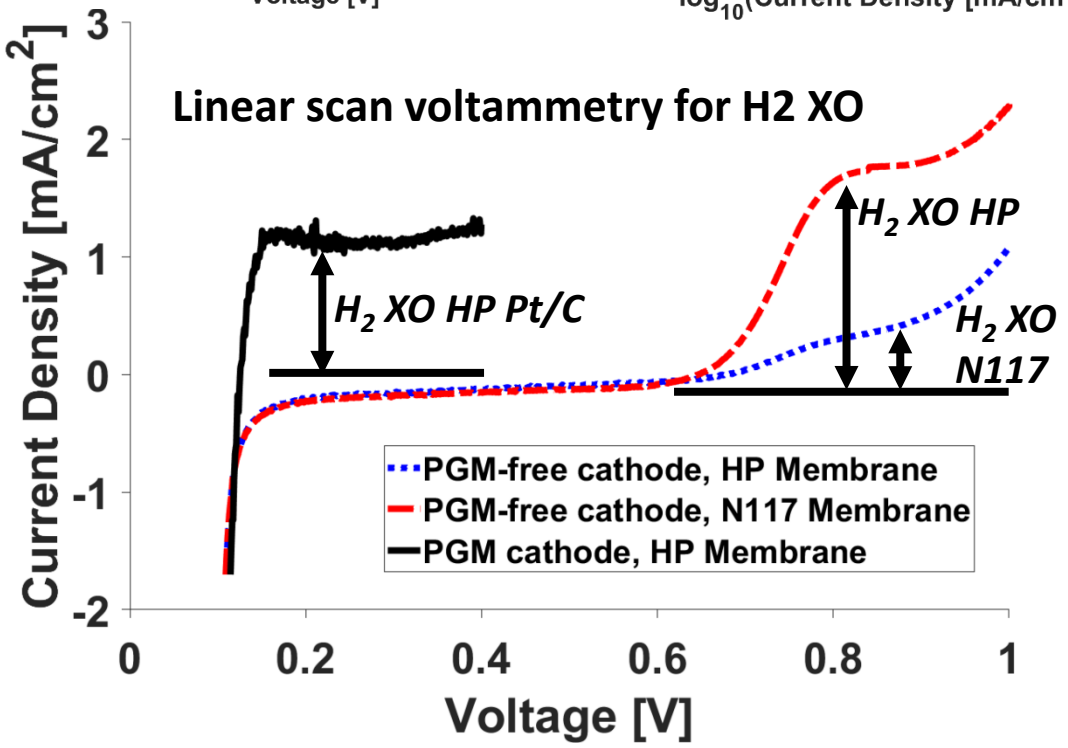
PGM-free Hydrogen Crossover (H_2 XO) Correction







- Impractical, thick membranes typically used to evaluate PGM-free MEA ORR activity due to higher activity values and the reasoning has been unclear.
- CMU performed a study of a hydrogen crossover as function of membrane thickness (N117 and HP) with same PGM-free cathode and a Pt/C cathode.
- LSV (bottom) shows that inactivity of the Fe-N-C catalyst to HOR pushes the crossover current to >0.7 V and limits at a similar value to Pt/C at >0.8 V
- H_2 crossover current evident in both CVs and the IV curves when comparing HP and N117 membranes

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Technology Transfer Activities

- Catalyst synthesis developed by UB scaled-up by Giner and distributed outside of project.

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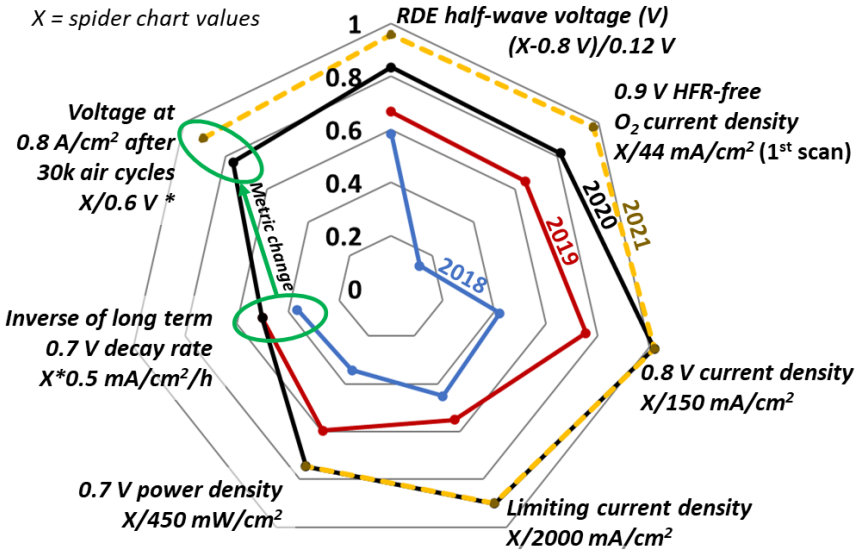
Contribution to Achievement of DOE Targets or Milestones

Property	DOE 2020 target	Present project status	Project end goal
PGM free catalyst activity (voltage at 0.044 A/cm²)	0.9 $V_{IR\text{-}free}$ (**2025**)	**0.90 $V_{IR\text{-}free}$, 43 mA/cm²** Ave. of 3 consecutive scans: 0.89 $V_{IR\text{-}free}$, 35 mA/cm²	>0.9 $V_{IR\text{-}free}$
Loss in initial catalyst mass activity	PGM: <40 %	**71%**	<50%
Loss in performance at 0.8 A/cm²	PGM: <30 mV	**30 mV**	<50 mV
MEA air performance @ 0.8 V	PGM: 300 mA/cm²	**153 mA/cm²**	>150 mA/cm²
MEA performance @ rated voltage	PGM: 1000 mW/cm²	**410 mW/cm² at 0.67 V (94°C)**	Stretch goal: >450 mW/cm²

Best metrics achieved up to each AMR year.

Normalization factors given. MEA at 80°C, 1.5 atm, 4 mg/cm²



**2020 0.8 A/cm² durability value is 2020 gen catalyst tested in 2021*

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