FC171

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

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Pittsburgh, PA

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DE-EE0008076

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*: $1,395,876
    * As of 4/30/2020

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 voltage

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

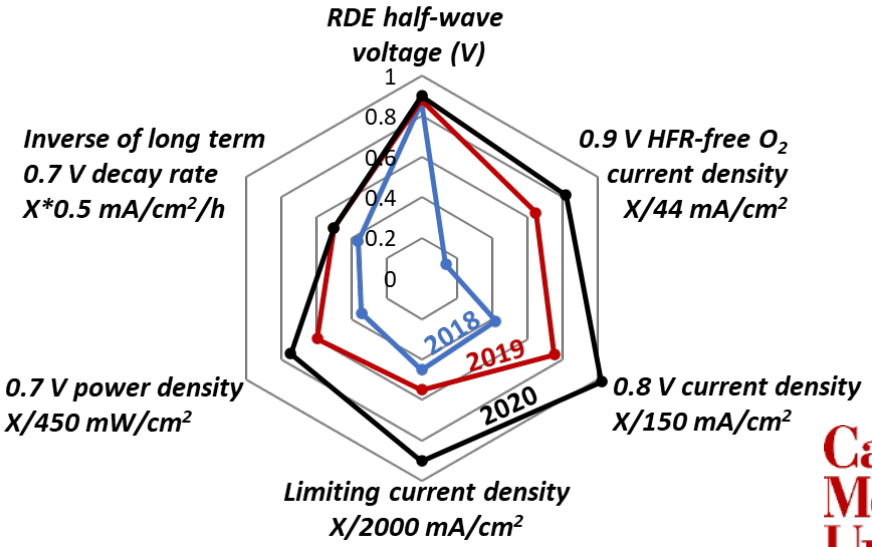
Property	DOE 2020 target	Present project status	Project end goal
PGM-free catalyst activity (voltage at 0.044 A/cm²)	0.9 $V_{IR\text{-}free}$ (**2025**)	**0.89 $V_{IR\text{-}free}$** 0.036 A/cm² at 0.9 $V_{IR\text{-}free}$ 2018: 0.028 A/cm² at 0.9 $V_{IR\text{-}free}$	>0.9 $V_{IR\text{-}free}$
Loss in initial catalyst mass activity	PGM: <40 %	-	<50%
Loss in performance at 0.8 A/cm²	PGM: <30 mV	-	<50 mV
MEA air performance @ 0.8 V	PGM: 300 mA/cm²	**153 mA/cm²** 2019 AMR: 113 mA/cm²	>150 mA/cm²
MEA performance @ rated voltage	PGM: 1000 mW/cm²	**410 mW/cm² at 0.67 V** 2018 AMR: 154 mW/cm²	Stretch goal: >450 mW/cm²

Objectives

- 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

Best metrics achieved up to each AMR year.

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



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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 VIR-free (RDE test); demonstrate MEA performance of 0.044 A/cm2 at >0.90 VIR-free	40%	RDE half-wave potential target achieved
Q12 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).	50%	

Project Team

Carnegie Mellon University (University prime)

Prof. Shawn Litster (PI), Dr. Bahareh Tavokoli, Dr. Aman Uddin, Lisa Langhorst, Diana Beltran, Shohei Ogawa, Leiming Hu, Yuqi Guo, 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), 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), Fan Yang, Shuo Ding, Zach Green

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)

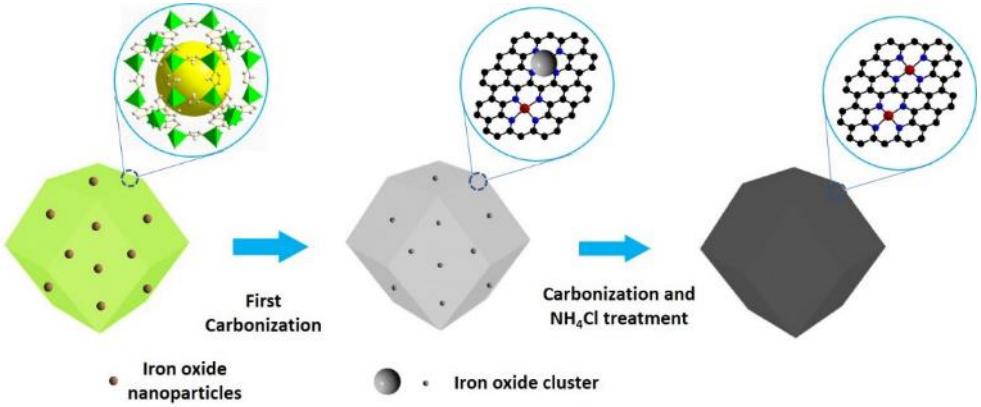
Ionomer supply and optimization support.

Electrocatalysis (ElectroCat) EMN Consortium Members (National Laboratories)

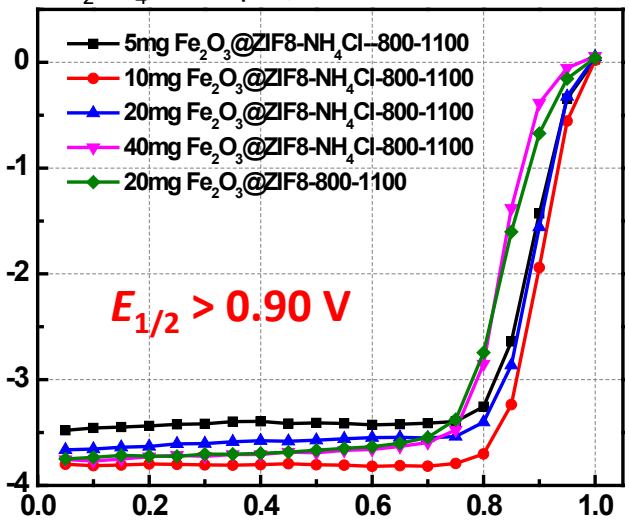
X-ray abs. spectroscopy, high-throughput electrodes (ANL), electron microscopy (ORNL), molecular probes studies (LANL & ANL), electrode development (NREL), fuel cell durability testing (LANL).

Solid State Synthesis of Atomically Dispersed Fe catalyst

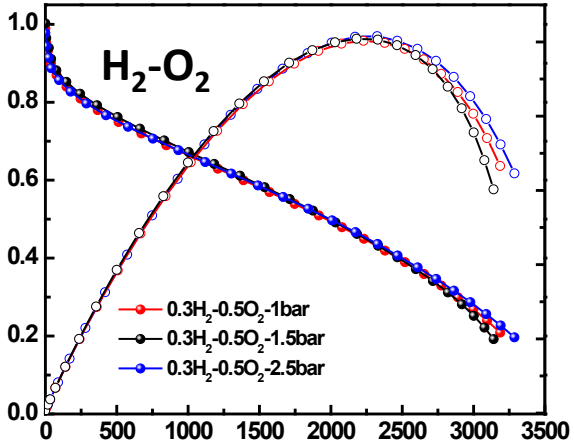
- Modified synthesis yielding significant increases in ORR activity
- RDE half-wave voltage >0.9 V and MEA air current density at 0.8 V >150 mA/cm^2, surpassing project target
- Durability and stability improvements required



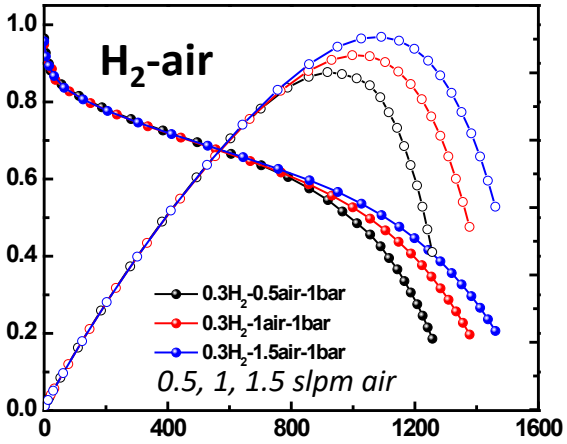
RDE: Loading: 0.6 mg cm^{-2}, 0.5M H_2SO_4, 900 rpm, 25°C



0.9 V: 36 mA/cm²



0.8 V: 153 mA/cm²



H_2/O_2 cell OCV: 0.977 V
36 mA/cm² at 0.9 V
439 mA/cm² at 0.8 V
1696 mA/cm² at 0.7 V

H_2/air cell OCV: 0.965 V
15 mA/cm² at 0.9 V
153 mA/cm² at 0.8 V

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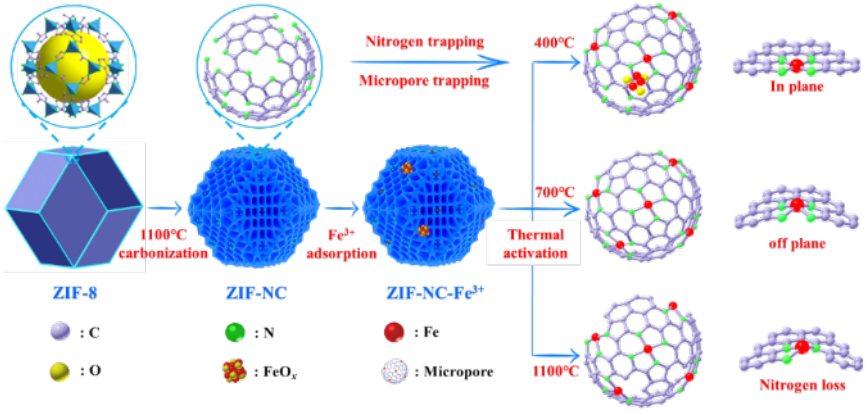
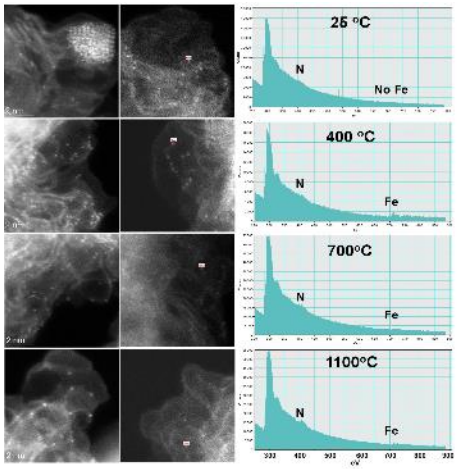
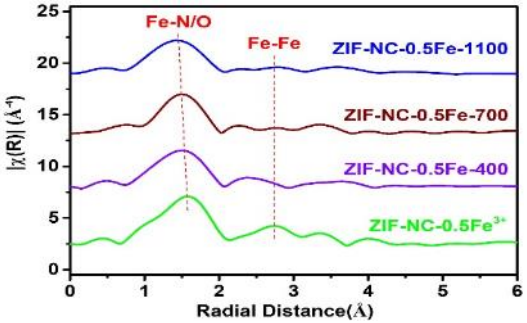
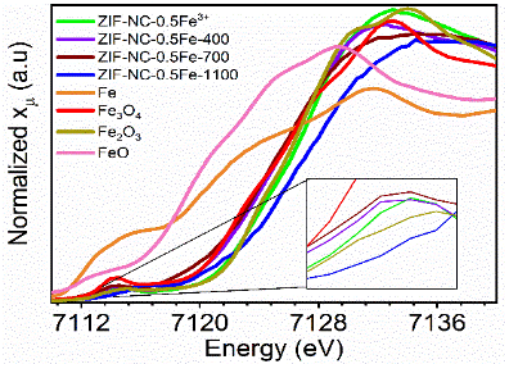
MEA: Fe-N-C catalyst loading: 4.0 mg/cm^2 ; Nafion 212; RH: 100 %; 80°C

Formation Mechanisms of FeN_4 Active Sites

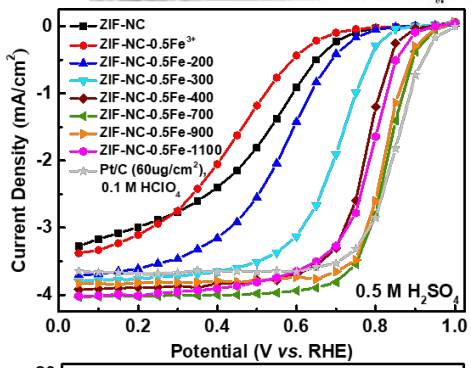


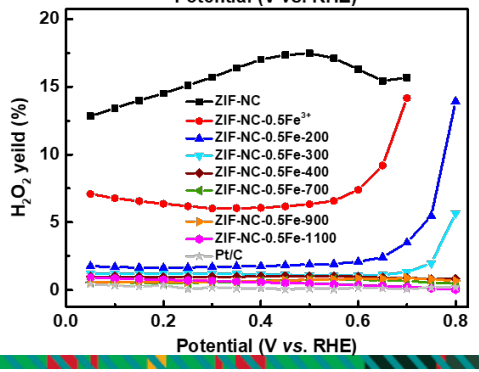






- FeN_4 formation during pyrolysis has remained unclear due to uncontrolled carbonization and nitrogen doping during heat treatments.
- Porous carbon derived from ZIF-8 with unique nitrogen-doping and microporous structure employed as a model substrate to adsorb Fe^{3+}
- The interactions between N and Fe^{3+} is the only variable factor during thermal activation.
- Inactive Fe-N configurations formed at room temperature; transformation from Fe-oxide to the atomic dispersion of FeN_4 up to 400°C
- Increasing from 400 to 700°C leads to the reduced oxidation state and low symmetry around Fe atom or shorter Fe-N bond length in FeN_4 configurations





- ***ORR activity increased up to 700°C***
- ***Even low temperature 400°C can generate high activity ($E_{1/2}$ =0.79 V)***
- ***Activity loss occurred at 1100 °C***
- ***Temperature >800°C not essential***

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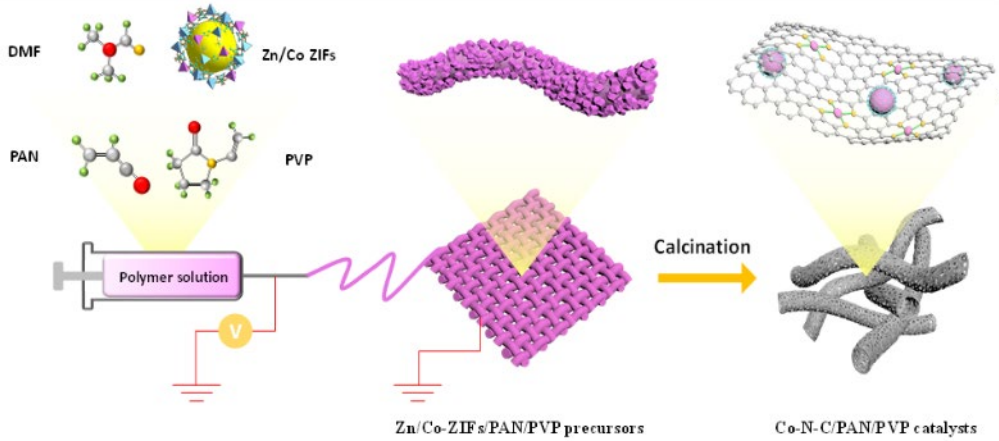
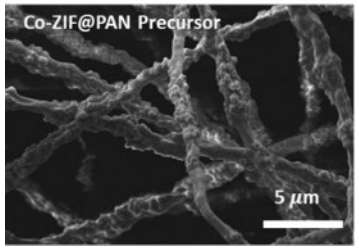
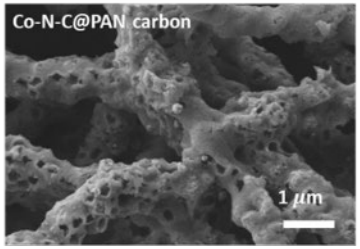
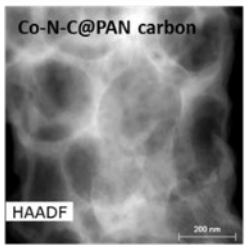
Synthesis of electrospinning Co-N-C catalysts

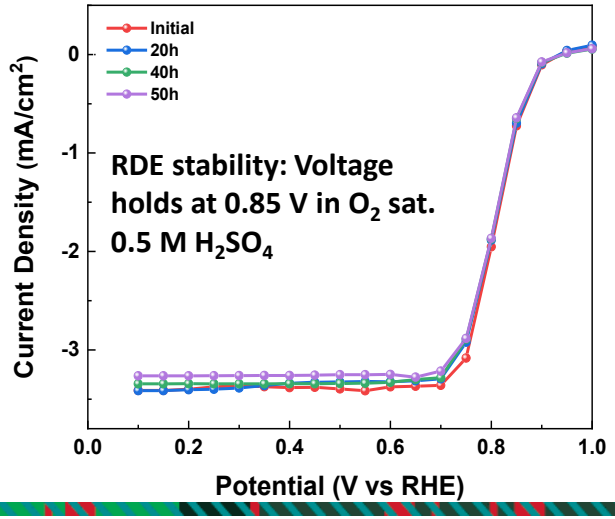


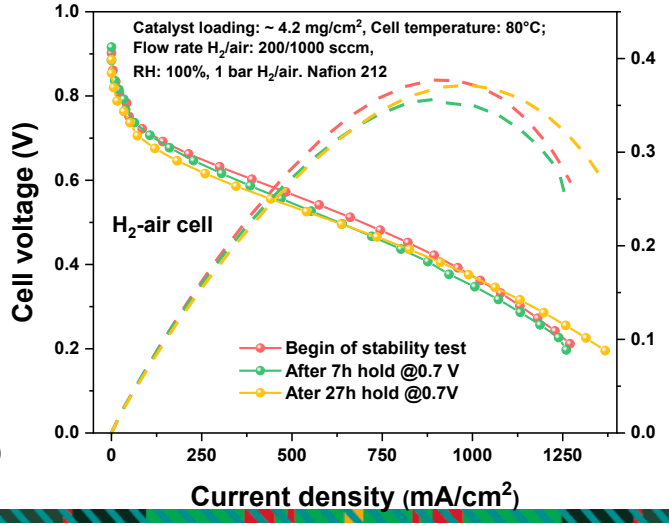


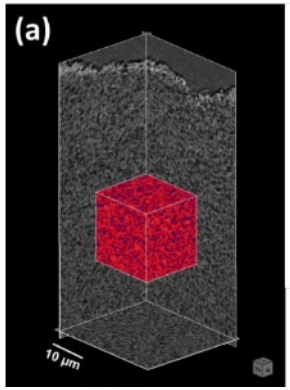


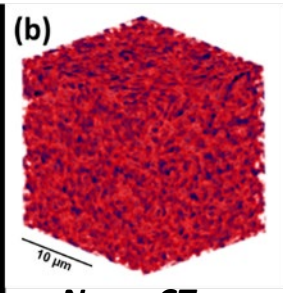


- Unique 1D structure, such as higher graphitization degree beneficial for electronic mobility
- 3D Hierarchical porosity facilitating the mass transport
- Rationally designed porous structure of M-N-C catalyst is essential to expose more accessible active sites and facilitate mass transport of reactants (O_2)and products (H_2O).
- Co-N_x active sites and Co clusters/particles are existing in the catalysts.
- Good ORR RDE activity with initial $E_{1/2}$ of ~0.81 V
- Nano-CT shows a compact cathode structure (higher vol. activity) and uniform ionomer coverage
- RDE and MEA show good stability during extended 0.7 V holds









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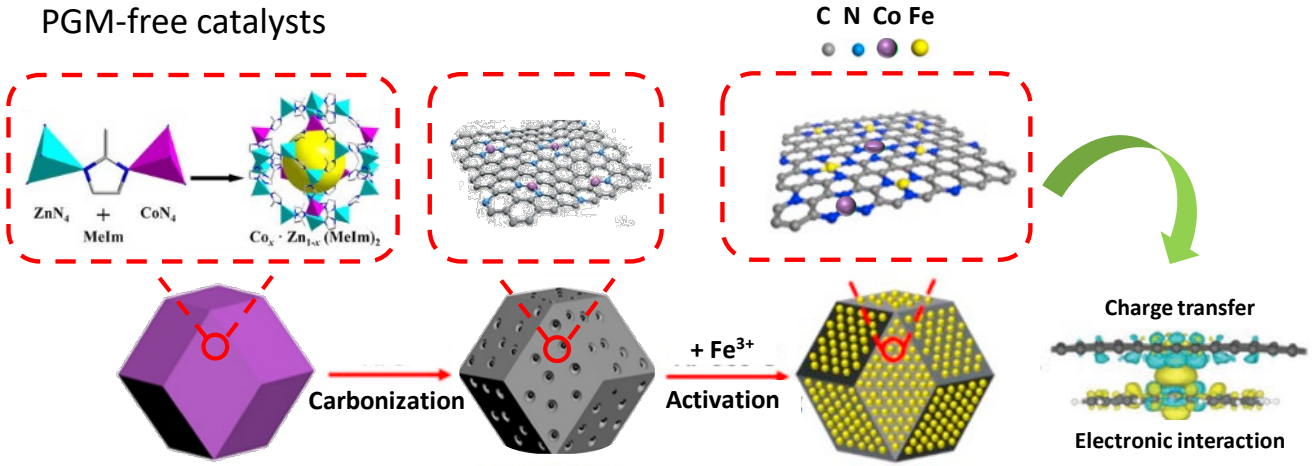
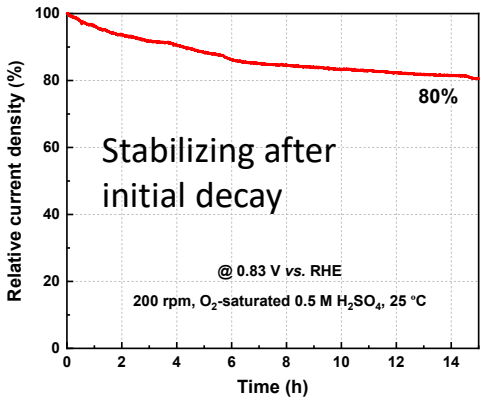
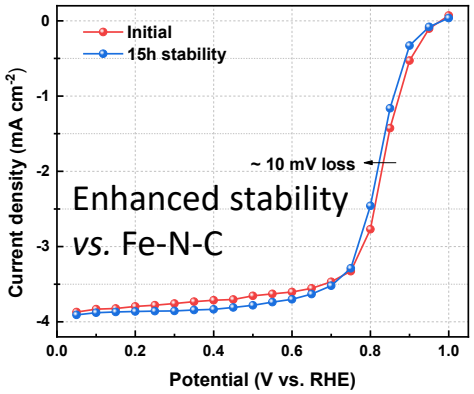
Synthesis of binary FeCo-N-C catalysts

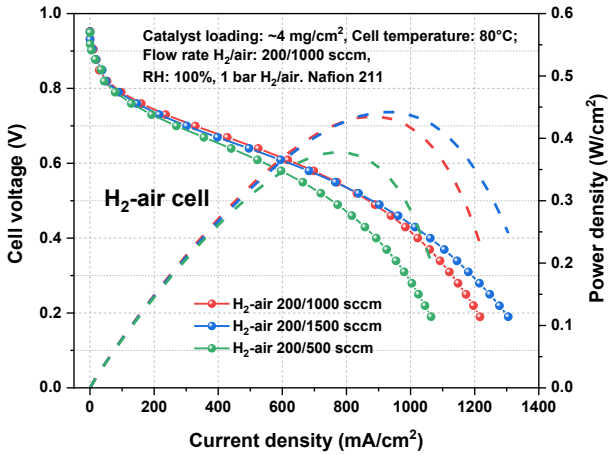
- Synergy with enhanced activity from Fe-N-C and improved stability from Co-N-C
- The FeCo catalyst exhibited enhanced RDE and MEA durability relative to the Fe-N-C catalyst (Zhang et al., Energy Environ, Sci, 2019).
- Development of innovative FeCo-N-C catalysts hold a promise to advance PGM-free catalysts

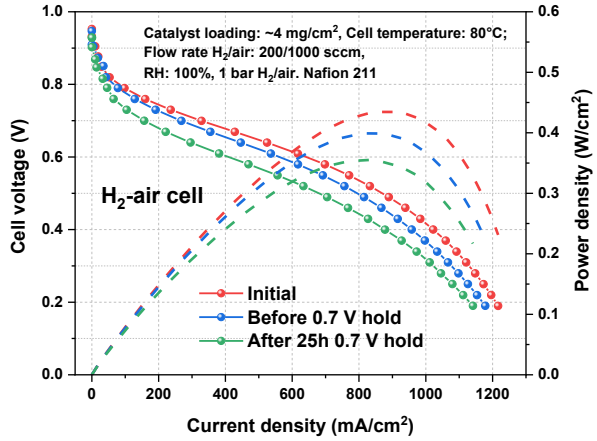


RDE Stability: constant 0.85 V, H_2-O_2









H_2/air cell
OCV: 0.95 V
0.8 V: 78 mA/cm^2
0.7 V: 302 mA/cm^2
Max Power: 442 mW/cm^2

MEA: Cathode loading: 4.0 mg/cm^2 ; Nafion 212;
RH: 100 %; 0.5 L/min O_2 or air, 1.0 bar

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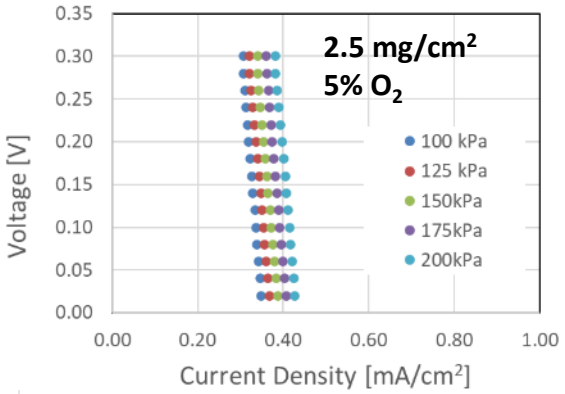
Limiting Current Measurements

- Thick PGM-free electrodes have large mass transport losses and unique catalyst structure
- Limiting current density measurements to determine the significance of each mass transport resistance



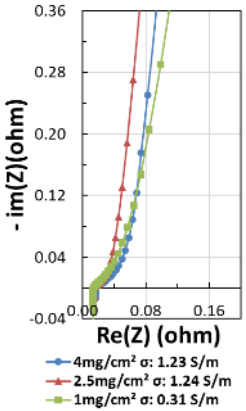
Measurements

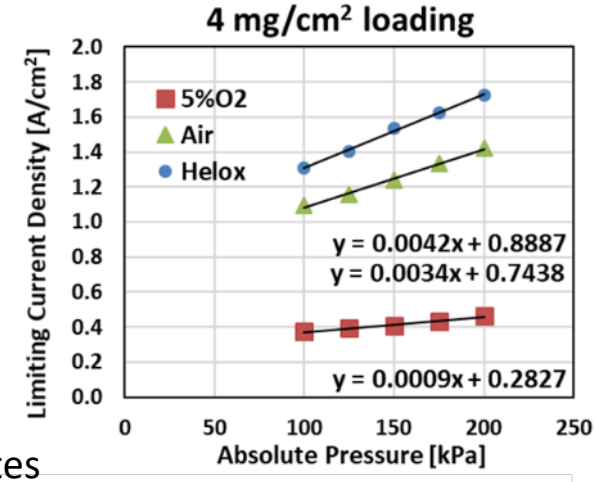
Limiting Current Density

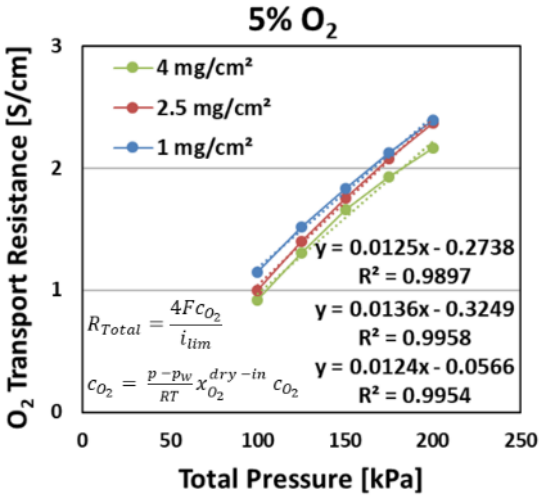
- Loading: 1 - 4 mg/cm²
- Pressure: 100 – 200 kPa
- O_2 concentration: 5 – 21%
- Carrier gas: N_2, H_2

O_2 transport resistance

- Slope: p-independent
- Intercept: p-dependent







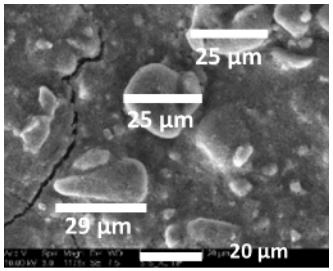
Thick Catalyst Layers

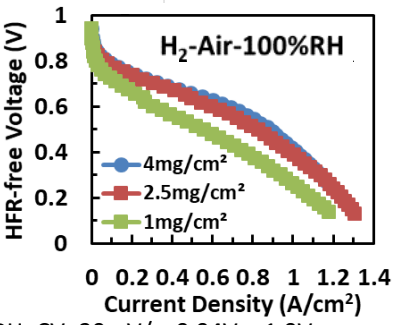
Broad size distribution of catalyst aggregates

- Primary particles size 100 nm
- Large catalyst aggregates (20 – 30 µm)

Less continuous structure at low loading

- At 1 mg/cm² electrode thickness is similar to the diameter of largest particles
- Conductivity outlier at 1 mg/cm²





i_{lim} measurement: H_2/(Lean Air /Air/Helox), 200 sccm/1000 sccm, An/Ca, 80°C, 0.30 V – 0.02 V, 0.02 V steps. Limiting current is taken as the current at 0.04 V.

Full MEA required to interpret oxygen transport resistances for thick electrode transport

Conditioning: N_2/N_2, 2h, 100%RH CV: 20mV/s, 0.04V – 1.0V
PEIS: 0.5V, 100mHz-100kHz 100% RH Polarization: H2/Air, 200sccm/1000sccm, an/ca, 80°C, 50kPa backpressure

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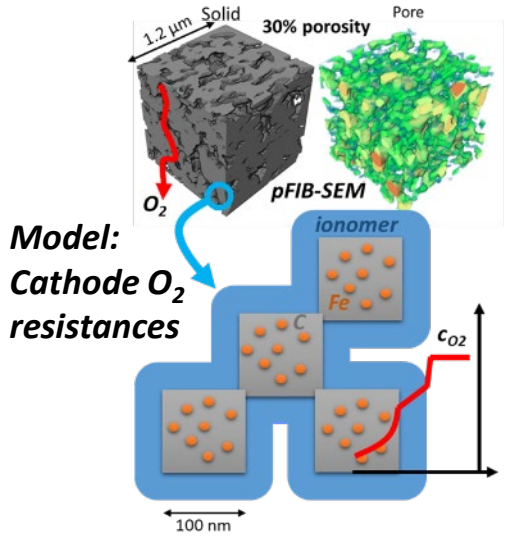
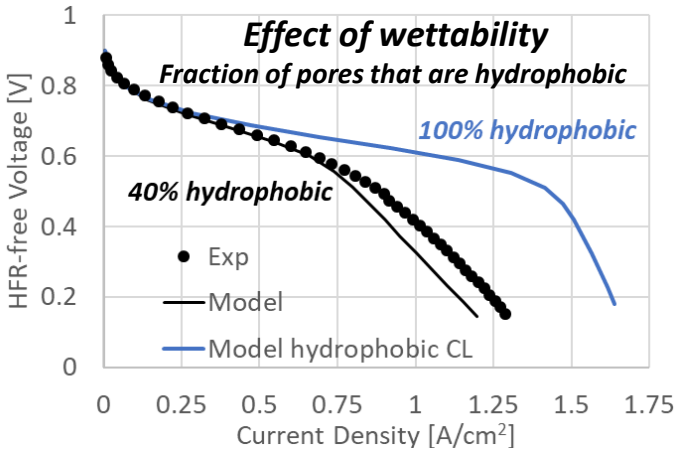
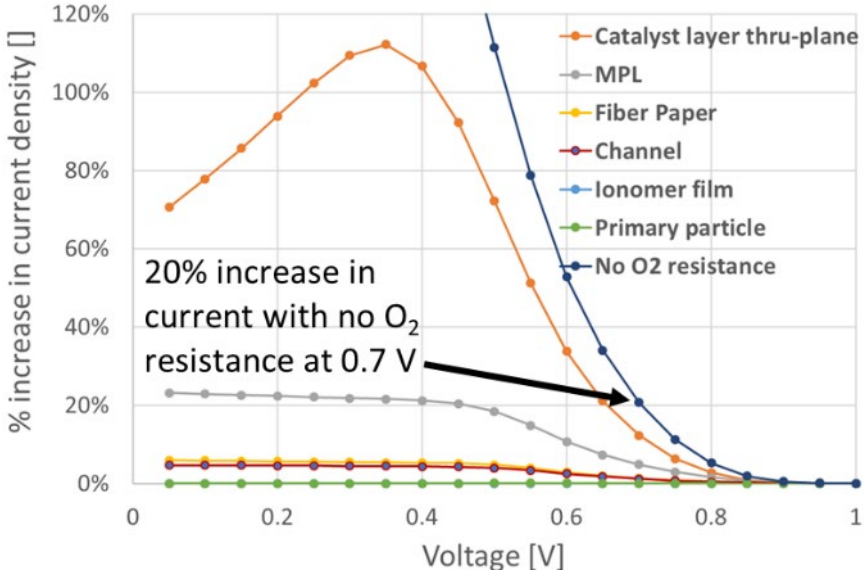
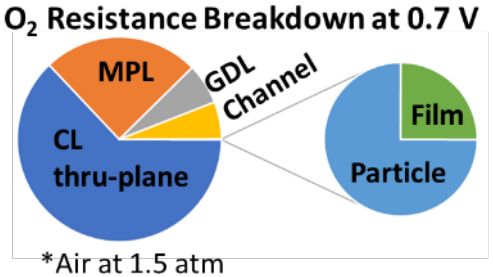
Transport Resistance Analysis

- Detailed model of cathode microstructure validated against O_2 limiting current study (see Technical Backup Slides) to resolve significant non-linear coupling of transport and ORR for thick electrodes
- Individual transport resistances estimated by computing polarization curves with that resistance set to zero
- Dominant resistances:
  1. Diffusion across flooded cathode
  2. Microporous layer
- Particle & ionomer film resistance negligible for 100 nm catalyst
- Performance improvements below 0.7 V assuming 100% hydrophobic catalyst layer pores versus fitted value of 40%









*Air at 1.5 atm

**Sums to 94% of no O_2 resistance

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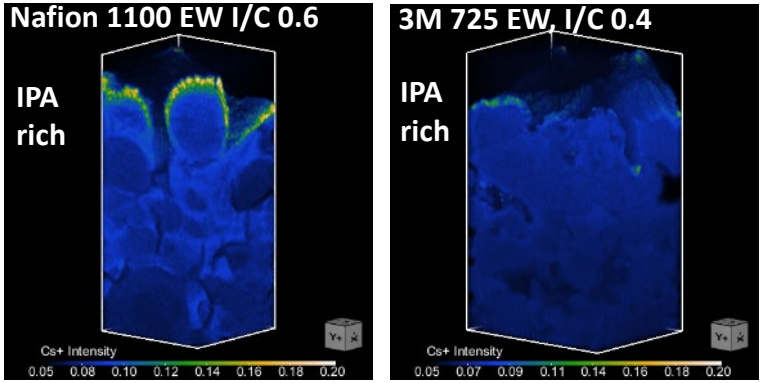
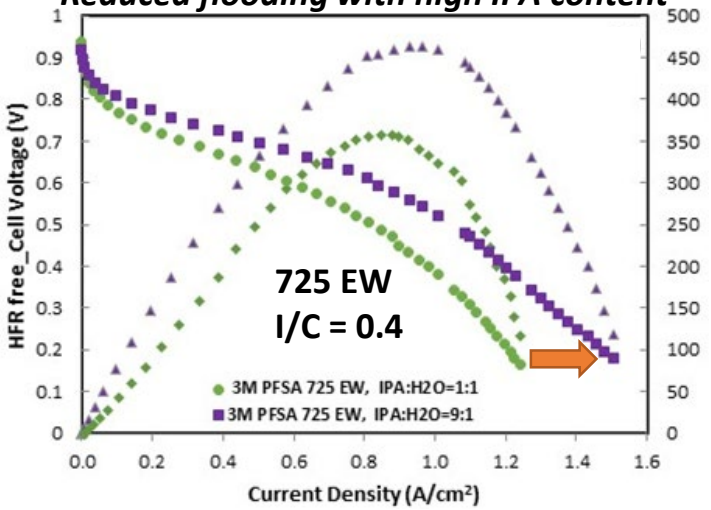
Enabling low EW ionomers

- Goal to use low EW ionomers in the electrode to reduce ohmic losses for more uniform catalyst utilization
- Comprehensive study of ink composition and ionomer type on PGM-free cathode performance (solid-solvent ratio, water-IPA ratio, 3M PFSA vs. Nafion, EW 725-1200)
- Severe flooding with low EW mitigated by lowering I/C and increasing IPA content versus water
- Increased hydrophobicity with lower I/C enabled by lower EW ionomers with higher conductivity
- Low dielectric constant (IPA-rich) solvent increases hydrophobicity
- ~50% reduction in resistance with 725 EW 3M PFSA vs. 1100EW Nafion both at I/C of 0.6
- 50 % increase limiting current density with 725 EW 3M PFSA by reducing I/C and using IPA-rich ink solvent

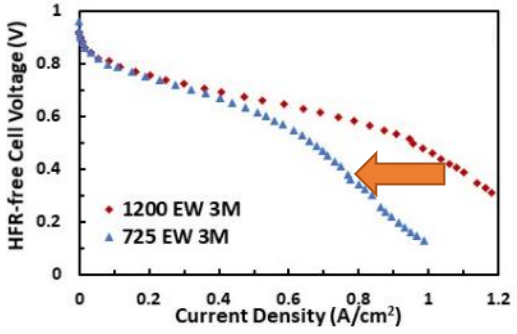
Nano-CT ionomer mapping



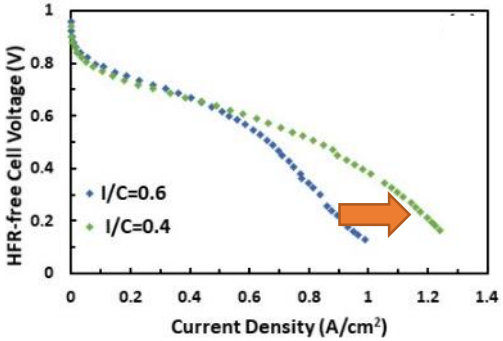
Reduced flooding with high IPA content



Increased flooding with lower EW



Reduced flooding with lower I/C



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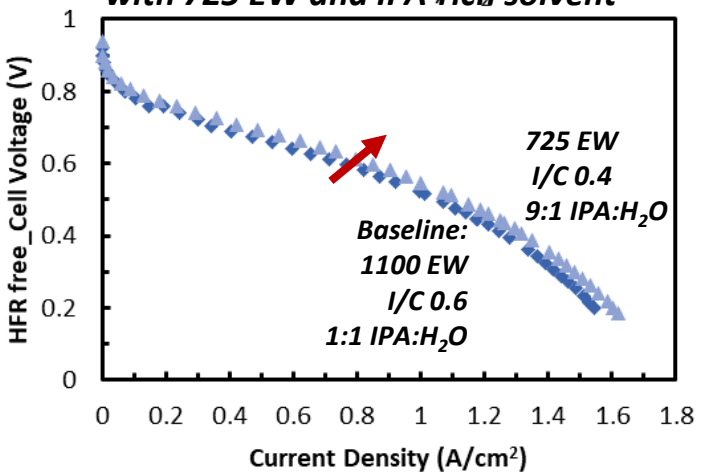
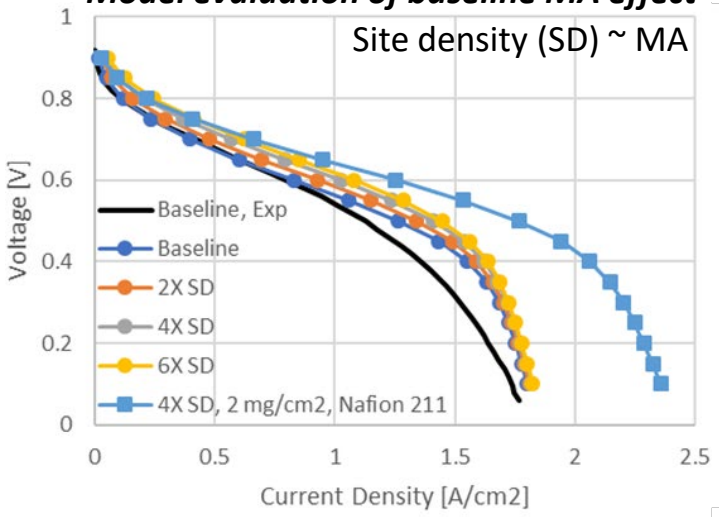
Meeting the 450 mW/cm^2 at 0.7 V Stretch Goal

- 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 Nafion 1100 EW electrode reaches target with 4X increase of mass activity with a loading of 2 mg/cm^2.
- Baseline: I/C = 0.6, 100 nm primary particles, Nafion 211 membrane, 2 mg/cm^2 loading (40 µm)
- **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

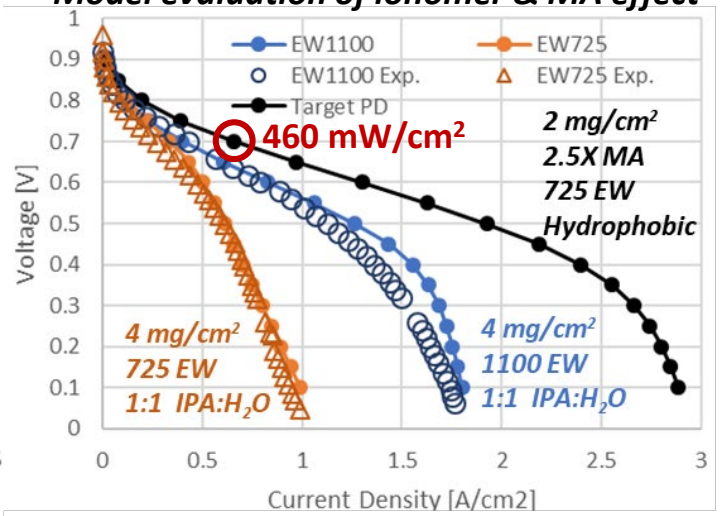
Improved performance with 2/3 ionomer with 725 EW and IPA-rich solvent



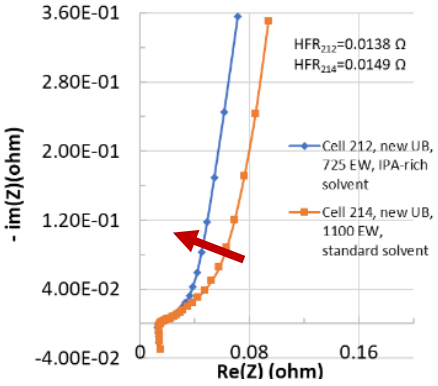
Model evaluation of baseline MA effect



Model evaluation of ionomer & MA effect



Reduced electrode resistance



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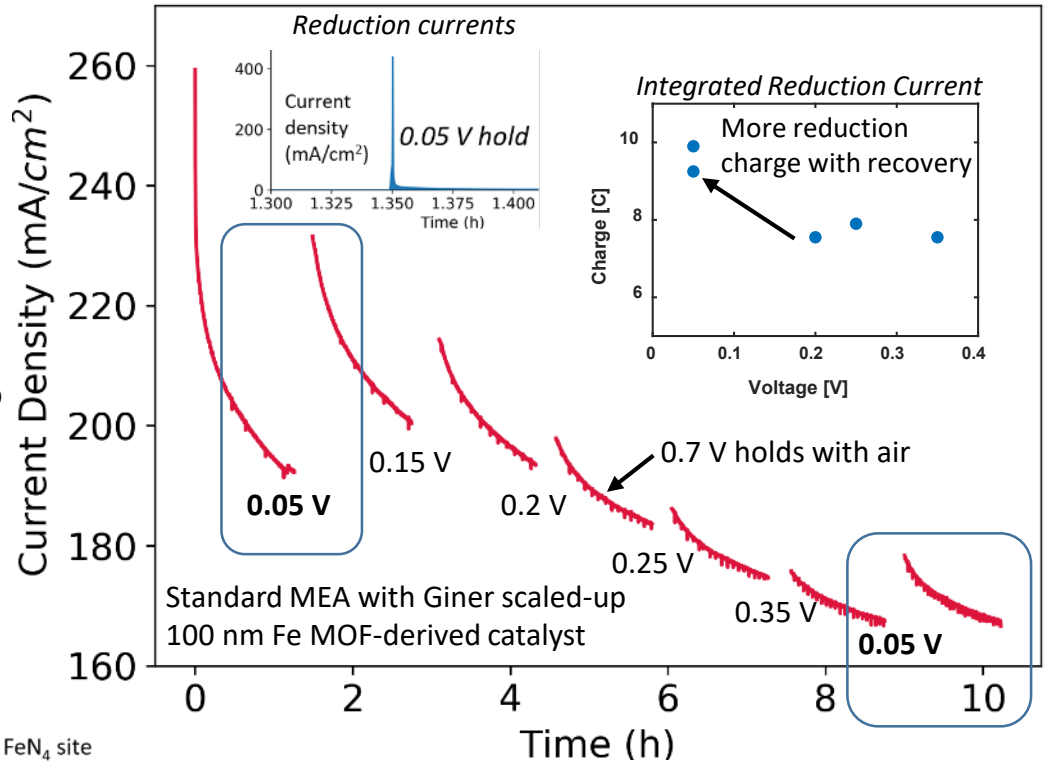
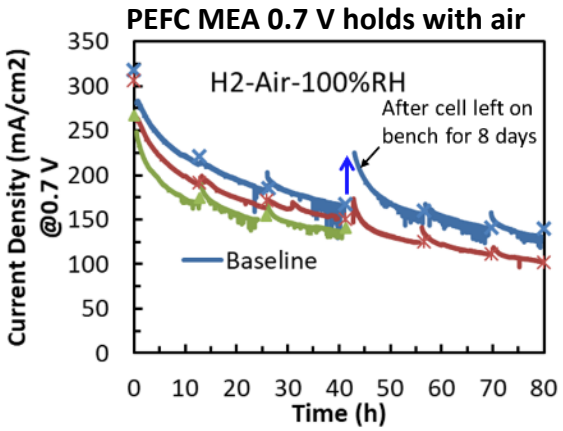
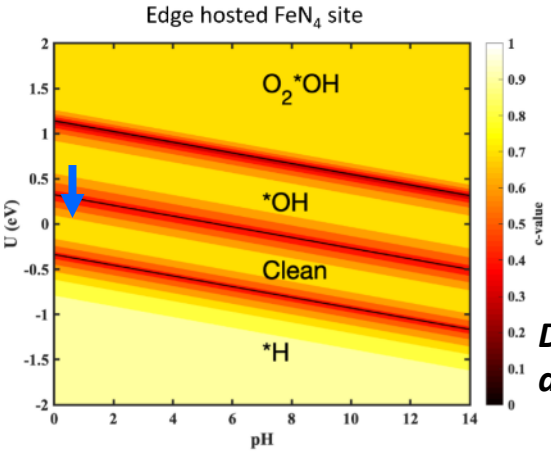
1. Beltrán & Litster, ACS Energy Letters, 2019

Potential Dependent Recovery of ORR Activity

- Development of rapid, in-situ activity recovery motivated by observed recovery in MEAs and RDE (e.g., 50% recovery after resting cell for 8 days).
- Recovers activity lost during initial fast performance loss. Not due to flooding.
- Identified low voltage holds in N_2 environment recovered performance
- Recovery coincides with a reduction current due to either $Fe^{3+} \rightarrow Fe^{2+}$ or reduction of adsorbate
- Reduced/negligible recovery and lower reduction currents for N_2 voltage holds above 0.2 V
- DFT studies suggest recovery could be due to reduction of adsorbed OH below 0.25 V.

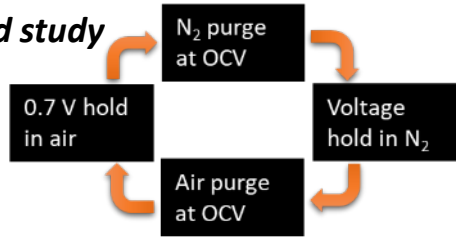






DFT-based Pourbaix diagram of FeN_4 site state

N_2 voltage hold study



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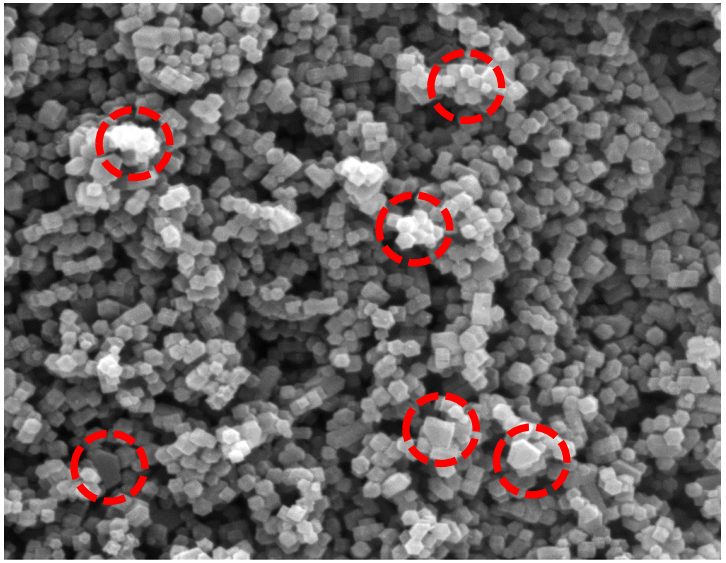
Catalyst Synthesis Scale-Up

20 L Reactor and Chiller

SEM images of 6L catalyst (100nm recipe)



- Giner leads the scale-up of catalyst synthesis and MEA evaluation.
- 20L reactor is used to produce large quantity precursors.
- Current catalyst yield is about 1-2g catalyst per batch and can be further improved using larger furnaces.
- Over 5 g catalysts have been sent to CMU and LANL for further studies.

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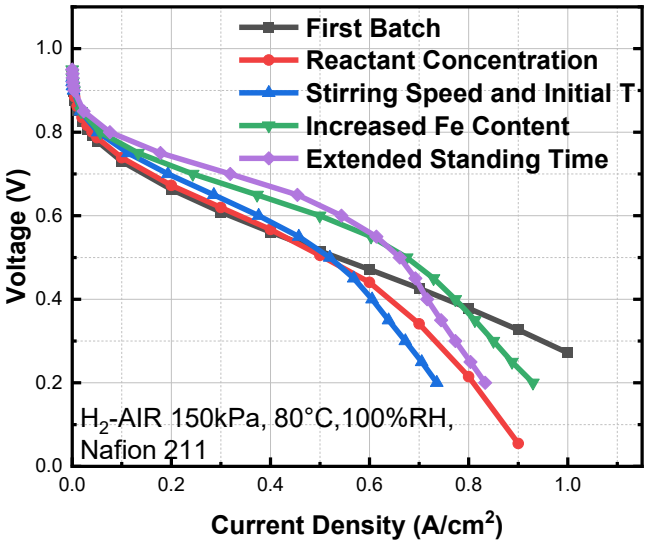
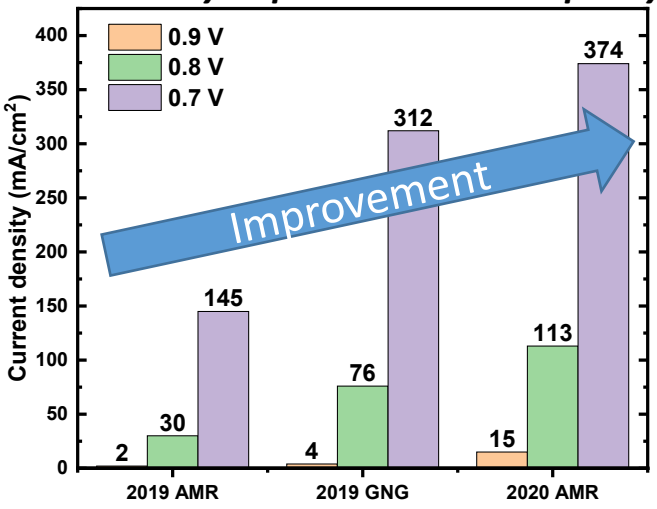
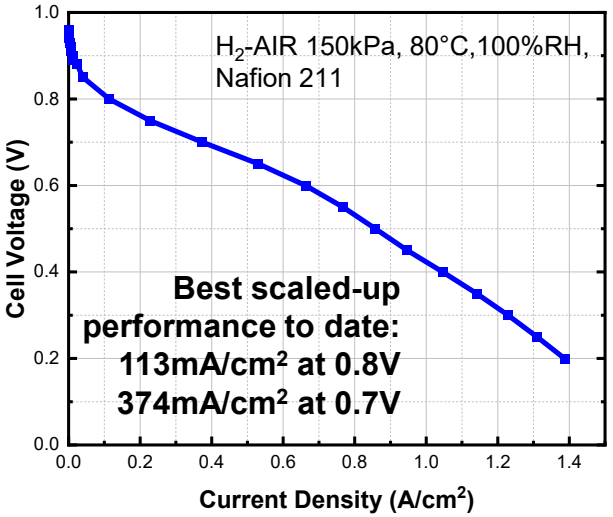
Optimization of Synthesis Scale-Up

MEA results in different optimizations



Current density improvement in the past year





- Several factors affecting catalyst scale-up have been identified and optimized, including reactant concentrations, initial temperature, stirring rate during process, standing time between mixing chemical solutions and heating up.
- Steady progress has been made towards catalyst performance improvement
- Best scaled-up catalyst batch matches 2019 AMR 0.8 V current density of 113 mA/cm^2
- Inconsistent particle size and huge aggregation exist in the large-scale synthesized catalyst, which may impact the MEA performance
- Further refinements in large batch processing needed for consistency

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Response to 2019 AMR Comments

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. Besides the 3D structuring, 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. 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 nearly fully 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 has 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

Durability and catalyst stability will be the primary focus for the remainder of the project, including the following specific areas:

- Stabilizing the new high activity Fe-MOF catalyst through improved graphitization
- Refining the FeCo-N-C catalyst for higher activity to leverage the potential for improved stability
- Establish an *in-situ*, rapid reactivation/recovery process for recovery the reversible, fast time-scale voltage loss that can be implemented in fuel cell systems.
- Evaluate long term stability of most promising catalysts through ASTs
- Evaluate the impact of atomically dispersed Fe-N-C catalysts on membrane degradation

Electrospining of Fe-N-C catalyst precursors to leverage the improved structures observed with the Co-N-C catalysts that did not feature problematic large dense aggregates or other methods to eliminate large aggregates

Scale-up of Catalysts and MEAs to support larger scale testing.

- Consistent synthesis of high activity Fe-MOF catalyst for 50 cm^2 MEA studies and for ElectroCat projects
- Fabrication and testing of 50 cm^2 PGM-free MEAs

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Summary

Accomplishments and Progress

- Significant increases in activity and mass transport properties in past year as shown in spider chart
- New synthesis for Fe-N-C catalyst yielding exceptionally high BOL ORR activity
- Electrospinning of precursors to eliminate large dense aggregates and demonstrate high performance with Co catalyst
- FeCo-N-C catalyst to potentially enhance stability
- Extensive study of ionomer and solvent composition in catalyst inks to yield high conductivity with low O_2 transport resistance
- O_2 transport resistance study identify flooding as dominant loss and local catalyst-scale losses to be negligible for 100 nm Fe-MOF catalysts
- Scale-up of high-performance catalyst and delivery outside of the project

Collaboration and Coordination with Other Institutions

- Rapid iteration cycle with catalyst development at UB and MEA fabrication and testing at CMU.
- 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

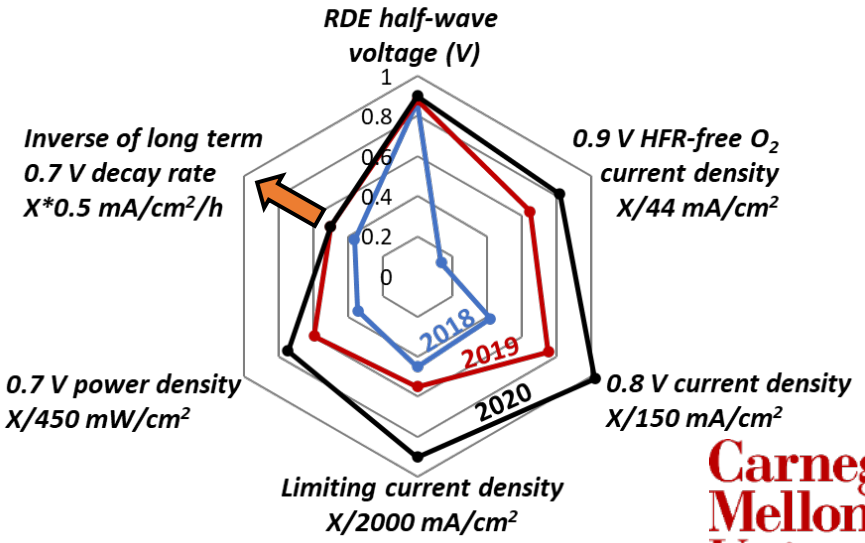
- Advancing synthesis of atomically dispersed active sites at high density with a simplified, low cost approach in order to meet activity and stability targets.
- Establishing new cathode designs specifically for PGM-free catalysts such that active sites are efficiently utilized to enable high power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

Proposed Future Work

- Stabilizing the new high activity Fe-MOF catalyst through improved graphitization
- Refining the FeCo-N-C catalyst for higher activity to leverage the potential for improved stability
- Establish an *in-situ*, rapid reactivation/recovery process for recovery the reversible, fast time-scale voltage loss that can be implemented in fuel cell systems.
- Evaluate long term stability of most promising catalysts through ASTs
- Evaluate the impact of atomically dispersed Fe-N-C catalysts on membrane degradation
- Electrospinning of Fe-N-C catalyst precursors to leverage the improved structures observed with the Co-N-C catalysts that did not feature problematic large dense aggregates or other methods to eliminate large aggregates
- Consistent synthesis of high activity Fe-MOF catalyst for 50 cm^2 MEA studies and for ElectroCat projects
- Fabrication and testing of 50 cm^2 PGM-free MEAs

Best metrics achieved up to each AMR year.

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



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Sunilkumar Khandavalli
Scott Mauger

Oak Ridge National Laboratory

Karren More
David Cullen

Technical Backup Slides

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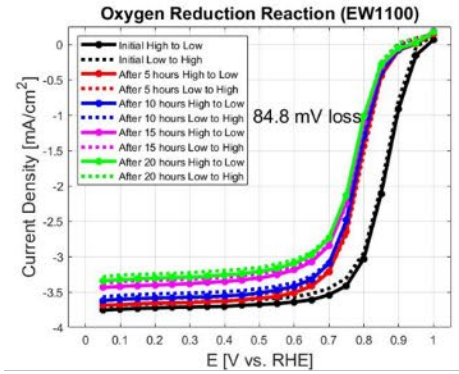
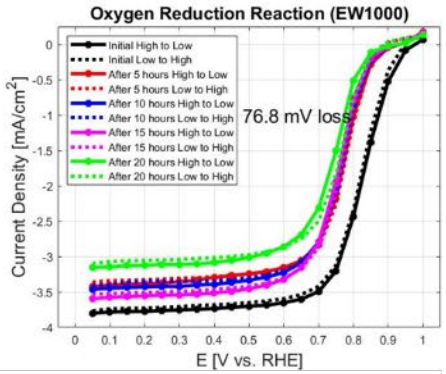
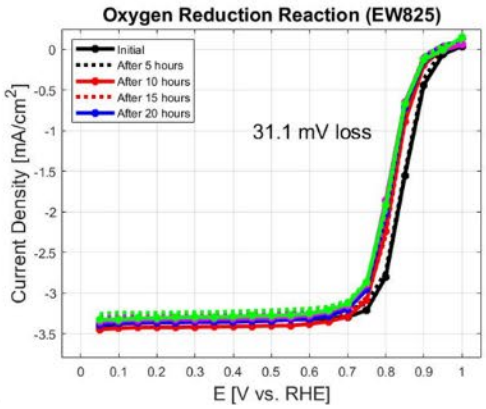
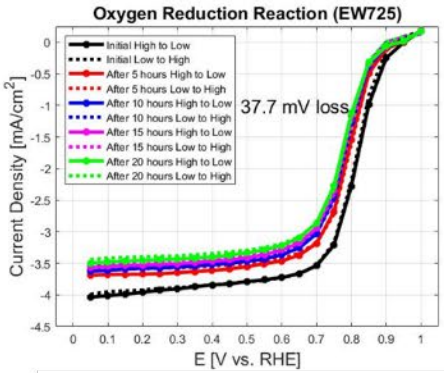
20-hr RDE 0.85 V Stability: Ionomer Effect

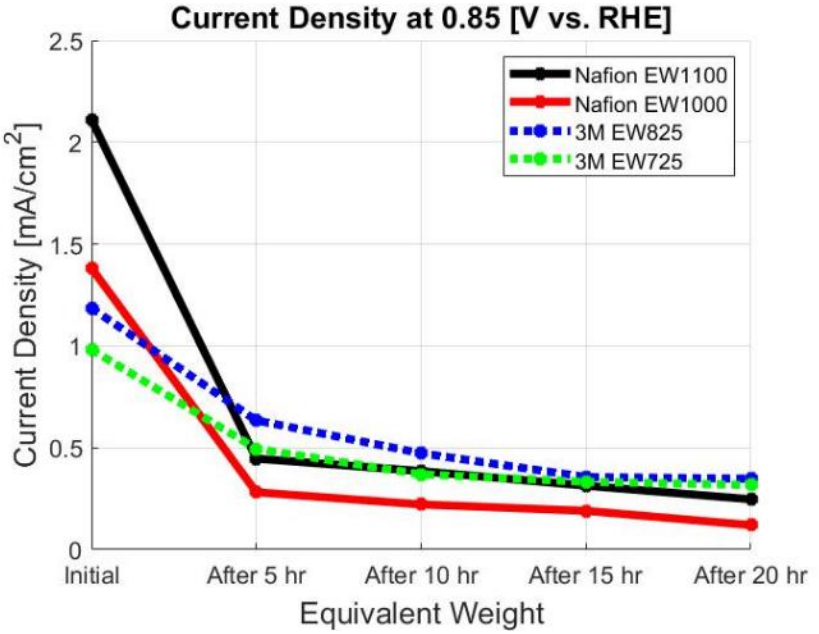








- RDE testing at CMU with varying ionomer type for stability over 20 hours at 0.85 V
- High initial activity with Nafion
- Lower initial ORR performance with 3M PFSA, but improved stability and greater ORR current over the duration
- 3M PFSA current stable after 10-15 hours



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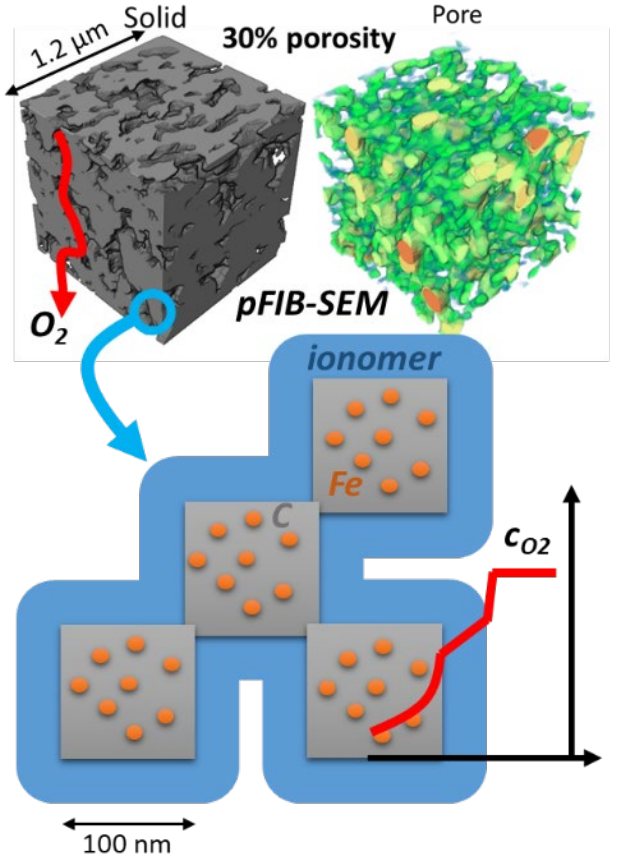
Model Summary & Validation

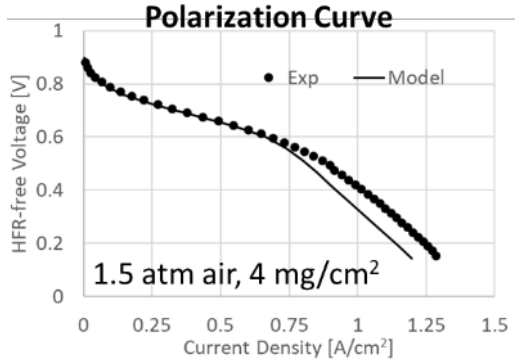
Computational Model-Based Interpretation

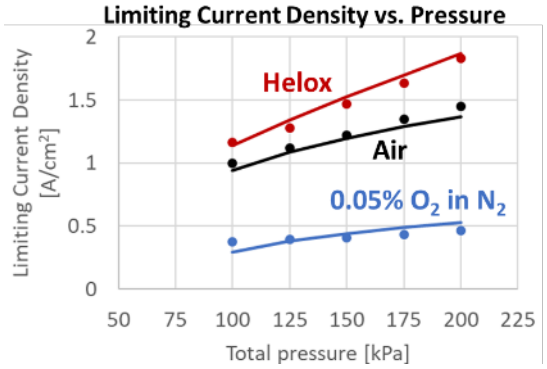
- Evaluate electrode-level transport losses in thick PGM-free electrodes
- Updated & improved multi-phase PEFC model (Komini Babu et al., JES, 2017)
- Agglomerate model treatment of volumetrically-active primary particles coated by ionomer
- Cathode morphology from pFIB-SEM

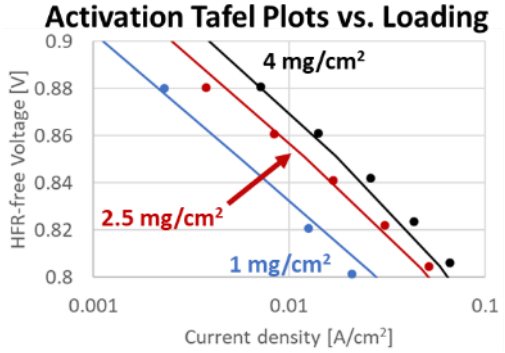


Model Predictions versus Experiment

- Evaluation of kinetics and transport modeling
- Tafel plot agreement at all loadings
- Strong limiting current agreement versus pressure and gas indicates transport resistances are well approximated by the model







Lines = Model, Symbols = Experiment

Modeled O_2 transport processes:

- Convective mass transport from channel to GDL (p-dep)
- Diffusion through carbon fiber paper GDL (p-dep)
- Diffusion through MPL (p-indep + p-dep)
- Diffusion across catalyst layer (p-indep + p-dep)
- Dissolution and diffusion across ionomer film (p-indep)
- Diffusion and ORR in primary particles (p-indep)

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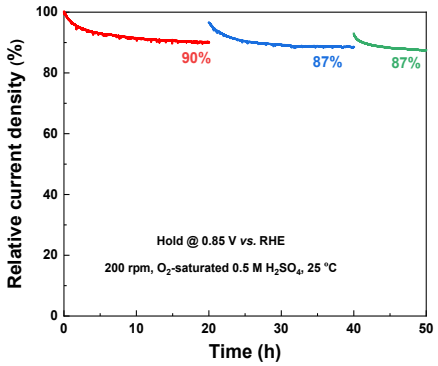
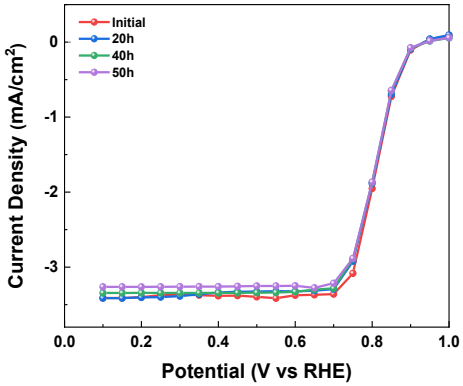
Technical Accomplishment

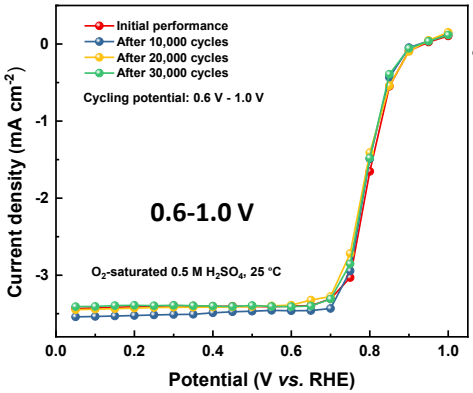
Improved stability of electrospinning Co-N-C catalysts

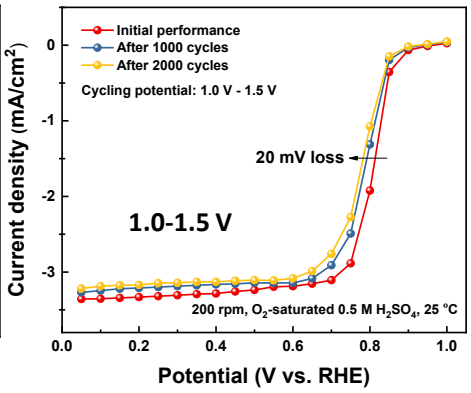
RDE stability: 0.85 V in 0.5 M H_2SO_4



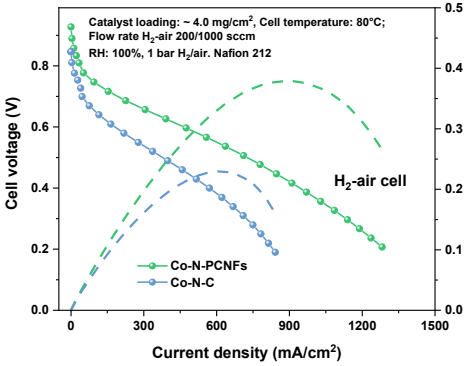


RDE stability: potential cycling

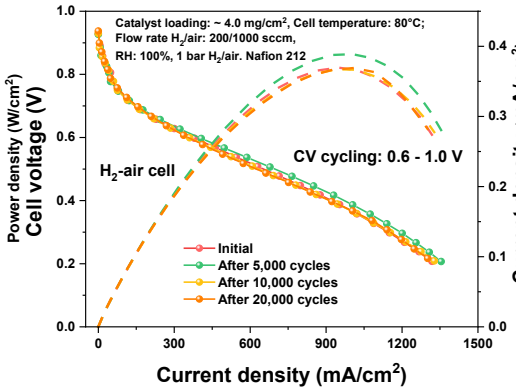




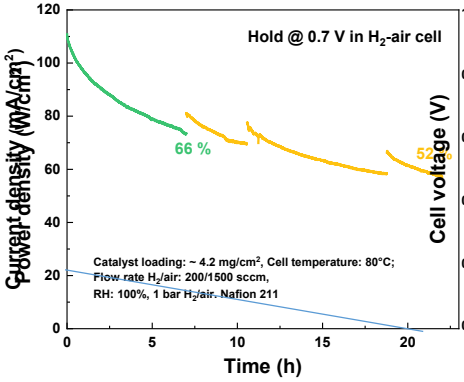
MEA: H_2-air, 1.0 bar

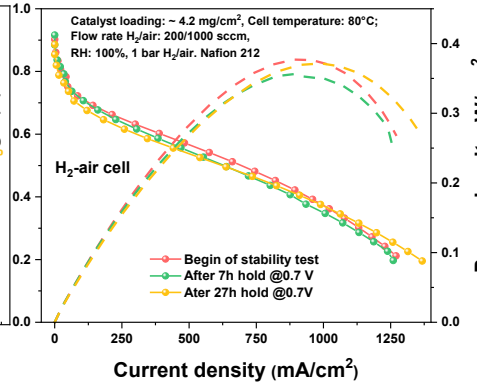


MEA Stability: voltage cycling 0.6-1.0 V, H2-air



MEA Stability: constant 0.7 V, H_2-air





- Electrospinning Co-N-C/PAN/PVP catalyst shows R**easonably Good initial ORR activity** in acidic media (with a half-wave potential of ~0.81 V); **Much Enhanced ORR stability** in acidic medium, which may be attributed to the higher graphitized carbon structure
- In MEA tests, the electrospinning Co-N-C/PAN/PVP catalyst showed comparable performance in kinetic area while **much better performance in mass transport area relative to traditional Co-N-C catalysts from ZIF-8.**
- Electrospinning Co-N-C/PAN/PVP catalyst showed **less degradation** in the voltage-current density plot, demonstrating the **improved stability and durability.**