U.S. DEPARTMENT OF ENERGY

Office of ENERGY EFFICIENCY & RENEWABLE ENERGY

ElectroCat (Electrocatalysis Consortium)

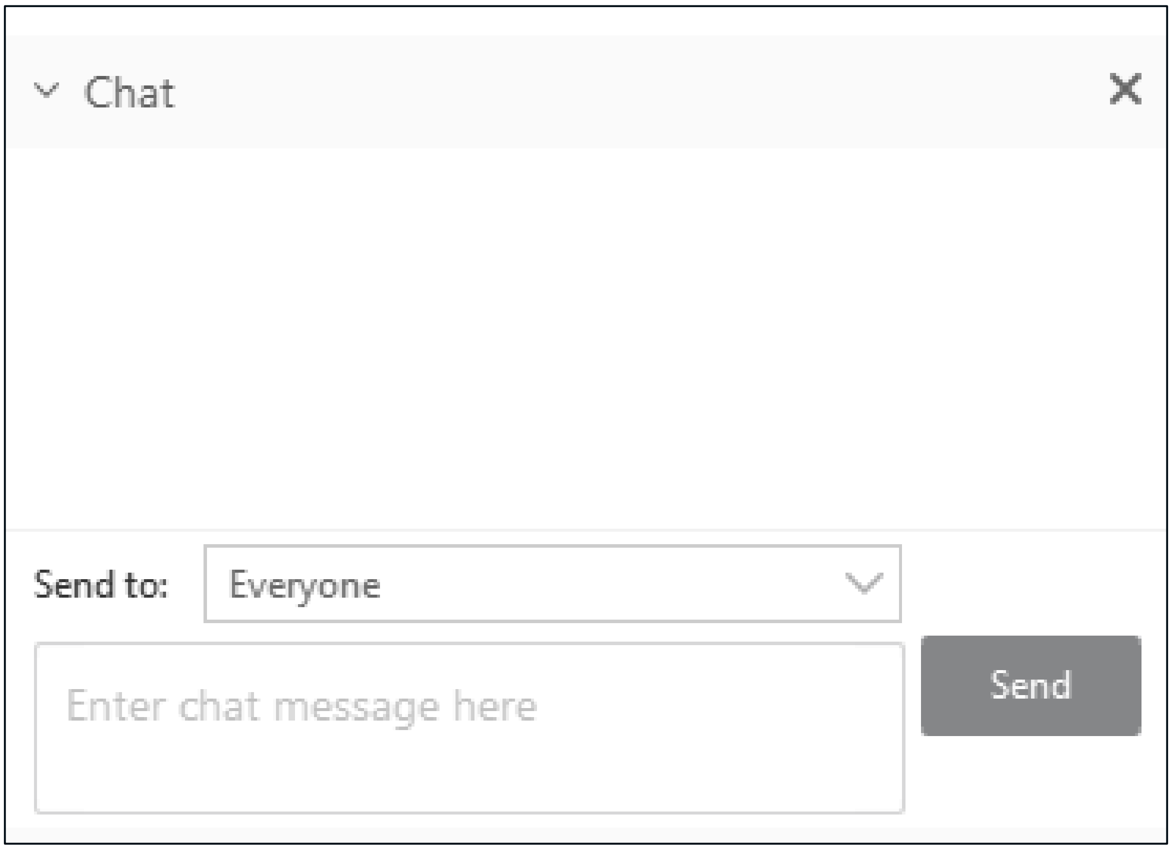
Deborah Myers, Argonne National Laboratory
Piotr Zelenay, Los Alamos National laboratory

Fuel Cell Technologies Office Webinar

September 26, 2018

Question and Answer

- Please type your questions to the chat box. **<u>Send to: (HOST)</u>**



Acknowledgement

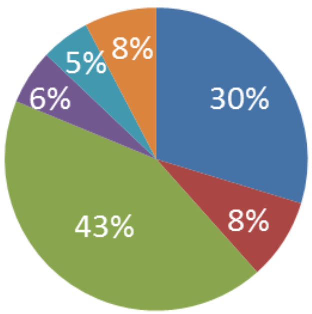
- The Electrocatalysis Consortium's early-stage R&D is funded by DOE's Fuel Cell Technologies Office (FCTO) in the office of Energy Efficiency and Renewable Energy (EERE)

Fuel Cell Stack Cost Challenge

Fuel cell system targets set to be competitive with ICEVs

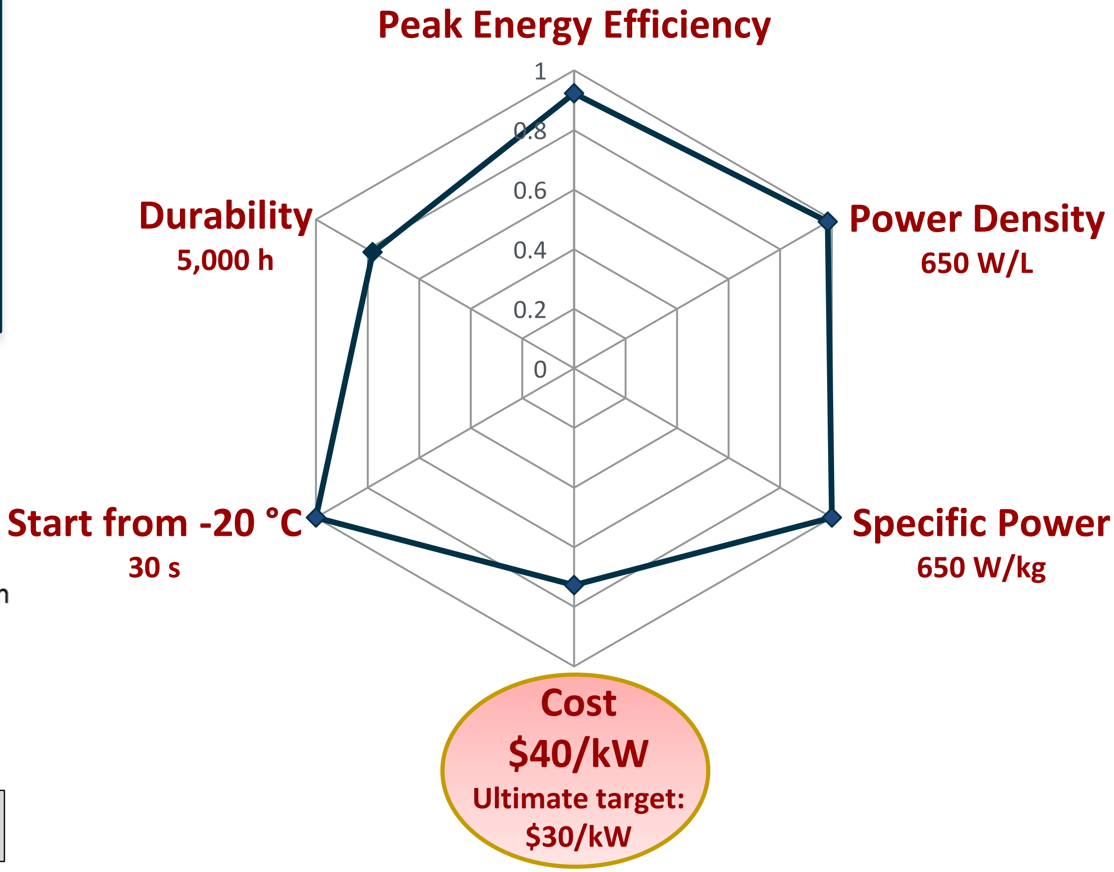
Durability and cost are the primary challenges to fuel cell commercialization and must be met concurrently

PGM Stack Cost Breakdown (500,000 systems/year)



https://www.hydrogen.energy.gov/pdfs/16020_fuel_cell_system_cost_2016.pdf

PGM-based System Automotive Stack Status



ElectroCat created as part of Energy Materials Network in February 2016
U.S. Department of Energy

Goal: Accelerate the deployment of fuel cell systems by eliminating the use of PGM catalysts

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Performance Targets

Table 3.4.7 Technical Targets: Electrocatalysts for Transportation Applications				
Characteristic	**Units**	**2018 PGM-free Status**	**2018 PGM Status**	**2020 Targets**
Platinum group metal total content (both electrodes)	g / kW (rated, gross) @ 150 kPa (abs)	N/A	0.109	0.125
Platinum group metal (pgm) total loading (both electrodes)	mg PGM / cm^2 electrode area	N/A	0.125	0.125
Mass activity	A / mg PGM @ 900 $mV_{iR\text{-}free}$	N/A	0.53	0.44
Performance at 0.8 V	A/cm^2	0.105	0.301	>0.3
Loss in initial catalytic activity	% mass activity loss	>50	15	<40
Loss in performance at 0.8 A/cm^2	**mV**	**>50**	**8**	**<30**
Loss in performance at 1.5 A/cm^2	mV	>500	>500	<30
PGM-free catalyst activity	A / cm^2 @ 900 $mV_{IR\text{-}free}$	0.021	N/A	>0.044

PGM-free activity target equivalent to PGM activity target:

$0.44\ A/mg_{PGM} \times 0.1\ mg_{PGM}/cm^2_{(electrode\ area)} \rightarrow$ **$0.044\ A/cm^2$**

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ElectroCat Objectives and Lab Roles

Mission: Develop and implement PGM-free catalysts and electrodes by streamlining access to unique synthesis and characterization tools across national labs, developing missing strategic capabilities, curating a public database of information.

Materials Discovery and Development	**Catalysts** for oxygen reduction in low-temperature PEFCs and PAFCs
	Catalysts for oxygen reduction and hydrogen oxidation in AMFCs
	Development of **electrodes** and **MEAs** compatible with PGM-free catalysts
Tool Development	Optimization of **atomic-scale** and **mesoscale models** of catalyst activity to predict macro-scale behavior
	High-throughput techniques for catalyst synthesis
	High-throughput techniques for characterization of catalysts, electrodes, and MEAs
	Aggregation of data in an easily searchable, public database to facilitate the development of catalyst materials and MEAs

Los Alamos National Laboratory

Argonne National Laboratory

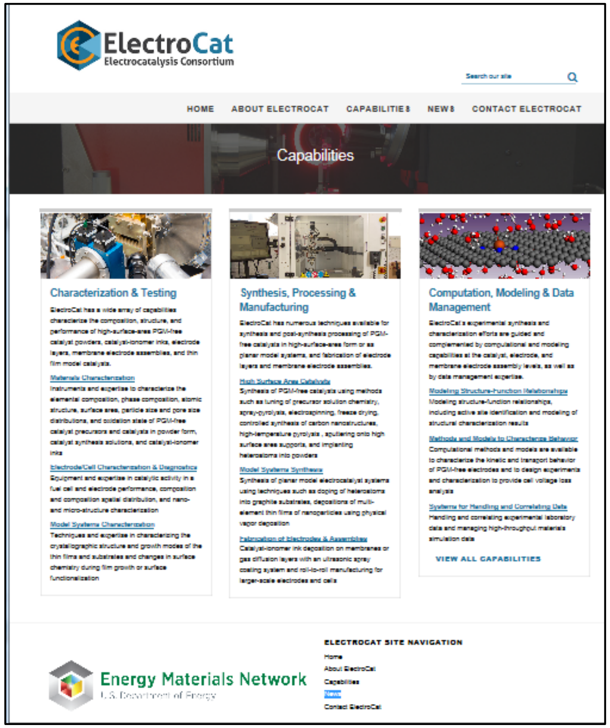
NREL National Renewable Energy Laboratory

Oak Ridge National Laboratory

LANL: PGM-free catalyst development, electrochemical and fuel cell testing, atomic-scale modeling
ANL: High-throughput techniques, mesoscale models, X-ray studies, aqueous stability studies
NREL: Advanced fuel cell characterization, high-throughput electrode fabrication and testing
ORNL: Advanced electron microscopy, atomic-level characterization, XPS studies

ElectroCat Capabilities Overview

http://www.electrocat.org/capabilities/



Synthesis, Processing and Manufacturing

Synthesis and post-synthesis processing of PGM-free catalysts in high-surface-area form or as planar model systems, and fabrication of electrode layers and MEAs

- ✓ High surface area catalysts
- ✓ Model systems synthesis
- ✓ Fabrication of electrodes and membrane-electrode assemblies

Characterization and Testing

Composition, structure, and performance of high-surface-area PGM-free catalyst powders, catalyst-ionomer inks, electrode layers, membrane electrode assemblies, and thin film model catalysts.

- ✓ Materials Characterization
- ✓ Electrode/Cell Characterization & Diagnostics
- ✓ Model Systems Characterization

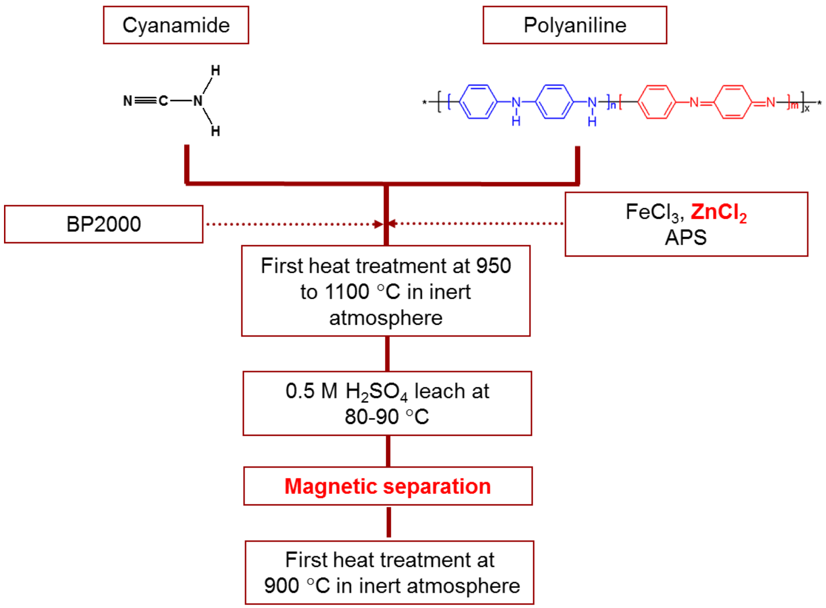
Computation, Modeling and Data Management

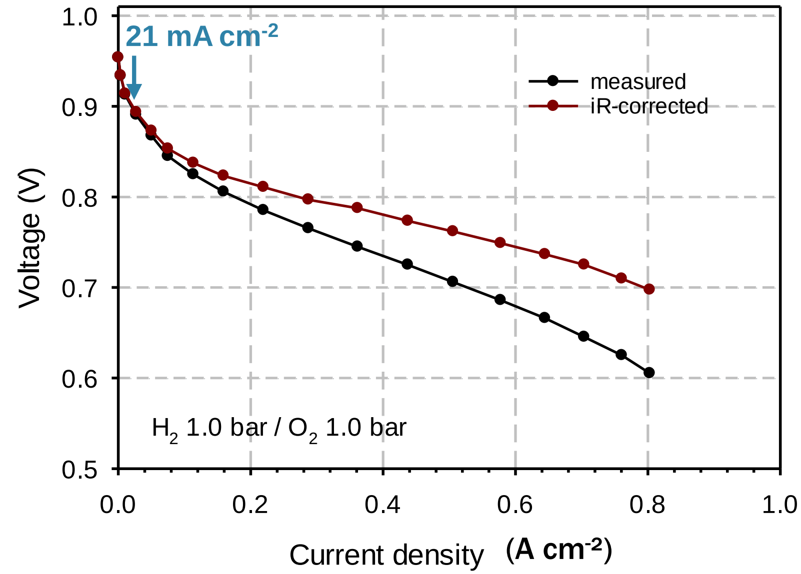
Guiding and complementing experimental efforts with computational and modeling capabilities at the catalyst, electrode, and membrane electrode assembly levels, as well as by data management expertise.

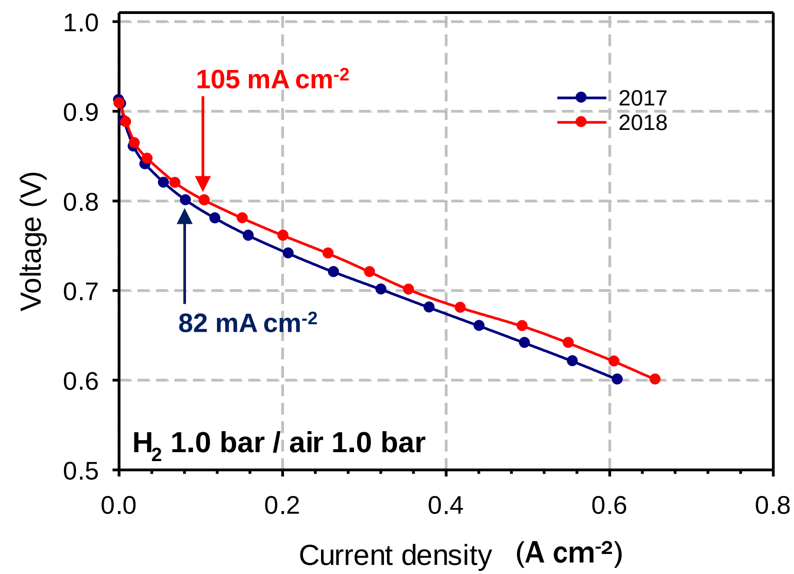
- ✓ Modeling structure-function relationships
- ✓ Methods and models to characterize behavior
- ✓ Systems for handling and correlating data

Status of PGM-free Fuel Cell Performance

Anode: 0.3 mg_{Pt} cm^{-2} Pt/C H_2, 200 sccm, 1.0 bar H_2 partial pressure; **Cathode**: ca. 4.8 mg cm^{-2} O_2, 200 sccm, 1.0 bar air partial pressure, 200 sccm; **Membrane**: Nafion®, 211; **Cell**: 5 cm^2, 80°C.



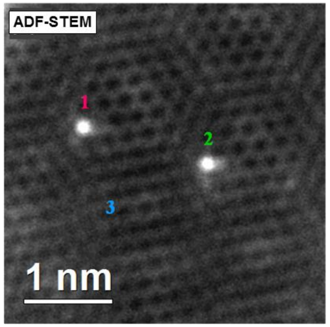


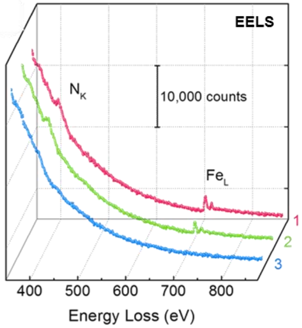


- H_2 / O_2 fuel cell performance of **CM-PANI-Fe-C(Zn)** catalyst measured at **21 mA cm^{-2}** (0.90 V, *iR*-free)
- H_2-air fuel cell performance at 0.80 V improved from 82 mA cm^{-2} to 105 mA cm^{-2} since June, 2017 (an increase of 28% in one year)

ElectroCat FY17 <u>Annual Milestone</u> of 20 mA cm^{-2} at 0.90 V (iR-free) achieved and exceeded!

Catalyst Development: Towards Atomically-Dispersed (AD) Catalyst

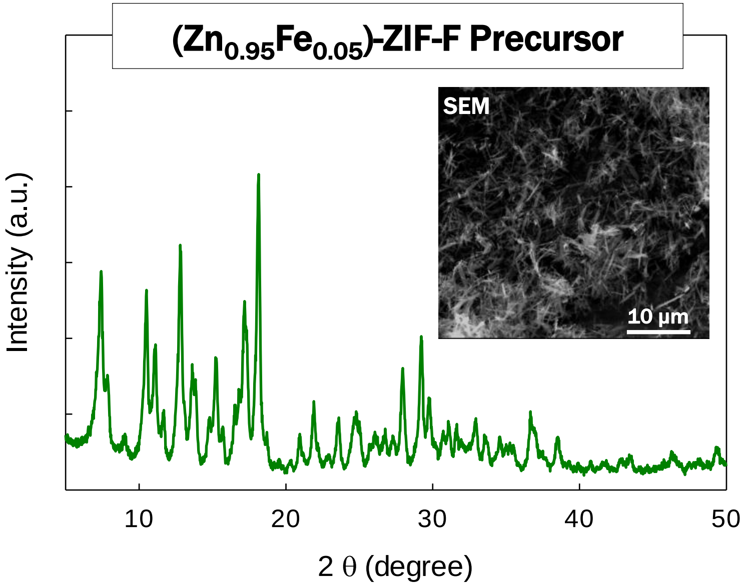




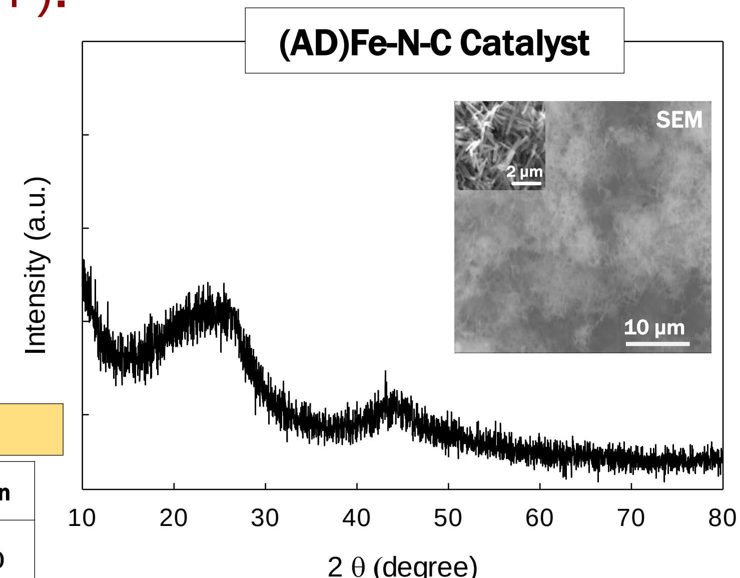
H. T. Chung, D. A. Cullen, D. Higgins, B. T. Sneed, E. F. Holby, K. L. More, P. Zelenay, *Science* **357**, 479-484, 2017

- **CM-PANI-Fe-C:** N associated with Fe in graphene layers, with an average Fe-to-N ratio of 1:4 pointing to **FeN_4** active site
- **Synthesis direction:** Atomic dispersion of the transition metal likely required to assure high initial ORR activity

(AD)Fe-N-C catalyst (derived from $(Zn_{0.95}Fe_{0.05})$ZIF-F):



Heat Treatment

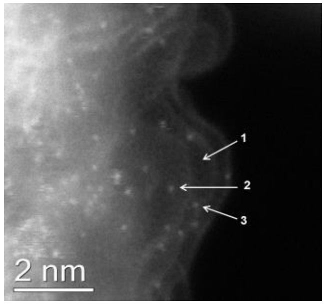


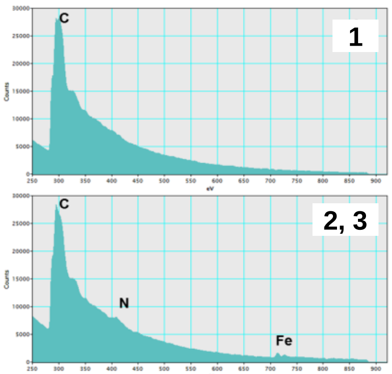
AD Catalyst XPS Analysis (at%)

C	Fe	N	O	Zn
92.5	0.6	2.1	4.7	0

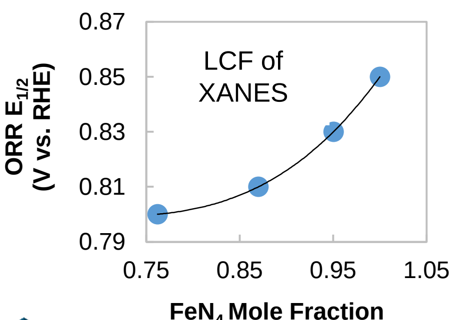
- ZIF-F(fiber) MOF successfully synthesized as AD catalyst precursor
- No near-surface Zn and Fe-rich nanoparticles (> ~ 2 nm) detected by XPS and XRD, respectively
- Initial ZIF-F morphology preserved in catalyst after heat treatment (important for future catalyst design)

Catalyst Development: (AD)Fe-N-C Dispersion and MEA Performance

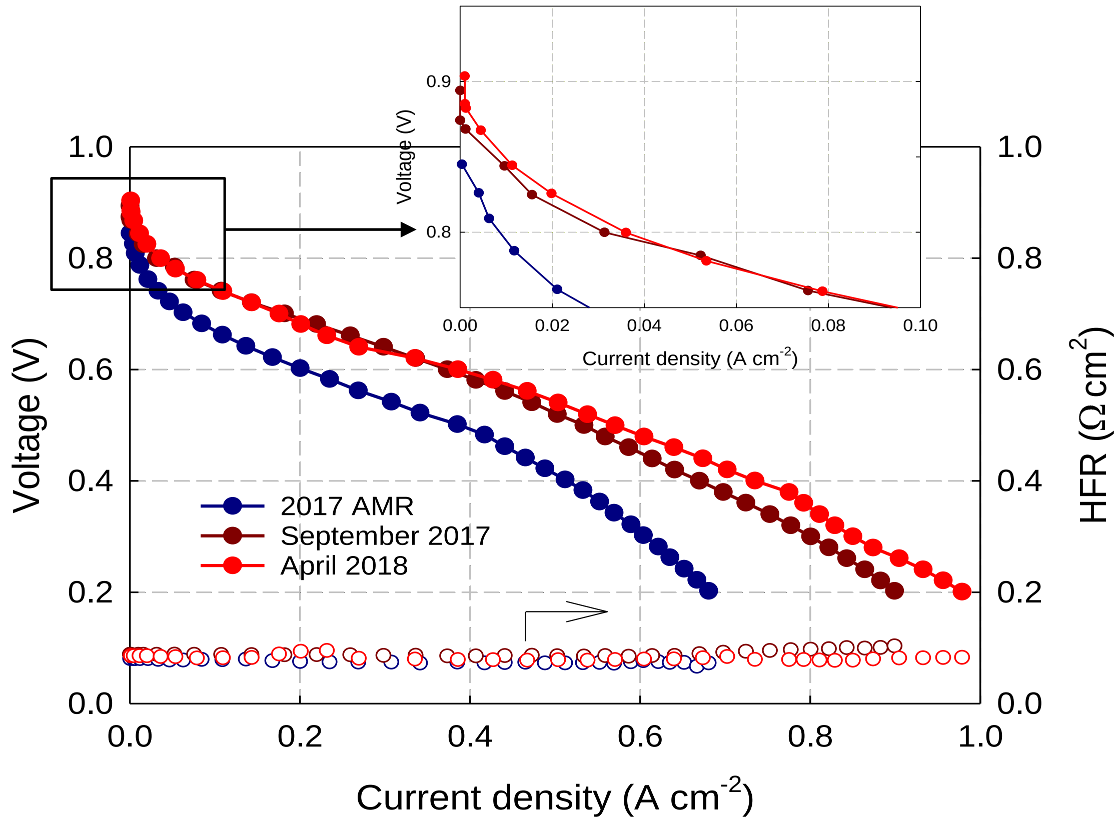




Path	CN	R (Å)
Fe-N/O	3.0 ± 0.4	1.837 ± 0.033
Fe-Fe	0.3 ± 0.3	2.983 ± 0.055



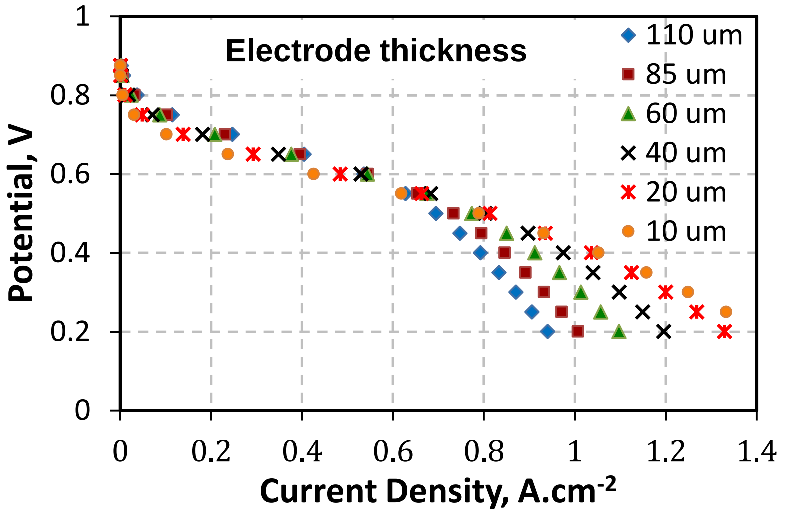
Anode: 0.2 mg_{Pt} cm^{-2} Pt/C H_2, 200 sccm, 1.0 bar H_2 partial pressure; **Cathode**: ~4 mg cm^{-2} air, 200 sccm, 1.0 bar air partial pressure; **Membrane**: Nafion®,211; **Cell**: 5 cm^2; 80°C



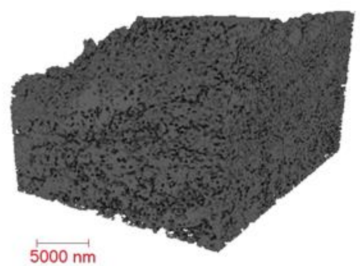
- Fe predominantly found in N-coordinated FeN_x sites
- ORR activity correlated with FeN_x content
- Single Fe atoms dispersions associated with basal-plane edges/step
- **Highlight: Four-fold improvement** of the H_2-air fuel cell performance at 0.80 V, from 9 mA cm^{-2} to 36 mA cm^{-2} since June, 2017

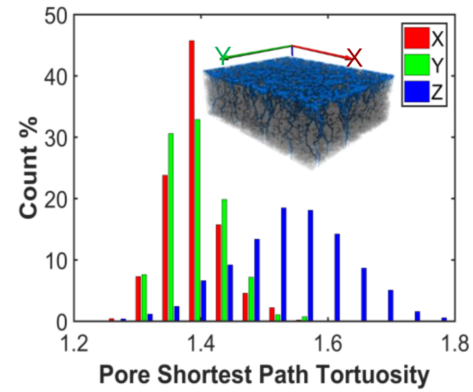
Methods for Improving High Current Density Performance

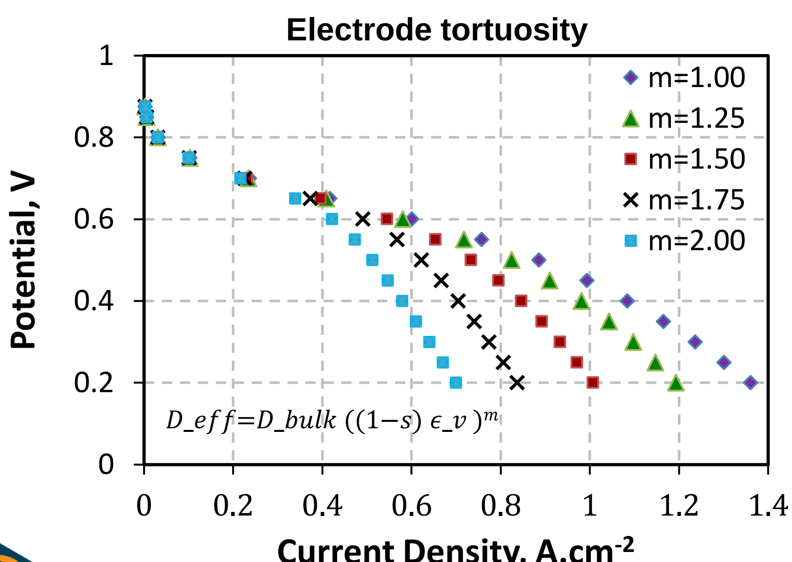
Highlight: High current density performance improved by decreasing electrode thickness, tortuosity (m), and size of micropores (rm) and increasing volume fraction (vf) of micropores

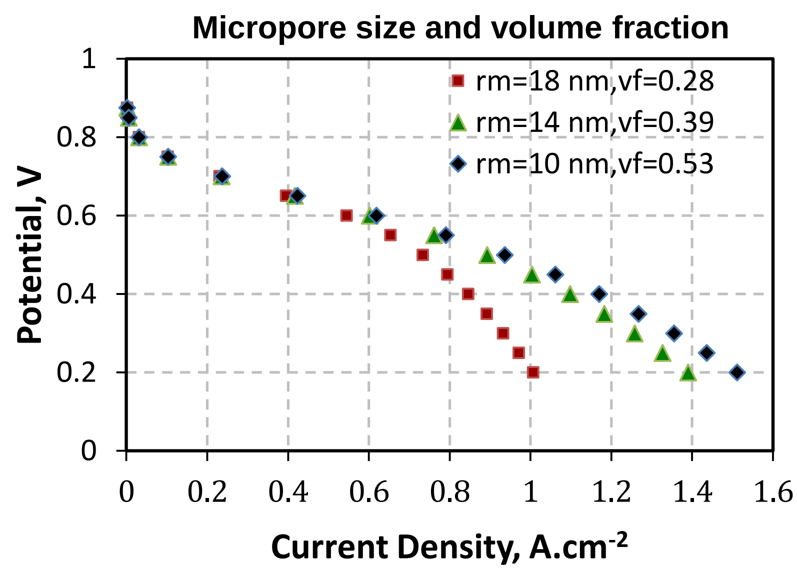


Nano-XCT Segmented Volume





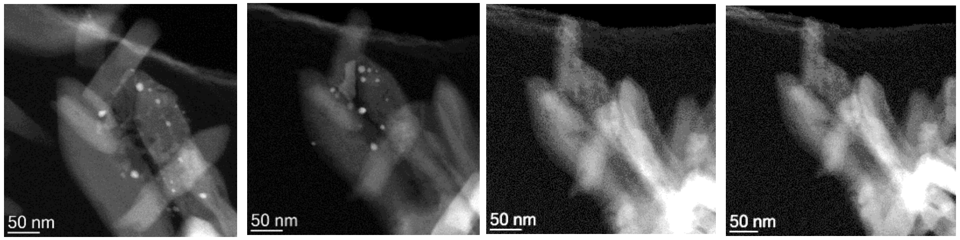


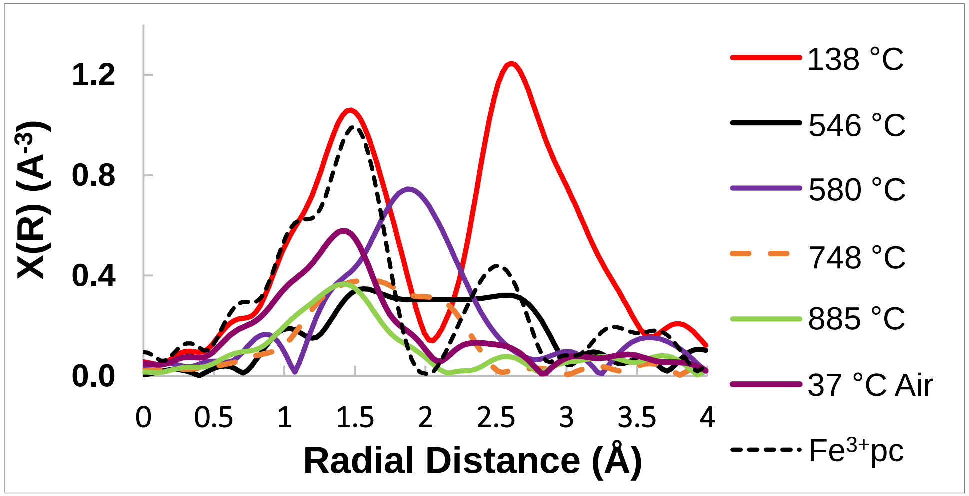


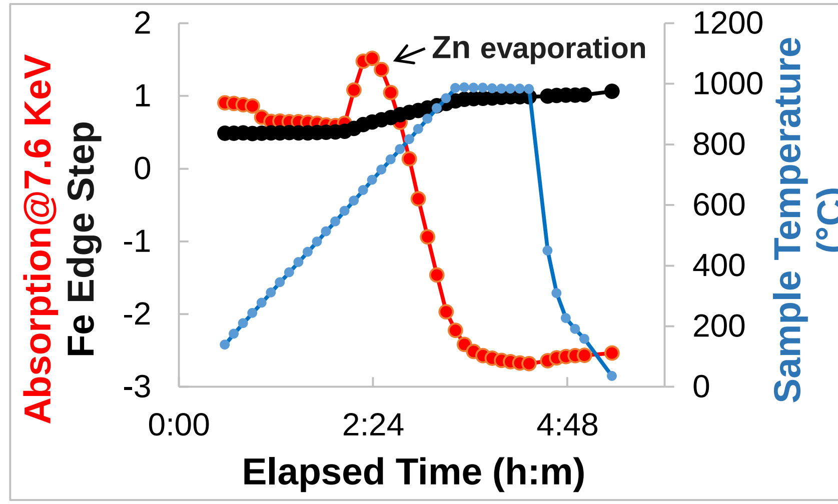
(AD)Fe-N-C: Fe Species & Structure Evolution During Heat Treatment

Fe K-edge XAFS and TEM during heat treatment of $(Zn_{0.975}Fe_{0.025})$ZIF-F; $FeSO_4$ used as Fe source for ZIF-F synthesis

500 °C **700 °C** **900 °C** **1100 °C**







- **500-546 °C:** Fe precursor reduced, particles, Fe-S coordination formed
- **580-650 °C:** Fe_3C phase formed; material density increased
- **650-885 °C:** Transition from Fe_3C phase to FeN_4-like phase concurrent with Zn loss; particles evaporating; no overall Fe loss during pyrolysis
- FeN_4 converted to Fe_3C and Fe metal in high Fe-content samples (≥ 5/95 Fe/Zn at.%) during 1000 °C hold

Highlight: ***In situ*** **characterization providing guidelines for catalyst synthesis procedure:**

- ✓ **Utilize temperatures as low as 900 °C to form FeN_4 and remove Zn**
- ✓ **Avoid long holds at >1000 °C to minimize Fe_3C and Fe metal formation**

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High-throughput Synthesis and Characterization

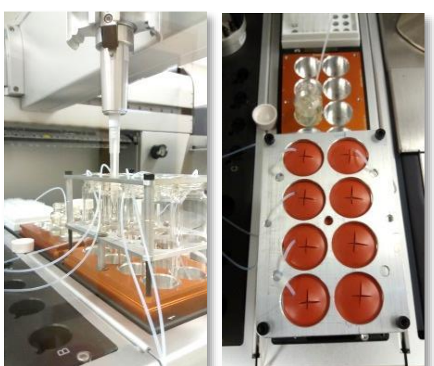
Purpose: Utilize Argonne's robotic system, simultaneous pyrolysis, high-throughput structural characterization using XRD and XAFS, and multi-channel flow double electrode cell for ORR activity characterization to explore catalyst composition and heat treatment effects.

Catalyst system: LANL's (AD)Fe-N-C selected due to high RDE ORR activity

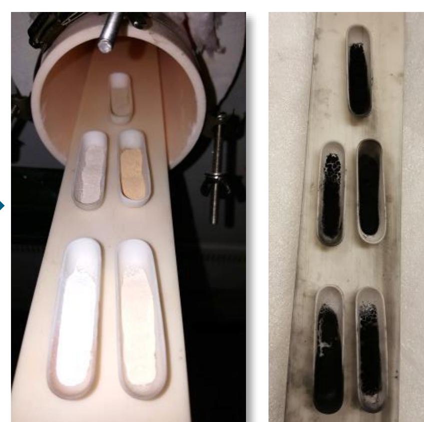
Parameters varied to obtain 40 unique samples:

- ✓ Fe-to-Zn ratio: 0, 1, 2.5, 5, and 7.5 at% Fe in precursors
- ✓ Fe salts: sulfate, nitrate, acetate
- ✓ Heat-treatment temperatures: 900, 1000, 1100 °C

Precursor synthesis: CM Protégé Robot



Heat Treatment



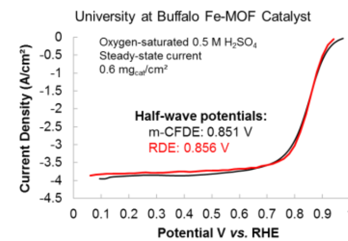
ORR Activity

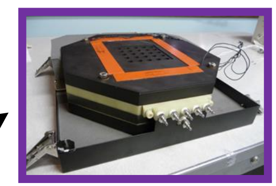
MEA Performance

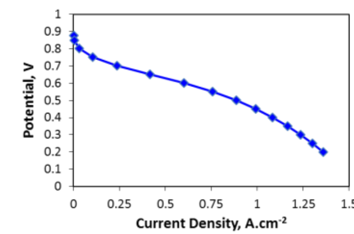
Phase Composition

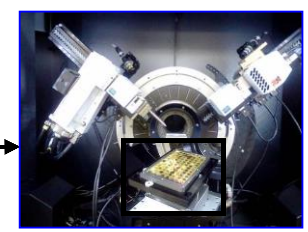
Atomic Structure

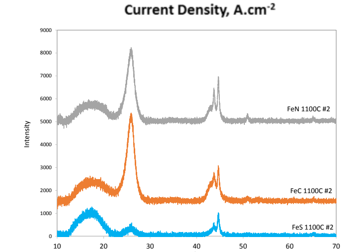
Characterization

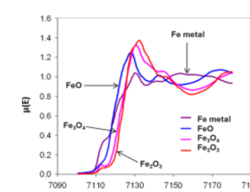






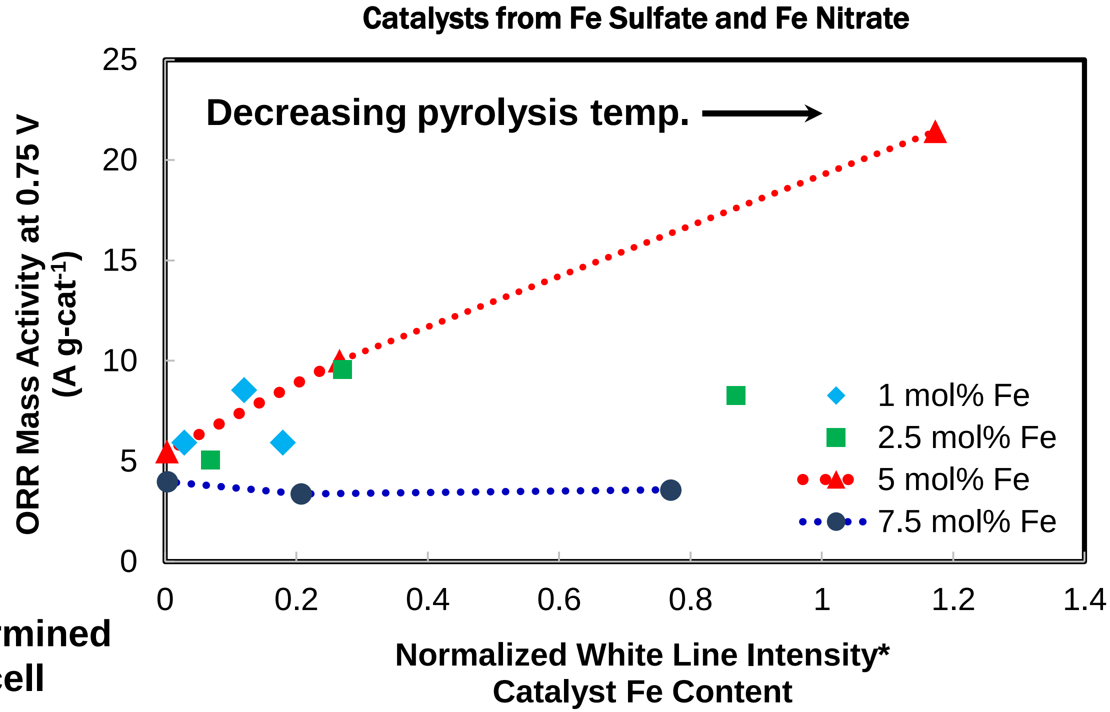


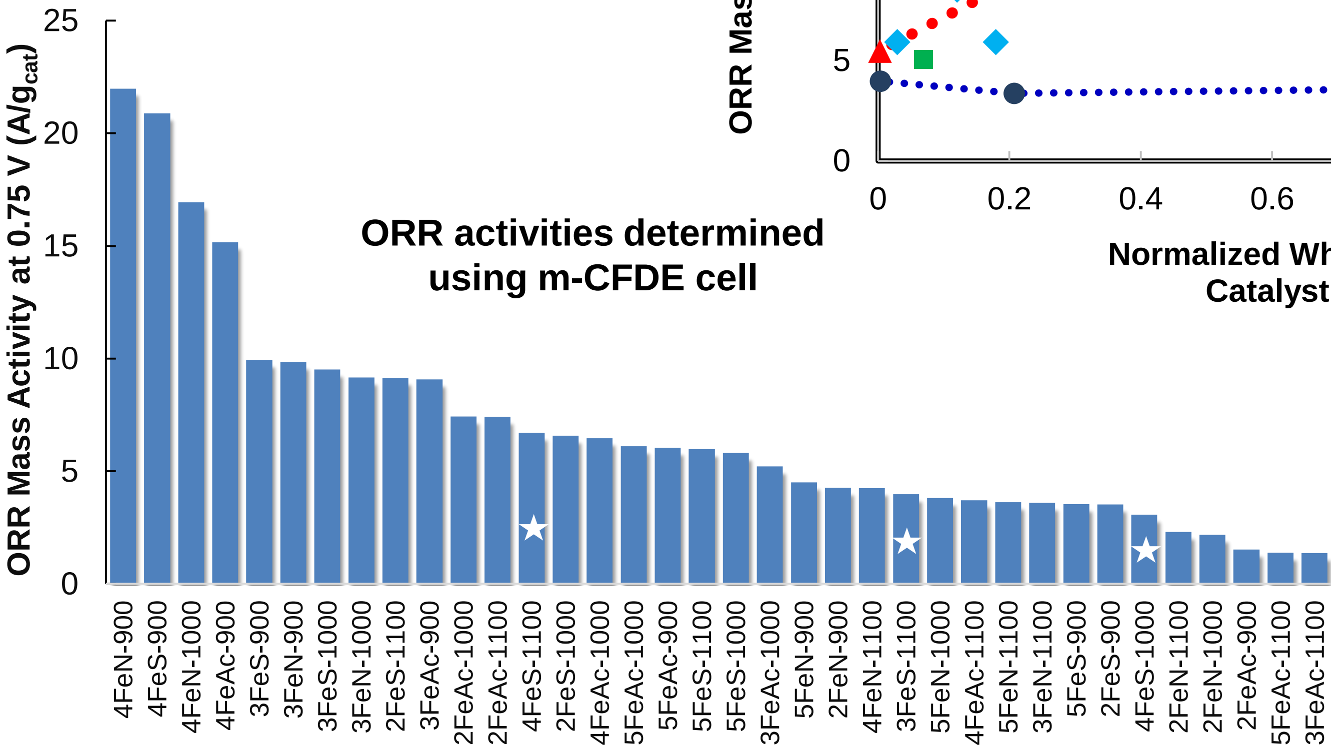




Activity Trends in Combinatorial ((Zn_xFe_{1-x}))ZIF-F-derived Catalysts

- Highest activities observed for iron nitrate and sulfate precursors, with pyrolysis temperatures of 900 °C and 1000 °C and intermediate iron to zinc atomic ratio (2.5/97.5, 5/95)
- ORR activity correlates with height of Fe XAFS white line (which correlates with fraction of Fe in FeN_4 coordination)



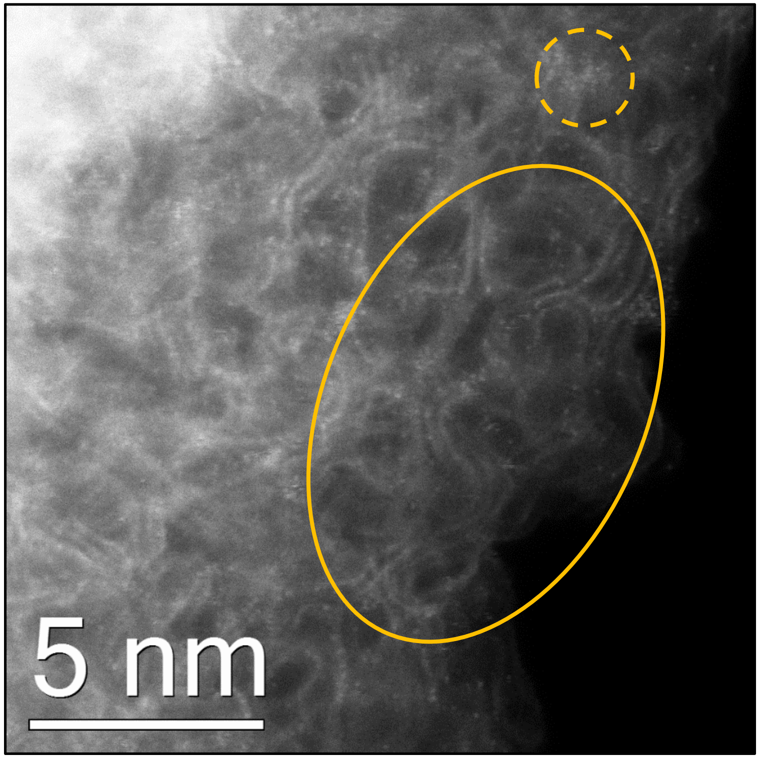


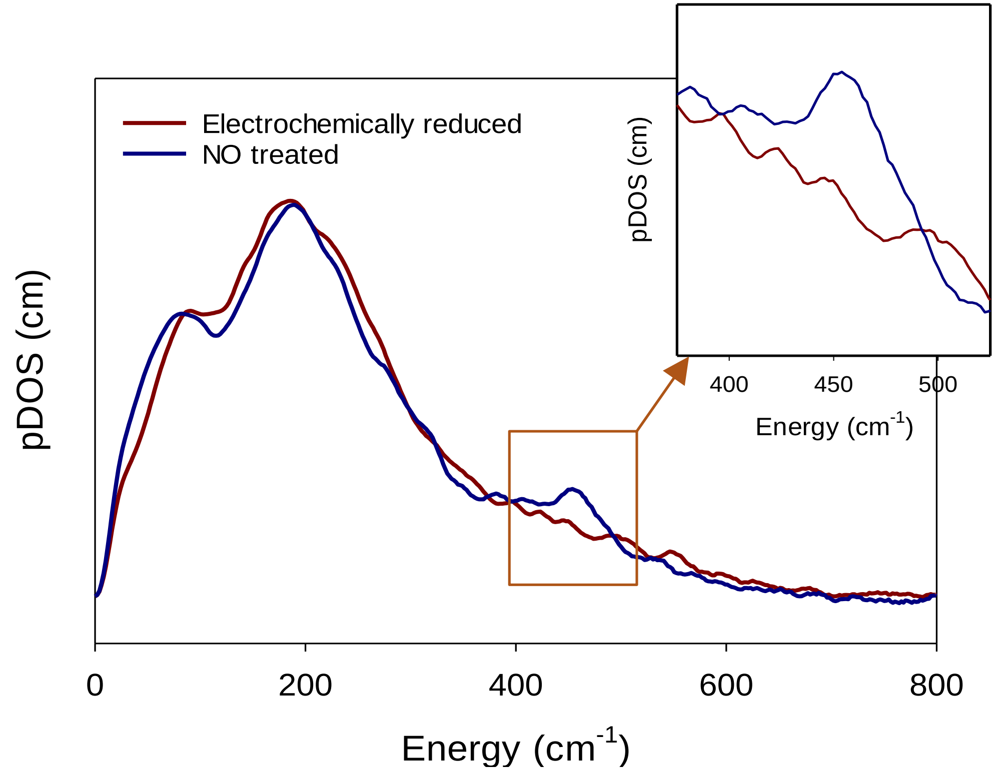
2:1 at% Fe, 3:2.5 at% Fe, 4:5 at% Fe, 5:7.5 at% Fe, FeN: Fe Nitrate, FeS: Fe Sulfate, FeAc: Fe Acetate

★ *Baseline materials explored by batch synthesis prior to initiation of combinatorial synthesis task*

- Materials with potentially > 5× ORR activity of baseline compositions identified in screening
- Next step: scale up of promising compositions and test performance in an MEA

Direct Detection of Fe Sites on (AD)^{57}Fe-N-C

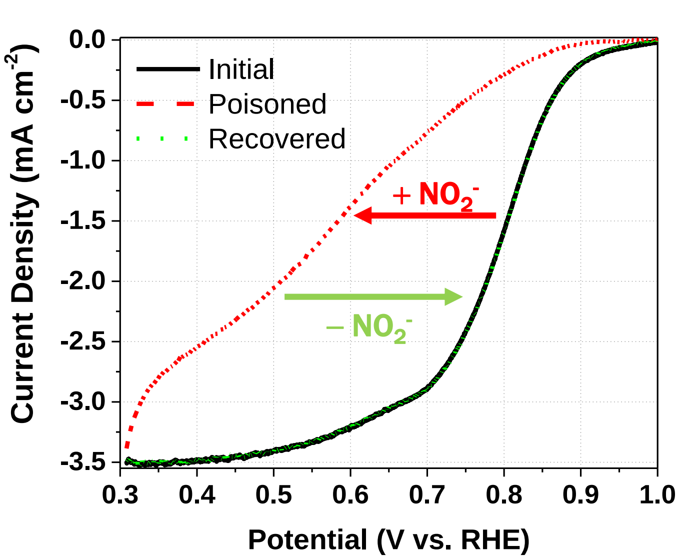


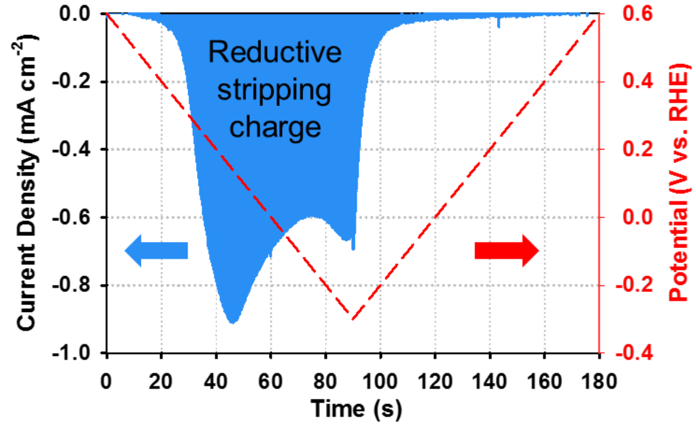


- ^{57}Fe-enriched catalyst demonstrating the same properties as non-enriched catalyst: atomically dispersed iron seen (solid yellow line), with some Fe-clustering (dashed yellow line)
- Nuclear resonance vibrational spectroscopy (NRVS) used with NO as a molecular probe (an O_2 analog) to detect iron sites on (AD)^{57}Fe-N-C catalyst; vibrational feature for NO-treated catalyst at a frequency of 450 cm^{-1}, likely corresponding to the Fe-NO bond stretch (assignment pending)

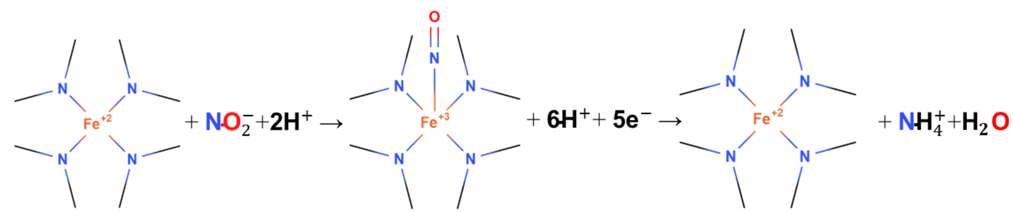
Highlight: Direct evidence of the presence of Fe sites on the surface of a PGM-free catalyst!

Molecular Probes: Calculation of Active Site Density in (AD)Fe-N-C





Poisoning and reductive stripping of PGM-free catalyst with NO_2^- as a molecular probe



Malko, D. *et al.*, *Nat. Commun.* 2016, **7**, 13285

$$Q_{strip}\left(C\ g^{-1}\right)=\frac{A_{curve}}{A_{RDE}\bar{V}L}$$

$$MSD\left(\text{sites cm}^{-2}\right)=\frac{Q_{strip}}{nSA_{DL}F}$$

$$TOF\ (s^{-1})=\frac{\Delta i_k}{F\ MSD}$$

Experimental values:
Catalyst loading (L): 0.6 mg cm^{-2}
RDE Area (A_{RDE}) = 0.1963 cm^2
Scan rate ($\bar{V}$) = 10 mV s^{-1}

TOF = 1.2 e$^-$ site^{-1} s^{-1} at 0.80 V

Area Specific Charge (μC cm^{-2})	Active Site Concentration* (sites cm^{-2})	Active Sites per Atom
2.35	3.0 10^{12}	0.001 per C atom 0.055 per N atom 0.498 per Fe atom

** Assuming 5e$^-$ transfer and catalyst area from double layer charging*

Highlight: Method for estimating active-site density in PM-free catalysts demonstrated

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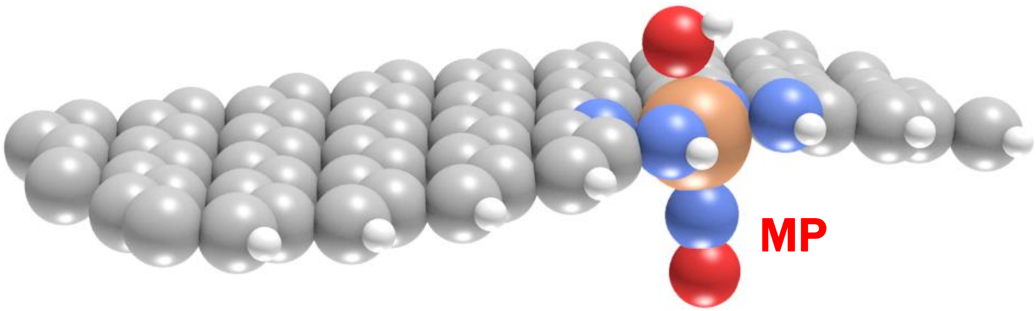
Molecular Probes: Probes and Active-Site Poisons from DFT

Density functional theory (DFT) used to calculate binding energies of possible probe/poison adsorbates to varied proposed active site structures hosted in graphene (bulk) and at nanoribbon zig-zag (ZZ) edges

Site Name	CO BE (eV)	NO BE (eV)	Cl BE (eV)	S BE (eV)	OH BE (eV)
FeN_4 - Bulk	-1.954	-2.334	-1.765	-0.059	-3.074
FeN_4OH - Bulk	-1.001	-1.603	-1.186	1.064	-1.608
FeN_4 - ZZ	-1.745	-2.416	-1.829	0.082	-3.033
FeN_4OH - ZZ	-0.494	-1.148	-0.923	1.638	-2.314

Relative binding energies show high poison tolerance and strong dependence on active site structure, molecular probe, and ligand

Further sites/species under consideration to extend library of probes/poisons



Highlight: Probe molecules identified binding to Fe with no binding to graphene without defects or epoxides local to FeN_4 sites

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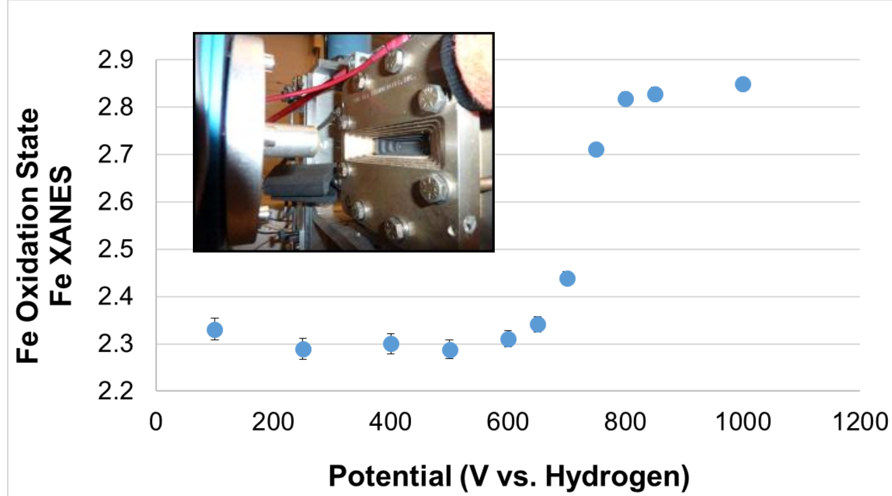
(AD)Fe-N-C Electrode: Potential Dependence of ORR Kinetics (MEA)

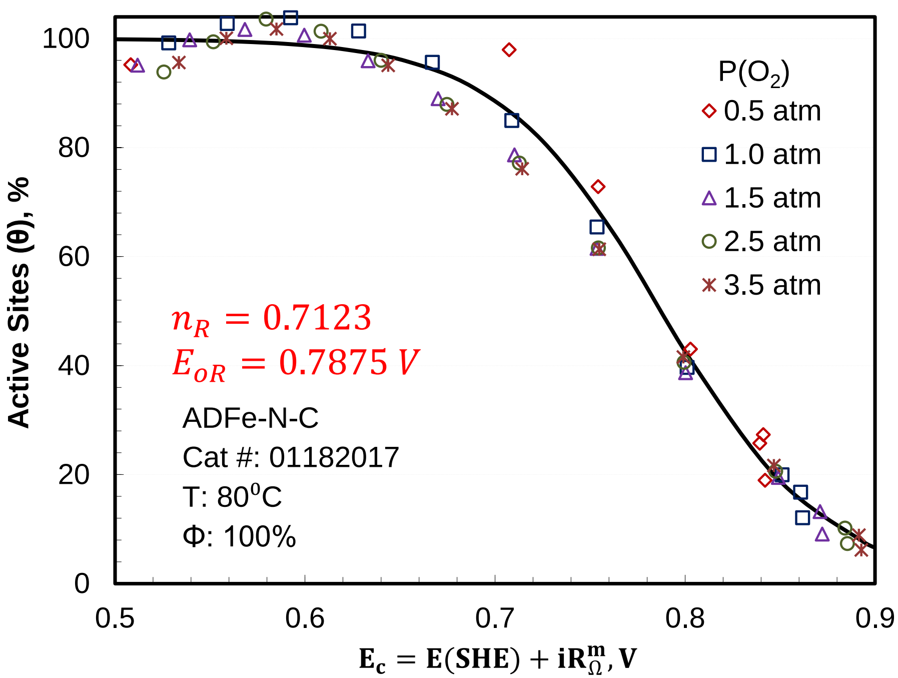
- **Available active sites (θ) depending on potential***

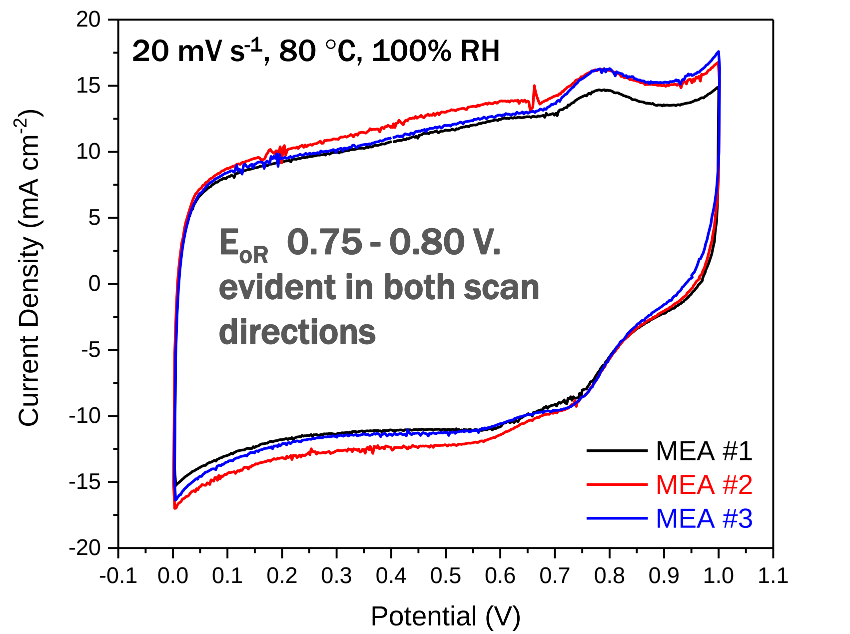
$$i + i_s = i_0 \theta e^{\frac{\alpha n F}{RT}\eta_s^c} \qquad \theta = \frac{1}{1 + e^{\frac{n_R F}{RT}(E_c - E_{0R})}}$$

E_c: cathode potential; E_{oR}: redox potential; n_R: effective number of electrons transferred

- **Near OCV, <10% of sites available**
- Literature models assume n_R=1 (*e.g.*, for Fe^{3+} to Fe^{2+})*



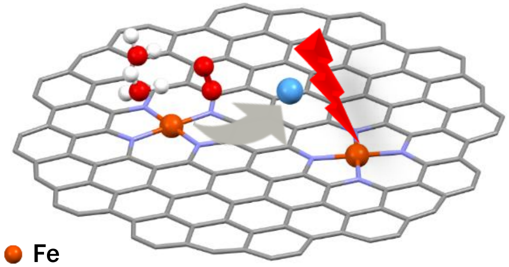




* Q. Jia *et al.*, *ACS Nano*, 2015, **9**, 12496-12505
J. Li *et al.*, *J. Am. Chem. Soc.*, 2017, **139**, 1384−1387

Catalyst Durability: Kinetic Models for Degradation in MEA

Two-step (autocatalytic) degradation



Fe
Deactivation agent

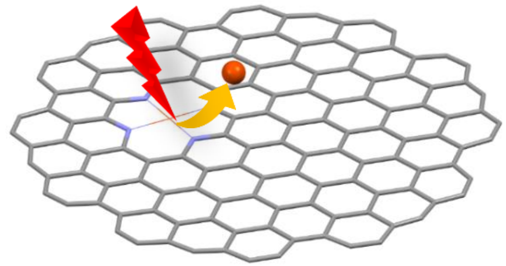
Reactants $\xrightarrow{k_1}$ Deactivation agent (D)

Active site + D $\xrightarrow{k_2}$ Deactivated site (DS)

Logistic decay:

$$\text{normalized } j_k = \frac{1}{1+k_{app}t}$$

1st order degradation

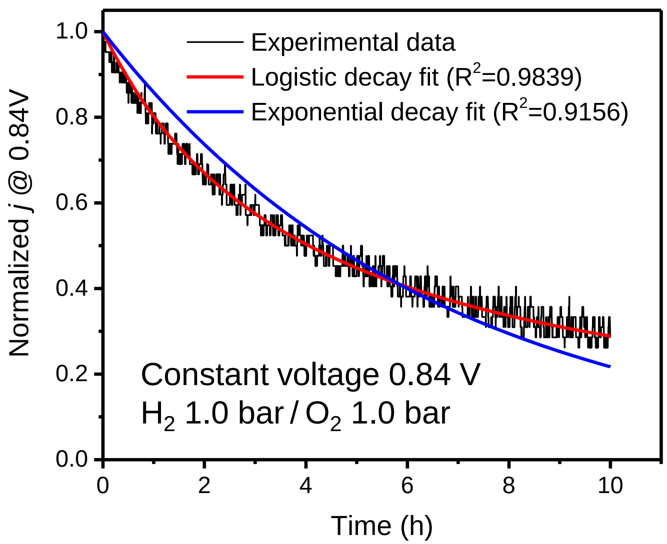


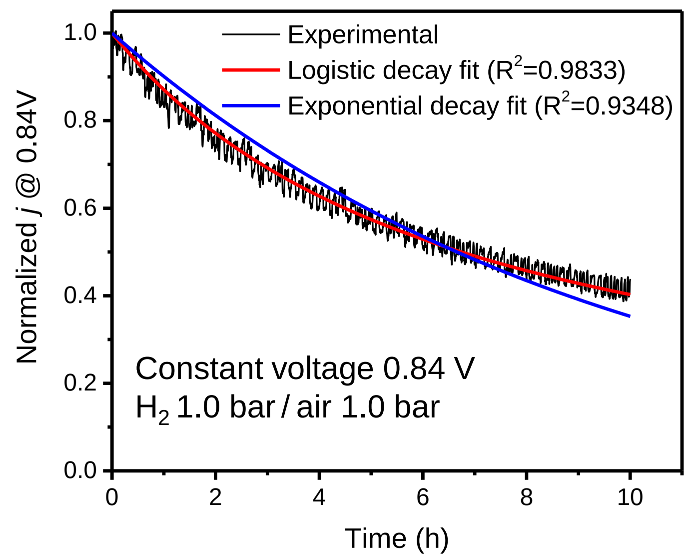
AS $\xrightarrow{k}$ DS

Exponential decay:

$$\text{normalized } j_k = e^{-k_{app}t}$$

Anode: 0.3 mg_{Pt} cm^{-2} Pt/C H_2, 200 sccm, 1.0 bar H_2 partial pressure; **Cathode:** **(CM-PANI)-Fe-C(Zn)** *ca.* 4.8 mg cm^{-2} air, 200 sccm, 1.0 bar O_2 or air partial pressure; **Ionomer:** Aquivion D83 (EW 830), 55 wt.%; Cell voltage: 0.84 V; **Membrane:** Nafion®211; **Cell:** 5 cm^2, 80 °C

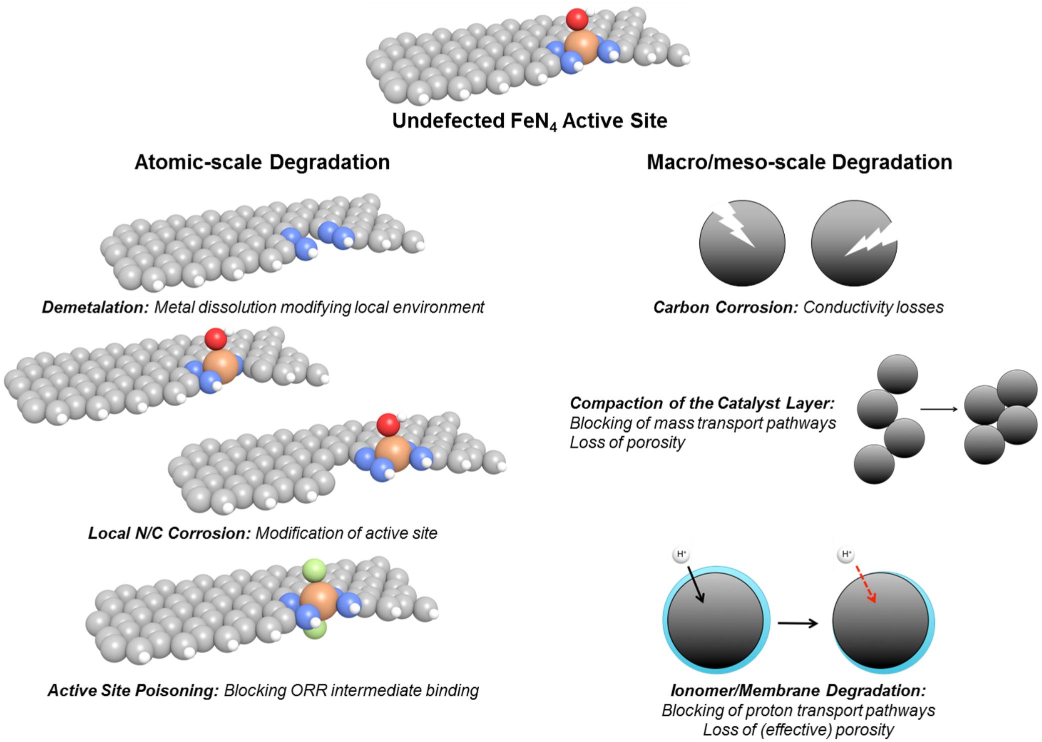




- **Two kinetic models with single parameter of apparent degradation rate constant, k_{app}**
- **Highlight:** Autocatalytic degradation mechanism suggested by better fitting of logistic decay model

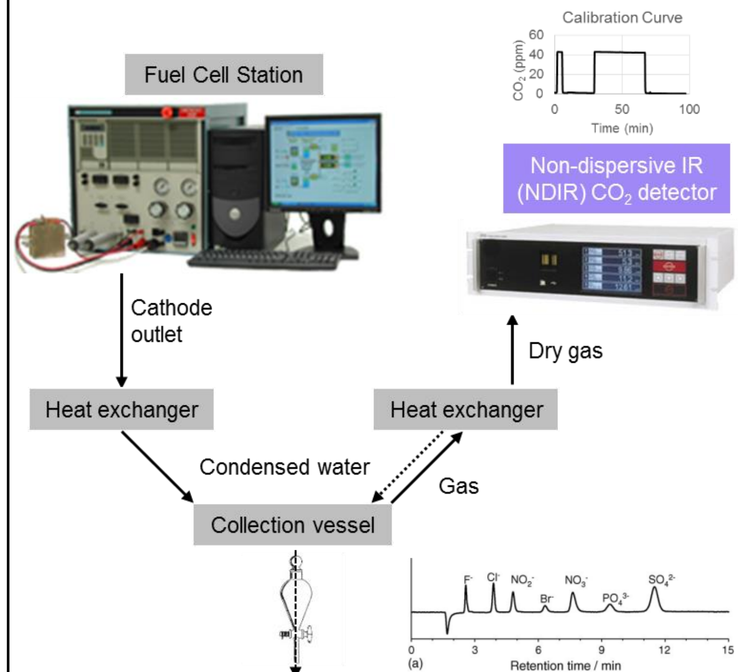
Catalyst Durability: Understanding Degradation Mechanisms

Possible degradation mechanisms of PGM-free electrocatalysts



U. Martinez, S. Komini Babu, E. F. Holby, and P. Zelenay, *Current Opinion in Electrochemistry*, 2018

Parallel measurements of CO_2, TM and F^- emissions during fuel cell operation

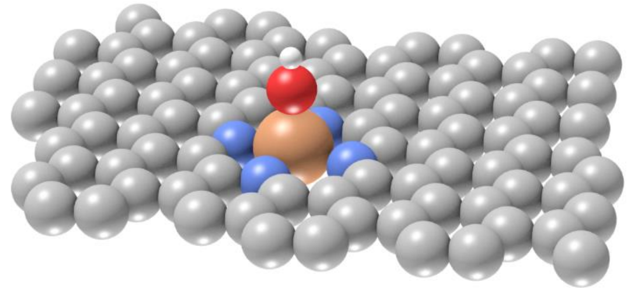


- Ion Chromatography (F^-, SO_4^{-2})
- Inductively Coupled Plasma (Transition metal content)

Durability Descriptor: KODTE Library

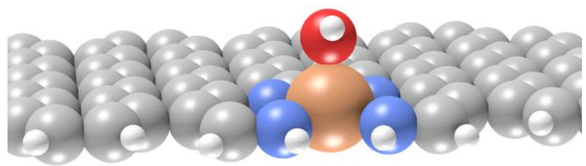
Structure	KODTE (kV)
FeN_4 bulk	90
FeN_4OH bulk	90
MnN_4 bulk	90
MnN_4OH bulk	90
CoN_4 bulk	90
CoN_4OH bulk	90
FeN_4 arm chair	35*
FeN_4OH arm chair	30*
MnN_4 arm chair	35*
MnN_4OH arm chair	25*
CoN_4 arm chair	35*
CoN_4OH arm chair	30*
FeN_4 zig zag	70
FeN_4OH zig zag	70
MnN_4 zig zag	65
MnN_4OH zig zag	70
CoN_4 zig zag	70
CoN_4OH zig zag	75
Fe_2N_5 bulk	60
Fe_2N_5OH bulk	60
$MnCoN_5$ bulk	60
$MnCoN_5OH$ bulk	60
Graphene	110
Arm chair edge	90
Zig zag edge	85

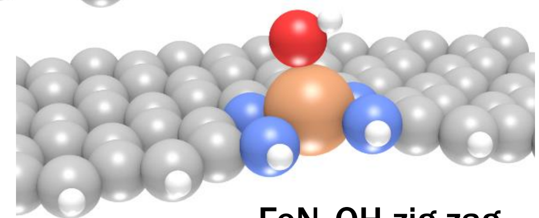
* some but not all bonds broken



FeN_4OH bulk

FeN_4OH arm chair





FeN_4OH zig zag

Findings thus far:

- N most susceptible to e^- beam damage → lowest knock-on displacement threshold energy (KODTE) in all considered cases
- Edge atoms more susceptible than bulk even for carbon supports, edge atom has lowest KODTE
- No large dependence on metal (M) speciation calculated
- No large dependence on *OH ligand calculated
- Need to test N-coordination (MN_3 structure) and other possible structural effects

Highlight: Successful completion of initial set of library calculations for bulk-C structures

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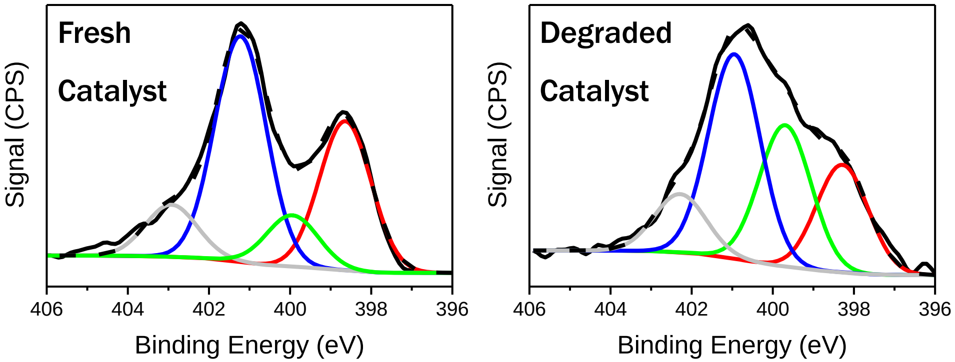
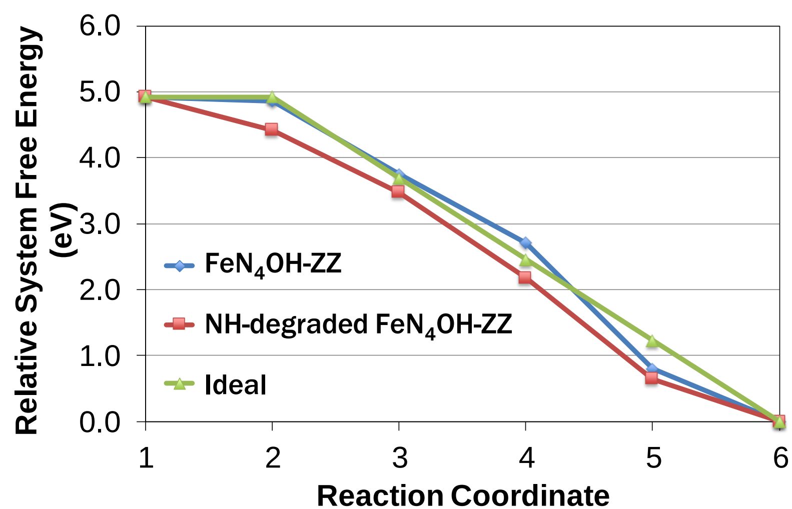
Catalyst Durability: Understanding through Experiment and Modeling

Nitrogen speciation before and after activity loss (XPS)



	$N_{pyridinic}$ (398.3 eV)	$N_{pyrrolic}$ (399.5 eV)	$N_{graphitic}$ (401.2 eV)	N_{oxide} (402.8 eV)
Fresh catalyst	**31.2**	10.7	47.2	10.9
Degradedc atalyst	**21.1**	27.6	39.9	11.4

- **Durability descriptor (knock on displacement threshold energy, KODTE) suggesting active site degradation *via* N removal**
- **Limiting potential calculation indicating significant decrease in activity following N removal (U_L = 0.80 V → 0.64 V *vs.* CHE)**
- **Effect of degraded structures on probe molecule binding underway for MP specificity as well as other degradation mechanisms**



- **Highlight: Durability and activity descriptors pointing to N loss being responsible for PGM-free catalyst activity decrease**
- **XPS results showing severe loss of $N_{pyridinic}$ during degradation**
- **Next step: Follow-on studies with probe molecules and XANES (Fe-N coordination)**

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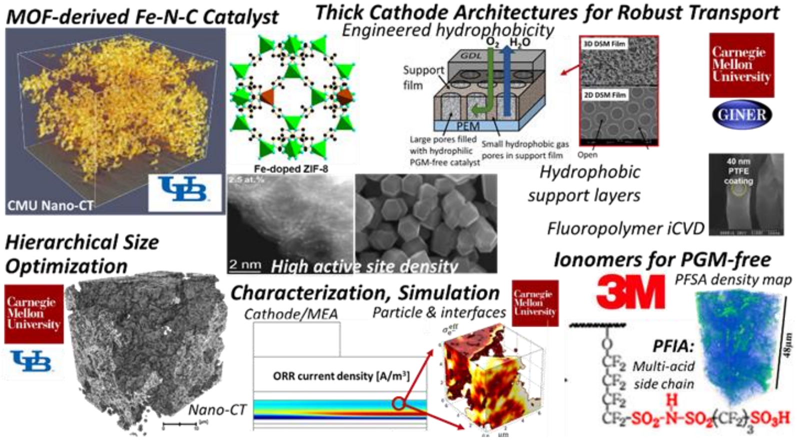
Remaining Challenges

- Insufficient stability of MOF-based catalyst powders and electrodes
- Limited stability of PGM-free electrodes under steady-state and load-cycling conditions
- Inadequate understanding of the catalyst and electrode degradation mechanism
- Oxygen reduction reaction activity of PGM-free catalysts in continued need of further improvement to reduce cathode thickness and lower cost of other stack components
- Development of surface-specific characterization techniques and molecular probes for carbon-based materials
- Electrode design and catalyst-ionomer integration to provide adequate ionic, electronic, and mass transport to and from active sites
- Replacement of Fe in catalyst with another PGM-free transition metal not catalyzing hydroperoxy radical formation and ionomer degradation
- Integration with existing automotive fuel cell stack and system technology

FOA Projects added in FY'17

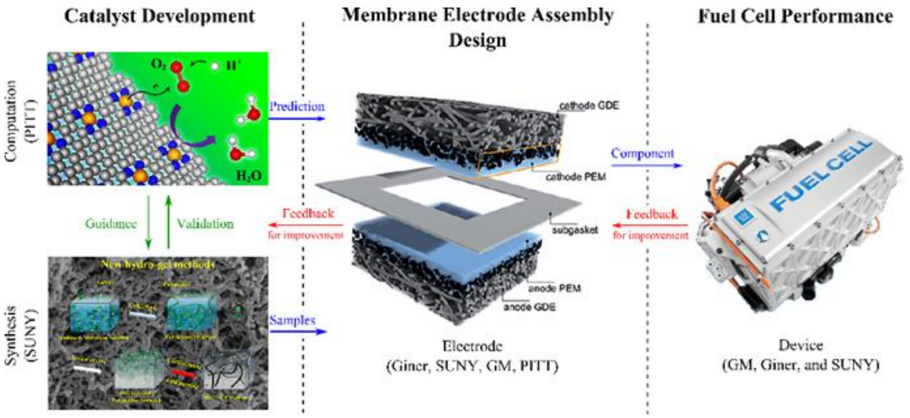
Carnegie Mellon University

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



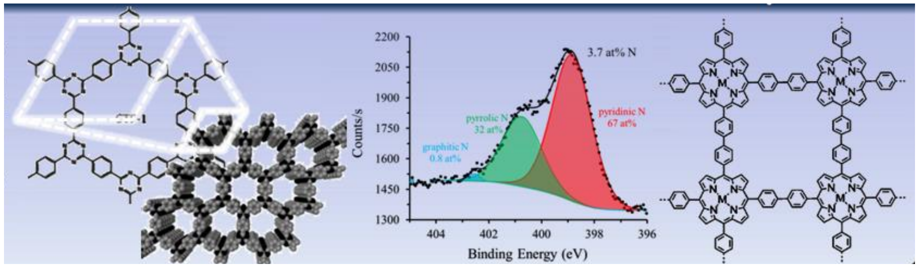
Giner Inc

Durable Mn-based PGM-Free Catalysts for Polymer Electrolyte Membrane Fuel Cells



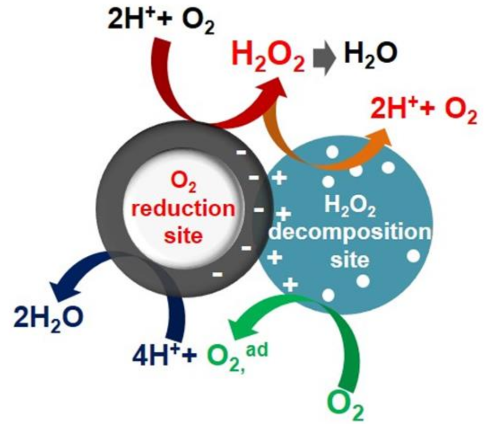
Greenway, LLC

PGM-free Engineered Framework Nano-Structure Catalysts



Pacific Northwest National Lab

Highly Active and Durable PGM-free ORR Electrocatalysts through the Synergy of Active Sites



FOA Projects added in FY'18

Selectee	Location (city, state)	Project Title
		Topic 1 ElectroCat
Northeastern University	Boston, MA	Developing Platinum Group Metal-Free Catalysts for Oxygen Reduction Reaction in Acid: Beyond the Single Metal Site
Indiana University Purdue University	Purdue, IN	Mesoporous Carbon-based PGM-free Catalyst Cathodes
Vanderbilt University	Nashville, TN	Fuel Cell Membrane-Electrode-Assemblies with PGM-free Nanofiber Cathodes
Pajarito Powder	Albuquerque, NM	Active and Durable PGM-free Cathodic Electrocatalysts for Fuel Cell Application
United Technologies Research Center	Hartford, CT	High Performance Non-PGM Transition Metal Oxide Oxygen Reduction Catalysts for Polymer Electrolyte Membrane Fuel Cells

Co-Authors

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

Piotr Zelenay (PI), Andrew Baker, Laura Barber, Hoon Chung, Edward (Ted) Holby, Siddharth Komini Babu, Ling Lin, Ulises Martinez, Geraldine Purdy, Xi Yin

High-throughput techniques, mesoscale models, X-ray studies, aqueous stability studies

Debbie Myers (PI), Jaehyung Park, Nancy Kariuki, Magali Ferrandon, Ted Krause, Dali Yang, Ce Yang, A. Jeremy Kropf, Rajesh Ahluwalia, C. Firat Cetinbas, Voja Stamenkovic, Eric Coleman, Pietro Papa Lopes, Ian Foster, Ben Blaiszik, Liz Jordan

Catalyst modification, model catalyst development, advanced fuel cell characterization

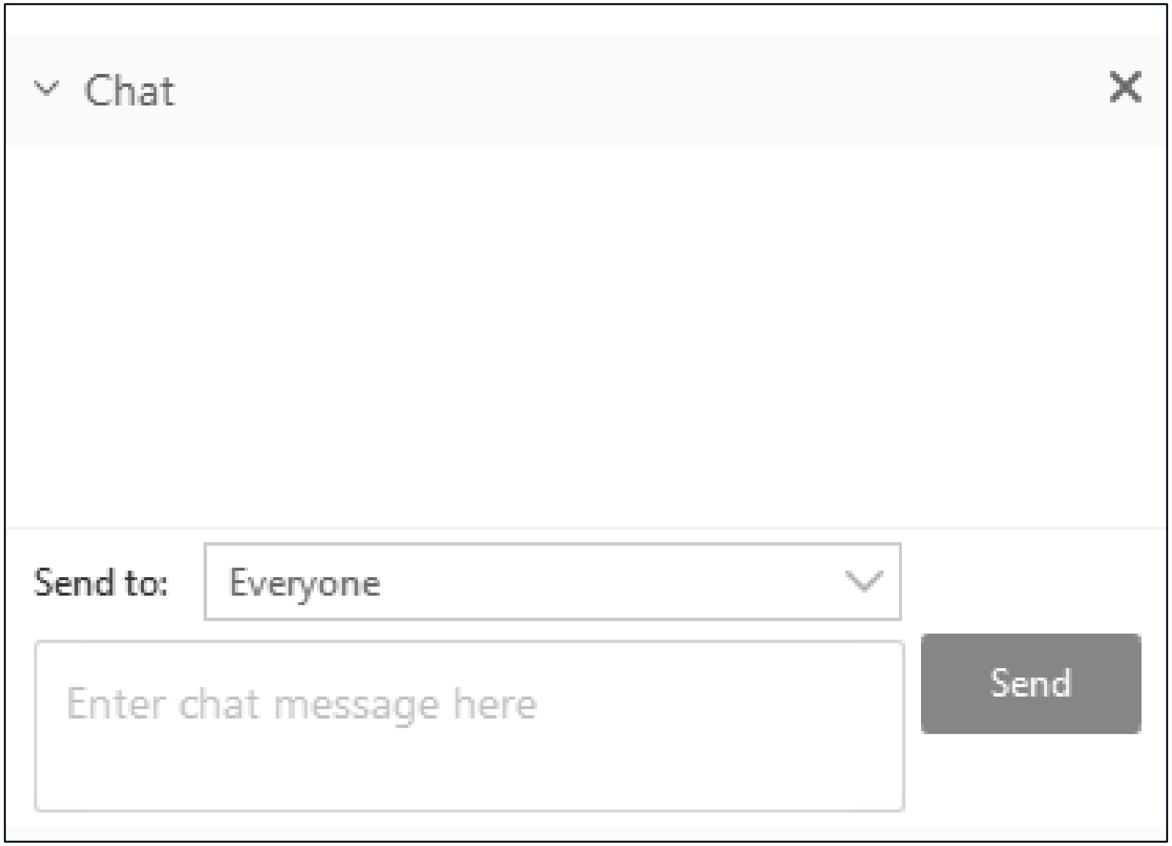
K.C. Neyerlin (PI), Luigi Osmieri, Sadia Kabir, Scott Mauger, Guido Bender, Michael Ulsh, Kristin Munch, Robert White, John Perkins

Advanced electron microscopy, atomic-level characterization, XPS studies

Karren More (PI), David Cullen, Harry Meyer III, Shawn Reeves, Brian T. Sneed

Question and Answer

- Please type your questions to the chat box. **<u>Send to: (HOST)</u>**



Thank you

Deborah Myers
dmyers@anl.gov

Piotr Zelenay
zelenay@lanl.gov

Dimitrios Papageorgopoulos
Dimitrios.Papageorgopoulos@ee.doe.gov

Eric Parker
DOEFuelCellWebinars@ee.doe.gov

hydrogenandfuelcells.energy.gov

Supplemental Slides

Publications (since June, 2017)

1. “Elucidation of role of graphene in catalytic designs for electroreduction of oxygen;” *Curr. Opin. Electrochem.*, P. J. Kulesza, J. K. Zak, I. A. Rutkowska, B. Dembinska, S. Zoladek, K. Miecznikowski, E. Negro, V. Di Noto, and P. Zelenay, https://doi.org/10.1016/j.coelec.2018.05.012, (published on-line on May 19, 2018).
2. “Durability Challenges and Perspective in the Development of PGM-free Electrocatalysts;” *Curr. Opin. Electrochem.*, U. Martinez, S. Komini Babu, E. F. Holby, and P. Zelenay, 10.1016/j.coelec.2018.04.010, 2018 (published on-line April 26, 2018).
3. “Metal-Organic Framework-Derived Nitrogen-Doped Highly Disordered Carbon for Electrochemical Ammonia Synthesis using N_2 and H_2O in Alkaline Electrolytes,” S. Mukherjee, D. A. Cullen, S. Karakalos, K. Liu, H. Zhang, S. Zhao, K. L. More, G. Wang, and G. Wu, *Nano Energy* **48** 217-226, 2018.
4. “Anion Exchange Membrane Fuel Cells: Current Status and Remaining Challenges;” S. Gottesfeld, D. R. Dekel, M. Page, C. Bae, Y. Yan, P. Zelenay, Y. S. Kim, *J. Power Sources*, **375**, 351-360, 2018.
5. “ElectroCat: DOE’s Approach to PGM-Free Catalyst and Electrode R&D,” S. T. Thompson, A. R. Wilson, P. Zelenay, D. J. Myers, K. L. More, K. C. Neyerlin, and D. Papageorgopolous, *Solid State Ionics*, **319**, 68-76, 2018.
6. “Effects of MEA Fabrication and Ionomer Composition on Fuel Cell Performance of PGM-free ORR Catalyst;” X. Yin, L. Lin, H. T. Chung, S. Komini Babu, U. Martinez, G. M. Purdy, and P. Zelenay, *ECS Trans.*, **77** (11) 1273-1281, 2017.
7. “ElectroCat (Electrocatalysis Consortium;” P. Zelenay, D. J. Myers, H. N. Dinh, and K. L. More, U.S. Department of Energy, Hydrogen and Fuel Cells Program; 2017 Annual Progress Report.

Publications II

8. “Direct Atomic-Level Insight into the Active Sites of a High-Performance PGM free ORR Catalyst;” H. T. Chung, D. A. Cullen, D. Higgins, B. T. Sneed, E. F. Holby, K. L. More, and P. Zelenay, *Science*, **357** (6350), 479-484, 2017.
9. “Modeling Electrochemical Performance of the Hierarchical Morphology of Precious Group Metal-free Cathode for Polymer Electrolyte Fuel Cell;” S. Komini Babu, H. T. Chung, P. Zelenay, and S. Litster, *J. Electrochem. Soc.*, **164** (9), F1037-F1049, 2017.
10. “A Combined Probe-Molecule, Mössbauer, Nuclear Resonance Vibrational Spectroscopy and Density Functional Theory Approach for Evaluation of Potential Iron Active Sites in an Oxygen Reduction Reaction Catalyst;” J. L. Kneebone, S. L. Daifuku, J. A. Kehl, G. Wu, H. T. Chung, M. Y. Hu, E. E. Alp, K. L. More, P. Zelenay, E. F. Holby, and M. L. Neidig, *J. Phys. Chem. C*, **121** (30), 16283-16290, 2017.

Presentations (since June, 2017)

1. American Chemical Society National Meeting and Exposition, March 18-22, 2018. Title: “Electrocatalysis without Precious Metals;” P. Zelenay (**invited lecture**).
2. Colorado School of Mines, Golden, Colorado, December 8, 2017. Title: “Oxygen Reduction at Platinum Group Metal-free Electrocatalysts: Progress in Performance and Understanding of Reaction Mechanism;” P. Zelenay (**invited lecture**).
3. 2nd International Fuel Cells Workshop, Ramat Gan, Israel, October 30-31, 2017. Title: “Recent Developments in PGM-free Electrocatalysis of Oxygen Reduction;” P. Zelenay (**invited lecture**).
4. 2nd International Fuel Cells Workshop, Ramat Gan, Israel, October 30-31, 2017. Title: “Activity, Performance, and Durability of Polymer Electrolyte Fuel Cell Catalysts and Electrodes;” D. Myers (**invited lecture**).
5. University of California Santa Cruz, Chemistry and Biochemistry, Santa Cruz, California, October 23, 2017. Title: “PGM-free Electrocatalysts for Oxygen Reduction Reaction in Fuel Cells: State of the Art and Challenges;” P. Zelenay (**invited lecture**).
6. University of California Merced, School of Natural Sciences, Chemistry and Chemical Biology, Merced, California, October 20, 2017. Title: “Electrocatalysis of Oxygen Reduction at Platinum Group Metal-free Catalysts;” P. Zelenay (**invited lecture**).
7. 232nd Meeting of the Electrochemical Society, National Harbor, Maryland, October 1-5, 2017. Title: ”Electron Microscopy Observations of Catalyst-Support Interactions in Polymer Electrolyte Membrane Fuel Cells;” D. A. Cullen, B.T. Sneed, G. Wu, J. Spendelow, H. T. Chung, P. Zelenay, and K. L. More.
8. 232nd Meeting of the Electrochemical Society, National Harbor, Maryland, October 1-5, 2017. Title: “Organic Molecular Catalyst for Electrochemical Production of Hydrogen Peroxide;” X. Yin, L. Lin, U. Martinez, H. T. Chung, and P. Zelenay.

Presentations II

9. 232nd Meeting of the Electrochemical Society, National Harbor, Maryland, October 1-5, 2017. Title: "High-Throughput Synthesis and Characterization of PGM-Free Oxygen Reduction Reaction Electrocatalysts;" D.J. Myers, M. Ferrandon, A.J. Kropf, D. Yang, N.N. Kariuki, J. Park, and S. Lee.
10. 232nd Meeting of the Electrochemical Society, National Harbor, Maryland, October 1-5, 2017. Title: "Microstructural Modeling of PEFC Catalyst Layer Performance and Durability;" S. Ogawa, S. Komini Babu, E. Padgett, H. T. Chung, P. Zelenay, A. Kongkanand, and S. Litster.
11. 232nd Meeting of the Electrochemical Society, National Harbor, Maryland, October 1-5, 2017. Title: "Modeling Durability of PGM-free Active Site Structures at the Atomic Scale;" E. F. Holby, U. Martinez, H. T. Chung, and P. Zelenay.
12. 232nd Meeting of the Electrochemical Society, National Harbor, Maryland, October 1-5, 2017. Title: "Atomically Dispersed (AD)Fe-N-C Oxygen Reduction Catalysts for Polymer Electrolyte Membrane Fuel Cells;" H. Chung, D. A. Cullen, B. T. Sneed, H. M. Meyer III, L. Lin, X. Yin, K. L. More, and P. Zelenay.
13. 232nd Meeting of the Electrochemical Society, National Harbor, Maryland, October 1-5, 2017. Title: "Structure-Activity-Durability Relationships of (CM+PANI)-Me-C PGM-free Catalysts;" U. Martinez, S. Komini Babu, H. T. Chung, L. Lin, G. M. Purdy, and P. Zelenay.
14. 232nd Meeting of the Electrochemical Society, National Harbor, Maryland, October 1-5, 2017. Title: "Influence of Transition Metal and Synthesis Methodology on the Active Site Density on the Surface of PGM-Free Catalysts;" S. Komini Babu, U. Martinez, H. Chung, L. Lin, X. Yin, and P. Zelenay.
15. 232nd Meeting of the Electrochemical Society, National Harbor, Maryland, October 1-5, 2017. Title: "PGM-Free Electrode Microstructure Analysis and Transport Modeling;" F. Cetinbas, N. Kariuki, R. Ahluwalia, H. T. Chung, P. Zelenay, and D. J. Myers

16. ElectroCat Modeling Workshop, Washington, D.C., USA. September 20, 2017. Title: "ElectroCat Overview;" P. Zelenay (**invited lecture**).
17. ElectroCat Modeling Workshop, Washington, D.C., USA. September 20, 2017. Title: "High-throughput Experimental Activities in ElectroCat;" D. Myers, J. Park, N. Kariuki, M. Ferrandon, A. J. Kropf, D. Yang, H. Lv, A. Zakutayev, G. Bender, and H. Dinh.
18. Microscopy & Microanalysis 2017, St. Louis, Missouri, August 6-10, 2017. Title: "Overcoming the Challenges of Beam-sensitivity in Fuel Cell Electrodes;" D.A. Cullen, B.T. Sneed, and K. L. More.
19. Milan Polytechnic, Milan, Italy, June 27, 2017. Title: "Platinum Group Metal-free Electrocatalysts for Oxygen Reduction in Fuel Cells;" P. Zelenay (**invited lecture**).
20. 21st International Conference on Solid State Ionics (SSI-21), Padua, Italy, June 18-23, 2017. Title: "PEFC Cathode Catalyst Layer Electrode Microstructure Analysis and Transport Modeling," C. F. Cetinbas, X. Wang, R. K. Ahluwalia, N. N. Kariuki, R. Winarski, V. J. De Andrade, and D. J. Myers (**invited lecture**).
21. U.S. Department of Energy, Energy Efficiency and Renewable Energy, Fuel Cell Technologies Program, 2017 Merit Review and Peer Evaluation Meeting, Washington, D.C., June 5-9, 2017. Title: "ElectroCat (Electrocatalysis Consortium);" P. Zelenay and D. M. Myers.
22. 231st Meeting of the Electrochemical Society, New Orleans, Louisiana, May 28-June 1, 2017. Title: "The Electrocat (Electrocatalysis) Consortium;" A. R. Wilson, D. C. Papageorgopoulos, D. J. Myers, P. Zelenay, H. N. Dinh, and K. L. More (**invited lecture**).
23. 231st Meeting of the Electrochemical Society, New Orleans, Louisiana, May 28-June 1, 2017. Title: "Porous Electrode Engineering for Platinum Group Metal-Free Oxygen Reduction Reaction Catalysts;" S. Komini Babu, S. Ogawa, H. T. Chung, P. Zelenay, and S. Litster (**invited lecture**).

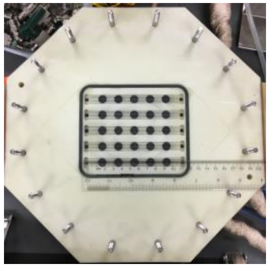
Presentations IV

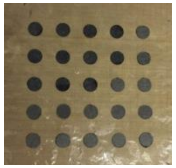
24. 231st Meeting of the Electrochemical Society, New Orleans, Louisiana, May 28-June 1, 2017. Title: "High-Performance PGM-Free Electrocatalysts for the Polymer Electrolyte Fuel Cell Cathode;" X. Yin, H. T. Chung, L. Lin, G. M. Purdy, U. Martinez, and P. Zelenay (**invited lecture**).
25. 231st Meeting of the Electrochemical Society, New Orleans, Louisiana, May 28-June 1, 2017. Title: "Effects of Porosity and Ionomer Composition on Fuel Cell Performance of PGM-Free ORR Catalysts;" X. Yin, L. Lin, H. T. Chung, S. Komini Babu, U. Martinez, G. M. Purdy, and P. Zelenay.
26. 231st Meeting of the Electrochemical Society, New Orleans, Louisiana, May 28-June 1, 2017. Title: "Metal-Organic Framework-Derived Atomic Iron-Dispersed Carbon Electrocatalysts for Oxygen Reduction in Acidic Polymer Electrolyte Fuel Cells;" H. Zhang, H. T. Chung, D. A. Cullen, K. L. More, P. Zelenay, and G. Wu.
27. Israel Research Center for Electrochemical Propulsion (INREP) Energy Conference, Bar-Ilan University, Ramat Gan, Israel, May 9-10, 2017. Title: "PGM-free ORR Electrocatalysis: Progress and Challenges on the Path to Viability;" P. Zelenay (**invited lecture**).
28. DOE Catalysis-Durability Working Group Meeting, Argonne National Laboratory, Lemont, Illinois, May 2-3, 2017. Title: "Introduction to PGM-free Catalysis and Protocols;" P. Zelenay.

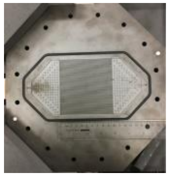
Capability Development: Combinatorial Fuel Cell Performance Testing

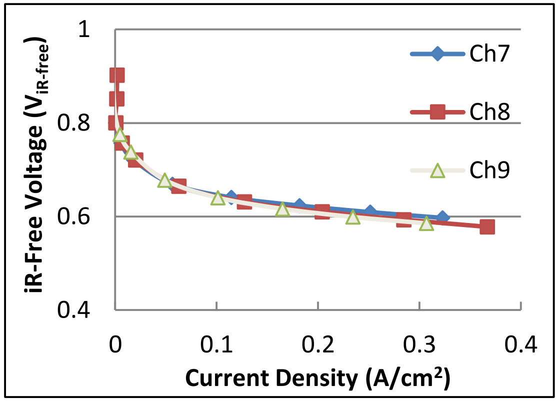
Purpose: Accelerate the optimization of the electrode composition and structure for PGM-free catalysts by developing methods for the high-throughput synthesis and deposition of catalyst-ionomer-solvent inks, and measuring ORR activity and fuel cell performance, using:

- **Combinatorial 25-electrode segmented electrode hardware from NuVant (ANL)**
  - ✓ Demonstrated for measuring ORR activities
  - ✓ Identical *iR*-corrected H_2-air polarization curves for different channels

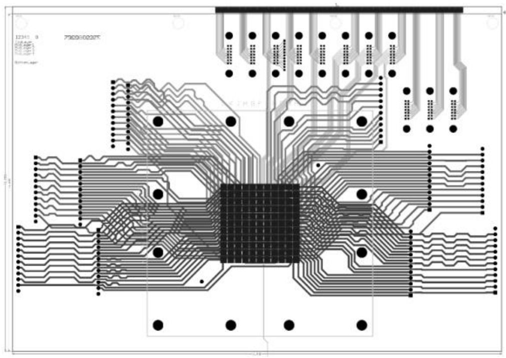


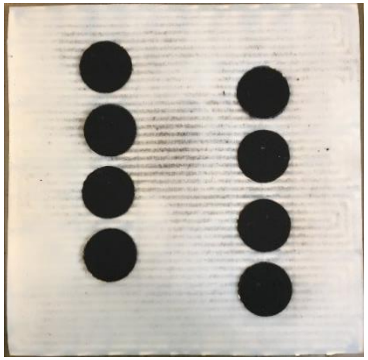






- **Segmented fuel cell hardware (NREL)**
  - ✓ Cross-talk between segments of cell hardware with common GDL quantified
  - ✓ Several approaches investigated to mitigate cross-talk and enhance ability to test combinatorial samples: (i) parallel flow field design; (ii) segmented GDLs; (iii) segmented electrodes





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