Hydrogen and Fuel Cells Program
2018 Annual Merit Review and Peer Evaluation Meeting
Washington, DC – June 13-15, 2018

ElectroCat (Electrocatalysis Consortium)

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Project ID: FC160

Overview

Timeline

• **Start date** (launch):	Feb 1, 2016
• **End date:**	Sep 30, 2020

Budget

• **FY17 funding total:**	$3,500k
• **FY18 core funding:**	$3,550k
FY18 FOA projects support:	$471k
• **FY18 funding total:**	$4,021k

Barriers

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

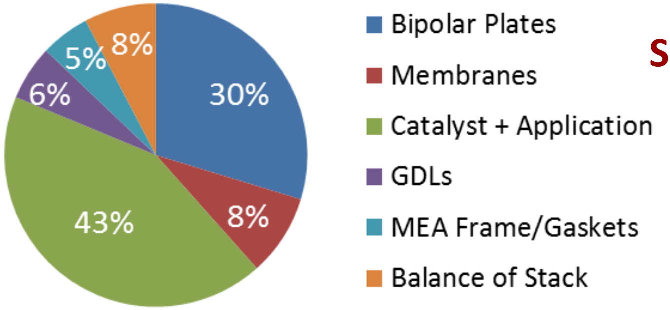
Partner	– PI
Los Alamos National Laboratory	– Piotr Zelenay
Argonne National Laboratory	– Deborah Myers
National Renewable Energy Laboratory	– Kenneth Neyerlin
Oak Ridge National Laboratory	– Karren More

Relevance: Fuel Cell Stack Cost Challenge

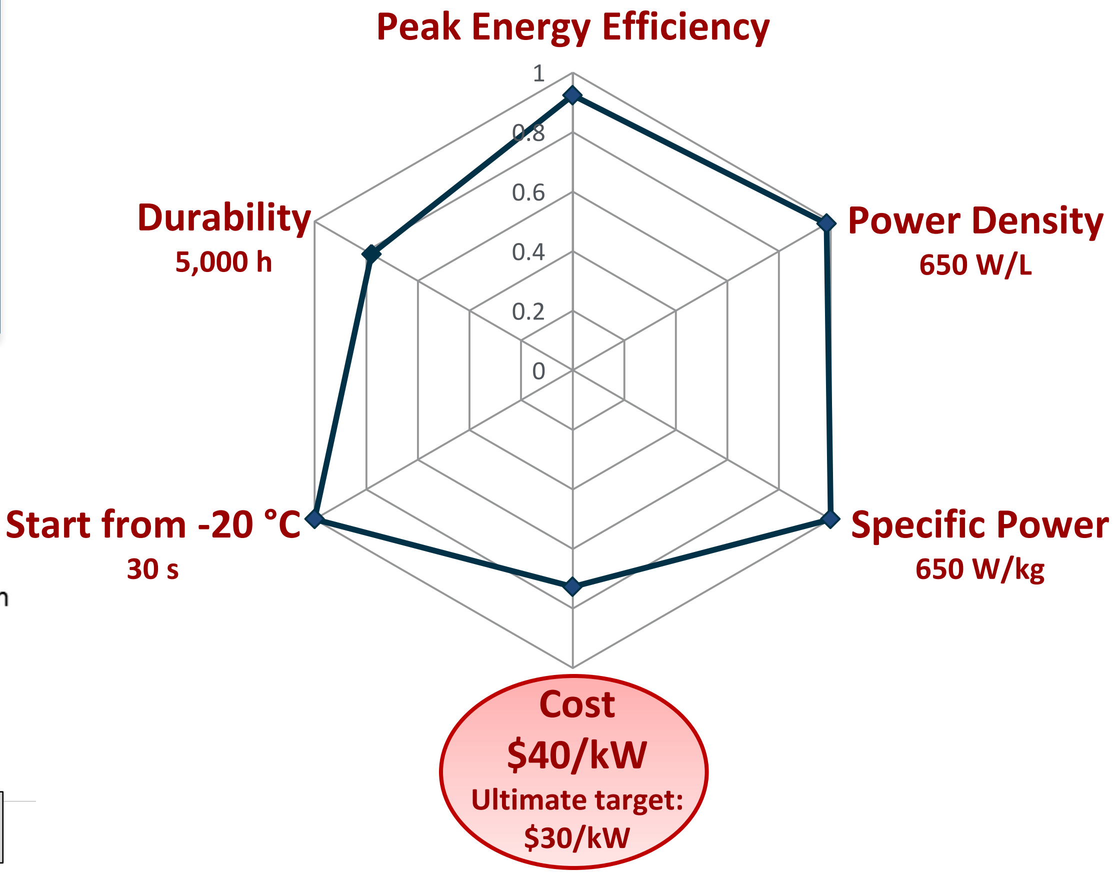
Fuel cell system targets set to be competitive with ICEVs

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



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

Approach: 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
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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

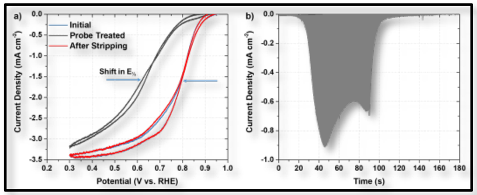
Capability Utilization, Management, and Development

Capabilities for Characterization

Argonne NATIONAL LABORATORY

Synchrotron X-ray Techniques

GINER
Carnegie Mellon University
Pacific Northwest NATIONAL LABORATORY



Los Alamos NATIONAL LABORATORY
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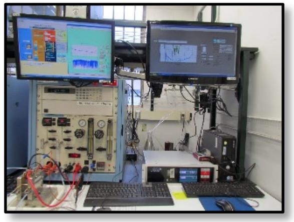
Molecular Probe Electrochemistry and X-ray Spectroscopy

Carnegie Mellon University



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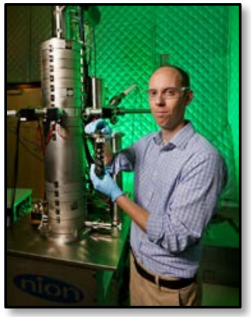
In situ Fluoride and CO_2 Emission Measurements

Pacific Northwest NATIONAL LABORATORY
Carnegie Mellon University



OAK RIDGE National Laboratory

Analytical Electron Microscopy

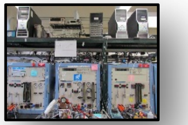
GINER
Pacific Northwest NATIONAL LABORATORY
Carnegie Mellon University
GWE GreenWayEnergy POWERFUL EXPERTS

Capabilities discontinued in FY18:

- ✓ Cube2: System for Sputtering and Implanting Powders
- ✓ Thin Film High-Throughput (HT) Experimental Capabilities

Capability Utilization, Management, and Development

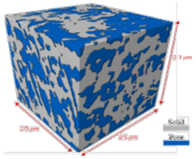
Synthesis and Diagnostics

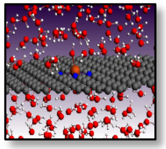


Los Alamos NATIONAL LABORATORY — **PGM-free Catalyst Synthesis, Analytical Characterization, Electrochemical and Fuel Cell Testing** — GreenWayEnergy POWERFUL EXPERTS

NREL NATIONAL RENEWABLE ENERGY LABORATORY — **Operando Differential Cell Measurements of Kinetics and Transport** — GINER; Pacific Northwest NATIONAL LABORATORY

Modeling

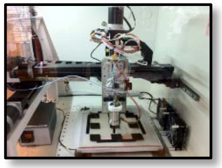




Argonne NATIONAL LABORATORY — **Electrode Microstructure Characterization and Simulation** — Pacific Northwest NATIONAL LABORATORY

Los Alamos NATIONAL LABORATORY — **Multi-scale Modeling for Rational Design of PGM-free Catalysts** — GreenWayEnergy POWERFUL EXPERTS

Fabrication



NREL NATIONAL RENEWABLE ENERGY LABORATORY — **Ultrasonic spray coating of MEAs** — Carnegie Mellon University

Los Alamos NATIONAL LABORATORY — **MEA Design and Fabrication** — GINER; GreenWayEnergy POWERFUL EXPERTS

Capabilities to be added in FY18:

Temperature-programmed desorption, model systems, wetting properties of catalysts, calculation of reaction energetics, electrospinning of electrodes

Approach: FY17 ElectroCat Milestone & Go/No-Go; FY18 LANL QPMs

FY17

Date	ElectroCat Annual Milestone	Status
September 2017 (FY17 Q4)	Demonstrate 20 mA cm^{-2} at 0.90 V (*iR*-corrected) in an H_2-O_2 fuel cell and 100 mA cm^{-2} at 0.80 V in an H_2-air fuel cell (measured); maintain partial pressure of O_2 + N_2 at 1.0 bar (cell temperature 80 °C).	**Completed** 21 mA cm^{-2} reached at 0.80 V (see slide 10 for details)

Date	ElectroCat Go/No-Go Decision	Criteria	Decision
June 2017 (FY17 Q3)	**TT/A Process:** Continuation of current path toward establishing a technology transfer and agreement (TT/A) process.	Short-form agreement for rapidly engaging industry established	**Go**

FY18

Date	LANL Quarterly Progress Measures	Status
December 2017 (FY18 Q1)	Demonstrate five-fold (400%) improvement in fuel cell performance of (AD)Fe-N-C catalysts at 0.80 V (measured) at 0.2 bar partial pressure of O_2 and cell temperature 80°C.	**Four-fold activity improvement** (see Slide 12)
March 2018 (FY18 Q2)	Evaluate active-site specificity of molecular probe methodology for PGM-free catalysts; compare binding motifs (structures and energies) of 3 different probe molecules adsorbed at no less than 3 sites local for selected Fe-based sites in activity/durability library *via* density functional theory (DFT).	**Completed** (see Slide 22)
June 2018 (FY18 Q3)	Identify possible degradation mechanisms via experiment and theory. — Validation and publication on DDCA-based modeling approach and calculation of activity descriptor for locally degraded structures (addition to calculated active site library); qualification and comparison of empirical activity-loss reaction kinetic model to DDCA atomic-scale model; corroboration from active-site probe methodology and CO_2/F^-/transition-metal emission measurements.	**On track**

Approach: FY18 ANL and NREL QPMs

Date	ANL Quarterly Progress Measures	Status
December 2018 (FY18 Q1)	Identity of X-ray absorption spectroscopy near edge and extended region features that are correlated with ORR activity for the (AD)Fe-N-C using XAFS data acquired from ex situ samples, in situ electrochemical experiments, and in situ pyrolysis experiments.	**Completed** (see Slide 15)
March 2018 (FY18 Q2)	Automated deposition of catalyst-ionomer inks on multi-channel flow double electrode glassy carbon electrodes demonstrated to result in ORR half-wave potentials within 10 mV of those measured using RDE	**Completed** (see Slide 35)
June 2018 (FY18 Q3)	Hydrogen-oxygen and hydrogen-air polarization curves measured for twenty-five electrodes simultaneously with different catalyst and ionomer to carbon ratios in the twenty-five cathode catalyst layers. Catalysts will include catalysts in (AD)Fe-N-C class arising from high-throughput synthesis task.	**On track**

Date	NREL Quarterly Progress Measures	Status
December 2017 (FY18 Q1)	Demonstrate that the PSIS-prepared PGM-free catalyst (e.g., deposited Fe_xN_y on black pearl) is capable of achieving a half-wave potential 0.70 V vs RHE for the ORR with 85% selectivity. Go/No-Go decision 12/31/17.	**No-Go**
December 2017 (FY18 Q1)	Demonstrate homogeneous current distribution in a subset of 6 - 7 segments located between the bend regions and along a straight channel section. The current densities of all segments in this subset must be within 10% of those in a standard 5 cm^2 test cell while using identical PGM-free electrode compositions in both cells. Go/No-Go decision 12/31/17.	**Completed** (see Slide 55)
March 2018 (FY18 Q2)	Demonstrate the capability to fabricate PGM-free electrodes with ionomer or electrocatalyst gradients in x, y and/or z dimensions. (Task 6)	**Completed** (see Slide 3)
June 2018 (FY18 Q3)	Separate the pressure dependent (Fickian) and independent (non-Fickian) transport resistances for at least two types of PGM-free electrocatalyst/ electrode combinations. (Task 3)	**On track**

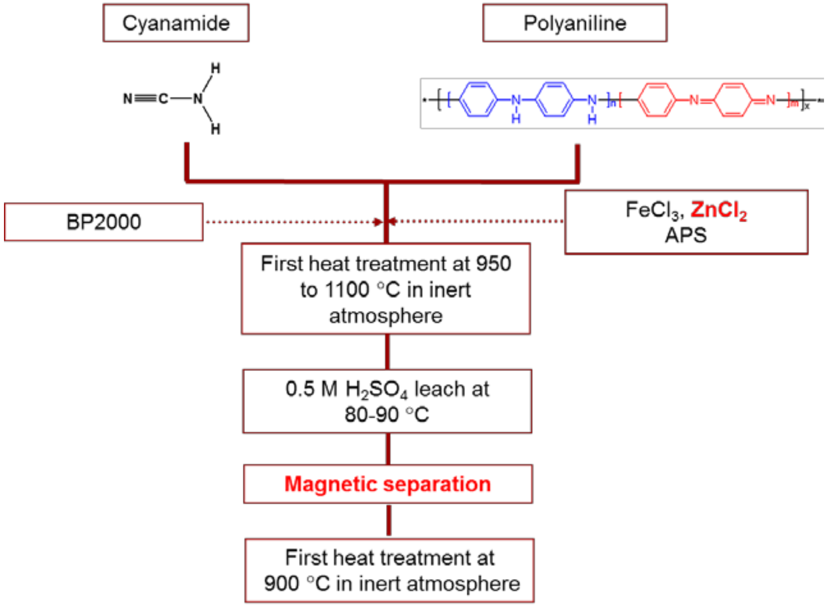
Approach: FY18 ORNL QPMs; ElectroCat Go/No-Go and Milestone

Date	ORNL Quarterly Progress Measures	Status
December 2017 (FY18 Q1)	Conduct high-resolution STEM imaging and spectroscopy on at least three (3) new (AD)-Fe-N-C catalysts and at least three (3) MOF/ZIF-derived catalysts in coordination with synthesis efforts at LANL and high-throughput methods at ANL. These studies will focus on understanding morphological aspects of catalysts in addition to identification of potential active sites.	**Completed**
March 2018 (FY18 Q2)	Characterize at least four (4) PGM-free MEAs before and after degradation testing using analytical electron microscopy and tomography. This effort will be highly coordinated with efforts at LANL to develop protocols to assess performance and durability of PGM-free catalysts and with X-ray tomography and XAFS efforts at ANL.	**Completed**
June 2018 (FY18 Q3)	Complete evaluation of ORNL's new "pixel array detector" combined with cryo-EM (imaging and spectroscopy) to image/analyze thin ionomer layers in optimized PGM-free electrode morphologies.	**On track**

Date	ElectroCat Annual Milestone	Status
September 2018 (FY18 Q4)	Achieve PGM-free cathode MEA performance in an H_2-O_2 fuel cell of 25 mA cm^{-2} at 0.90 V (*iR*-corrected) at 1.0 bar partial pressure of O_2 and cell temperature 80°C; define performance-limiting catalyst and electrode properties to guide the synthesis of PGM-free catalysts and fabrication of electrodes/MEAs (LANL, ANL, ORNL, NREL).	**On track**

ElectroCat FY2017 Annual Milestone Achieved

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.



Cyanamide

Polyaniline

BP2000

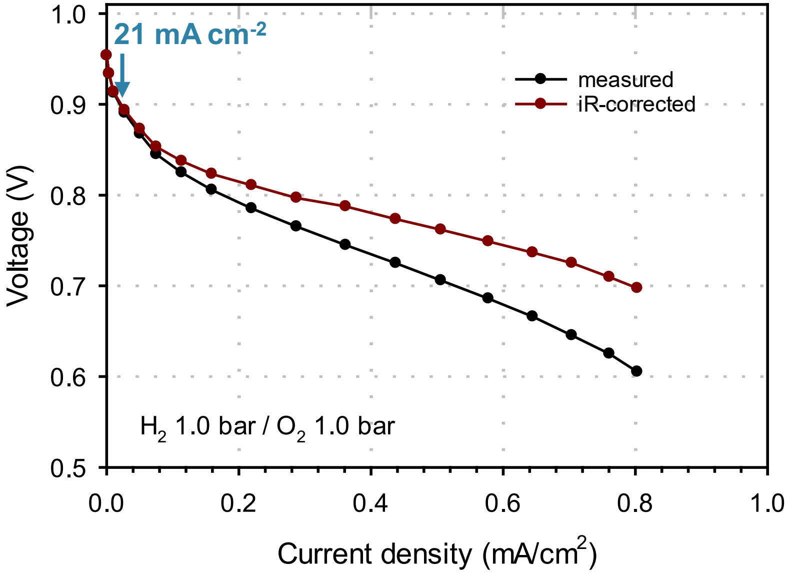
$FeCl_3$, **$ZnCl_2$**
APS

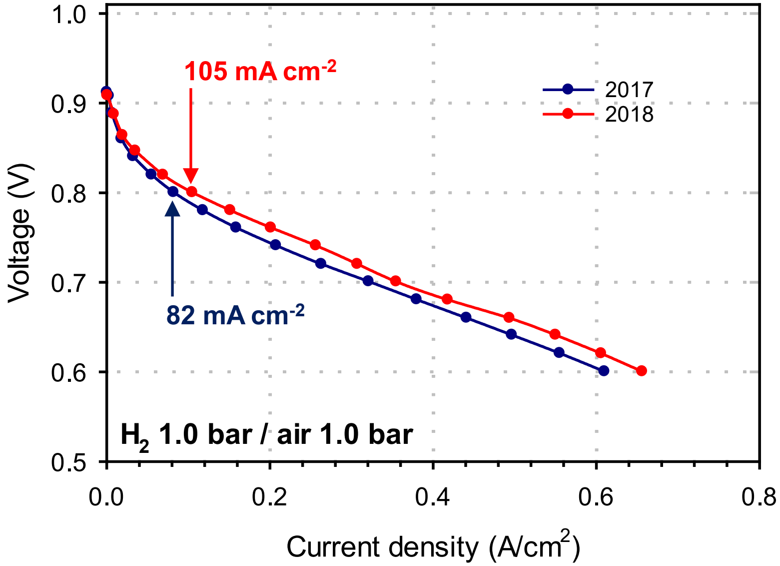
First heat treatment at 950 to 1100 °C in inert atmosphere

0.5 M H_2SO_4 leach at 80-90 °C

Magnetic separation

First heat treatment at 900 °C in inert atmosphere

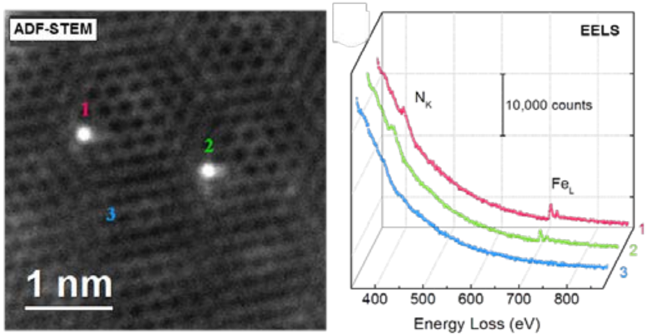




- H_2 / O_2 fuel cell performance of **CM-PANI-Fe-C(Zn)** catalyst measured at **21 mA cm^{-2}** (0.90 V, *iR*-free)
- H_2-air fuel cell performance at 0.80 V improved from 82 mA cm^{-2} to 105 mA cm^{-2} since 2017 AMR (an increase of 28% in one year)

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

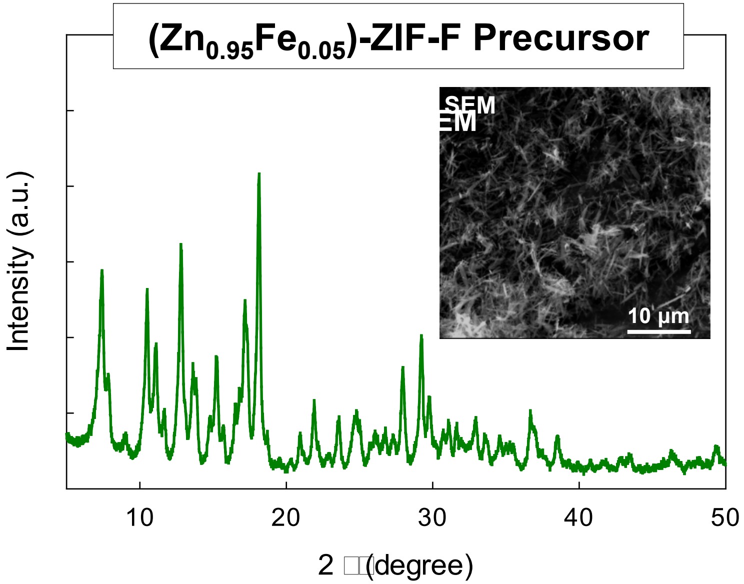
Catalyst Development: Towards Atomically-Dispersed (AD) Catalyst



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

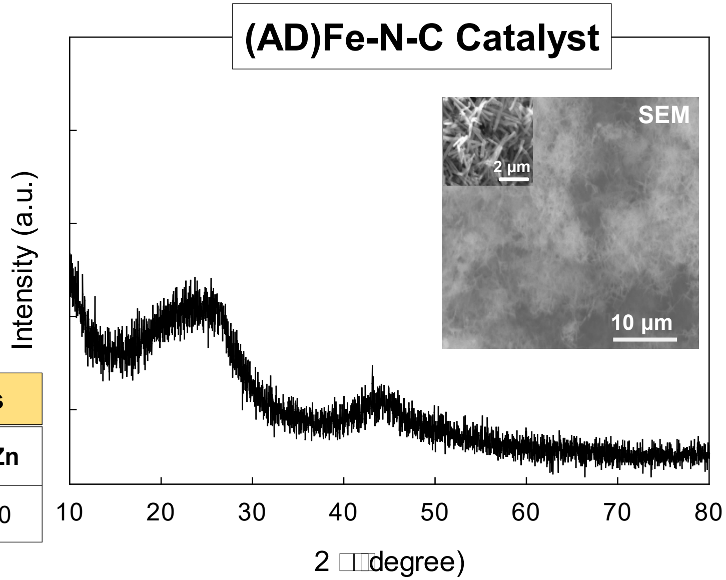
(AD)Fe-N-C catalyst (derived from ($Zn_{0.95}Fe_{0.05}$)ZIF-F):


($Zn_{0.95}Fe_{0.05}$)-ZIF-F Precursor

Heat Treatment

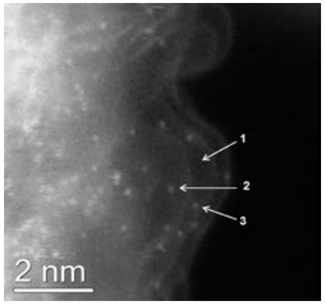
AD Catalyst XPS Analysis

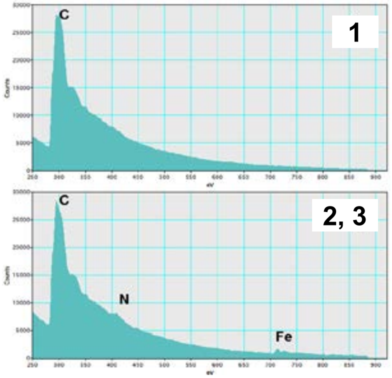
C	Fe	N	O	Zn
92.5	0.6	2.1	4.7	0


(AD)Fe-N-C Catalyst

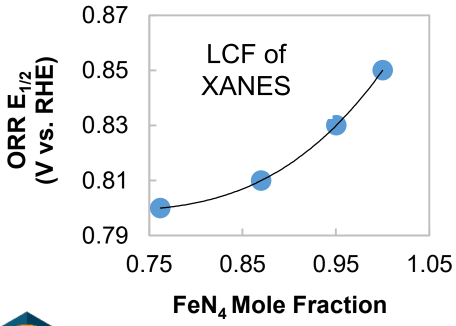
- ZIF-F(fiber) MOF successfully synthesized as AD catalyst precursor
- No near-surface Zn and Fe-rich nanoparticles (> ~ 2 nm) detected by XPS and XRD, respectively
- Initial ZIF-F morphology preserved in catalyst after heat treatment (important for future catalyst design)

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

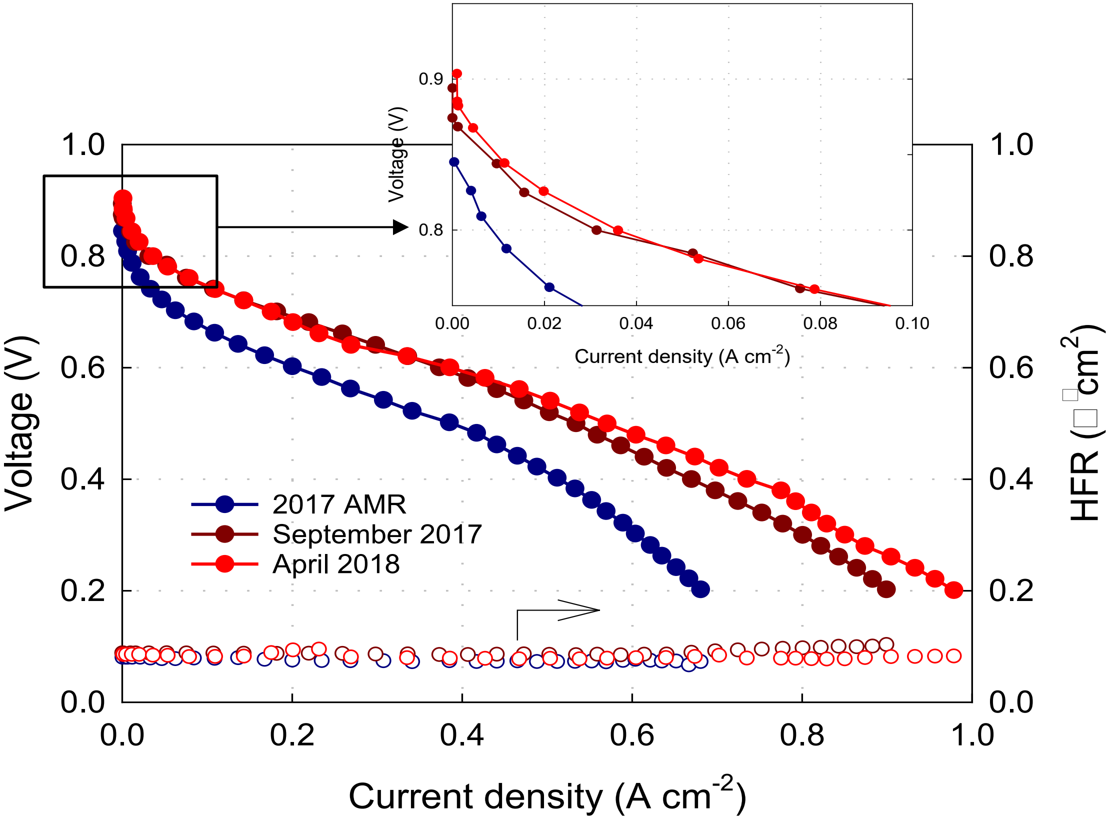




Path	CN	R (Å)
Fe-N/O	3.0 ± 0.4	1.837 ± 0.033
Fe-Fe	0.3 ± 0.3	2.983 ± 0.055



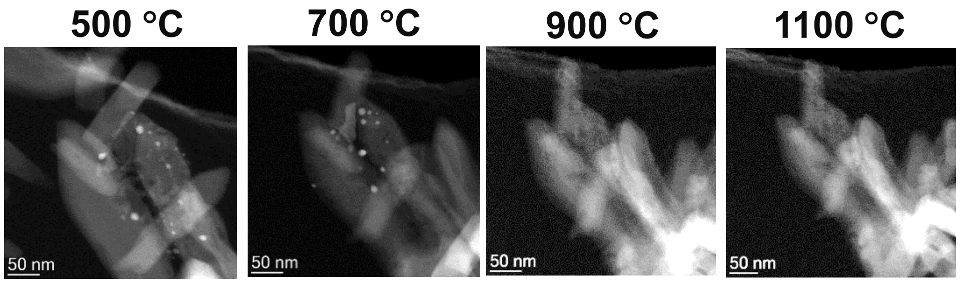
Anode: 0.2 mg_{Pt} cm^{-2} Pt/C H_2, 200 sccm, 1.0 bar H_2 partial pressure; **Cathode**: ~4 mg cm^{-2} air, 200 sccm, 1.0 bar air partial pressure; **Membrane**: Nafion®-211; **Cell**: 5 cm^2; 80°C

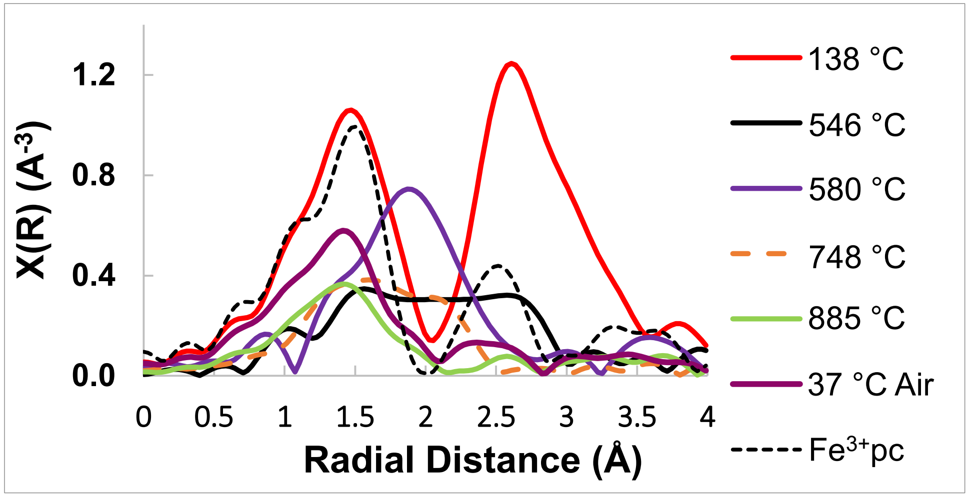


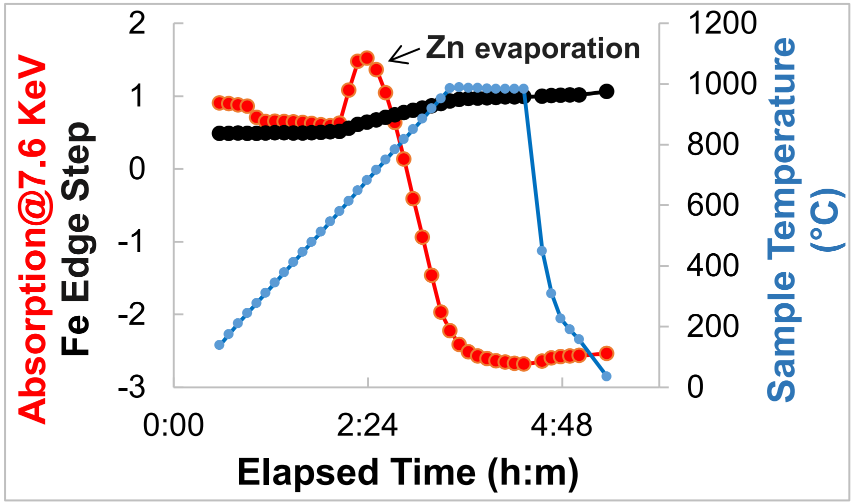
- Fe predominantly found in N-coordinated FeN_x sites
- ORR activity correlated with FeN_x content
- Single Fe atoms dispersions associated with basal-plane edges/step
- **Highlight: Four-fold improvement** of the H_2-air fuel cell performance at 0.80 V, from 9 mA cm^{-2} to 36 mA cm^{-2} since 2017 AMR **(FY18 Q2 QPM)**

(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







- **500-546 °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

High-throughput Synthesis, Characterization, Performance Evaluation

Catalyst system: LANL's (Zn_xFe_{1-x})ZIF-F system selected due to high RDE ORR activity

Parameters varied to obtain 40 unique samples:

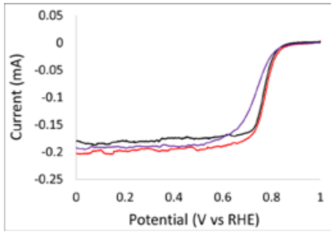
- Fe-to-Zn ratio: 0, 1, 2.5, 5, and 7.5 mol% Fe in precursors
- Fe salts: sulfate, nitrate, acetate
- Heat-treatment temperatures: 900, 1000, 1100°C

Precursor synthesis: CM Protégé Robot

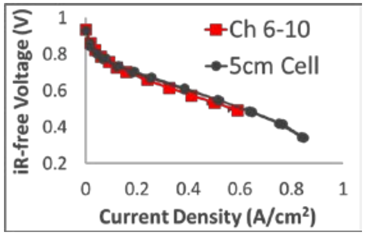
Multi-sample pyrolysis

Characterization

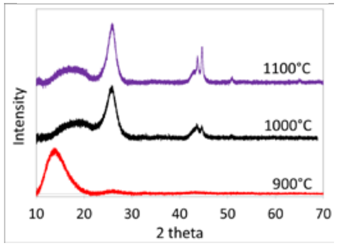
4 Sample Electrochemical Flow Cell



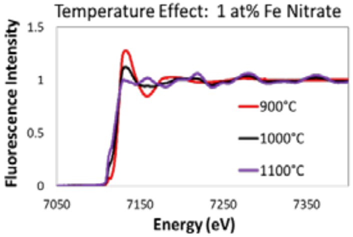
25-electrode segmented MEA hardware



96-sample XRD



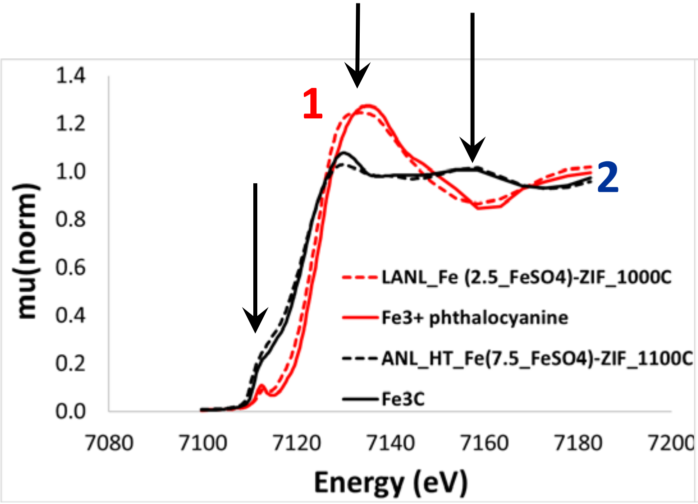
XAFS

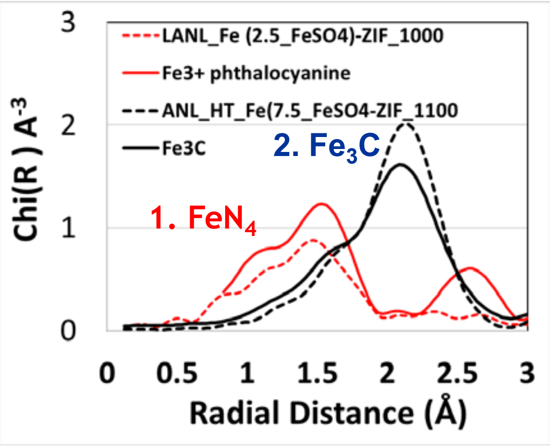


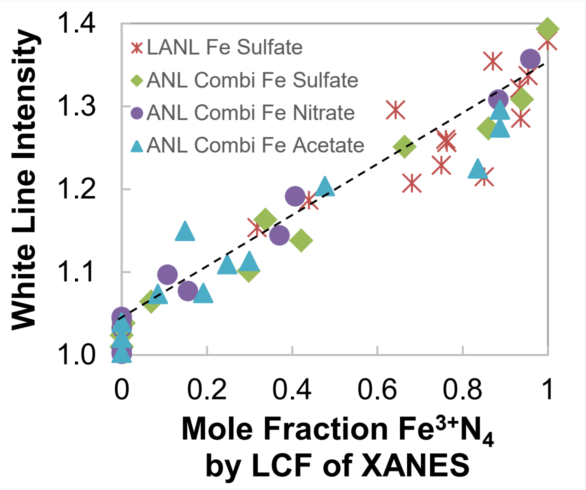
A 2017 reviewer comment and response (more comments & responses in upcoming slides)**:**

"High-throughput methods of synthesis and testing are of questionable value for non-Pt catalysts, the performance of which depends less on chemical composition and more on details of processing. The physical vapor deposition (PVD) generation of thin-layer model catalyst systems is unlikely to be useful…"
– High-throughput synthesis of high-surface area catalysts does encompass processing conditions as a variable. PVD methods were being used to attempt to fabricate model systems.

Fe X-ray Absorption Spectroscopy of Heat-Treated (Zn_xFe_{1-x})ZIF-F

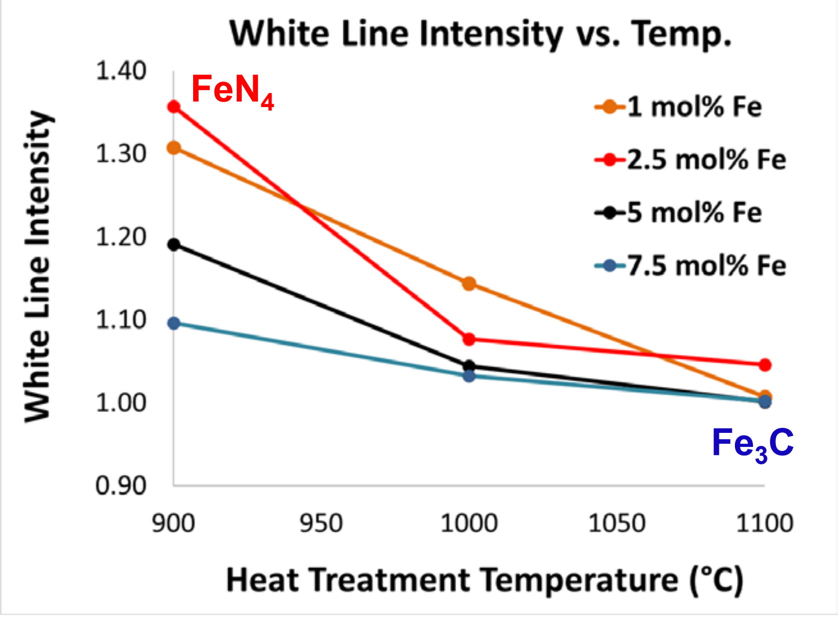






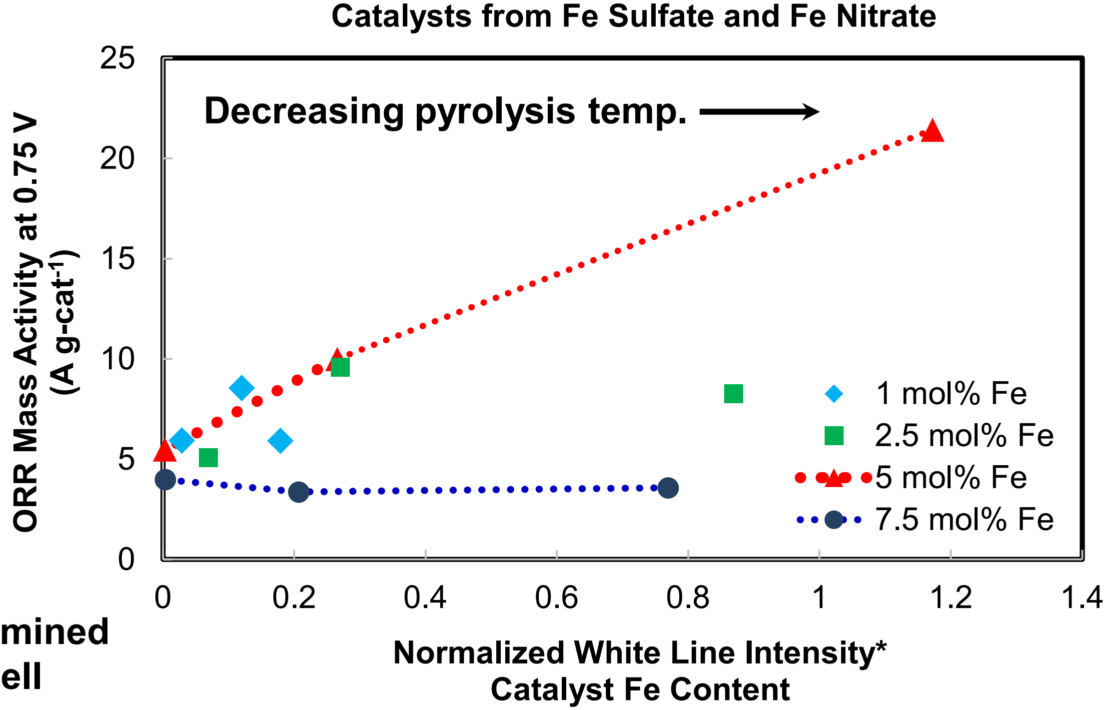
- Fe XAFS of catalysts range from spectra with:
  - ✓ **1. Low pre-peak, high white line, and low post-peak intensity ($Fe^{3+}N_4$)**
  - ✓ **2. High pre-peak, low white line, and high post-peak (Fe_3C)**
- Linear combination fitting (LCF) of XANES region showing correelation between white line intensity and $Fe^{3+}N_4$ content
- Spectral signatures of Fe_3C increasing and of Fe-N_4 decreasing with an increase in heat-treatment temperature and Fe content

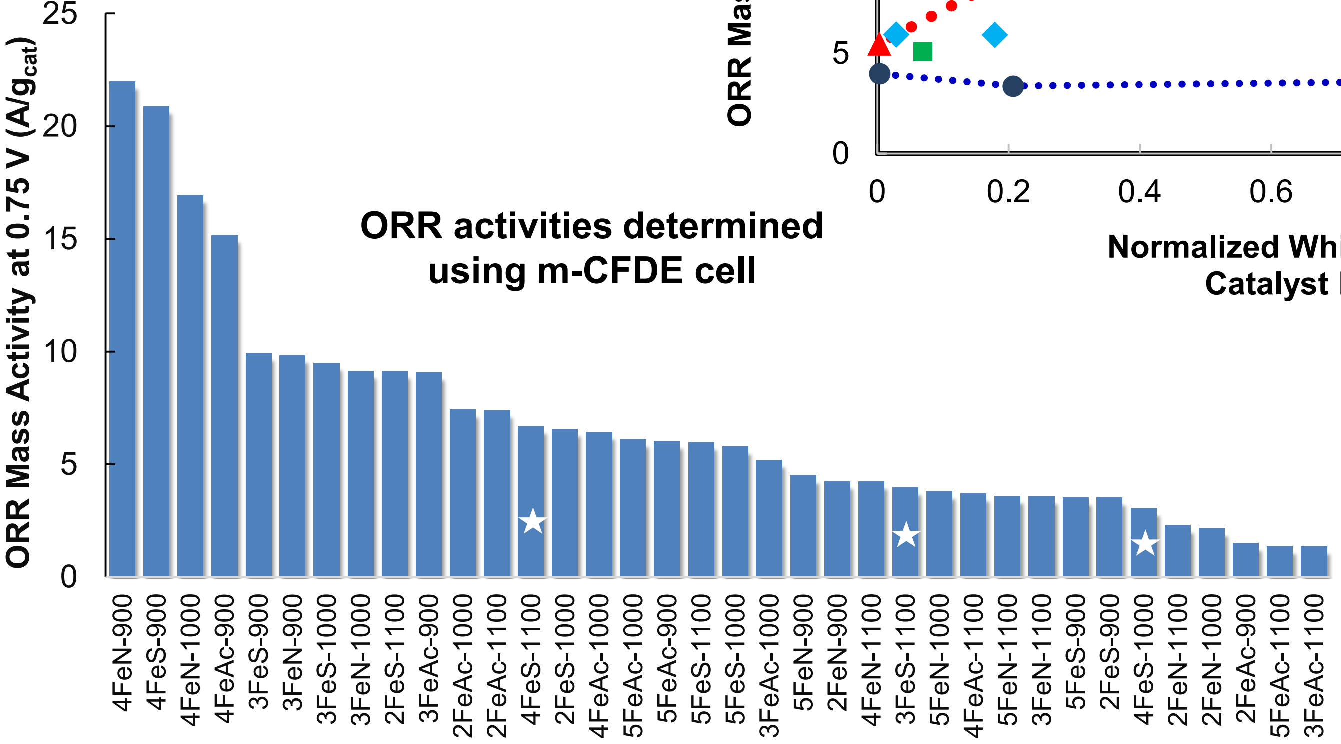
Fe Nitrate Precursor



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)





ORR activities determined using m-CFDE cell

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

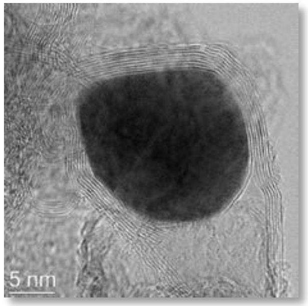
★ *Baseline materials explored by batch synthesis prior to initiation of combinatorial synthesis task*

- 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

Carbon Structure and XPS Data for Heat-Treated (Zn_xFe_{1-x})ZIF-F

Combinatorial $(Zn_{0.95}Fe_{0.05})$ZIF-F
(Fe Nitrate)

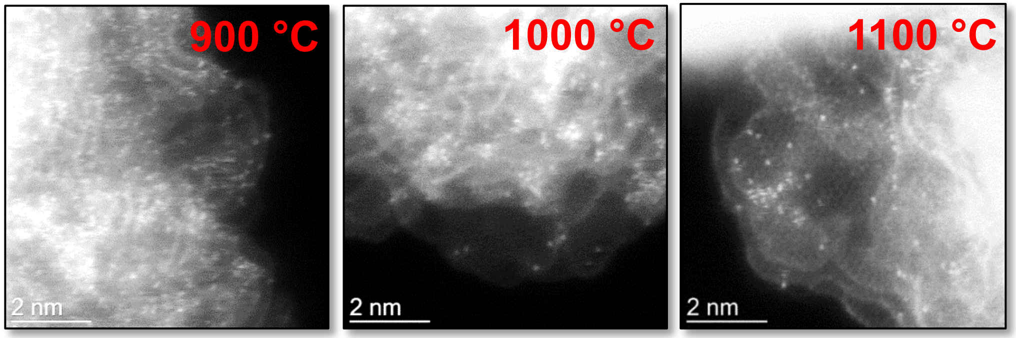
- Heat-treated material composed of a mixture of regions with atomically-dispersed Fe and regions with graphite-encased Fe or Fe_3C particles
- Increase in heat-treatment temperature resulting in:
  - ✓ Decrease in near-surface Fe and FeO content
  - ✓ Decrease in near-surface pyridinic N
  - ✓ Decrease in near-surface C/N
  - ✓ Increase in near-surface N/Fe
  - ✓ Increase in (AD)Fe clustering
  - ✓ Increases in degree of graphitization of the carbon matrix
  - ✓ Decrease in ORR activity



Graphite-encased Fe carbide particle

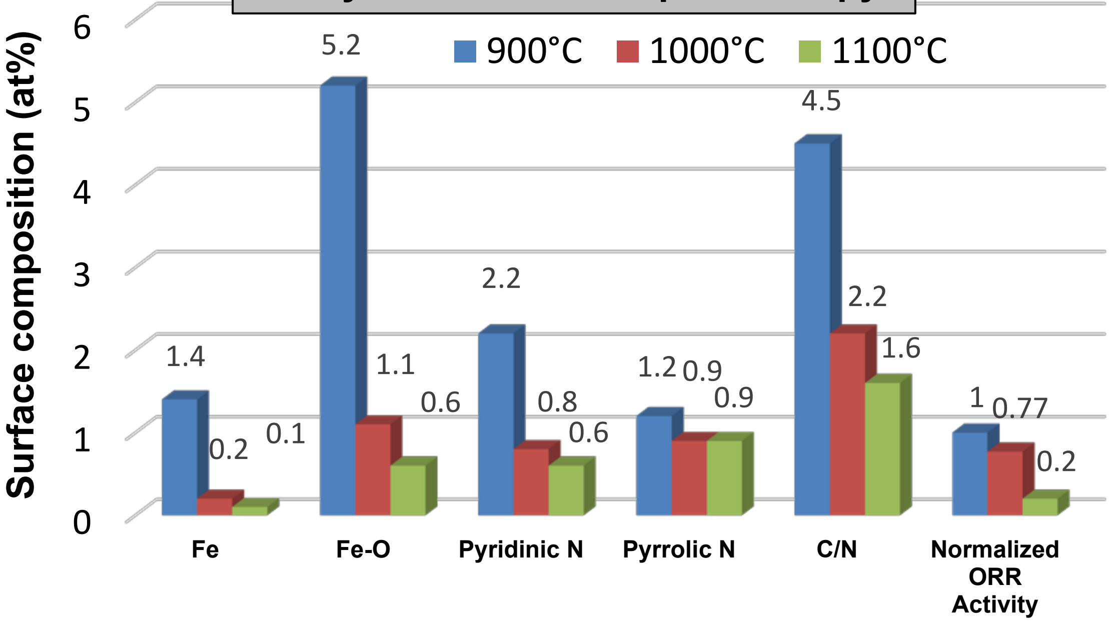
Composition of atomically-dispersed Fe regions (EELS)

Fe: 1.2 at%	Fe: 0.5 at%	Fe: 0.1 at%
N: 6.4 at%	N: 2.6 at%	N: 1.1 at%

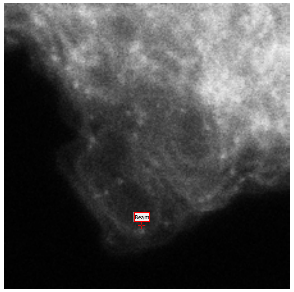


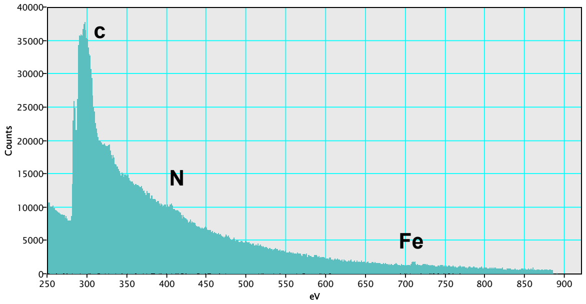
64 at% sp^2 C | 77 at% sp^2 C | 83 at% sp^2 C

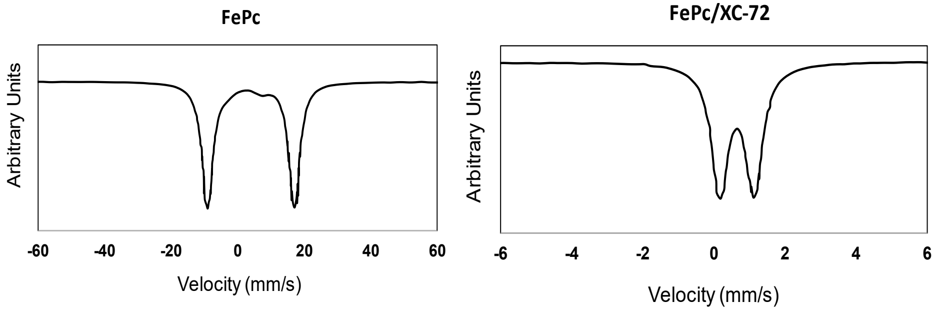
X-ray Photoelectron Spectroscopy



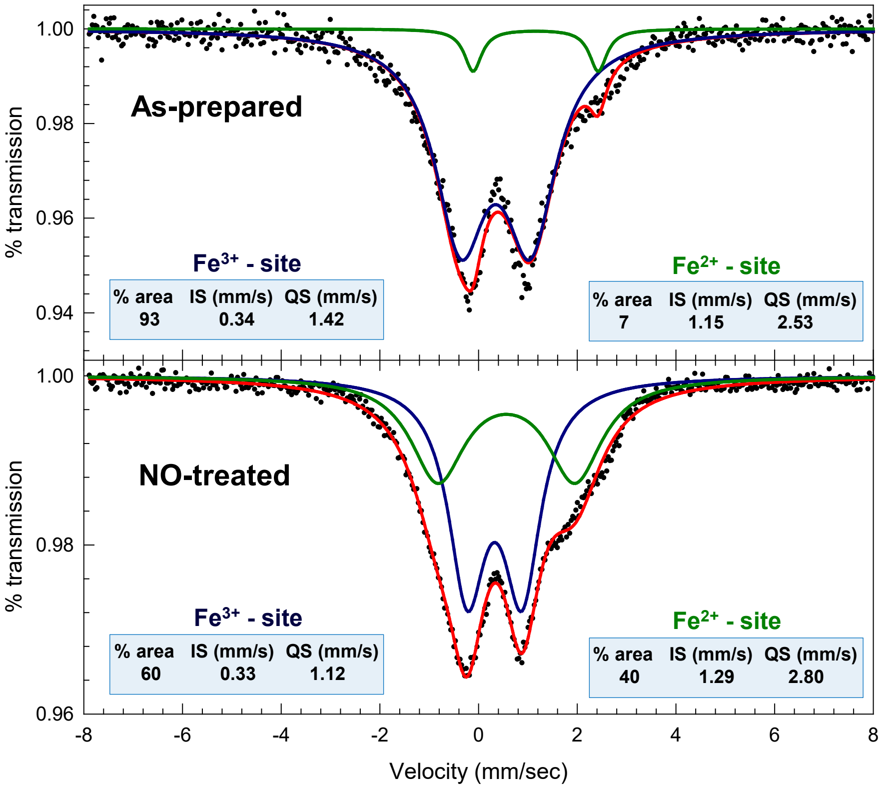
(AD)Fe-N-C Catalyst (100% ^{57}Fe-enriched)**: Mössbauer Characterization**







Mössbauer spectroscopy of iron phthalocyanine (FePc) and FePc dispersed on XC-72 carbon (based on E. B. Yeager *et al.*, *J. Electroanal. Chem.*, **184**, 419, 1985)



- Broad FWHM possibly indicating diverse FeN_x moieties (not a single FeN_4) and/or formation of ferric oxy-hydroxide (FeOOH)
- NO (an O_2 analog) inducing evident change in isomer shift and quadrupole splitting for Fe^{3+} and Fe^{2+}

Highlight: Direct evidence of NO interaction with Fe^{2+} ions in FeN_x moieties on the surface of a PGM-free catalyst

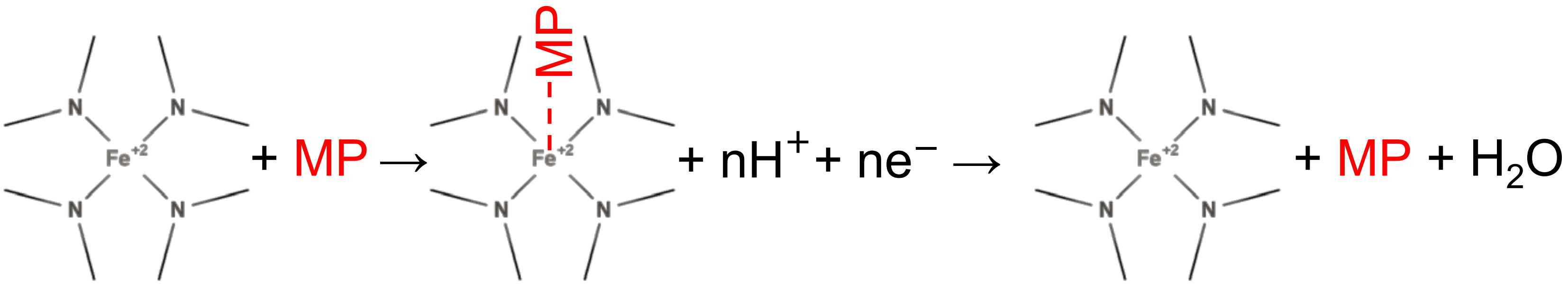
Linear Combination Fitting of Fe XANES of NO-treated

Fe Species	at%
$Fe^{3+}N_4$	56
$Fe^{2+}N_4$	32
Fe_3C	12

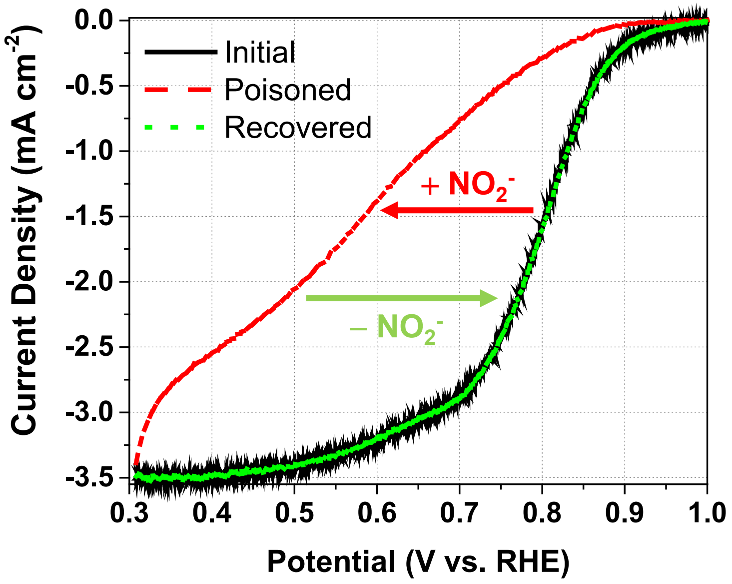
Molecular Probes for Active-Site Identification/Quantification

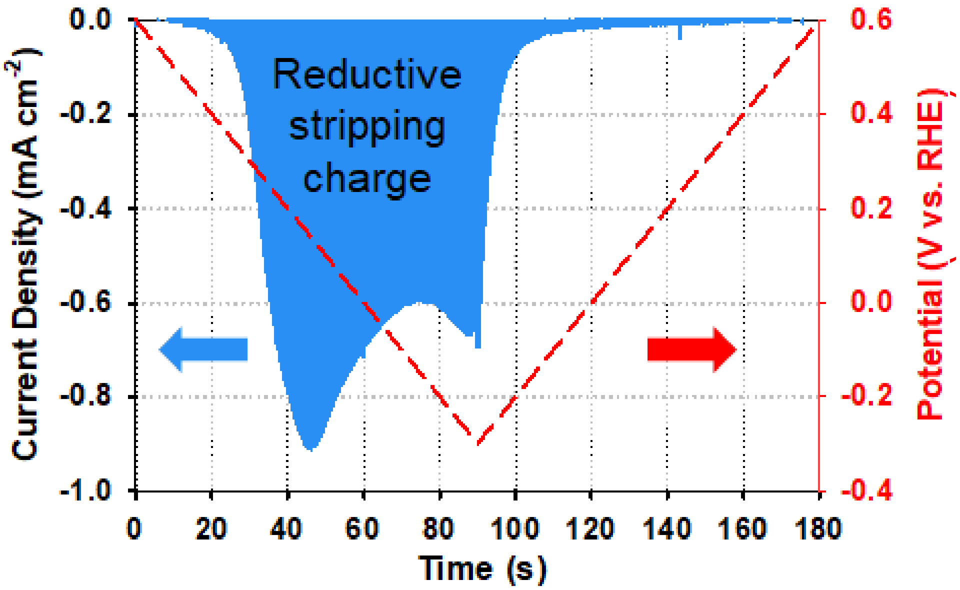
Molecular probe (MP) poisoning

Reductive MP stripping



RDE: 0.6 mg/cm^2 (AD)Fe-N-C; 0.5 M H_2SO_4; 1600 rpm; 25ºC; Ag/AgCl (3 M KCl) reference electrode; graphite counter electrode; LSV 10 mV/s





Highlight: NO_2^- successfully used as a molecular probe for (AD)Fe-N-C catalyst

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

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

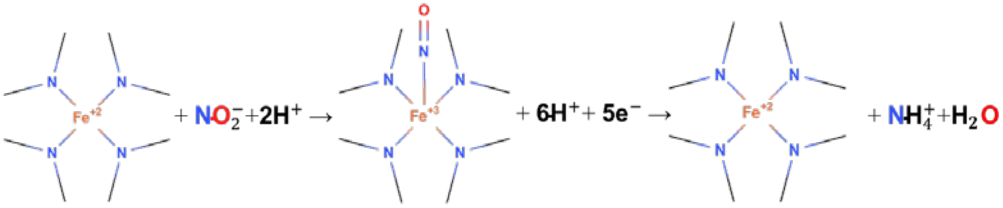
$$MSD\left(sites\ cm^{-2}\right)=\frac{Q_{strip}}{nSA_{DL}F}$$

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

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 = 1.7 e^- $site^{-1}$ s^{-1} at 0.80 V

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



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

Area Specific Charge (µC cm^{-2})	**Active Site Concentration*** (sites cm^{-2})	**Active Sites per Atom**
2.35	2.99 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*

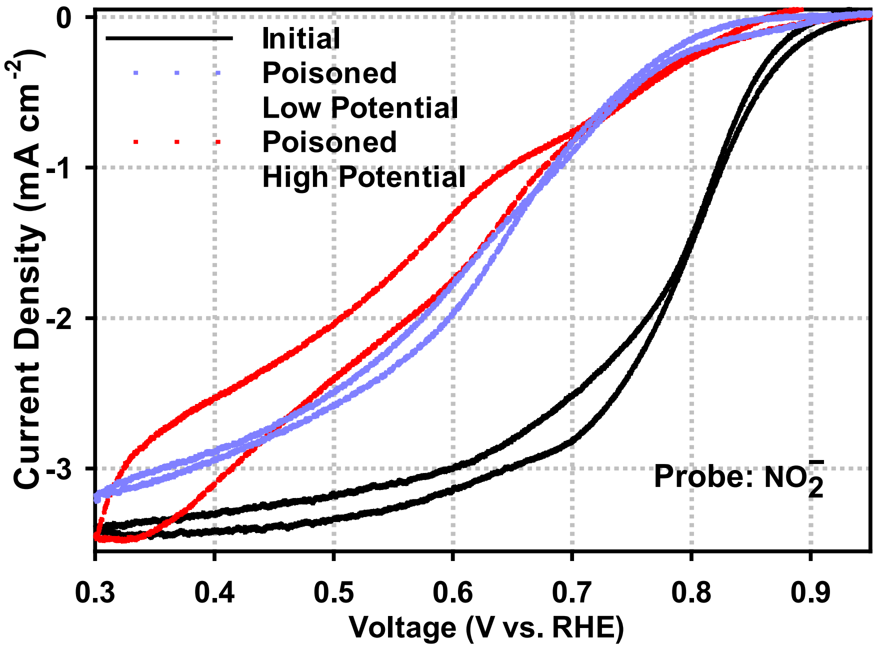
Highlight: Method for estimating active-site density demonstrated

"…just what is the active site, how many of them are there, and why do they stop working?" – **Development of an active site characterization and quantification technique will contribute to the understanding of the active site structure as well as its degradation or poisoning.**

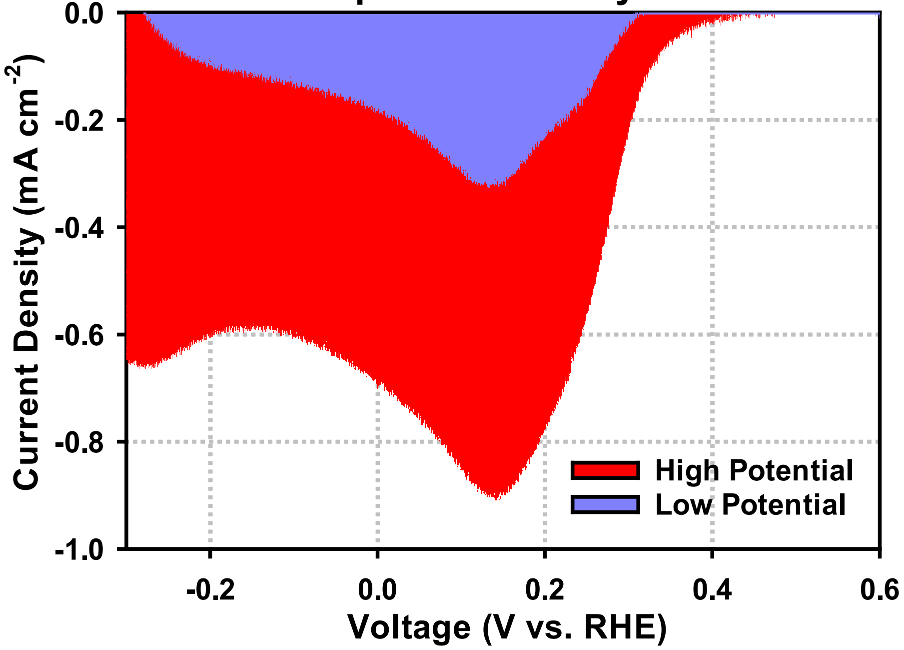
Molecular Probes: Effect of Applied Potential on Poisoning

RDE: 0.6 mg/cm^2 (AD)Fe-N-C; 0.5 M H_2SO_4; 1600 rpm; 25ºC; Ag/AgCl (3 M KCl) reference electrode; graphite counter electrode; LSV 10 mV/s

(AD)Fe-N-C catalysts poisoned at low and high potentials



Reductive stripping charge for poisoned catalysts



Scattering Path	Coordination Number	R (Å)
Fe-N (NO)	1.0 ± 0.6	1.759 ± 0.061
Fe-N (pc)	3.1 ± 0.9	1.964 ± 0.027
Fe-Fe	0.9 ± 0.3	2.493 ± 0.023

- Similar $E_{½}$ decrease for poisoning at low and high potentials
- Hysteresis loop observed for high potential poisoning and increased reductive stripping charge might indicate difference in poisoning mechanism at high and low potentials
- EXAFS shows addition of Fe-NO coordination with nitrite exposure at low potentials and no change in Fe coordination with exposure at high potentials

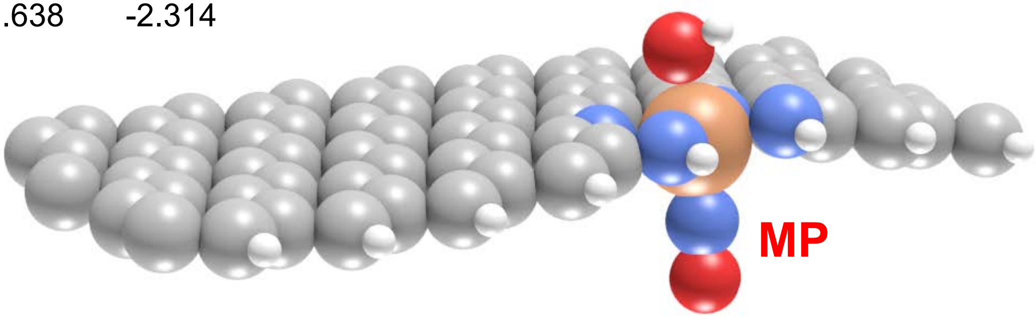
Molecular Probes: Probes and Active-Site Poisons from DFT

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 **(FY18 Q2 QPM)**

Site Name	**CO BE (eV)**	**NO BE (eV)**	**CI 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

"Computation and modeling are not integrated with the experimental efforts" – **Modeling is key for understanding specificity of probe molecules used in experimental efforts to quantify active-site density in synthesized and degraded materials.**

(AD)Fe-N-C Electrode: ORR Kinetics

MEA composition and fabrication

- Cathode catalyst: AD(Fe)-N-C, ~3.8 $mg_{catalyst}cm^{-2}$
- CCMs: hand-painted (HP) or ultrasonic-sprayed (US), no hot-pressing
- Anode: 0.2 $mg_{Pt}cm^{-2}$, commercial Pt on HSAC

Distributed ORR kinetic model, 100% active sites

- $\alpha n = 0.5$, b =140 mV dec^{-1} at 80 °C
- For Tafel kinetics, ORR (η_s^c) and CCL Ohmic (iR_Ω^c) overpotentials treated separately

$$\eta_c = E_N - Ecell - iR_\Omega^m - \eta_s^a$$

$$E_N = E_{N0}(T) + \frac{RT}{nF} ln(\frac{P_{O_2}^{1/2} P_{H_2}}{P_{H_2O}})$$

$$\eta_c = \eta_s^c + iR_\Omega^c\,(\frac{i\delta_c}{b\sigma_c})$$

$$i = i_0 e^{\frac{\alpha nF}{RT}\eta_s^c}$$

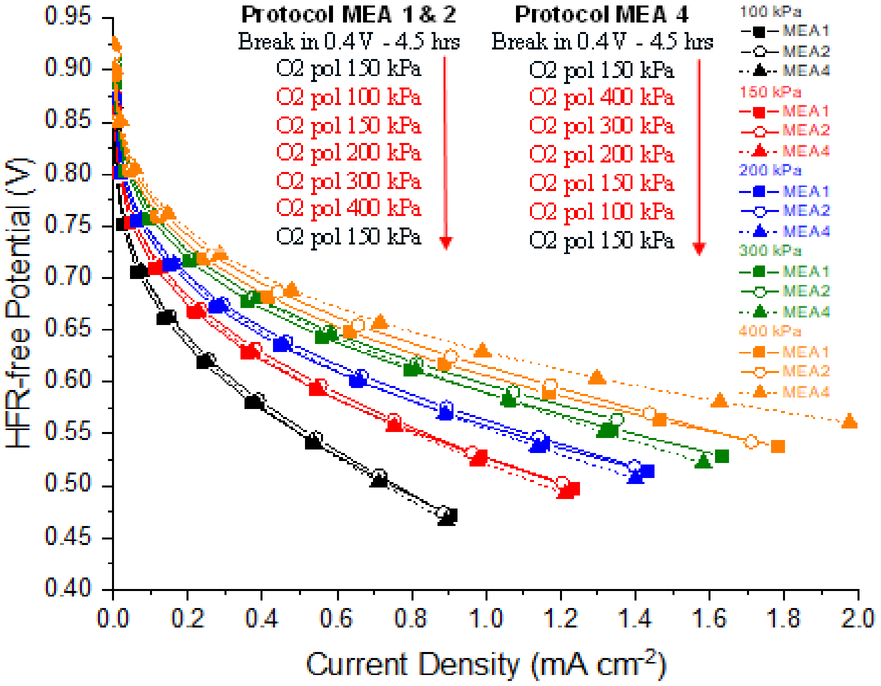
η_c: cathode overpotential

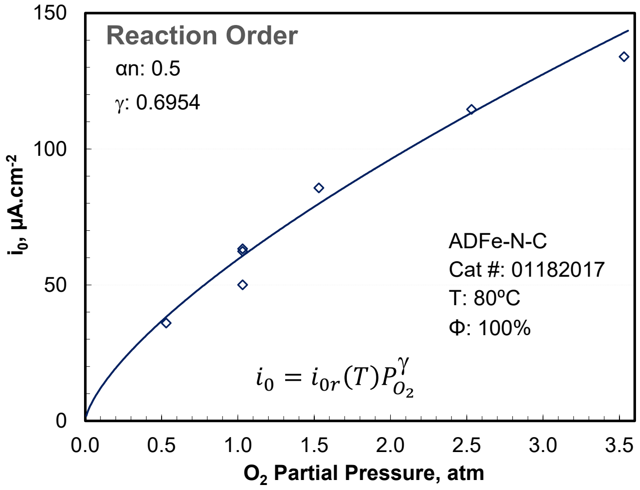
η_s^c: ORR kinetic overpotential

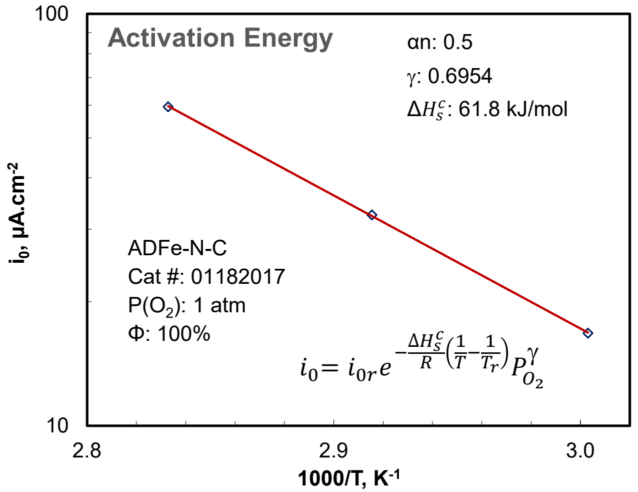
δ_c: electrode thickness

σ_c: ionomer conductivity

b: $RT/\alpha nF$







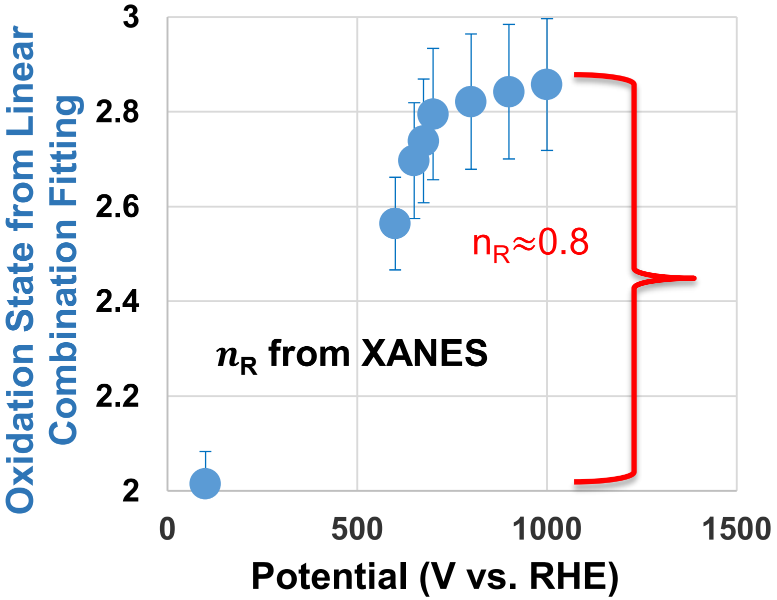
(AD)Fe-N-C Electrode: Potential Dependence of ORR Kinetics (MEA)

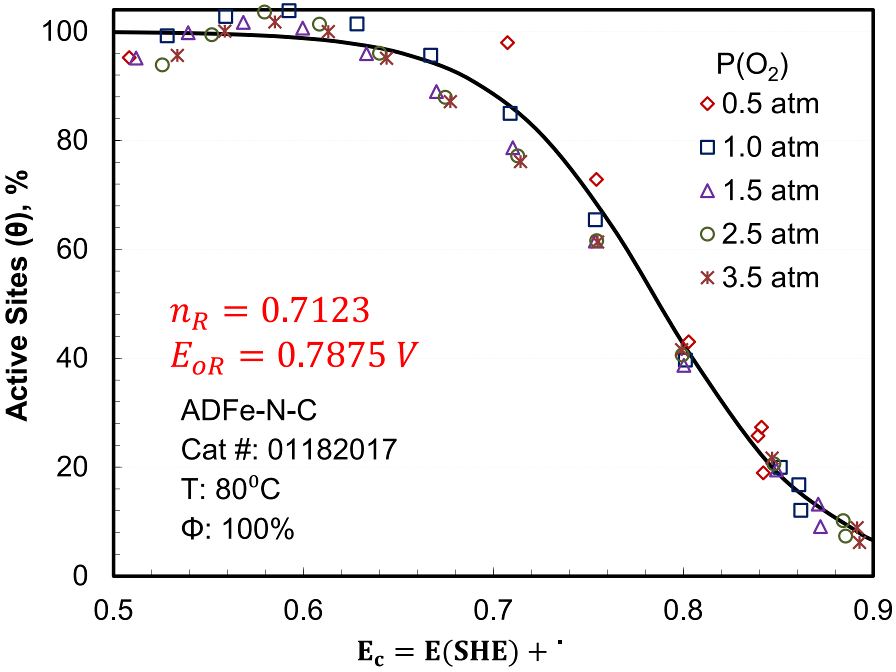
- Available active sites (θ) depending on potential*

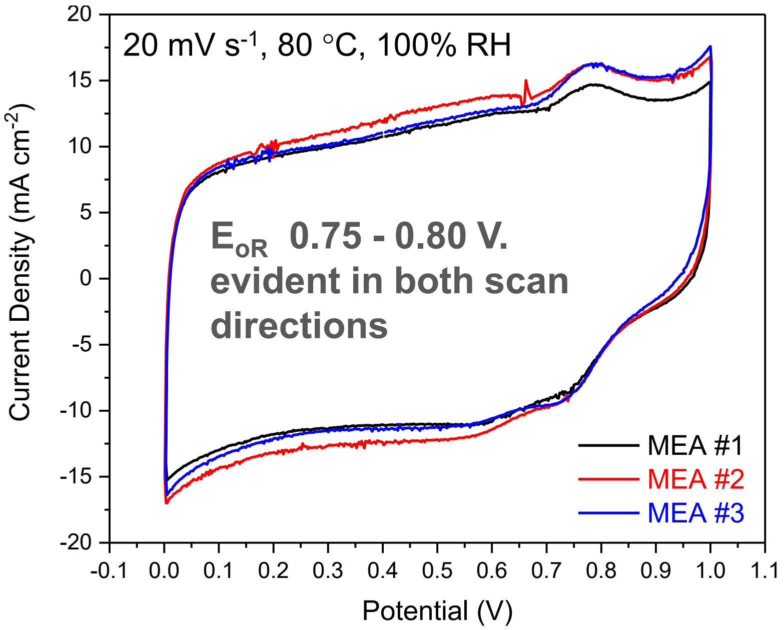
$$i + i_s = i_0 \theta e^{\frac{\alpha n F}{RT}\eta_s^c} \qquad \theta = \frac{1}{1 + e^{\frac{n_R F}{RT}(E_c - E_{0R})}}$$

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+})*



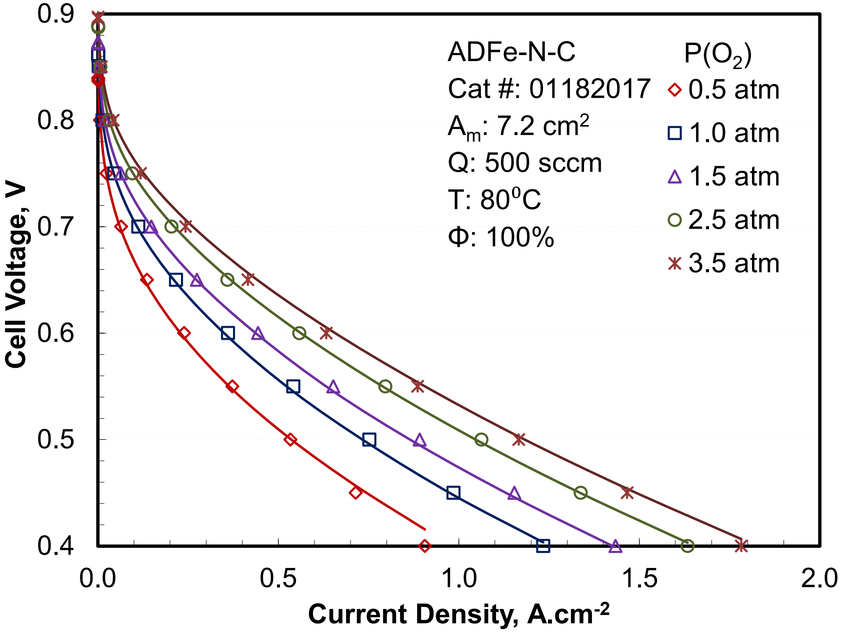


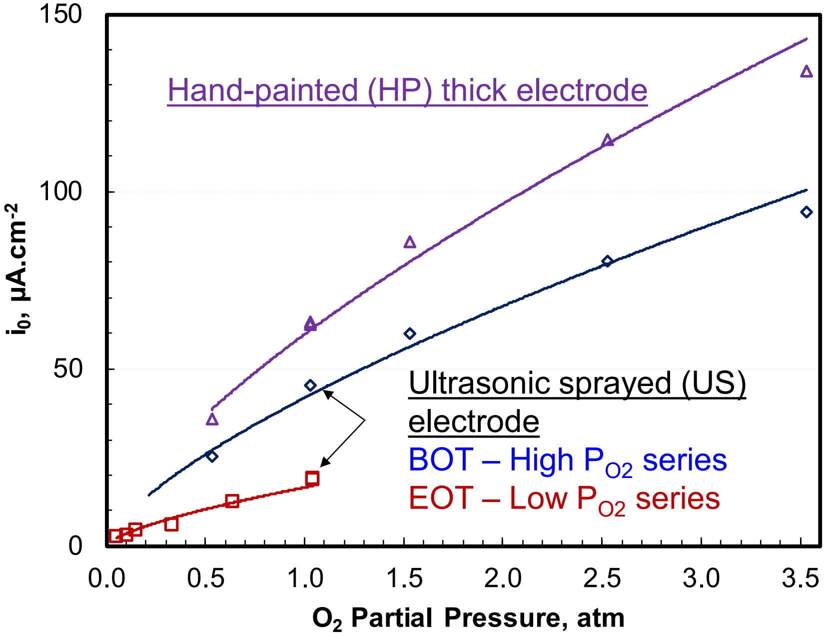


E_{oR} 0.75 - 0.80 V. evident in both scan directions

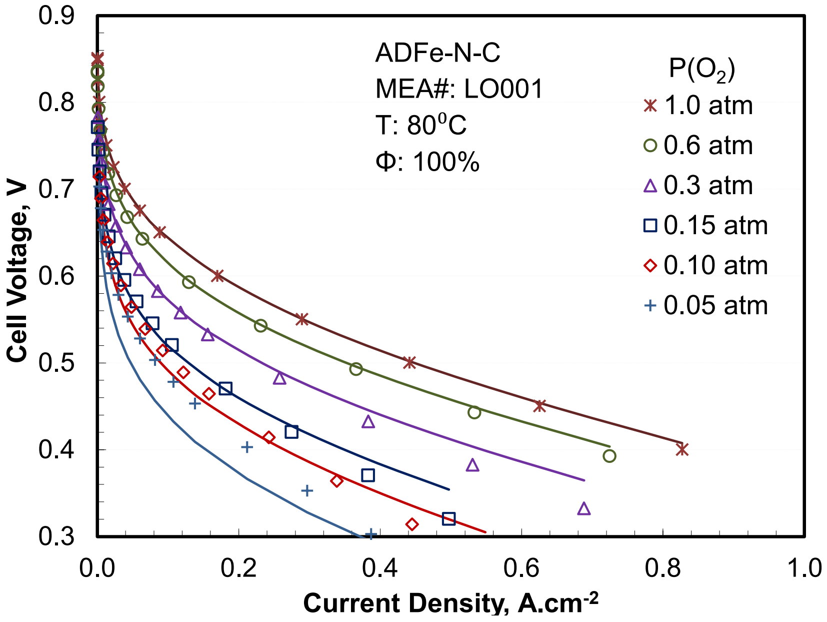
* Q. Jia *et al.*, *ACS Nano*, 2015, **9**, 12496-12505
J. Li *et al.*, *J. Am. Chem. Soc.*, 2017, **139**, 1384−1387

(AD)Fe-N-C Electrode: Kinetic Model Validation



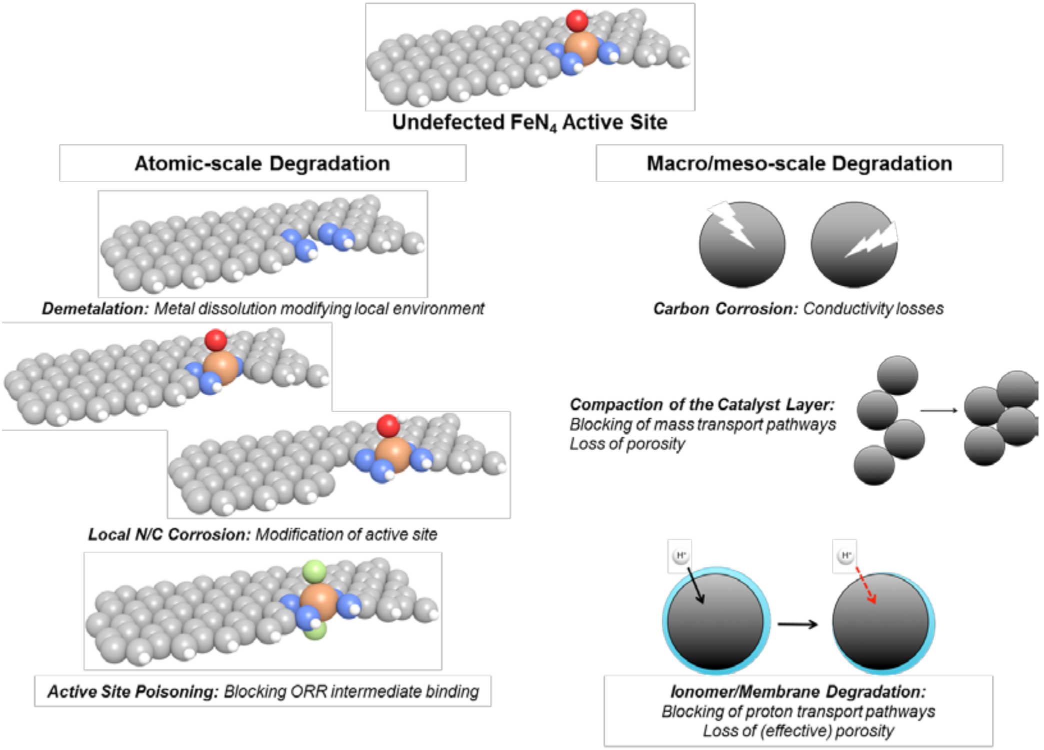


- Similar kinetic performance of MEAs made by HP and US, when adjusted for loading difference, can be described by the same kinetic constants as previously derived
- HP and US MEAs performing similarly performance after correcting for differences in HFR (66% higher for US) and CCL resistance (67% lower for US)
- The kinetic model also applicable at lower P_{O2} (0.6 to 0.05 atm pure oxygen) after accounting for degradation



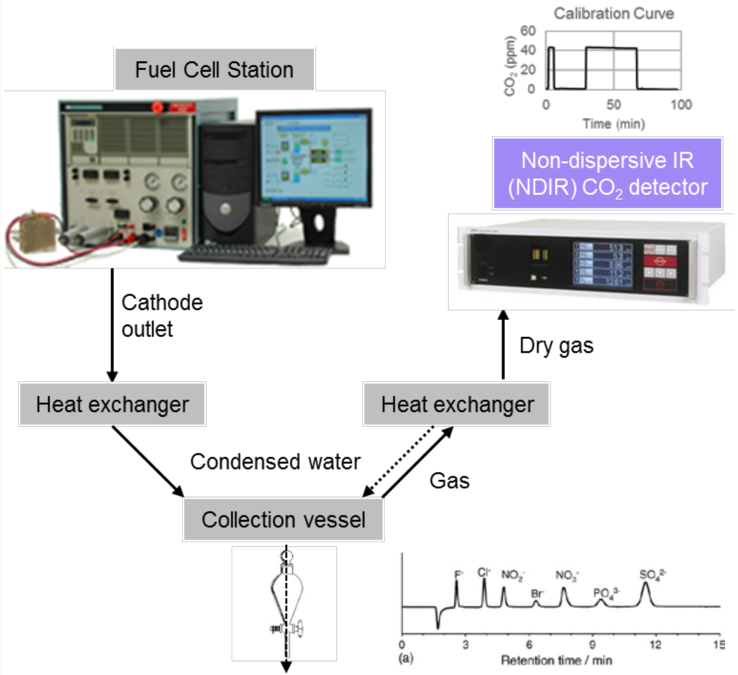
Catalyst Durability: Understanding Degradation Mechanisms

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

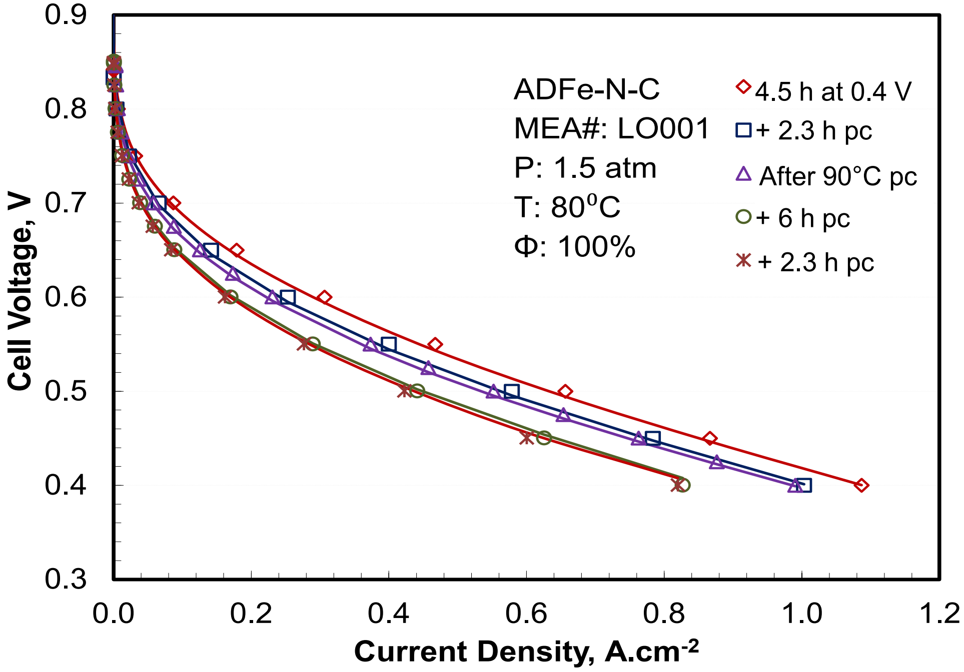


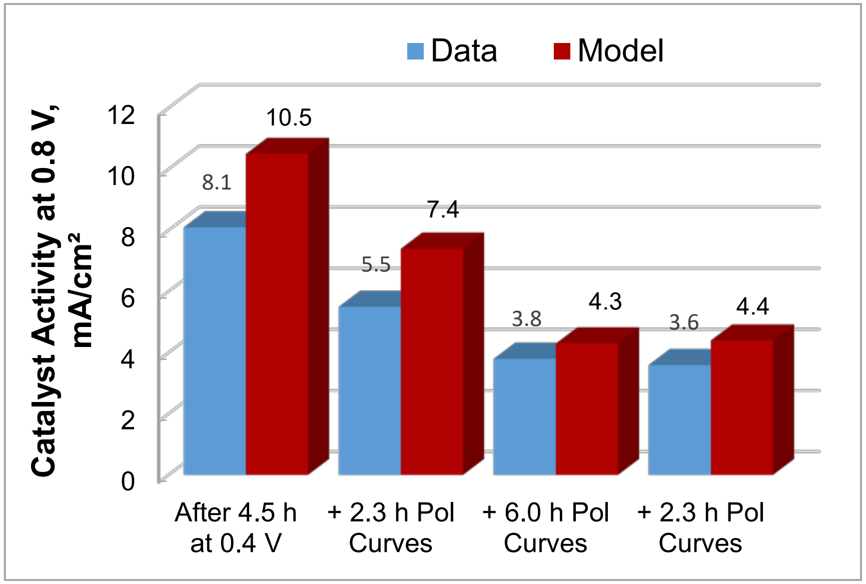
- Ion Chromatography (F^-, SO_4^{-2})
- Inductively Coupled Plasma (Transition metal content)

"The only minor concern is that some of the initial focus seems to be on improving activity; however, until degradation is well-understood, activity and durability should be examined in parallel to prevent development of really good catalysts that may never last more than 100 hours." – **We have implemented a system for parallel studies of F^-, CO_2, and transition metal (TM) emissions at various operating conditions in order to gain better understanding about possible degradation mechanisms of PGM-free catalysts.**

Catalyst Durability: Degradation Studies in Fuel Cell Operating on O_2

(AD)Fe-N-C catalyst degradation in a H_2/O_2 cell during extended testing

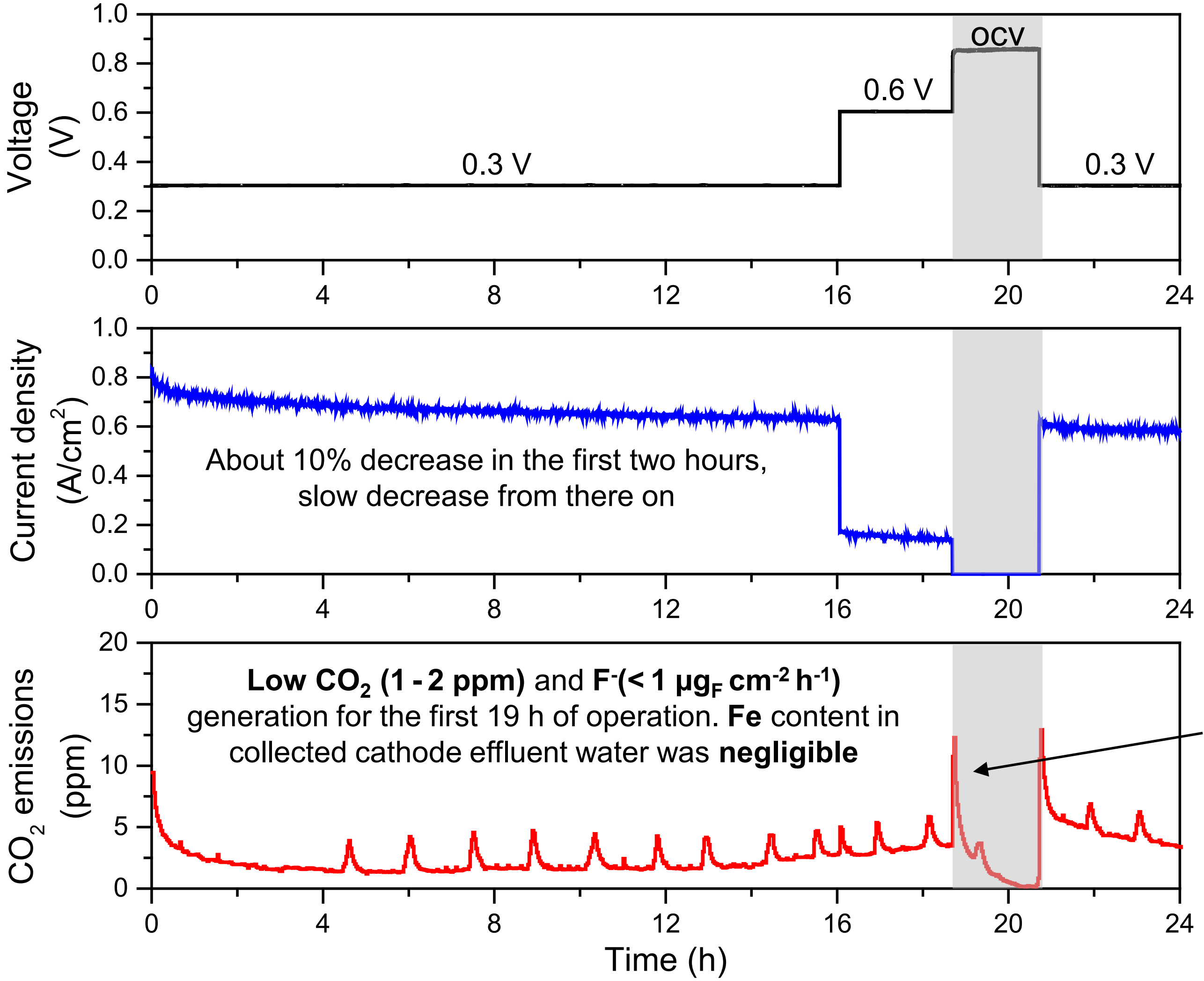




- (AD)Fe-N-C electrode layer exhibiting signs of performance degradation after extended testing involving voltage hold and polarization-curve testing
- More than 50% drop in ORR kinetic activity over 15 h of voltage testing
- Polarization curve modeling pointing to the majority of performance loss due to a loss in ORR kinetics (50 mV increase in kinetic overpotential and 10 mV increase in mass transfer overpotential at 0.8 A cm^{-2})

Catalyst Durability: Degradation Studies in Fuel Cell Operating on Air

Anode: 0.2 $mg_{Pt}\,cm^{-2}$ Pt/C H_2, 200 sccm, 1.0 bar H_2 partial pressure; **Cathode**: **(CM+PANI)-Fe(Zn)-C**, air, 300 sccm, 1.0 bar air partial pressure; **Cell**: Nafion®212; 5 cm^2; 80 ºC; 50% RH, constant voltage: 0.3 V, 0.6 V, OCV



About 10% decrease in the first two hours, slow decrease from there on

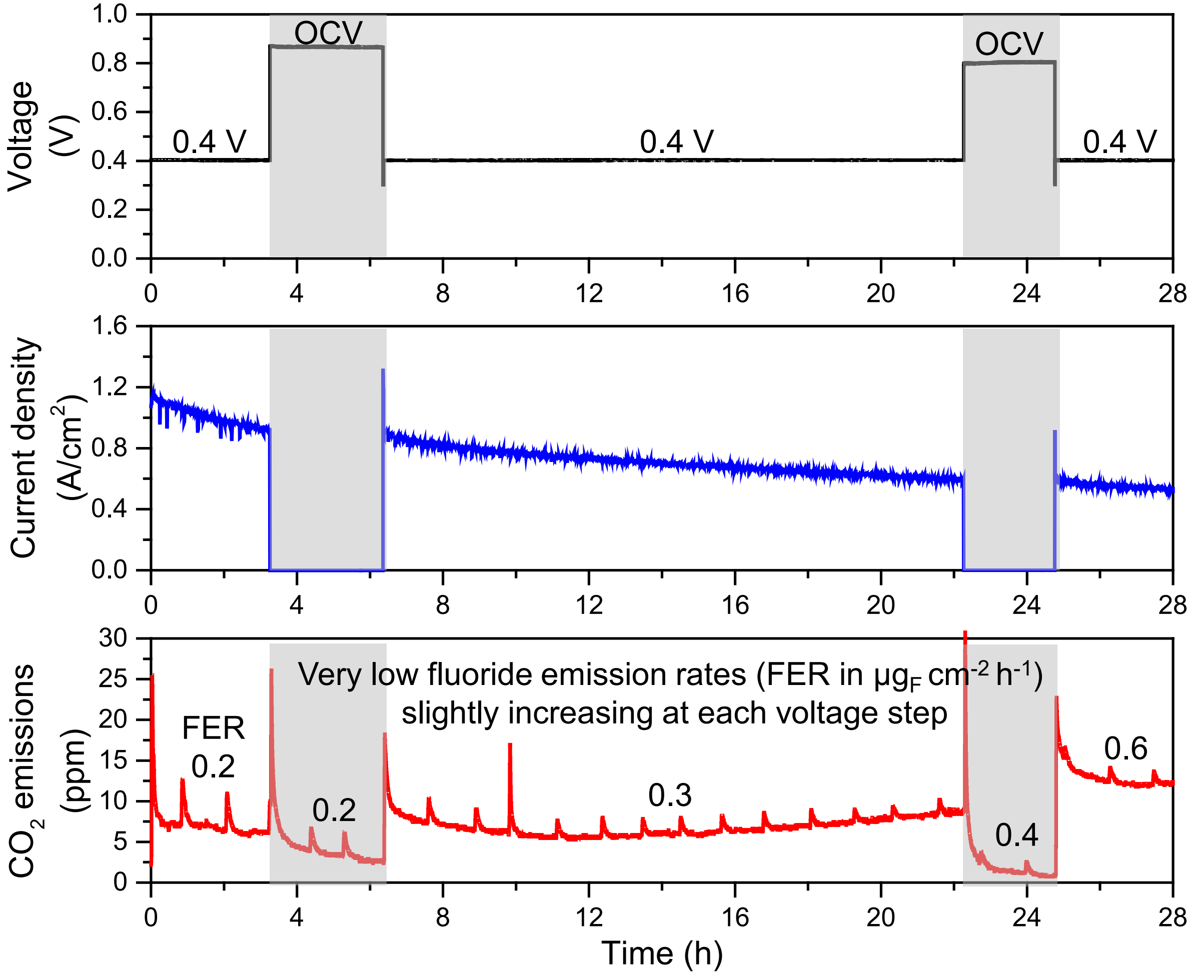
Low CO_2 (1 - 2 ppm) and **F^-(< 1 $\mu g_F\,cm^{-2}\,h^{-1}$)** generation for the first 19 h of operation. **Fe** content in collected cathode effluent water was **negligible**

Initial sharp increase in CO_2 generation at OCV, but eventually decreased to 0 ppm, F^-(~0.5 $\mu g_F\,cm^{-2}\,h^{-1}$)

Highlight: Low CO_2 and F^- emissions observed during operation on air

Catalyst Durability: Degradation Studies in Fuel Cell Operating on O_2

Anode: 0.2 $mg_{Pt}\ cm^{-2}$ Pt/C H_2, 200 sccm, no backpressure; **Cathode**: **(CM+PANI)-Fe(Zn)-C**, O_2, 200 sccm, no backpressure; **Cell**: Nafion®211; 5 cm^2; 80 ºC; 50% RH, constant voltage: 0.4 V, OCV



Very low fluoride emission rates (FER in $\mu g_F\ cm^{-2}\ h^{-1}$) slightly increasing at each voltage step

- Increased CO_2 generation, from **1-2** on air to **6-12** ppm, when operated on O_2
- **Highlight:** Relatively low FER (< 1 $\mu g_F\ cm^{-2}\ h^{-1}$) pointing to the catalyst rather than membrane degradation as a primary source of detected CO_2

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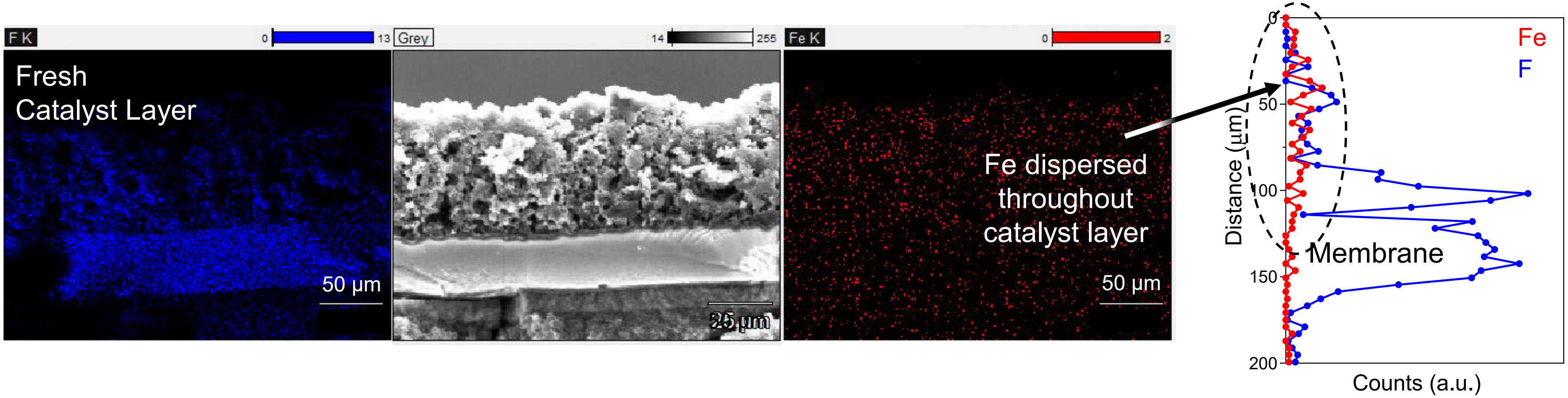
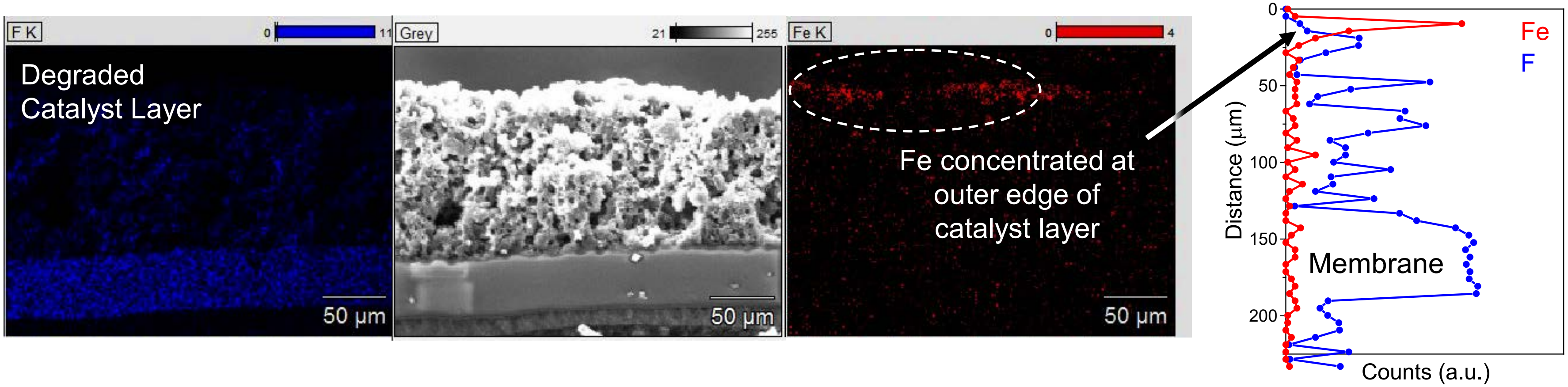
Catalyst Durability: Characterization of Degraded Catalyst Layer

(CM+PANI)-Fe(Zn)-C

Line scans



Fe dispersed throughout catalyst layer



Fe concentrated at outer edge of catalyst layer

“While very important, the project does not appear to have a strong apparent focus on addressing the key durability concerns with carbon-based structures.” – **Preliminary studies suggest de-metalation as the main mechanism for activity loss of (CM+PANI)-Fe(Zn)-C**

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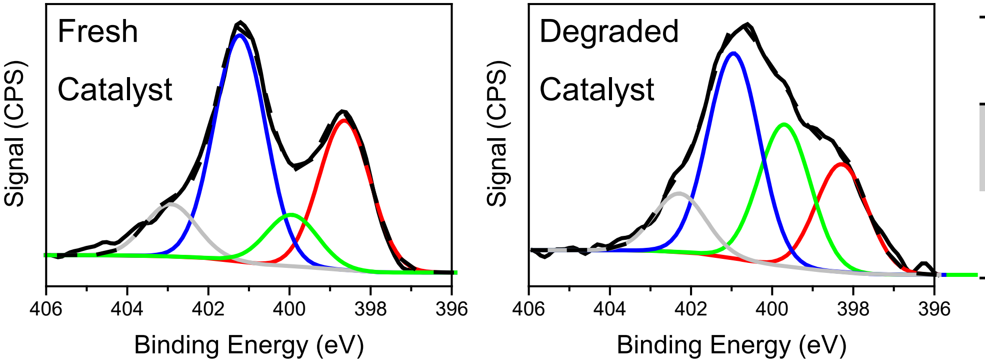
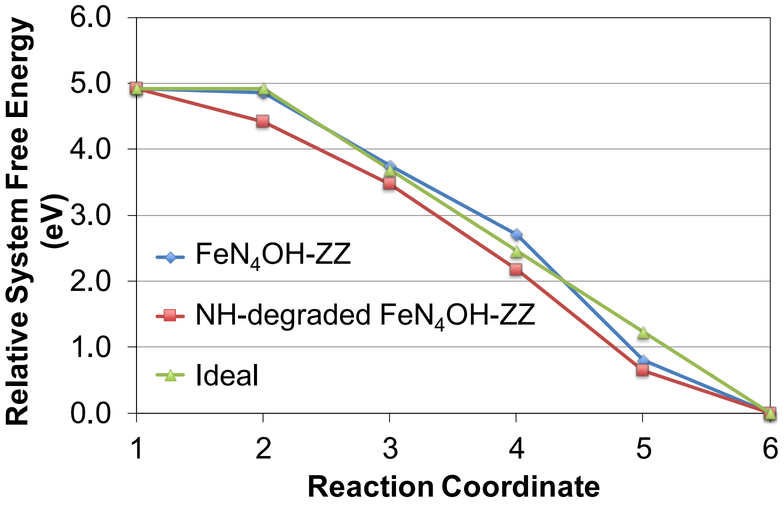
Catalyst Durability: Understanding through Experiment and Modeling

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
Degraded catalyst	**21.1**	27.6	39.9	11.4

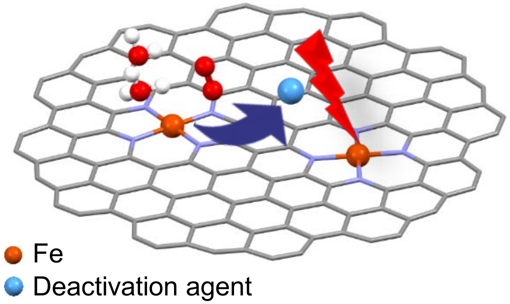
- Durability descriptor (knock on displacement threshold energy, KODTE) suggesting active site degradation *via* N removal
- Limiting potential calculation indicating significant decrease in activity following N removal (U_L = 0.80 V → 0.64 V *vs.* CHE)
- Effect of degraded structures on probe molecule binding underway for MP specificity as well as other degradation mechanisms (**FY18 Q2 QPM**)



- **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)

Catalyst Durability: Kinetic Models for Degradation in MEA

Two-step (autocatalytic) degradation



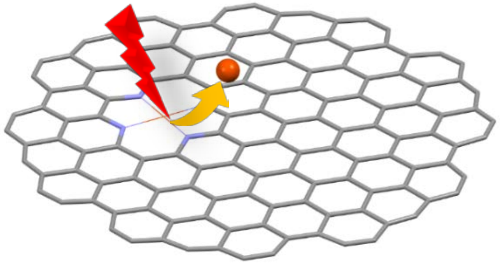
$$\text{Reactants} \xrightarrow{k_1} \text{Deactivation agent (D)}$$

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

Logistic decay:

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

1st order degradation

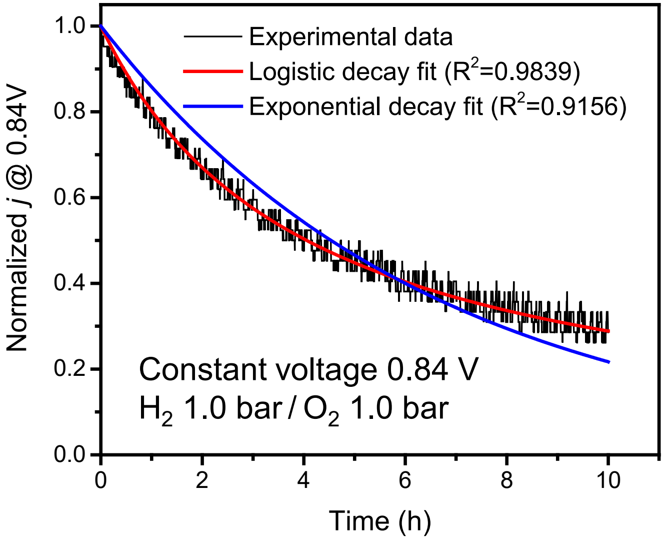


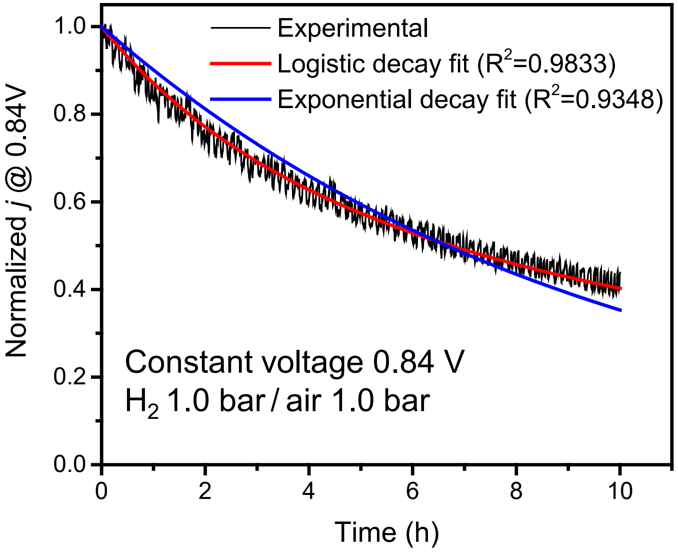
$$\text{AS} \xrightarrow{k} \text{DS}$$

Exponential decay:

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

Anode: 0.3 $\mathrm{mg_{Pt}\,cm^{-2}}$ Pt/C H_2, 200 sccm, 1.0 bar H_2 partial pressure; **Cathode: (CM-PANI)-Fe-C(Zn)** *ca.* 4.8 mg $\mathrm{cm^{-2}}$ 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 $\mathrm{cm^2}$, 80 °C





- Two kinetic models (details in slide 51) with single parameter of apparent degradation rate constant, k_app
- **Highlight:** Autocatalytic degradation mechanism suggested by better fitting of logistic decay model

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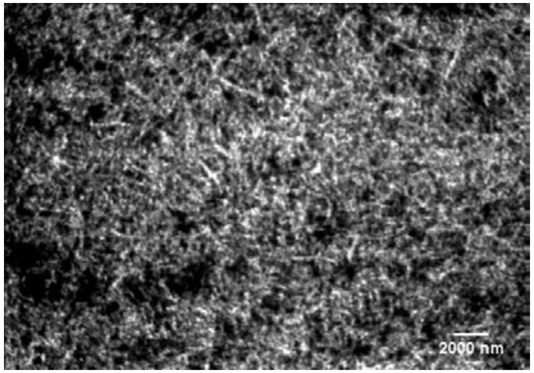
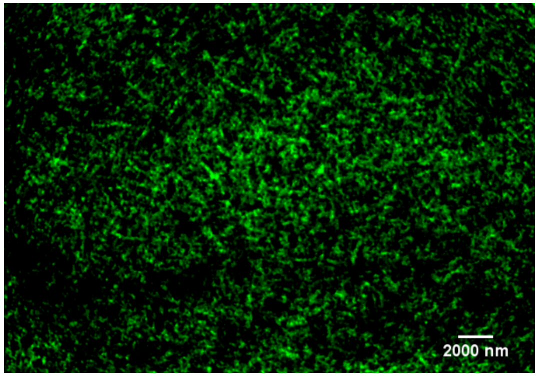
(AD)Fe-N-C Electrodes: Structural Characterization

X-ray nano-tomography and TEM used to resolve distribution of pores, carbon/catalyst, and ionomer in electrode, as input to transport model, and to guide optimization of electrode fabrication

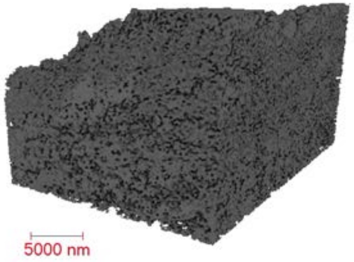
Phase Contrast Nano-XCT



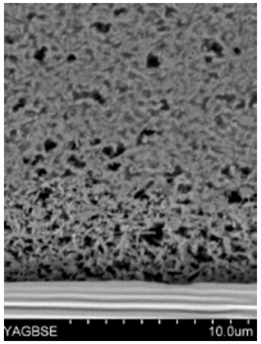
Absorption Contrast Nano-XCT



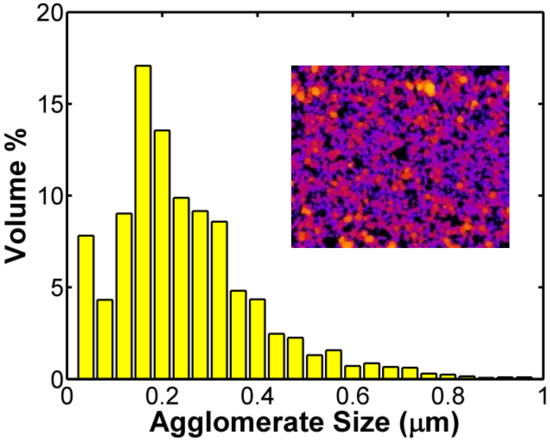
Nano-XCT Segmented Volume



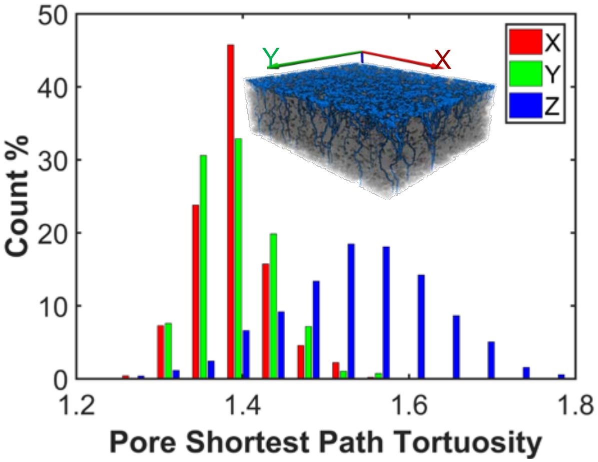
TEM



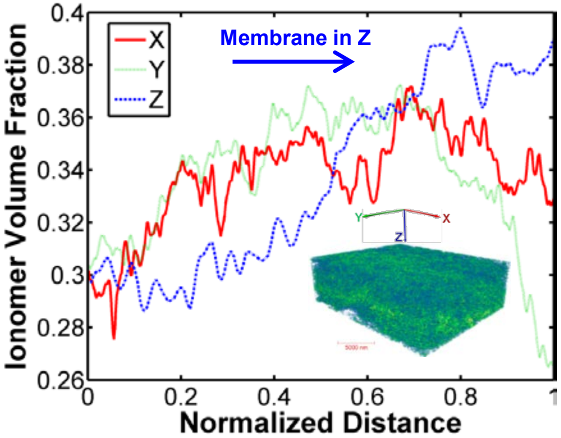
Bi-modal solid agglomerate size distribution corresponding to prismatic geometry of carbon plates in the electrode



Significantly higher tortuosity in thickness direction (Z), compared to in-plane directions (X,Y)



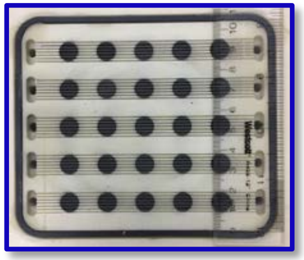
Non-uniform electrode composition; ionomer volume graded towards the membrane boundary



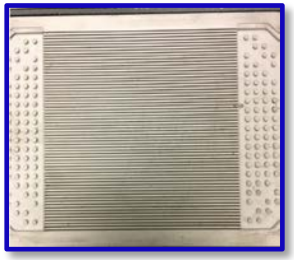
Capability Development: Combinatorial Fuel Cell Testing

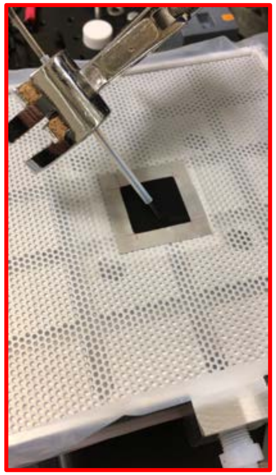
NuVant 25 Segmented-Electrode Hardware

Cathode

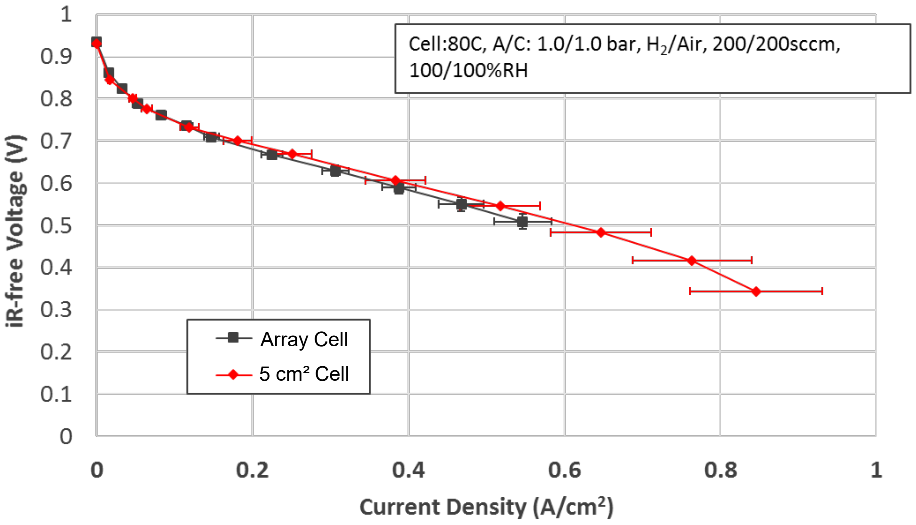


Anode





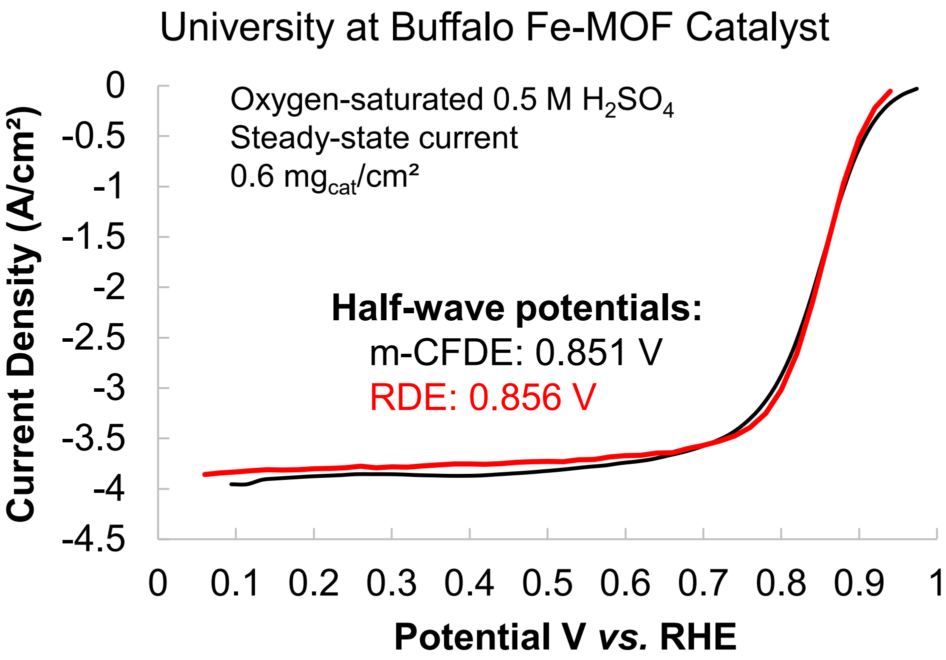
Anode: 0.2 $mg_{Pt}\,cm^{-2}$ Pt/C onto 29BC GDL; **Cathode:** (CM+PANI)-Fe(Zn)-C on 29BC GDL, Membrane: Nafion® XL



- **FY’17 Q4 QPM:** Demonstrate current densities in the 25-electrode high-throughput MEA test setup for all 25 electrodes within 10% of those in a standard 5 cm² test cell using identical PGM-free electrode compositions in both cells
- Array electrode performance falling within 10% of the 5 cm² single cell performance at < 0.5 A/cm²
- Differences between 5 cm² cell and array cell performance due to edge effects and non-uniform compression of the 25 GDEs. Addressing these issues by:
  - ✓ Developing system for automated ink deposition onto heated membrane to make 25-electrode catalyst-coated membrane
  - ✓ Utilizing electrodes larger than GDLs to minimize edge effects
  - ✓ Utilizing staged gasketing to improve compression uniformity

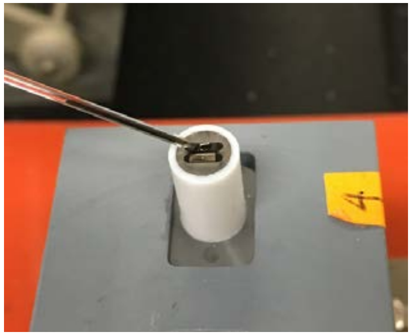
Capability Development: Combinatorial Screening of Catalyst Activity

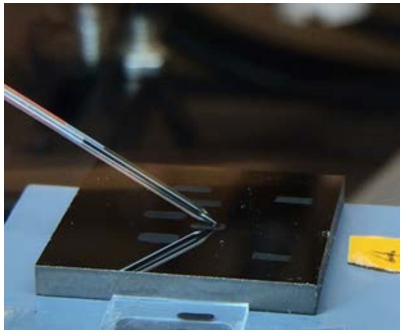
- **FY'18 Q2 QPM**: Automated deposition of catalyst-ionomer inks on multi-channel flow double electrode (m-CFDE) glassy carbon electrodes demonstrated to result in ORR half-wave potentials using m-CFDE within 10 mV of those measured using RDE
- **Last year's status:** m-CFDE $E_{½}$ agreeing with RDE $E_{½}$ to within 30 mV
- **This year:** Developed system for automated deposition of inks resulting in $E_{½}$ agreement between m-CFDE and RDE of 5 mV
- Automated deposition of inks with programmable XY stage (resolution: 0.04μm) and nanoliter injector (minimum injection rate: 1 nL/sec)


University at Buffalo Fe-MOF Catalyst

Oxygen-saturated 0.5 M H_2SO_4
Steady-state current
0.6 mg_{cat}/cm^2

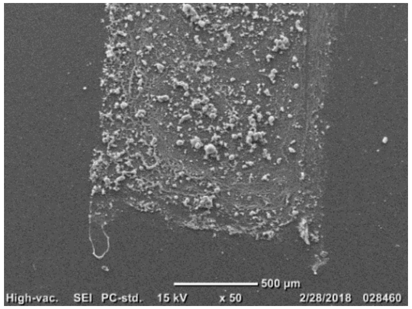
Half-wave potentials:
m-CFDE: 0.851 V
RDE: 0.856 V

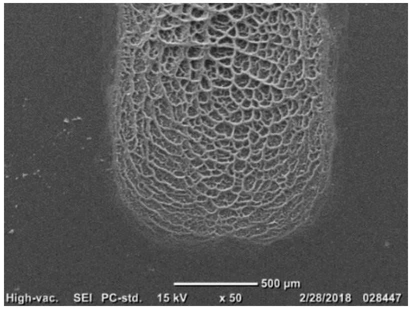




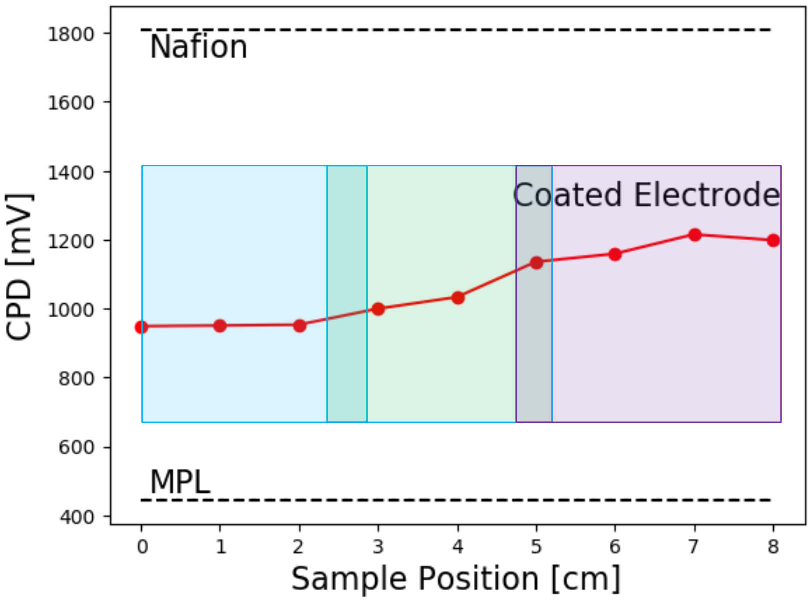
Manual ink deposition using micro-liter pipet

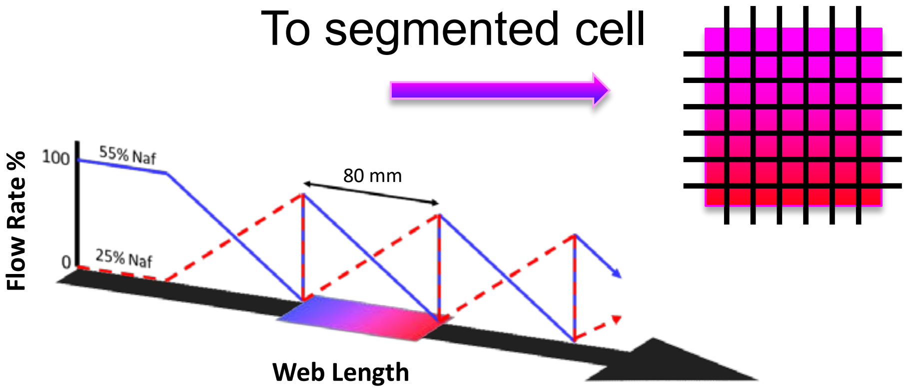
Automated deposition using nano-liter injector

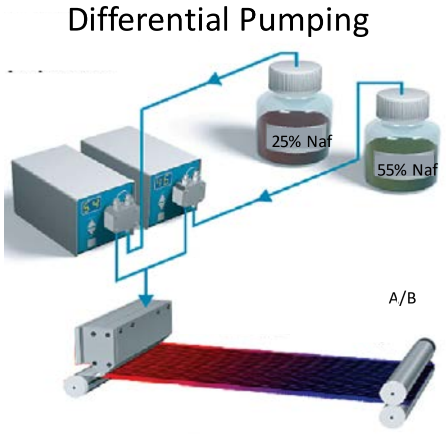




Capability Development: Gradient Composition Electrode Fabrication







- Fabricated electrode with catalyst/ionomer gradient over 8 cm length
- Measured contact potential difference (CPD) showing expected trend, validating Kelvin probe as a quick screening tool to quantify ionomer gradients
- **Next step:** Spatially-resolved performance testing using segmented cell

Collaboration and Coordination

ElectroCat members: Four national laboratories with highly complementary skills and capabilities:

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

ElectroCat FOA projects support:

- Carnegie Mellon University (Shawn Litster*), Advanced PGM-free Cathode Engineering for High Power Density and Durability* – XAS, microscopy, molecular-probe catalyst characterization
- Giner (Hui Xu), *Durable Mn-based PGM-Free Catalysts for Polymer Electrolyte Membrane Fuel Cells* – microscopy and XAS characterization, MEA design and fabrication, fuel cell testing
- Greenway Energy (Prabhu Ganesan), *PGM-free Engineered Framework Nano-Structure Catalysts* – multi-scale modeling, MEA fabrication, fuel cell testing, catalyst synthesis
- Pacific Northwest National Laboratory (Yuyan Shao), *Highly Active and Durable PGM-free ORR Electrocatalysts through the Synergy of Active Sites* – F^- and CO_2 emissions, microscopy and XAS characterization

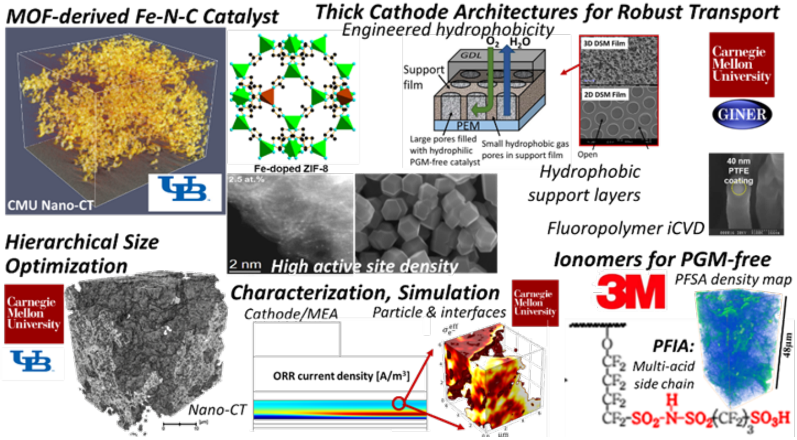
No-cost collaborators, not directly participating in ElectroCat:

- University at Buffalo (SUNY), Buffalo, New York – novel PGM-free catalyst synthesis
- Pajarito Powder, Albuquerque, New Mexico – catalyst scale-up, PGM-free electrode design, catalyst commercialization
- Technical University Darmstadt, Germany – catalyst characterization by Mössbauer spectroscopy and synchrotron X-ray techniques
- CEA – LITEN/DEHT/SCGE, Grenoble, France – MEA optimization and characterization
- Colorado School of Mines, Golden, Colorado – XPS characterization
- University of Warsaw, Poland – role of graphite in PGM-free catalyst design
- Institut national de la recherche scientifique (INRS), Montreal, Canada – PGM-free catalyst design
- Chevron Energy Technology Company, Richmond, California *–* patent application with LANL on non-electrochemical uses of PGM-free carbon-based materials

Collaboration and Coordination: FOA Projects added in FY’17

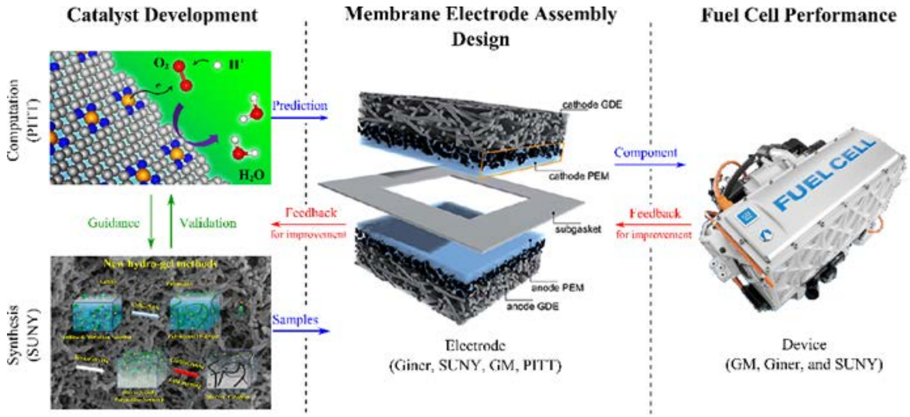
Carnegie Mellon University

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



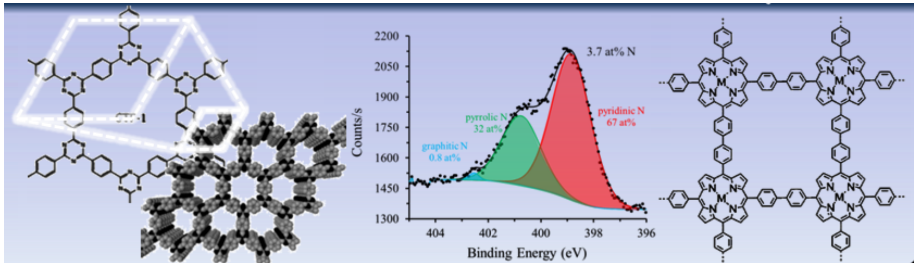
Giner Inc

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



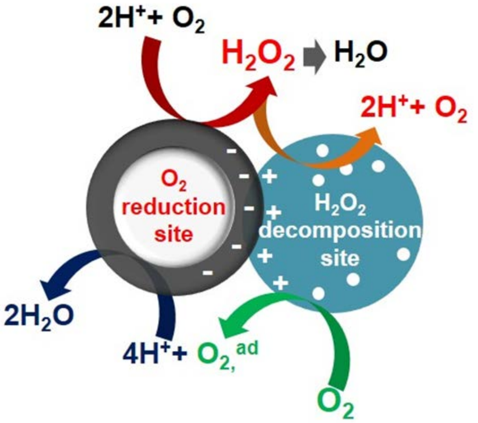
Greenway, LLC

PGM-free Engineered Framework Nano-Structure Catalysts



Pacific Northwest National Lab

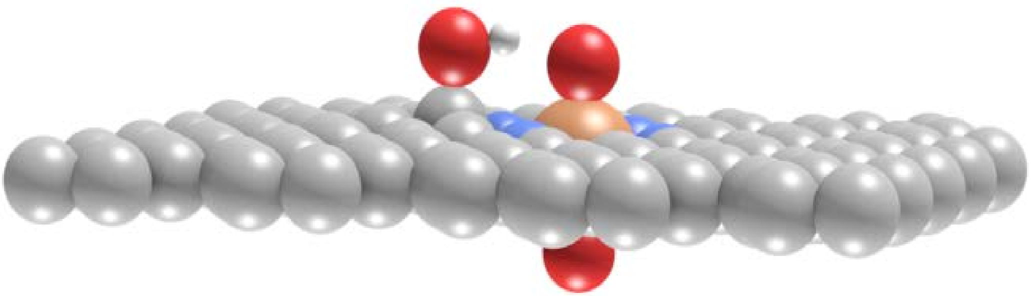
Highly Active and Durable PGM-free ORR Electrocatalysts through the Synergy of Active Sites



FOA Project Support: Greenway Energy (Modeling Support)

Aiding in target site identification for synthesis *(Greenway Energy project; with Professor Alfred B. Anderson at CWRU leading modeling effort)*

- Comparison of Computational Hydrogen Electrode (CHE) and Linear Gibbs Energy Relationship (LGER) computational approaches to ORR activity
- Effect of altering exchange-correlation potentials on results
- Consideration of FeN_4 as Fe(II), FeN_4OH as Fe(III), and FeN_4O as Fe(IV)
- Consideration of proposed OOH dissociation to O + OH with OH binding possible on neighboring C
- Addition of C-neighbor as a possible poisoning site with alternative pathway



Highlight: Qualitative agreement between activity descriptors; Possible new reaction pathway for bulk-hosted structures determined; bulk-hosted Fe(IV) structures with new reaction pathway have promising calculated ORR activity descriptors with both models

"Experimental efforts from catalyst activity improvement to active site identification can all benefit from appropriate modeling work." – **Example of a collaborative effort between ElectroCat and FOA projects, this one targeting theoretical identification of the ORR active sites to guide catalyst synthesis.**

Remaining Challenges and Barriers

- 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

Proposed Future Work

- **ElectroCat Development**
  - ✓ Demonstrate and/or utilize recently selected national laboratory capabilities
  - ✓ Incorporate collaborators from DE-FOA-0001874 into ElectroCat and coordinate activities of all ElectroCat partners
  - ✓ Populate Data Hub with datasets from national laboratory and FOA partners; implement automated methods for data capture and publication
  - ✓ Develop automated artificial intelligence and machine learning techniques for data correlation and experimental design
- **Improvement in Performance and Durability of Catalysts and Electrodes**
  - ✓ Further identify primary factors governing the durability of PGM-free catalysts and electrodes and develop means to prevent performance degradation
  - ✓ Advance fuel cell performance of catalysts by maximizing volumetric density and accessibility of active sites, through **(i)** the development of novel synthesis approaches, using information from *in situ* characterization techniques and **(ii)** optimization of hierarchical pore-size and ionomer distribution, using information from imaging, X-ray scattering, and multi-scale modeling efforts
  - ✓ Verify synthesis and activity of promising materials (*e.g.*, 900 °C, 5 at% Fe) identified in initial screening, scale-up synthesis, and test fuel cell performance and durability
  - ✓ Continue to develop surface-specific methods for the ORR active-site determination (*e.g.*, probe molecules)

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

Summary

- **ElectroCat Development and Communication**
  - ✓ National laboratories are supporting four newly-established FOA projects with 10 capabilities
  - ✓ New national laboratory capabilities were submitted and reviewed in April 2018, and selected by DOE and Steering Committee
  - ✓ A publically-accessible data management hub for national laboratory and FOA project datasets was developed and launched (https://datahub.electrocat.org)
  - ✓ Nine papers published, including one in *Science,* 28 presentations given (11 invited)
- **Progress in Performance**
  - ✓ ElectroCat FY'17 Annual Milestone of 20 mA cm^{-2} at 0.90 V (H_2/O_2, iR-free) exceeded
  - ✓ 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 2017 AMR
  - ✓ Achieved half-wave potential ($E_{½}$) of 0.85 V with (AD)Fe-N-C in RDE testing, an increase of 0.02 V over the 2017 status
  - ✓ PGM-free catalyst activity in an MEA: 21 mA/cm^2 at 0.90 $V_{iR\text{-}free}$ and 0.044 A/cm^2 at 0.88 V
- **Characterization and Capability Development**
  - ✓ Determined that FeN_4 site is formed and Zn is removed from Fe-Zn-ZIF at temperatures as low as 900 °C
  - ✓ Correlated ORR activity with FeN_4 content; identified signatures of FeN_4 content
  - ✓ Successfully used NO and NO_2^- as molecular probes for ORR-active surface sites
  - ✓ Obtained further direct evidence of a majority of Fe sites being atomically dispersed and on the (AD)Fe-N-C catalyst surface using TEM, a molecular probe, and X-ray spectroscopy

Summary (Continued)

- ✓ Used TEM and X-ray absorption to characterize Fe species and structure evolution during heat treatment, obtaining guidance for improved catalyst synthesis
- ✓ Characterized the atomic structure and ORR activity of 40 combinatorial $(Zn_{1-x}Fe_x)$ZIF-F catalysts using X-ray absorption and multi-channel flow double electrode cell, identifying materials with potentially > 5× ORR activity of baseline composition
- ✓ Developed system for automated deposition of multiple inks resulting in $E_{\frac{1}{2}}$ agreement between m-CFDE and RDE of 5 mV for PGM-free catalyst
- ✓ Further refined the capability to characterize by XAFS the atomic structure of catalysts during heat treatment, determining the evolution of Fe species
- ✓ Acquired MEA kinetic data for (AD)Fe-N-C cathode and applied the distributed ORR model to determine reaction order, activation energy, and the potential dependence of active site availability

- **ORR active-site activity and durability modeling**
  - ✓ Calculated binding energies of potential probes/poisons to various active site structures
  - ✓ Utilized model descriptors to determine that N loss is likely responsible for PGM-free catalyst activity decrease
  - ✓ Logistic decay model developed and utilized to describe autocatalytic degradation mechanism of PGM-free catalysts

- **Project performance measures**
  - ✓ ElectroCat milestones and quarterly progress measures (QPMs) for all four labs either completed, on track, or task no-goed (PSIS-prepared PGM-free catalyst)

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

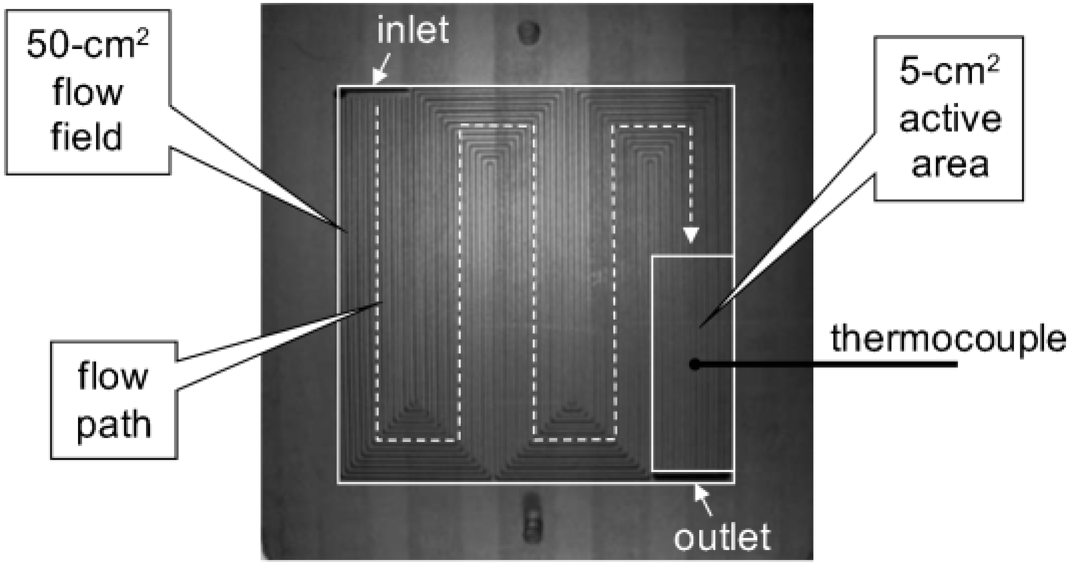
Advanced electron microscopy, atomic-level characterization, XPS studies

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

Technical Back-Up Slides

Experimental Details for MEA ORR Kinetic Study

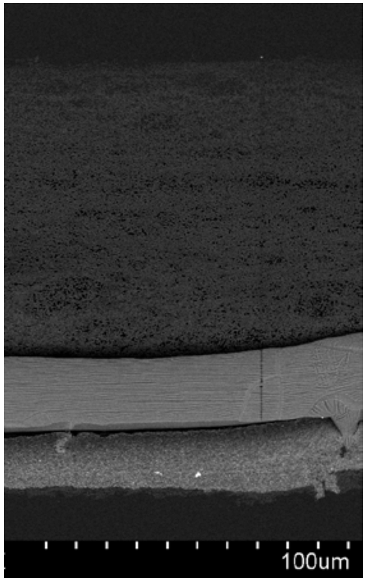
- LANL made AD(Fe)-C-N electrocatalyst (#01182017)
- 5 cm^2 MEAs with ~3.8 mg_{cat} cm^{-2}
- Cathode proton resistance determined at 100% RH 80 °C H_2/N_2
- Oxygen reaction order determined at 100% RH, 80 °C across 50-350 kPa p_{O2}
- Activation energy determined at 100% RH, 100 kPa p_{O2}, across 60, 70 and 80 °C



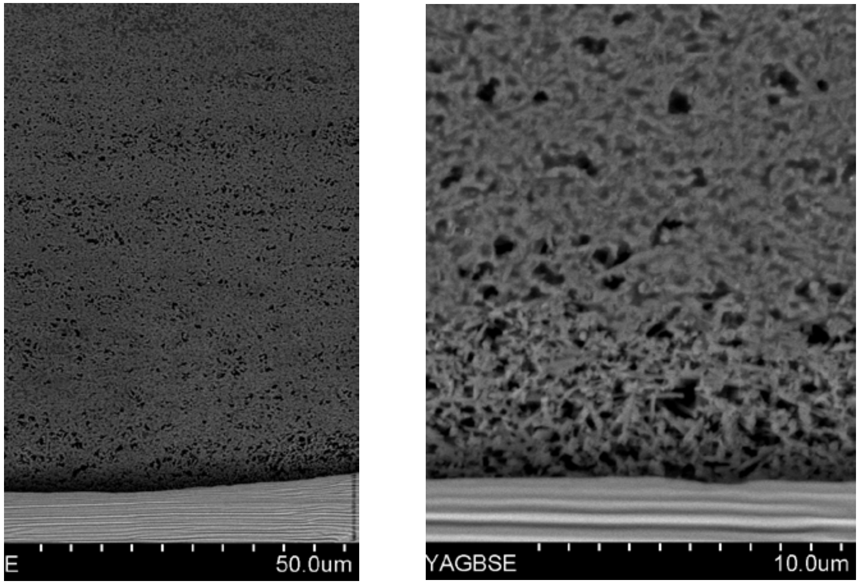
D. R. Baker, D. A. Caulk, K. C. Neyerlin, and M. W. Murphy, *Journal of The Electrochemical Society*, **156**, B991 (2009)
T. A. Greszler, D. Caulk, and P. Sinha, *Journal of The Electrochemical Society,* **159**, F831 (2012)

(AD)Fe-N-C Catalyst: MEA Fabrication and Electrode Characterization

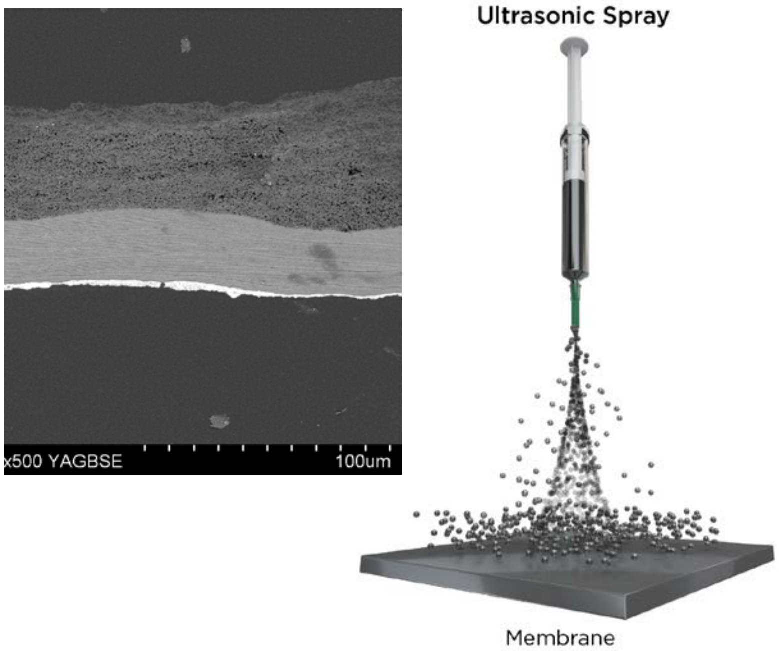
Hand Painted

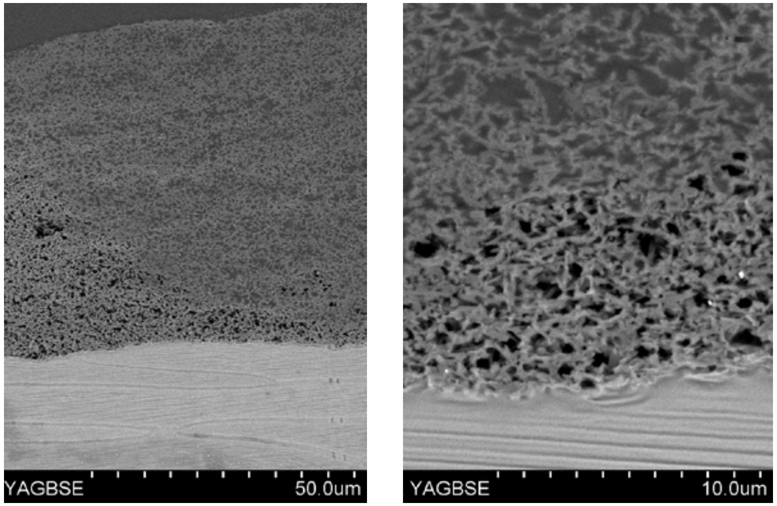


(AD)Fe-N-C cathode
~ 80 mm thick HP
~ 50 mm thick for US
Variations on par with loading



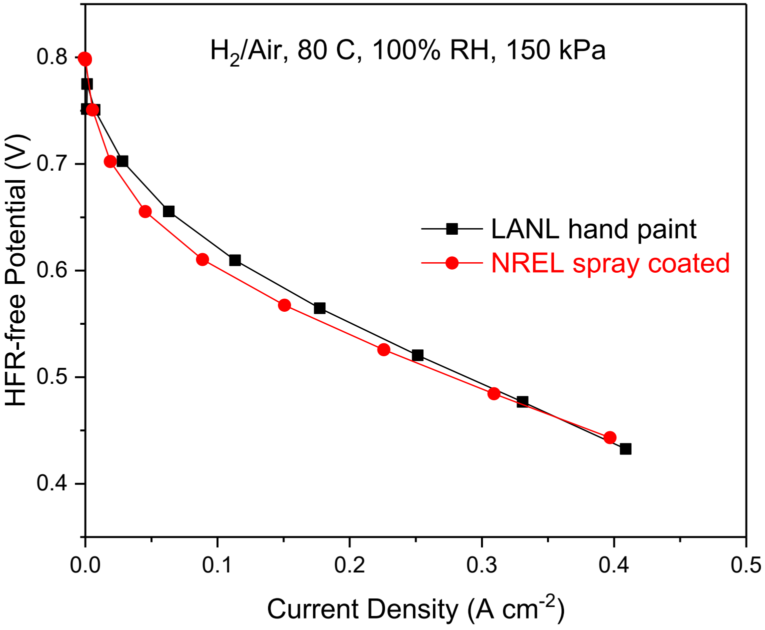
Ultrasonically Sprayed

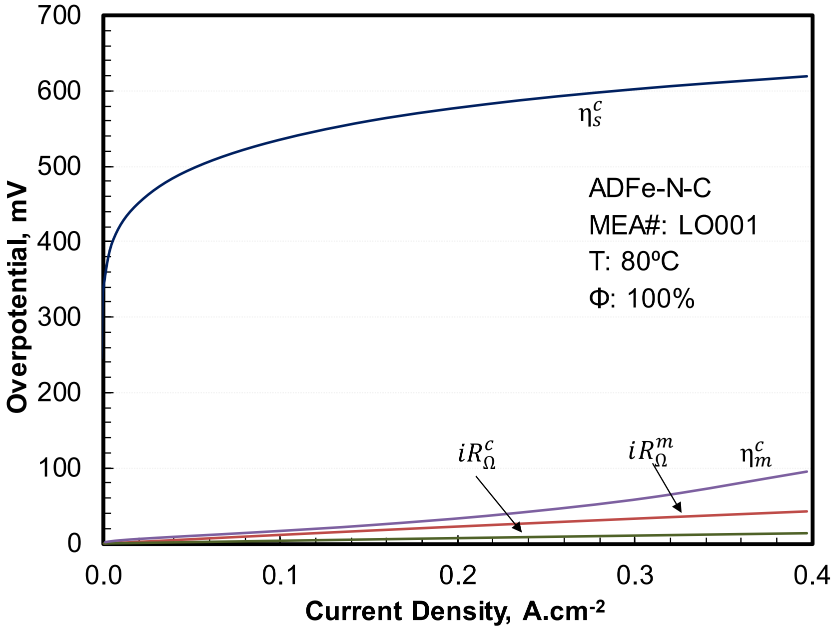




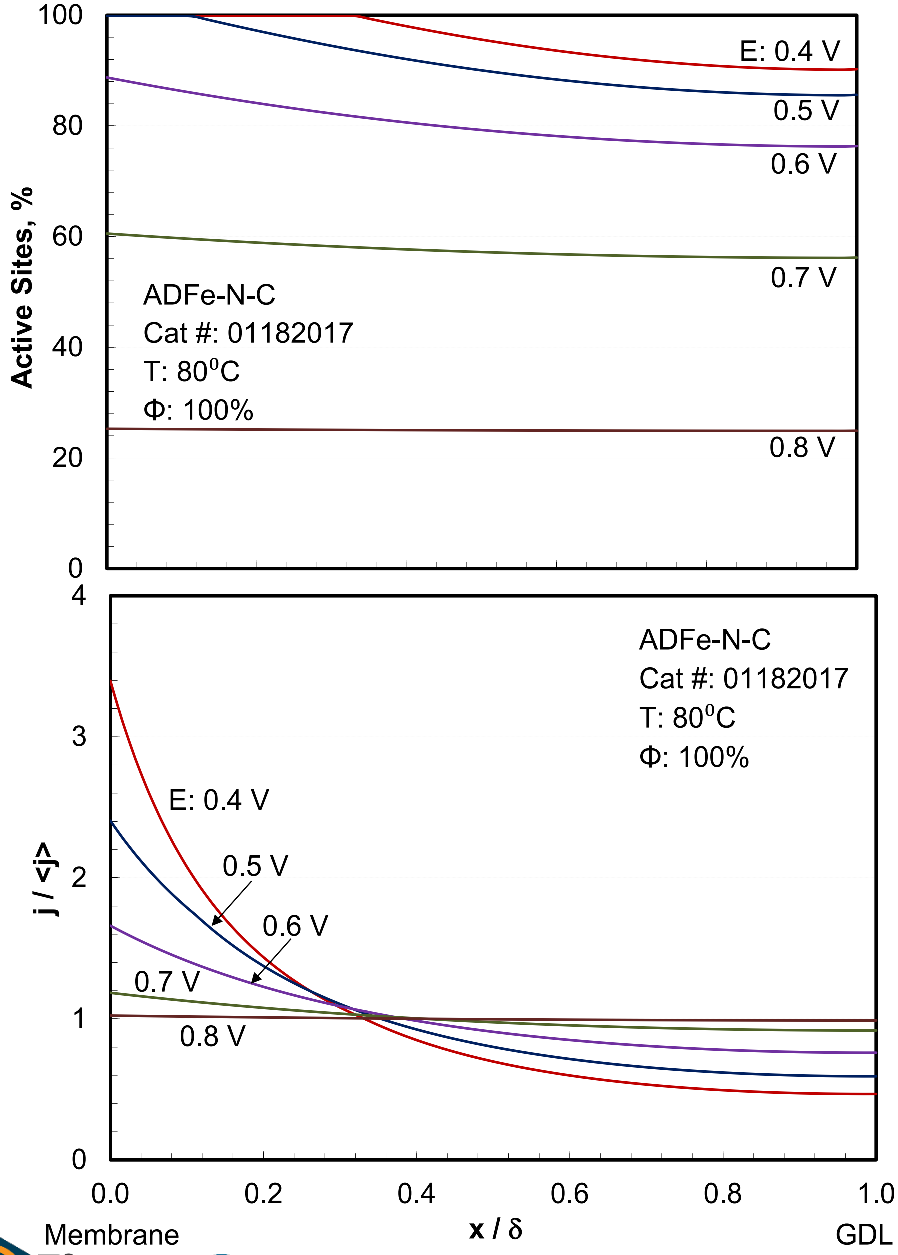
Electrode Performance Model: Separation of Transport Losses

- Currently, the performance in air is limited by the slow ORR kinetics (η_s^c)
- However, the mass transfer overpotential (η_m^c), ~100 mV at just 0.4 A/cm^2, will require attention after improving the ORR kinetics

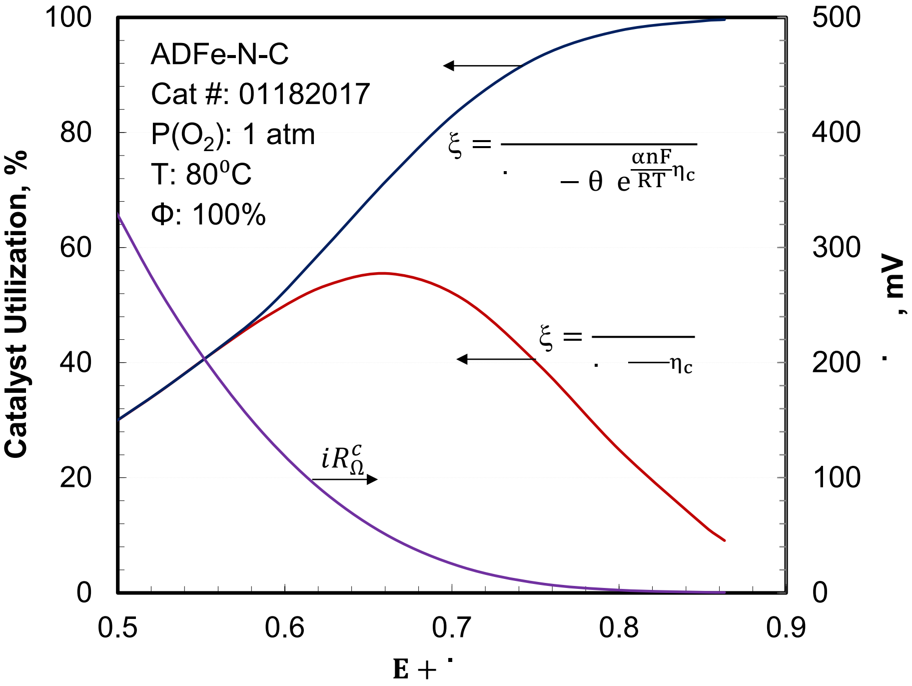




Electrode Performance Model: Distributions in Electrodes

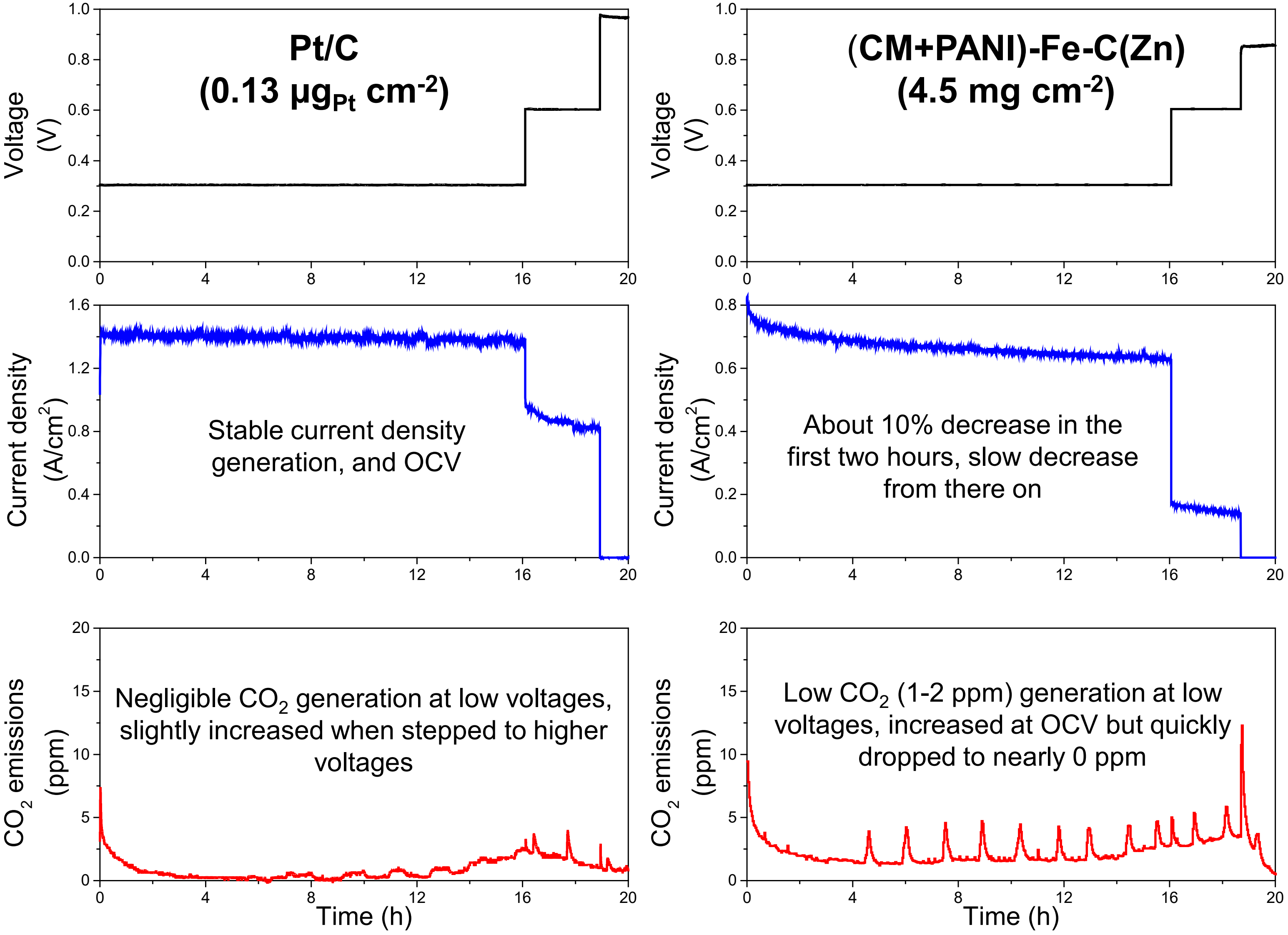


- θ is potential dependent but quite uniform across the electrode thickness, except at low cell voltage
- Highly non-uniform ORR kinetics at low E
- Low catalyst utilization (ξ) in thick PGM-free electrode



Catalyst Durability: Degradation Studies Compared to Pt-MEA in Air

Anode: 0.2 mg_{Pt} cm^{-2} Pt/C H_2, 200 sccm, 1.0 bar H_2 partial pressure; **Cathode**: air, 300 sccm, 1.0 bar air partial pressure; **Cell**: Nafion®, 212; 5 cm^2; 80 ºC; 50% RH, constant voltage: 0.3 V, 0.6 V, OCV



Pt/C
(0.13 μg_{Pt} cm^{-2})

(CM+PANI)-Fe-C(Zn)
(4.5 mg cm^{-2})

Stable current density generation, and OCV

About 10% decrease in the first two hours, slow decrease from there on

Negligible CO_2 generation at low voltages, slightly increased when stepped to higher voltages

Low CO_2 (1-2 ppm) generation at low voltages, increased at OCV but quickly dropped to nearly 0 ppm

ElectroCat
Electrocatalysis Consortium

Catalyst Durability: Kinetic Models

Overall ORR reaction

$$\mathrm{X} + \mathrm{O_2} + 4\mathrm{H}^+ + 4\mathrm{e} \xrightarrow{k_1} \mathrm{X} + 2\mathrm{H_2O}$$

X: active site

At fixed potential, the kinetic current can be expressed as

$$j_k = -4F \cdot k_1[\mathrm{O_2}][\mathrm{X}]_s$$

$[X]_S$: surface concentration of active sites

First order degradation reaction

$$\mathrm{X} \xrightarrow{k_2} \mathrm{X_D}$$

X_D: de-activated site

$$\frac{d[\mathrm{X}]_s}{dt} = -k_2[\mathrm{X}]_s$$

Exponential decay

$$\boxed{\frac{j_k}{j_{k,t=0}} = e^{-k_{app}t}}$$

Autocatalytic degradation reaction

$$\mathrm{X} + \mathrm{R} \xrightarrow{k_3} \mathrm{X} + \mathrm{D}$$

R: reactants, *e.g.*, O_2, H_2O, H^+, e^-;

$$\mathrm{X} + \mathrm{D} \xrightarrow{k_4} \mathrm{X_D}$$

D: de-activation agent, *e.g.*, H_2O_2, ·OH

$$\frac{d[\mathrm{X}]_s}{dt} = -k_4[\mathrm{D}][\mathrm{X}]_s$$

$$k_3[\mathrm{O_2}][\mathrm{X}]_s - [\mathrm{D}]*v - k_4[\mathrm{D}][\mathrm{X}]_s = 0$$

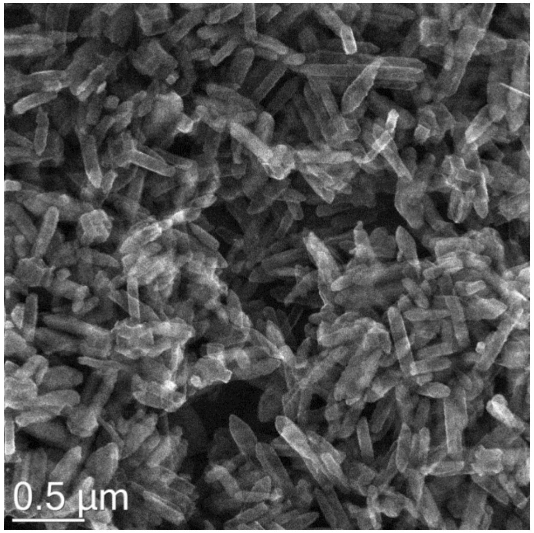
Logistic decay

$$\boxed{\frac{j_k}{j_{k,t=0}} = \frac{1}{1 + k_{app}t}}$$

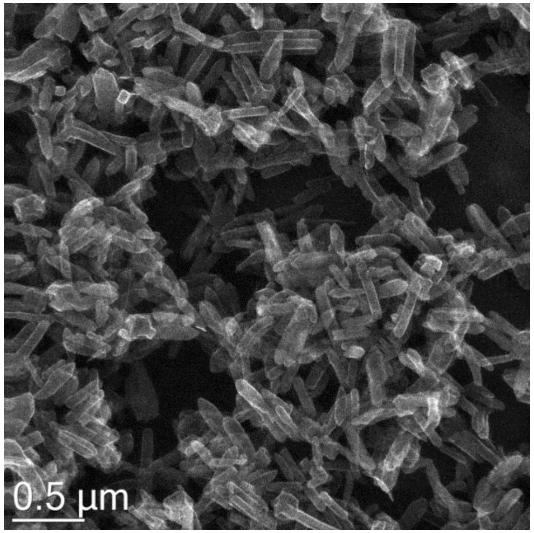
Highlight: Quantitative kinetic model describing performance loss in time

Microscopy of $(Zn_{0.975}Fe_{0.025})$ZIF-F During Heat Treatment

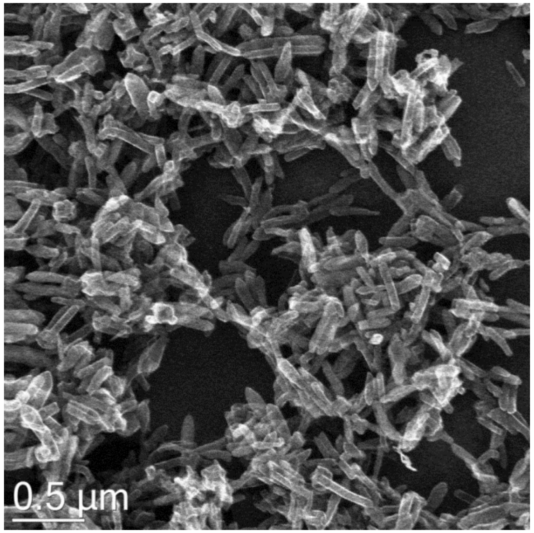
250 °C



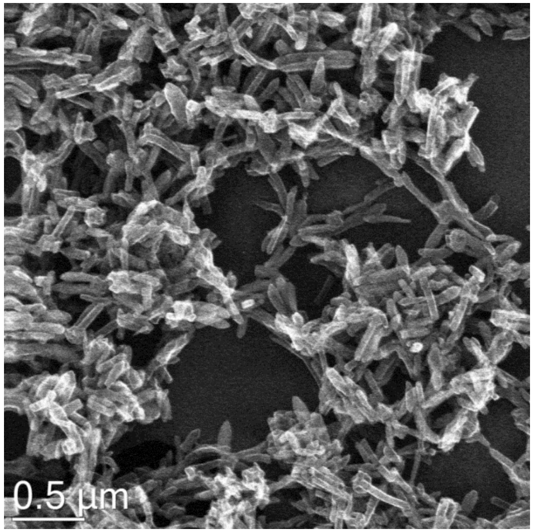
500 °C



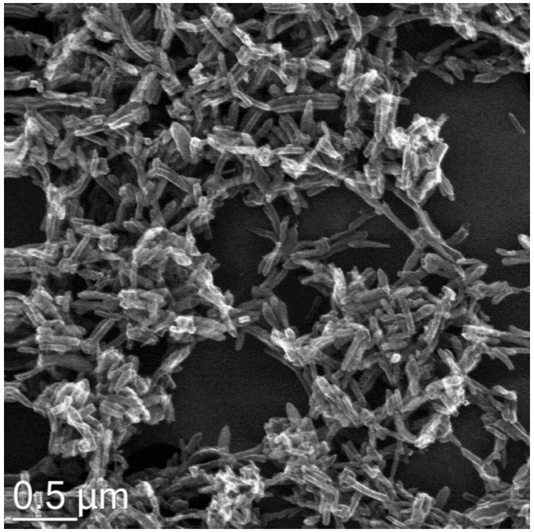
700 °C



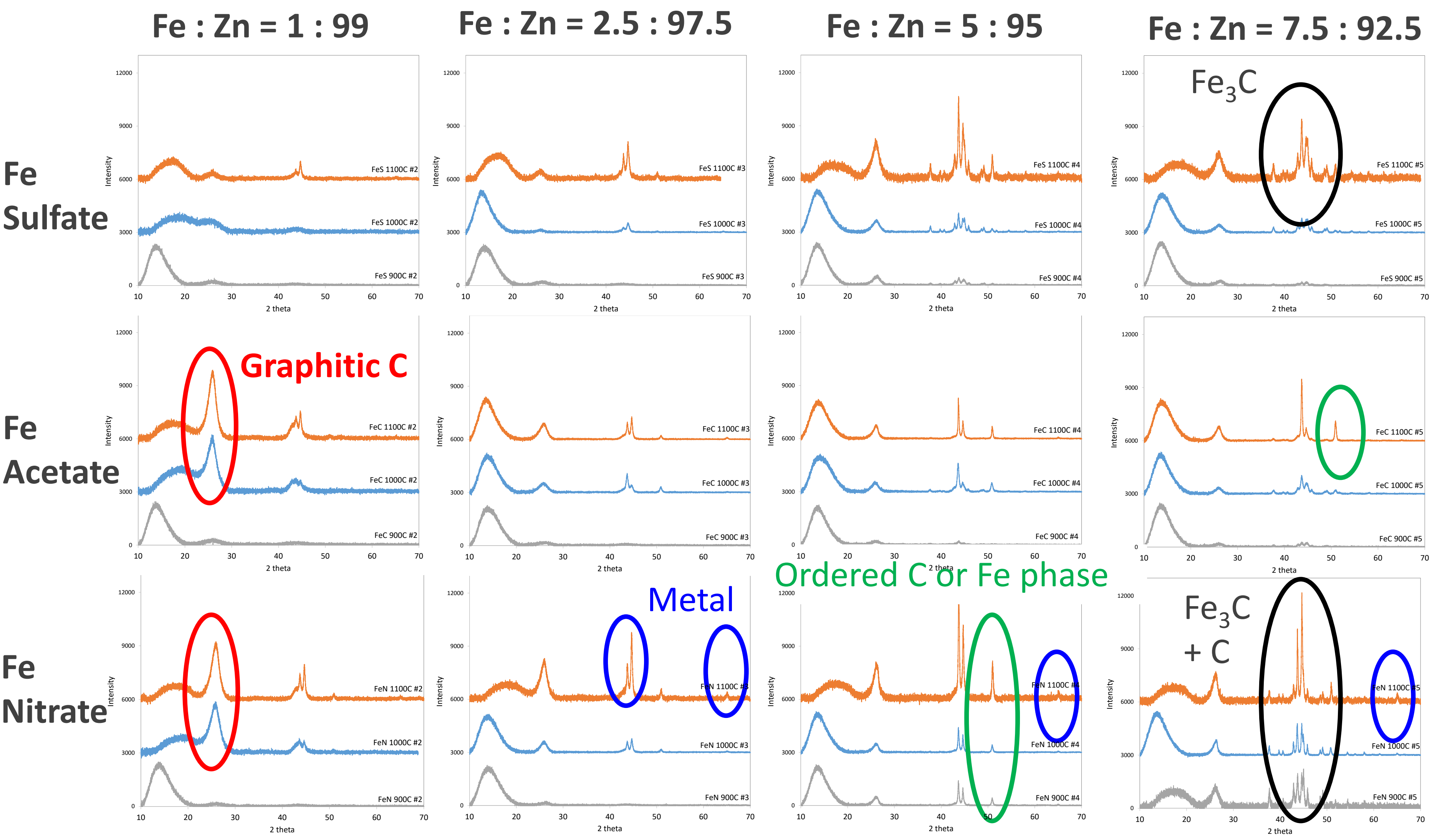
900 °C



1100 °C



XRD of Heat-Treated ((Zn_xFe_{1-x}))-ZIF-F Precursors



Fe_3C

Graphitic C

Metal

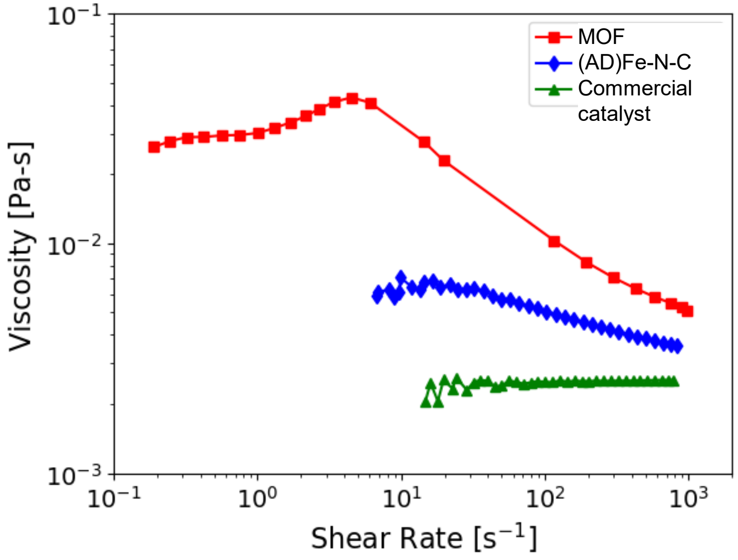
Ordered C or Fe phase

Fe_3C + C

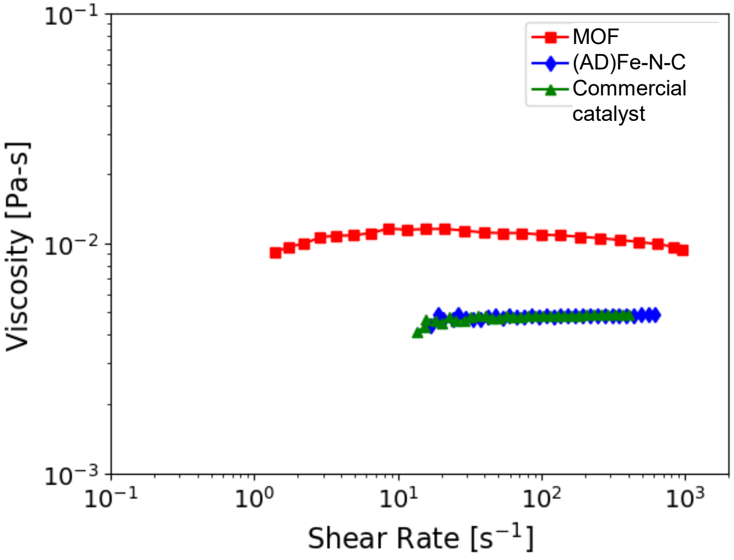
Grey – 900 °C, Blue – 1000 °C, Orange – 1100 °C

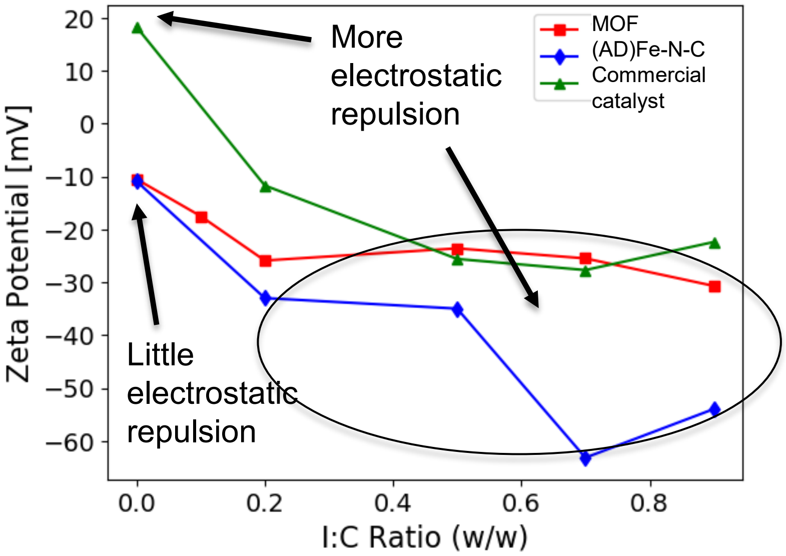
PGM-free Ink Formulation and Inter-particle Interactions

Without Ionomer



With Ionomer (0.5 I:C)



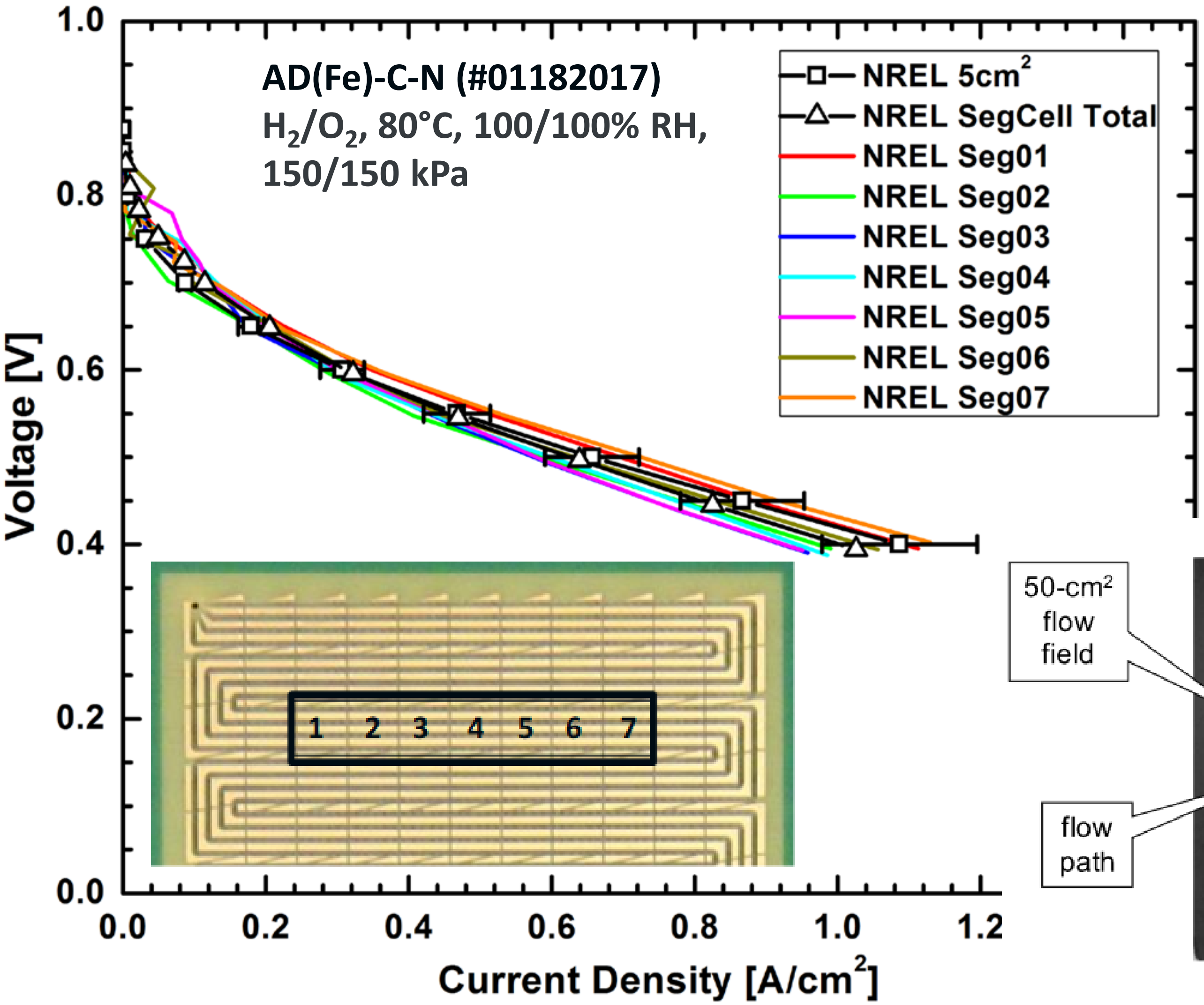


- Rheology characterizes agglomeration of catalyst inks
- Zeta potential characterizes particle surface energy and ionomer-particle interactions
- Understanding MEA fabrication/ processing parameters could help improve electrode transport phenomena by reducing agglomerates

Capability Development: Segmented Cell Testing and Development

Each of the 7 segments falls within ~10% of 5 cm^2 differential cell data at <0.5 A/cm^2

Next generation hardware will improve the utility and accuracy of the system



Next Generation Hardware:

- ✓ True 4-wire measurement for voltage sense
- ✓ Identical resistances of the 121 current paths
- ✓ Flexible flow-field designs including parallel, differential and interdigitated