Hydrogen and Fuel Cells Program
2016 Annual Merit Review and Peer Evaluation Meeting
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Non-Precious Metal Fuel Cell Cathodes: Catalyst Development and Electrode Structure Design

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Project ID: FC107

Overview

Timeline

- **Project start date:** April 1, 2013
- **Project end date:** March 31, 2016
  (summer 2016 for IRD and GM due to delay in the implementation of contracts)

Budget

- **FY15 DOE funding:** $1,275K
- **Estimated FY16 funding:** $780K
- **Total DOE project value:** $3,999K
- **Cost share:** 20.1%

Barriers

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

Partners – Principal Investigators

Carnegie Mellon University

Carnegie Mellon ENGINEERING – CARNEGIE INSTITUTE OF TECHNOLOGY – Shawn Litster

University of Rochester

MELIORA – UNIVERSITY of ROCHESTER – Michael Neidig

University of Waterloo

University of Waterloo – Zhongwei Chen

Oak Ridge National Laboratory

OAK RIDGE National Laboratory – Karren More

IRD Fuel Cells

IRD – POWERING PEOPLE ANYWHERE – Madeleine Odgaard

General Motors

GM – Joseph Ziegelbauer

Relevance: Objectives and Technical Targets

Objectives

Advance non-PGM cathode technology through the development of new materials and implementation of novel electrode concepts to assure:

(a) ORR activity viable for automotive systems

(b) practical catalyst durability

(c) high ionic/electronic conductivity within the cathode

(d) efficient oxygen transport and effective removal of the product water

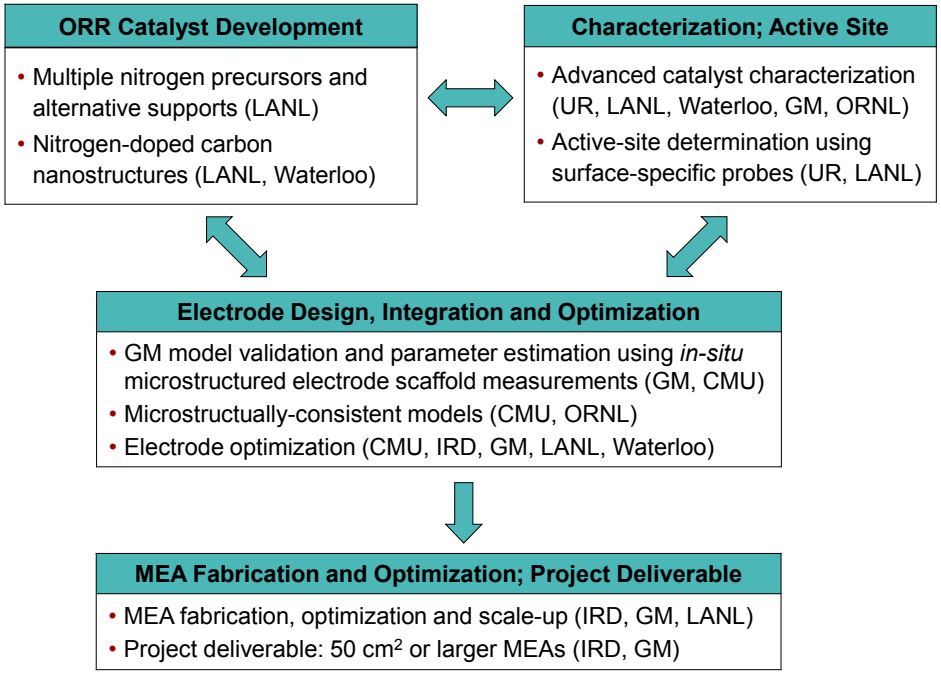
Technical Targets

Characteristic	Unit	2018 Target	2020 Target
Voltage at 0.044 A/cm^2	V	0.88	0.90
Current density loss at target voltage after 30,000 cycles	%	< 50	< 40
Loss in performance at 0.8 A/cm^2	mV	< 60	< 30
Loss in performance at 1.5 A/cm^2	mV	< 60	< 30

Approach: Details and Impact to Date

Catalyst Activity:

- Develop new synthesis paths to increase active site density
- Tune porosity to enhance accessibility of ORR active sites to oxygen
- Probe active sites to understand structure-activity relationships
- Explore synergies between multiple metal and nitrogen precursors



Durability:

- Use durable non-carbon supports to mitigate corrosion; determine corrosion rates
- Minimize and eliminate spectator species in Fe-based catalysts; explore catalysts synthesized using Fe-free precursors, especially based on other transition metals
- Improve durability by advanced cathode design (effective water management)

MEA Performance: Image, model and optimize performance of non-PGM cathode structures

Selected Impacts to Date:

- Catalysts with activity on track to meeting 2018 intermediate target (0.88 V at 0.044 A/cm^2)
- Significant progress in the durability of Fe-based and Fe-free catalysts
- Understanding of main design factors determining performance of non-PGM cathodes

Approach: Project Milestones

Date	Quality Performance Measures and Milestone	Status	Comments
Dec 2015	Using fuel cell simulations with a microstructurally consistent cathode model, perform a multi-parameter optimization to identify ideal electrode structures as a function of non-PGM catalyst ORR activity. **QPM**	**Complete**	Performed multi-parameter studies to identify key factors for electrode development and for further increasing active-site density needed to meet power density targets.
Mar 2016	Complete the synthesis and deliver four 2.5 g batches (10 g total) of pre-selected non-PGM catalyst for 50 cm^2 MEA optimization and project deliverable with the following target ORR performance: 100 mA/cm^2 at 0.8 V (MEA, 80°C, 1.0 bar air pressure) and 97% selectivity at 0.8 V vs. RHE (RDE testing). **QPM**	**Complete**	Three 2.5-gram batches of pre-selected PANI-CM-Fe-C catalyst with specified target performance delivered to IRD; supply of 4^{th} batch deferred for as long as catalyst from the 3^{rd} batch satisfies IRD's needs.
Jun 2016	Deliver two optimized 50 cm^2 MEAs with non-PGM cathode to DOE-designated test facility. **Milestone/Deliverable**	**Pending**	No delay expected.

Responses to Previous Year Reviewers' Comments

"Ultimately, the catalyst must not include Fe to be compatible with membranes and the ionomer. The approach allows for Fe-free catalysts to be made and tested."

In the past year, research has focused much more than before on catalysts derived from Fe-free precursors. RDE activity of the best-performing alternative catalysts is within 20-30 mV of Fe-based counterparts. Cycling durability enhancement has been observed with Mn-based catalyst.

"It is not clear how many heat treatment and leaching steps are involved for the catalyst synthesis."

Our most advanced synthesis process for Fe-(CM+PANI)-C catalysts involves two heat treatments, with one intermediate leaching step. In one of the recent approaches, no acid leach has been used.

"It is unclear whether the modeling implicitly suggests that CM-PANI-Fe-C-based catalysts are [performance] limited."

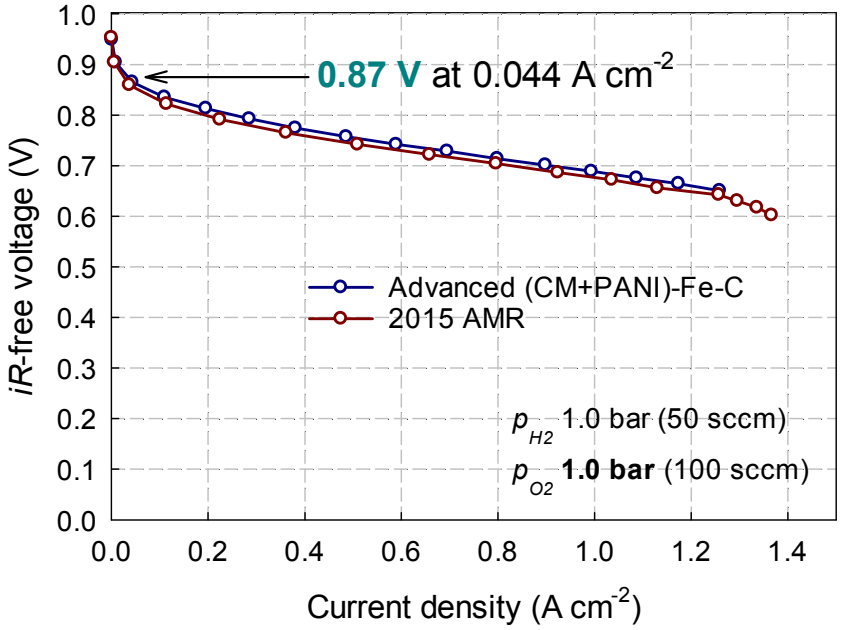
Current calculations suggest that certain active site structures should have activities (calculated *via* limiting potential) similar to Pt. Recent efforts in understanding the effect of ligand modification of sites suggest the possibility of tuning active site structures *via* persistent ligands to further improve activity. Combining these two points, modeling indicates that further improvement in ORR activity for non-PGM materials is achievable.

"The model is validated for the shape of the curves and trends for Nafion® content and water content, but absolute performance values are not predicted. […] The thinner CL and resulting significantly improved performance data shown is on oxygen. If there are O_2 mass transport limitations, then they are very severe. This result should be further explored with the model."

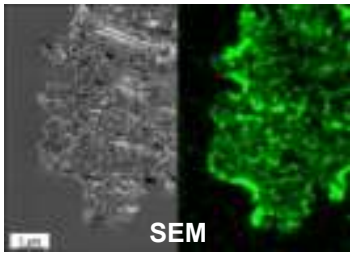
A loading modeling study has been performed, as well as a loading versus active site density parametric study. Significant increases in limiting current are predicted with thinner electrodes. However, there is a substanial loss in the activity/Ohmic regions of the polarization curves with thicknesses below 60 μm.

Accomplishment: Advanced (CM+PANI)-Fe-C Catalyst

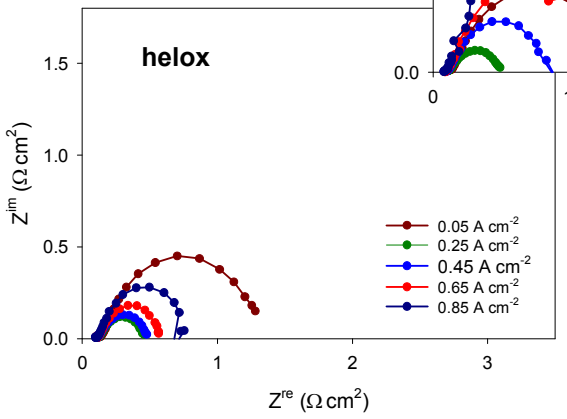
Anode: 0.2 $mg_{Pt}\,cm^{-2}$ Pt/C H_2, 50 sccm, 1.0 bar H_2 partial pressure; **Cathode:** *ca.* 4.0 mg cm^{-2} O_2, 100 sccm, 1.0 bar O_2 partial pressure; **Membrane:** Nafion®,117; **Cell size:** 5 cm^2

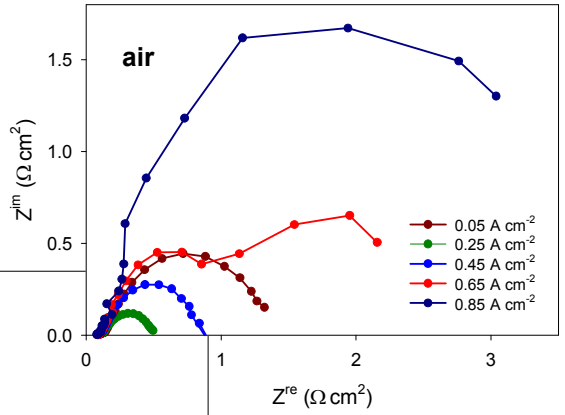


Fluorine mapping



Impedance spectroscopy



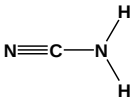


- Improved ORR activity achieved through modifications to (CM+PANI)-Fe-C catalyst synthesis and improvements in electrode design, enhancing O_2 transport within the catalyst layer
- 0.044 A cm^{-2} reached at **0.87 V** (*iR*-free) in the H_2-O_2 fuel cell test

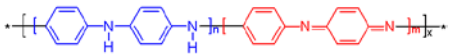
Project catalyst activity target accomplished!

Accomplishment: Enhancement of ORR Activity for Fe-free Catalysts

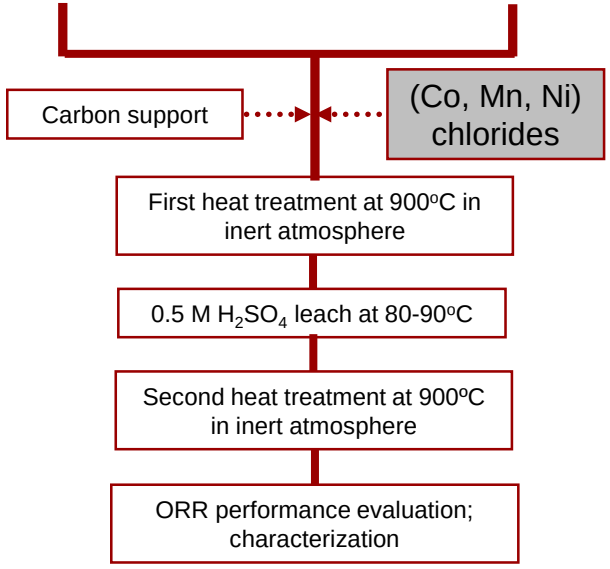
*Alternative transition metal precursors (Co, Mn, Ni) studied to mitigate possible Fenton reaction (Fe^{2+}/H_2O_2) or Fenton-like reaction (Fe^{3+}/H_2O_2) producing harmful **hydroperoxyl radicals***



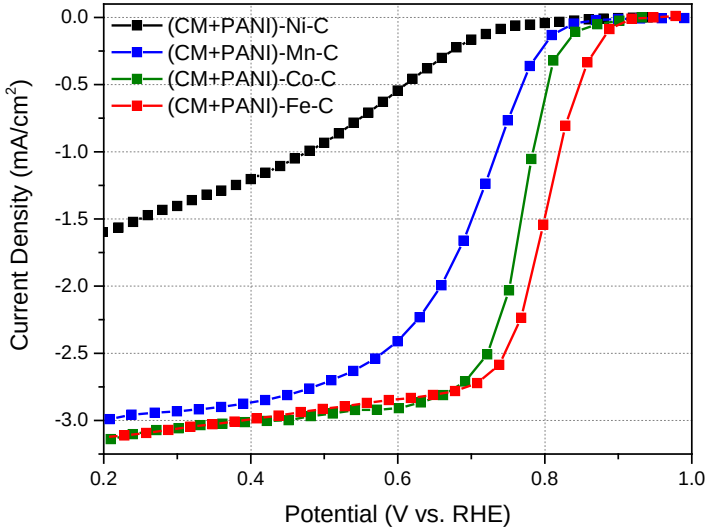
Cyanamide



Polyaniline



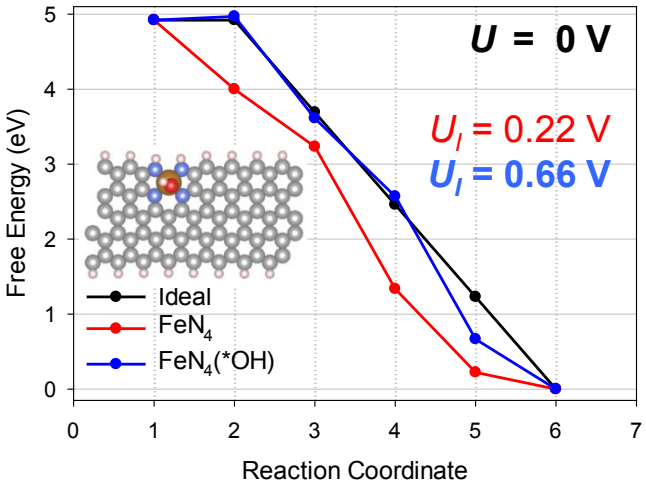
ORR: 0.6 mg/cm^2; 0.5 M H_2SO_4; 900 rpm; 25ºC; Ag/AgCl (3M) reference electrode; graphite counter electrode; steady-state potential program: 30 mV steps, 30 s/step

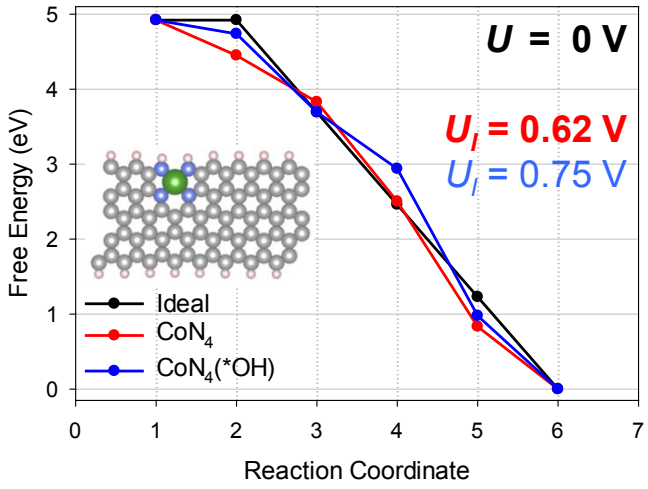


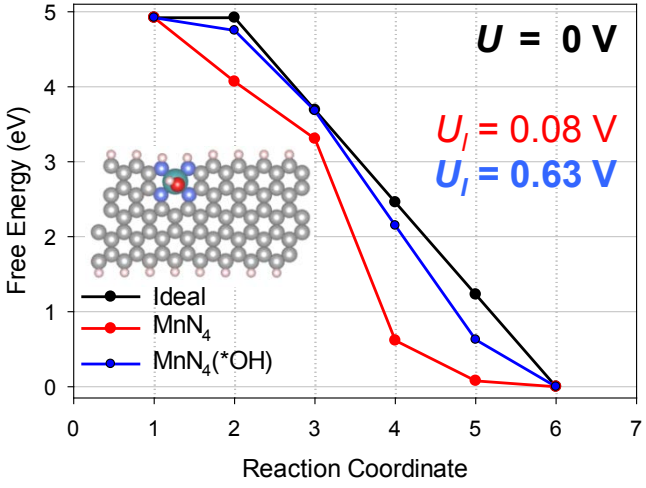
- Very promising ORR activity observed from Mn- and Co-based catalysts as alternative to Fe-based ORR catalysts
- Following acid leaching and 2nd heat treatment all catalysts are predominantly *Me*-N-C without metallic crystalline phases

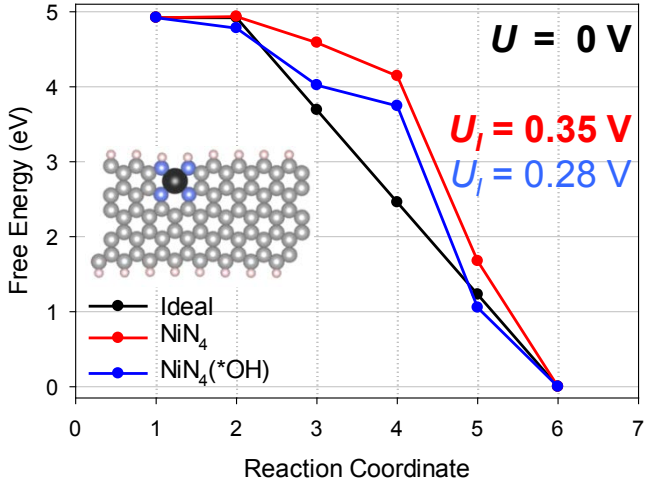
Highlight: $E_{½}$ of **0.77 V** achieved with entirely Fe-free non-PGM ORR catalyst

Accomplishment: Modeling of Fe-free ORR Potential Energy Surfaces





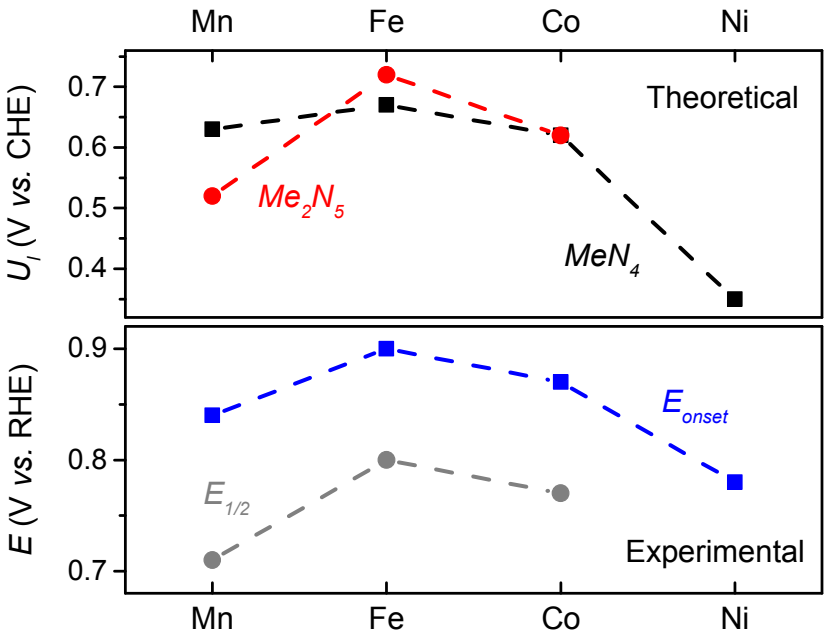




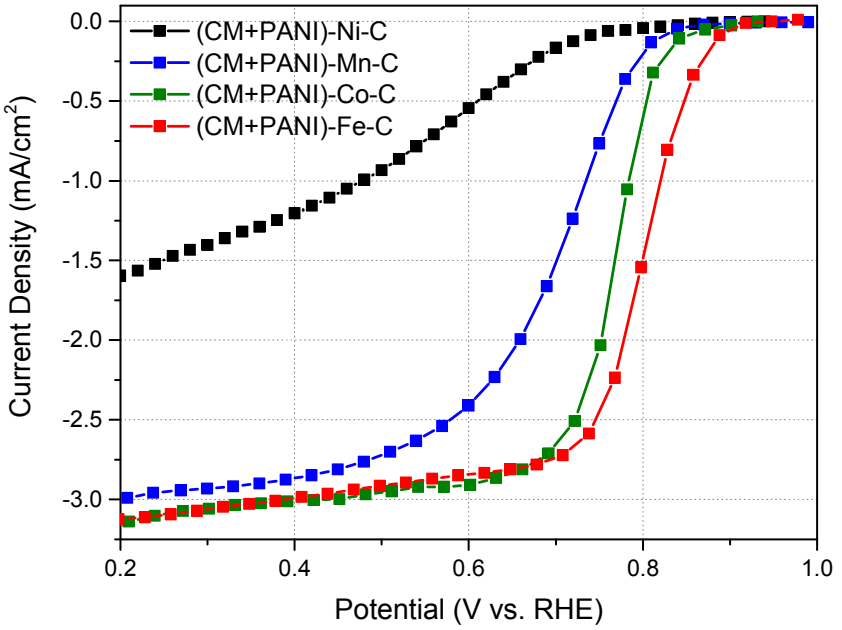
- Calculation of **ORR pathway** → persistent *OH for edge MnN_4 and FeN_4 (but not CoN_4 or NiN_4)
- Activity descriptor, U_l, prediction without *OH modification: $U_{l,Co} > U_{l,Fe} > U_{l,Mn} > U_{l,Ni}$
- With *OH modification of Mn and Fe: $U_{l,Fe} > U_{l,Mn} \approx U_{l,Co} > U_{l,Ni}$

Accomplishments: Fe-free Catalysts – Experiment Supported by Theory

Calculated U_l using computational hydrogen electrode (CHE) formalism and DFT (GGA)



ORR: 0.6 mg/cm^2; 0.5 M H_2SO_4; 900 rpm; 25ºC; Ag/AgCl (3.0 M KCl) reference electrode; graphite counter electrode; steady-state potential program: 30 mV steps, 30 s/step

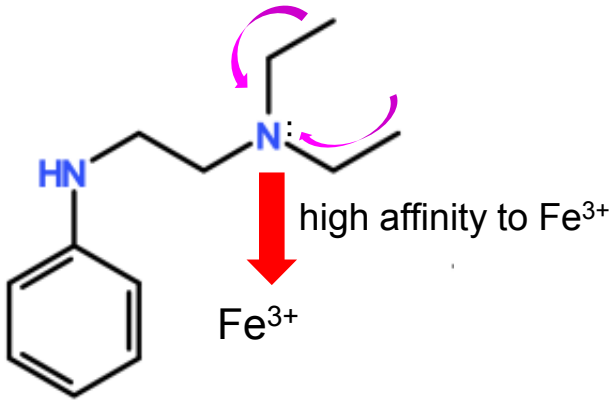


ORR pathways: **(1)** *OH modification for **MnN_4**, **FeN_4** and ***Me_2N_5*** **(2)** no *OH modification for **CoN_4** and **NiN_4**

Highlight: Theoretical prediction of spontaneous *OH ligand modification of active site structures explains shift in activity trend with *Me*-N-C catalysts

$$U_{l,Fe} > U_{l,Co} \geq U_{l,Mn} > U_{l,Ni}$$

New Synthesis Approach: Innovative Catalyst Template Design



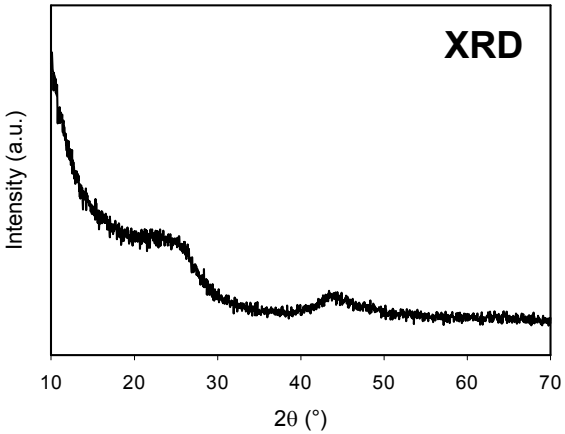
"polymerizable" aniline group

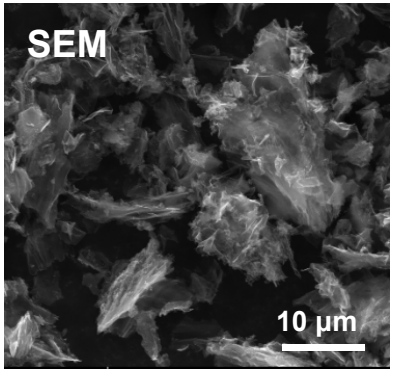
Affinity to Fe^{3+}:

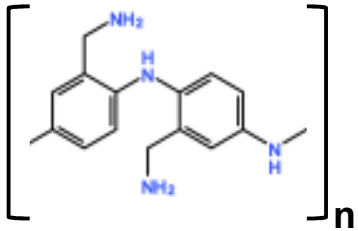
diethyl-N- > NH_2- > phenylamine

- Rational catalyst design based on known amine affinity to Fe^{3+}
- **Purpose:** Increase in active site density *via* addition of polymer side chains

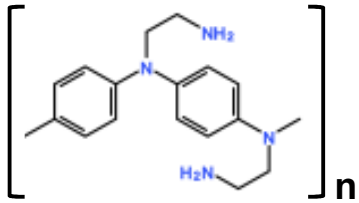
Two-stage Heat-treated Catalysts



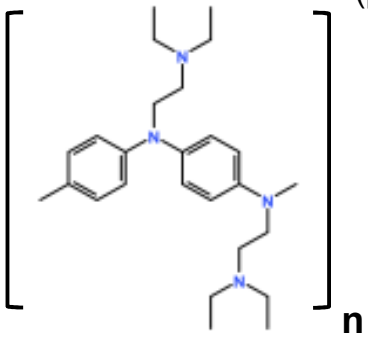




polyaminobenzylamine (**polyABA**)



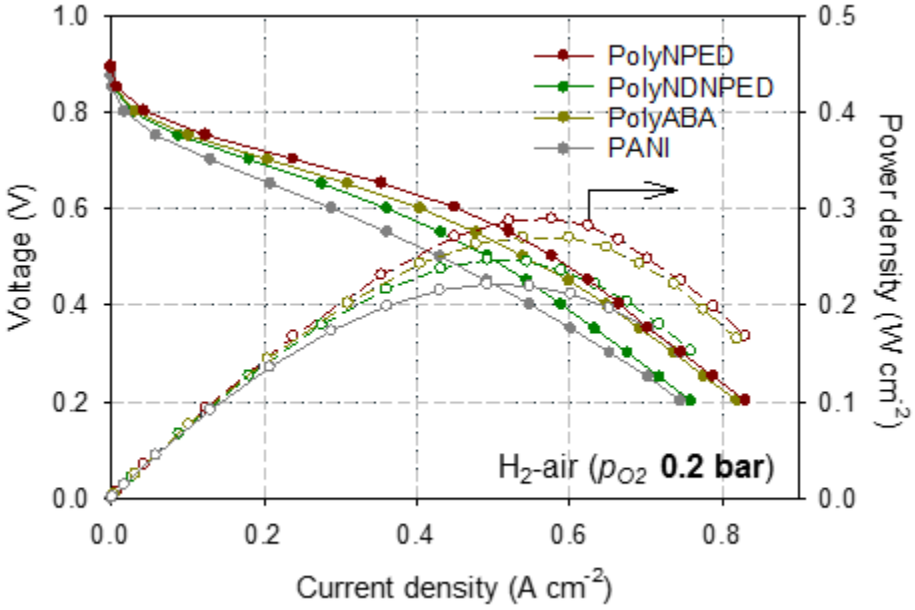
poly(N-phenylethylenediamine) (**polyNPED**)



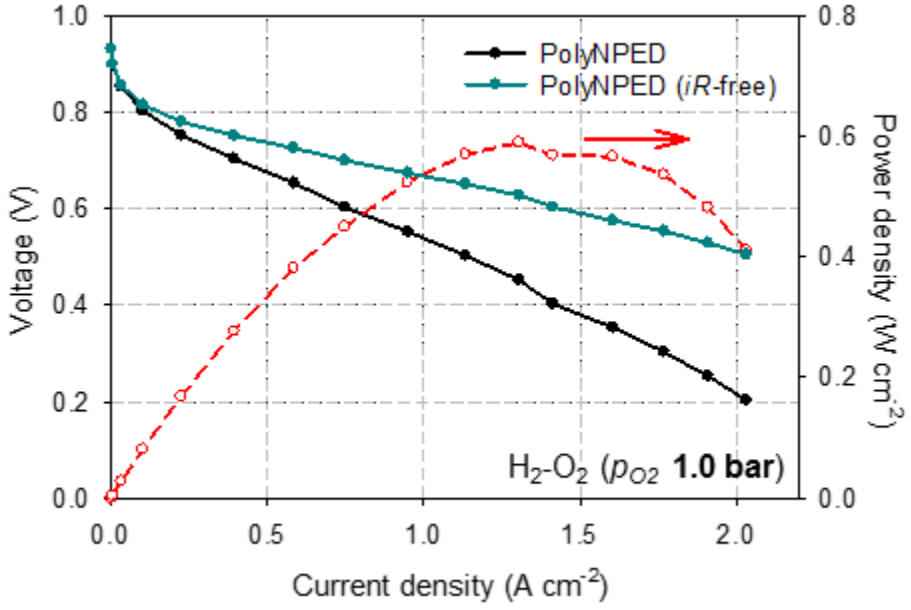
poly(N,N-diethyl-N'-phenylethylenediamine) (**polyNDNPED**)

Accomplishment: Performance of Side-Chain Templated Catalysts

Anode: 0.2 mg_{Pt} cm^{-2} Pt/C H_2, 200 sccm, 1.0 bar H_2 partial pressure; **Cathode:** *ca.* 4.8 mg cm^{-2} air, 200 sccm, 1.0 bar air pressure; **Membrane:** Nafion®211; **Cell size:** 5 cm^2

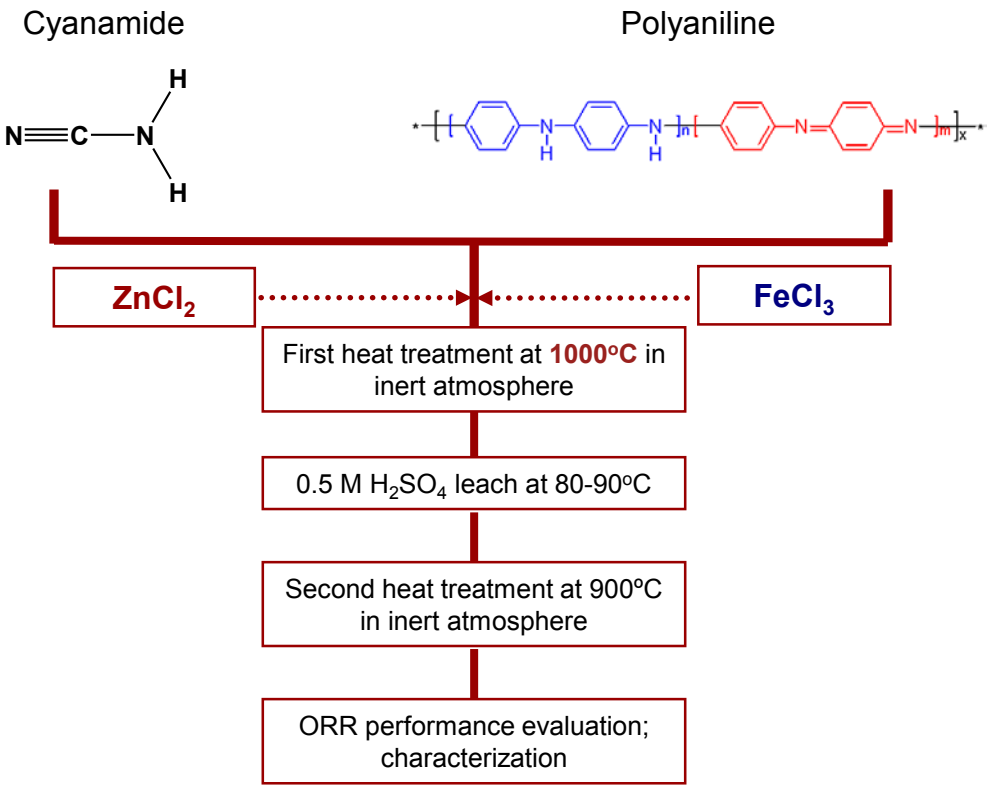


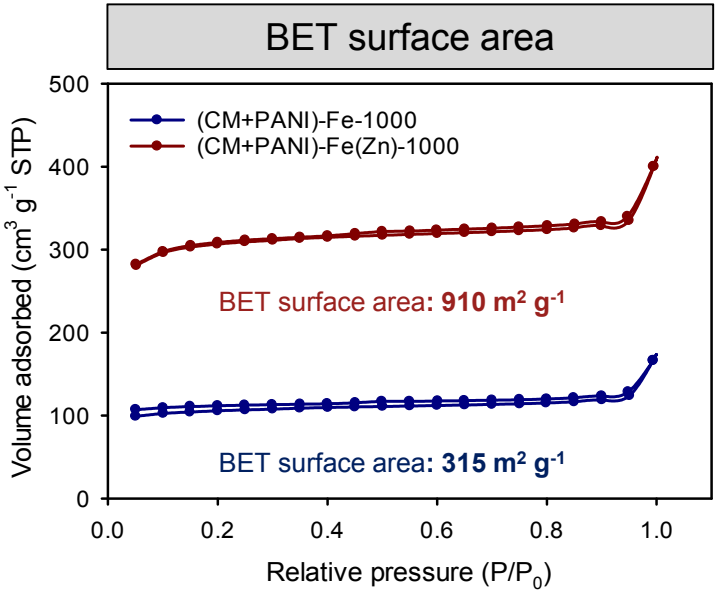
Anode: 0.2 mg_{Pt} cm^{-2} Pt/C H_2, 200 sccm, 1.0 bar H_2 partial pressure; **Cathode:** *ca.* 4.8 mg cm^{-2} air, 200 sccm, 1.0 bar O_2 partial pressure; **Membrane:** Nafion®212; **Cell size:** 5 cm^2

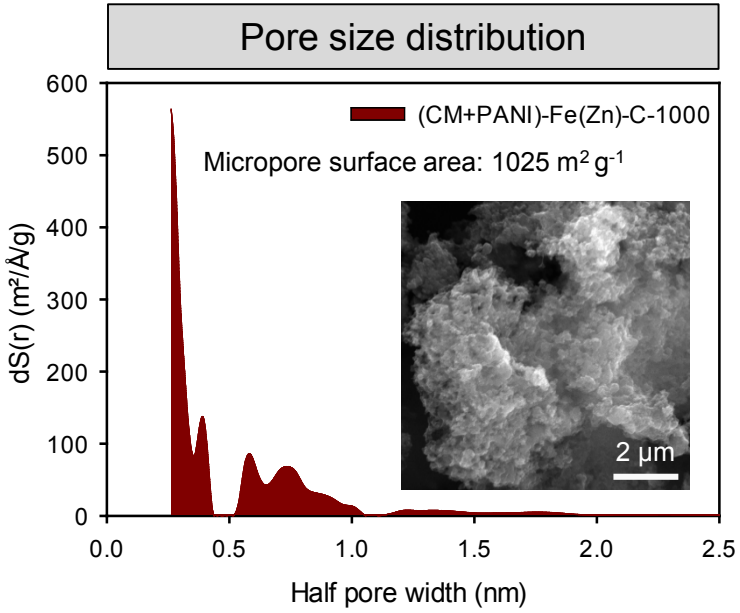


- **Highlight:** Innovative precursor design resulting in catalysts with ORR activity higher than that of unsubstituted-PANI-derived reference catalyst (H_2-air testing, p_{O2} 0.2 bar)
- High N-to-C ratio benefiting ORR activity

New Catalyst Synthesis Approach: Zn-induced Microporosity





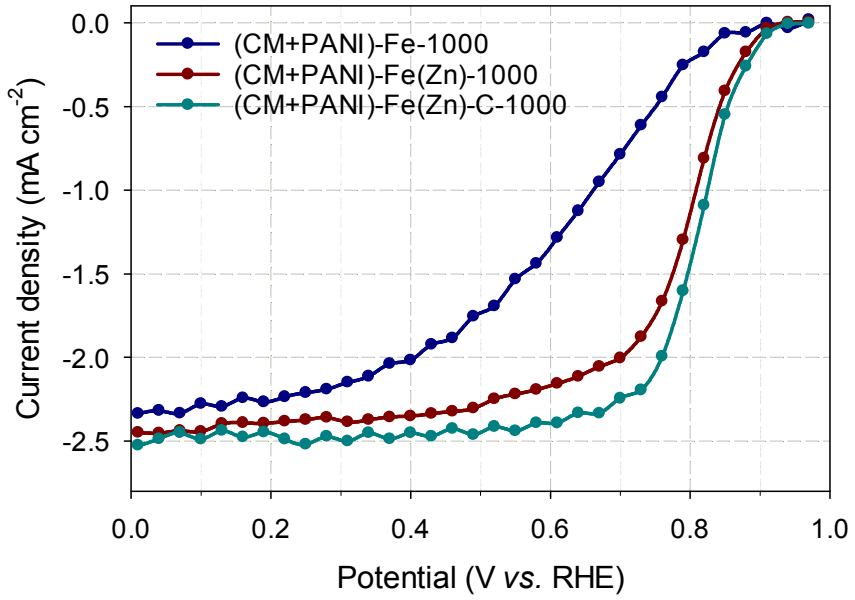


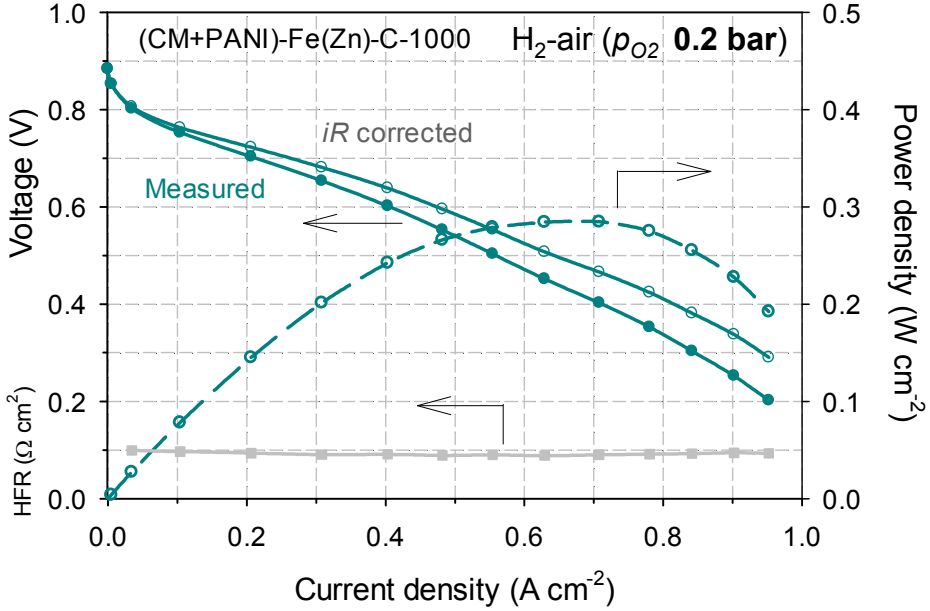
- Treatment at 1000°C to ensure complete Zn evaporation and reach improved catalyst stability
- BET surface area of "unsupported" catalyst increased **threefold** by using Zn in the synthesis
- Carbon addition for fine-tuning of microporous content

Accomplishment: RDE and Fuel Cell Performance of (CM+PANI)-Fe(Zn)

ORR: 0.6 mg cm^{-2}; 0.5 M H_2SO_4; 900 rpm; $Hg/HgSO_4$ reference electrode; graphite counter electrode; steady-state potential program: 30 mV steps, 30 s/step

Anode: 0.2 mg_{Pt} cm^{-2} Pt/C H_2, 200 sccm, 1.0 bar H_2 partial pressure; **Cathode:** *ca.* 4.0 mg cm^{-2} air, 200 sccm, 1.0 bar air pressure; **Membrane:** Nafion®,211; **Cell size:** 5 cm^2; **Cell:** 80 °C; 100% RH



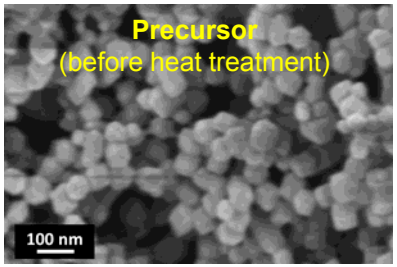


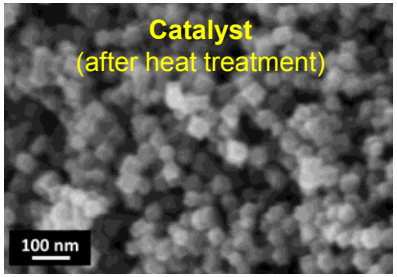
Highlights: **(1)** Catalyst with Zn-induced microporosity obtained without using a MOF precursor

(2) Approach allowing high-temperature processing, potentially enhancing durability (tests ongoing)

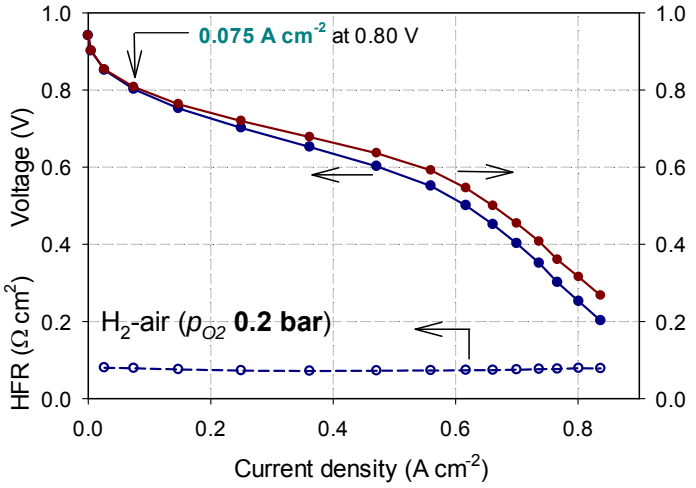
(3) Very high $E_{½}$ of **0.81 V** in RDE testing and promising activity at very low O_2 partial pressure (0.2 bar) demonstrated in the first round of fuel cell testing

Accomplishment: Major Progress in Durability at High Fuel Cell Voltage

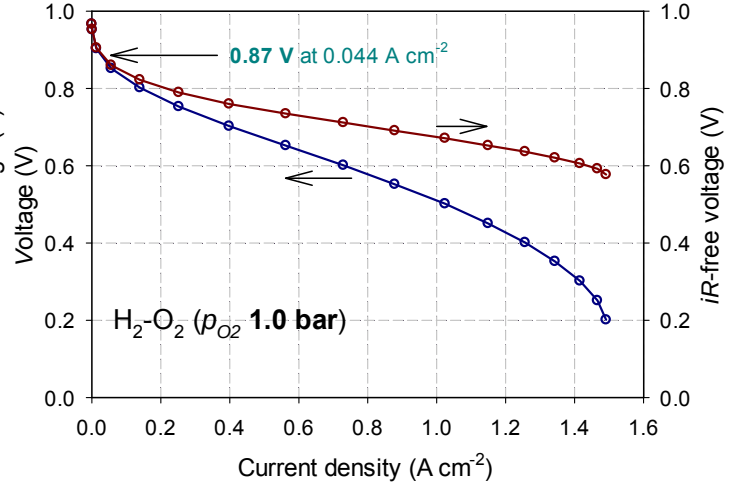


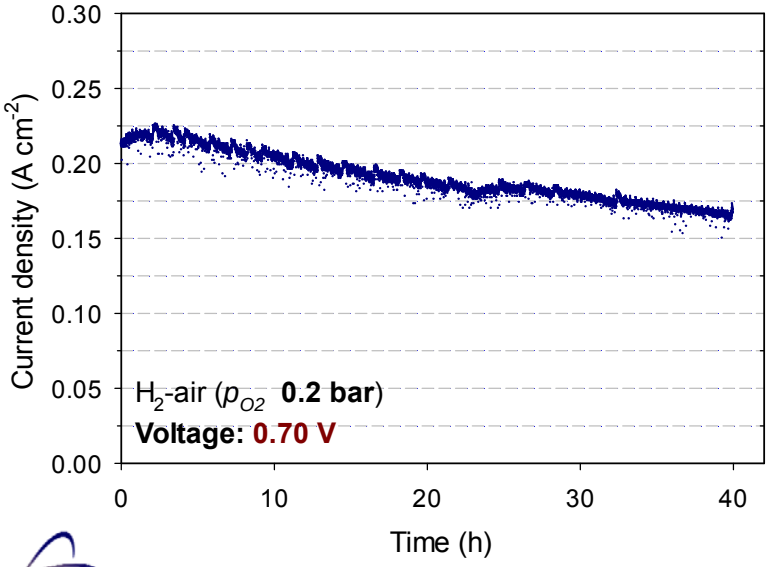


Anode: 0.3 mg_{Pt} cm^{-2} Pt/C, H_2, 200 sccm, p_{H2} 1.0 bar; **Cathode:** 4.0 mg cm^{-2}, air, 200 sccm; **Membrane:** Nafion®211; **Cell:** 80°C, 100%RH



Anode: 0.3 mg_{Pt} cm^{-2} Pt/C, H_2, 50 sccm, p_{H2} 1.0 bar; **Cathode:** 4.0 mg cm^{-2}, O_2, 100 sccm; **Membrane:** Nafion®115; **Cell:** 80°C, 100%RH

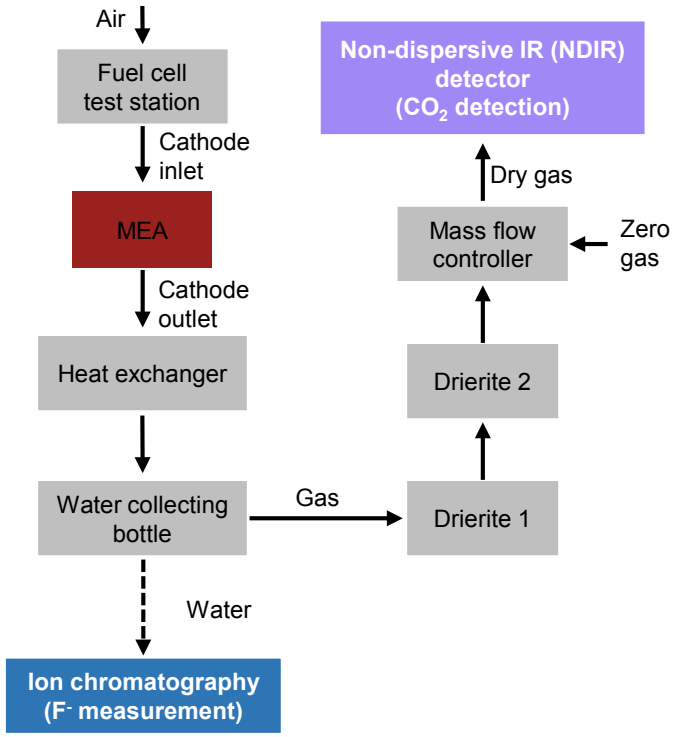




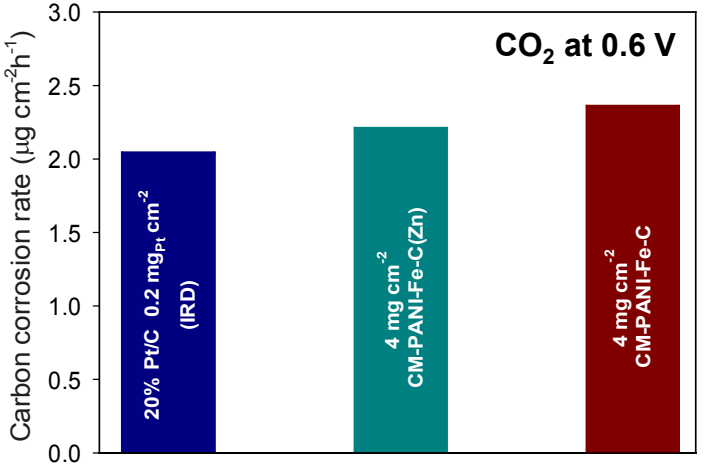
- UB unsupported catalyst derived from a homemade "Fe-MOF" precursor; unique cubic morphology preserved after heat treatment; all Fe atomically dispersed
- High ORR activity in H_2-air (**0.075 A/cm²** at **0.80 V**) and H_2-O_2 fuel cell (**0.87 V** at **0.044 A/cm²**, *iR*-free)
- **Highlight:** Initial testing (April 2016) revealing for the first time very promising performance durability of a non-PGM catalyst under viable fuel cell operating conditions: **ambient air feed** and **high voltage** (0.70 V)

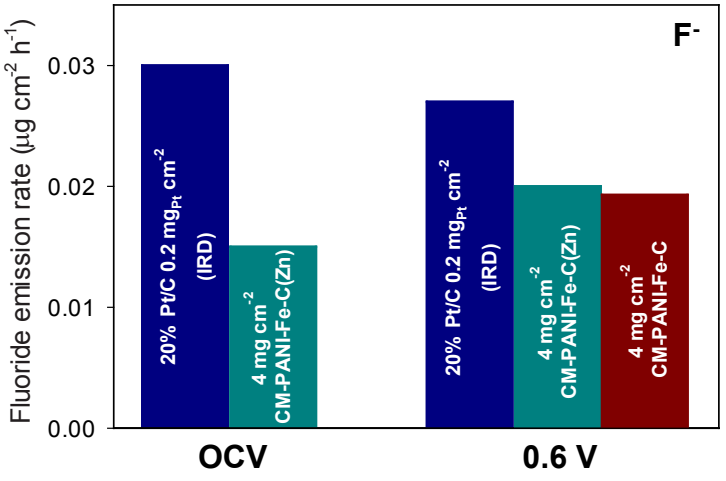
Accomplishment: Fluoride and CO_2 Emissions in Operating Fuel Cell

Schematic for Parallel Measurements of CO_2 and F^- Emissions from Fuel Cell Cathode



Anode: 0.2 $mg_{Pt}\,cm^{-2}$ Pt/C H_2, 200 sccm, 1.0 bar H_2 partial pressure; **Cathode:** air, 200 sccm, 1.0 bar air partial pressure; **Membrane:** Nafion®,212; **Cell size:** 5 cm^2; **Cell:** 80 °C; 50% RH; OCV (0.94 V – Pt/C; 0.93 V – non-PGM catalysts)



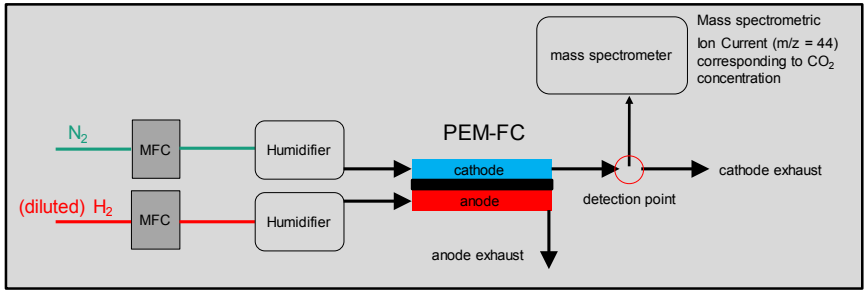


Highlights:

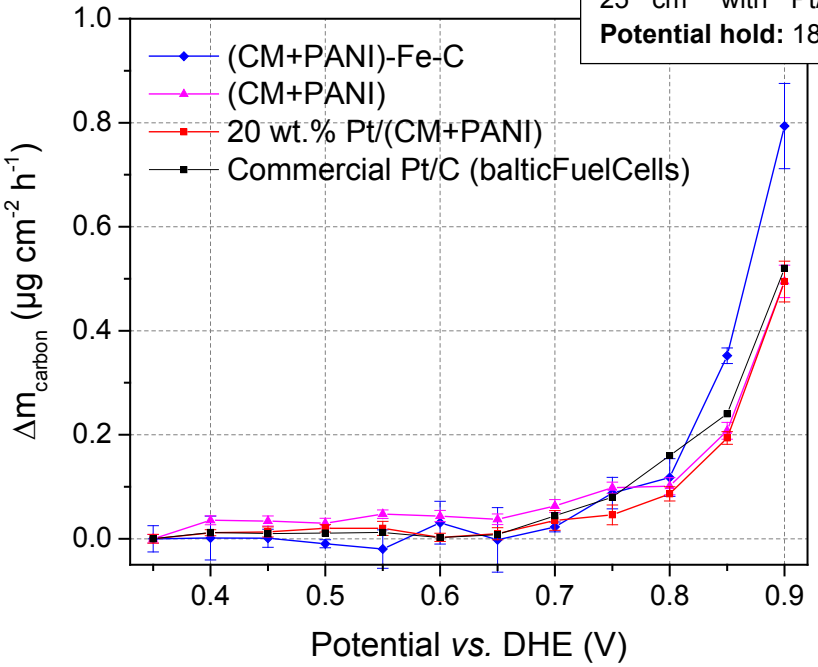
(1) Similar CO_2 emissions measured with two Fe-based, acid-leached non-PGM and reference Pt/C catalysts

(2) Low fluoride emission observed with non-PGM Fe-based cathodes; slightly lower than from Pt/C cathode

Accomplishment: CO_2 Emission Measurements in N_2 (Driven Cell)

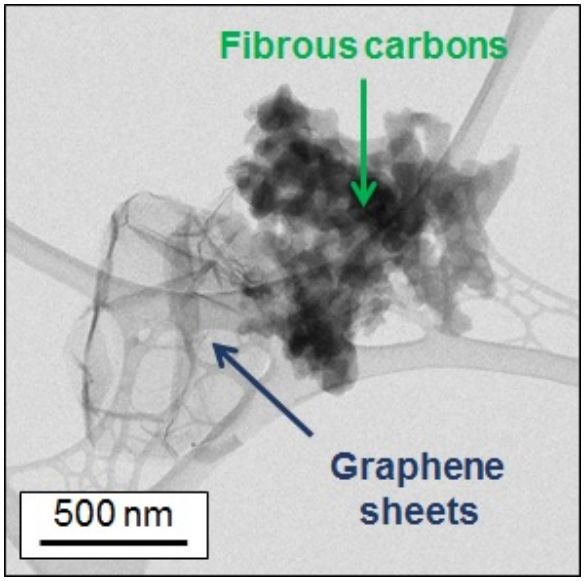


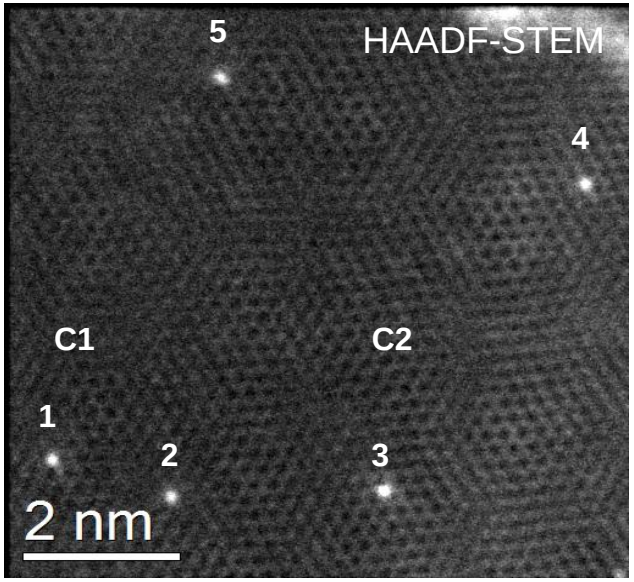
Measured electrode: 25 cm^2 with non-PGM or Pt reference catalyst, N_2, 100% relative humidity; **Counter/quasi-reference (DHE) electrode:** 25 cm^2 with Pt/C catalyst, H_2, 100% RH; **Potential hold:** 180 s; **Cell temperature:** 80°C

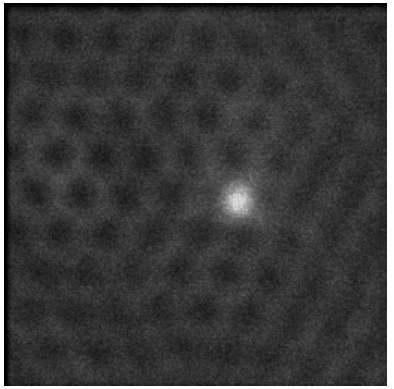


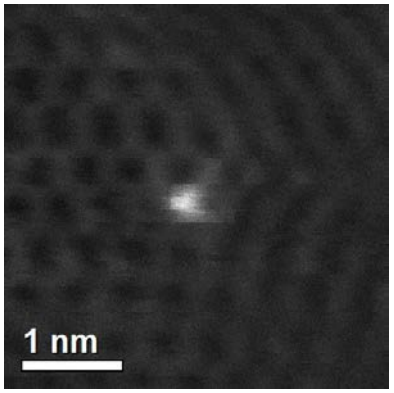
- **Highlight:** Differential electrochemical mass spectrometry (DEMS) revealing very similar CO_2 generation patterns in nitrogen for all studied cathodes up to 0.80 V
- Markedly higher carbon loss observed with Fe-based catalyst above 0.80 V
- Carbon loss at 0.6 V reduced by nearly two orders of magnitude in N_2 relative to air

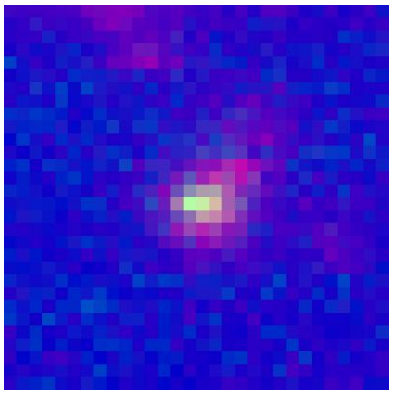
Accomplishment: First Insight into Atomic-Level FeN_x Sites











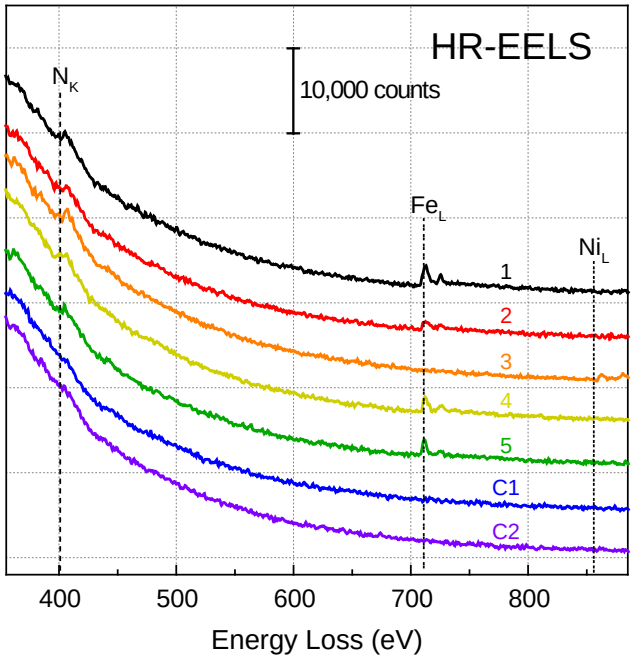
EELS quantification:

N 79.5 at.%

Fe 20.5 at.%

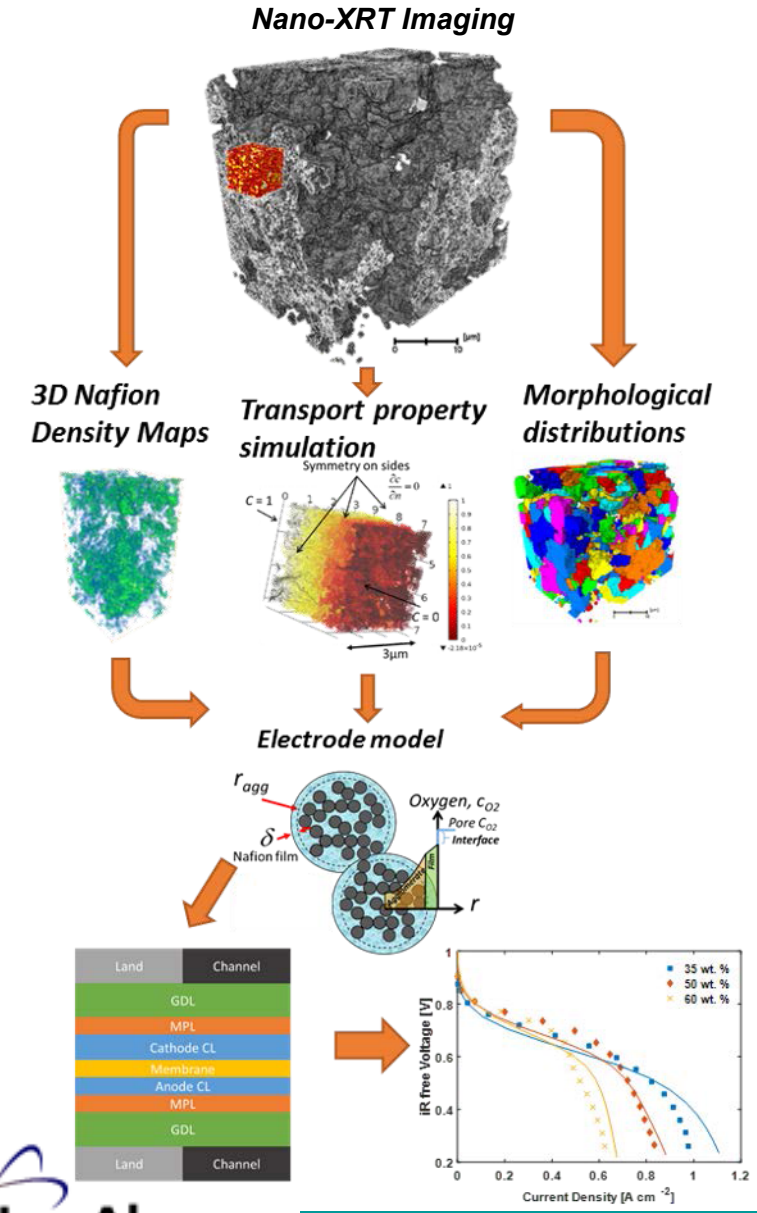
- Individual Fe atoms detected on (CM+PANI)-Fe-C catalyst surface
- Nitrogen found to be associated with iron at a ratio of 4:1

First direct observation of FeN_4 on non-PGM catalyst surface!

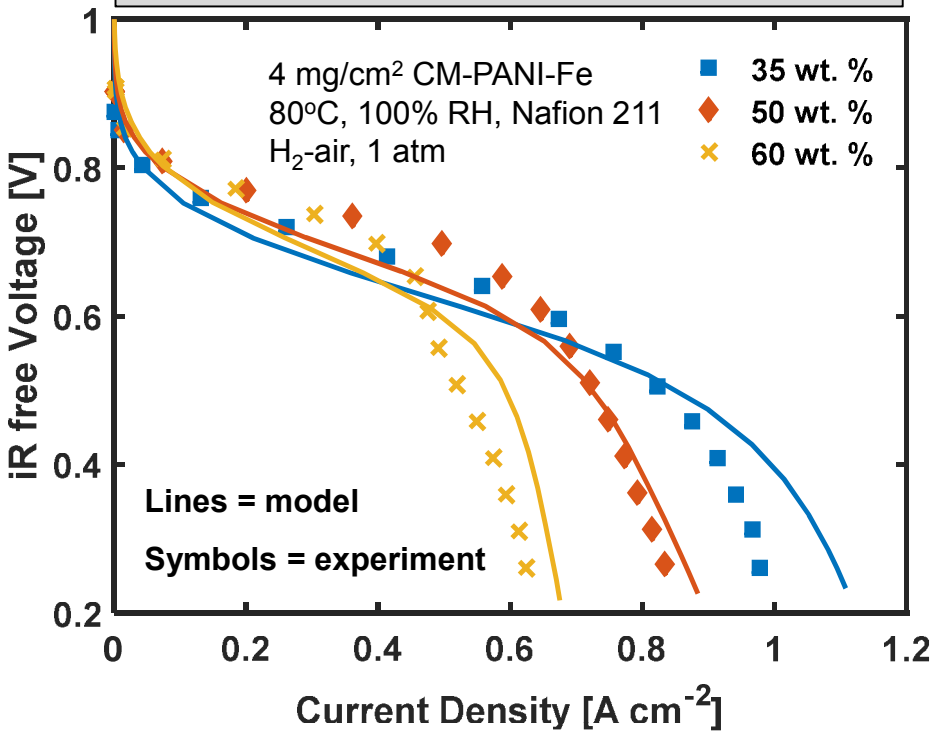


Accomplishment: Cathode and Fuel Cell Modeling

Microstructurally Consistent Model Framework



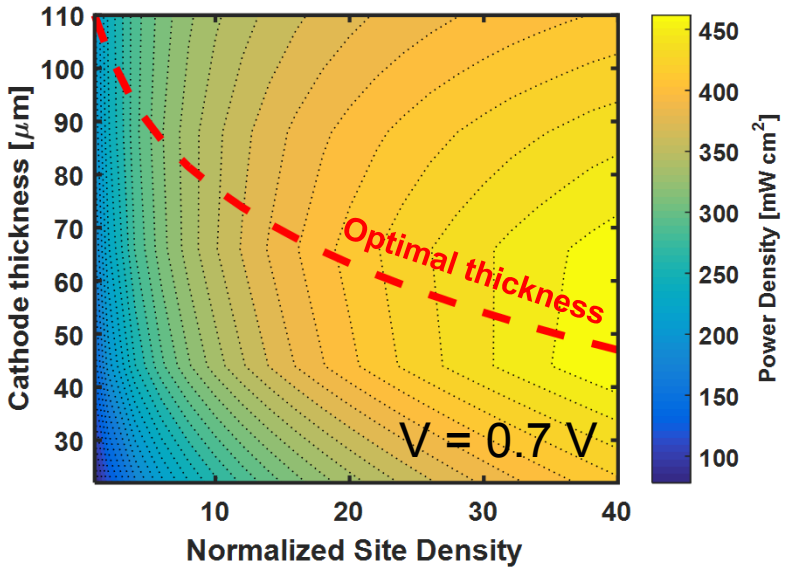
Fuel Cell Polarization Curve Comparison

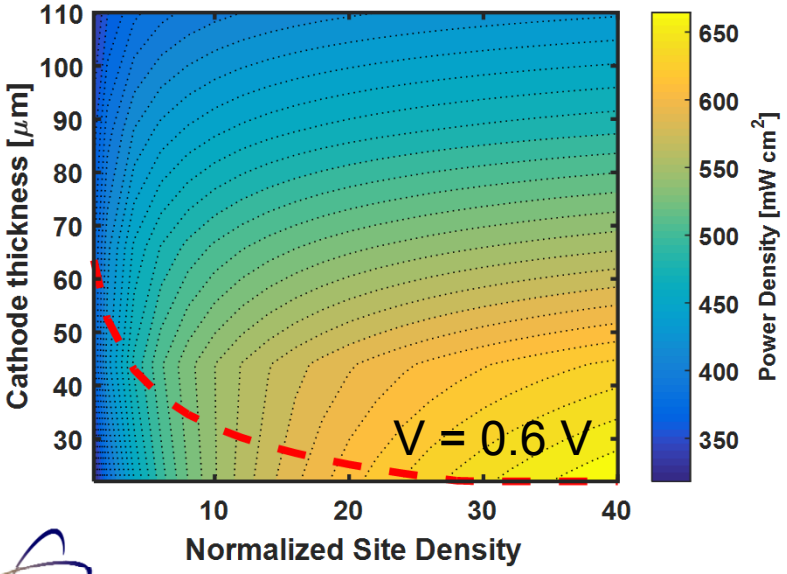


- Microstructurally consistent cathode model with morphology and transport property inputs from nano-XRT imaging and analysis
- Fitting of site activity site density at 0.8 V; conductivity from nano-XRT ionomer imaging and MES data
- **Highlight:** Trends and values consistent with experiments

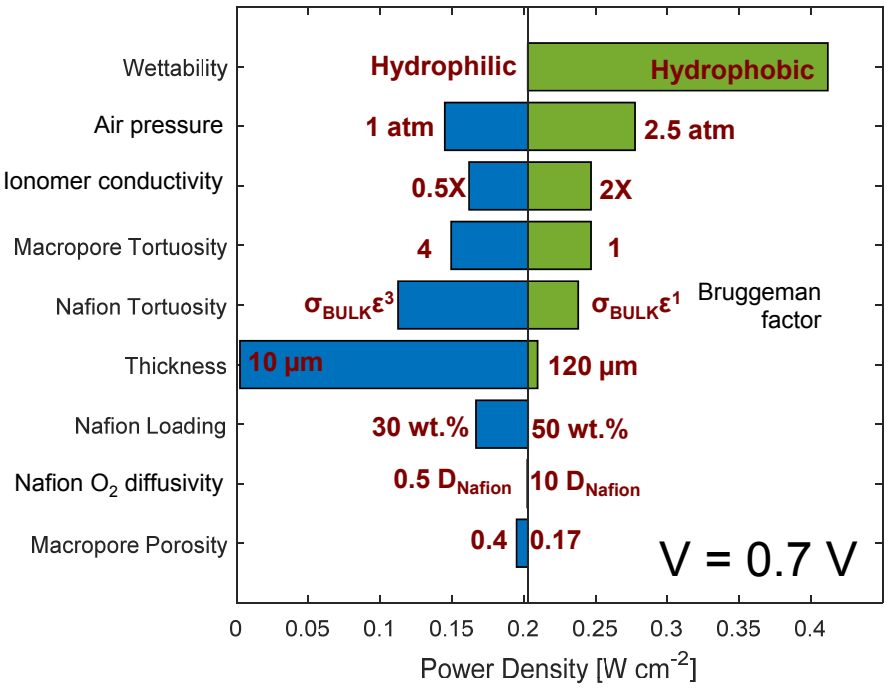
Accomplishment: Parametric Study of Cathode Performance

Power Density *vs.* Thickness and Site Density/Activity





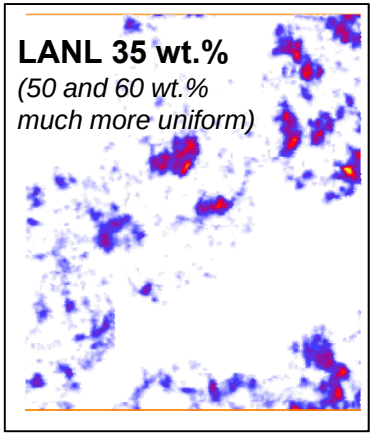
Cathode Parameter Sensitivity

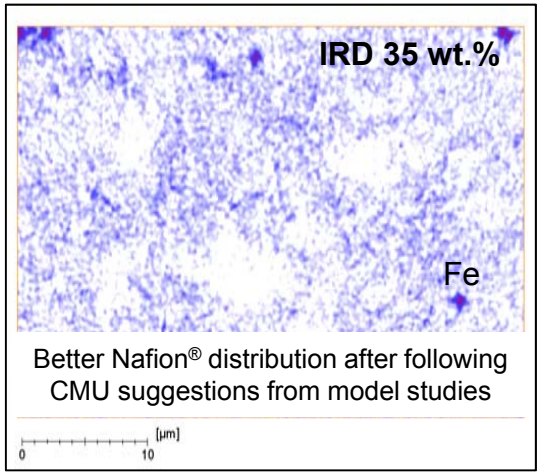


- **Highlight:** Increase in active site density/activity needed for power density targets at optimal thickness:
  - **15×** for **0.4 W/cm²** at **0.70 V**
  - **5×** for **0.5 W/cm²** at **0.60 V**
- **Highlight:** Key properties for electrode development:
  - More electrode hydrophobicity to reduce flooding
  - Higher conductivity or lower tortuosity of the ionomer

Microstructural Analysis: Progress in Electrode Design

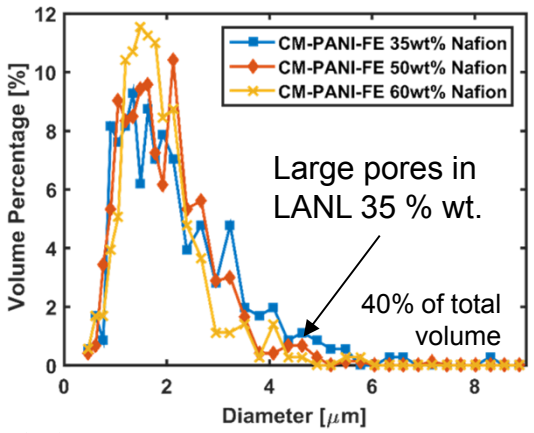
Nafion® distribution

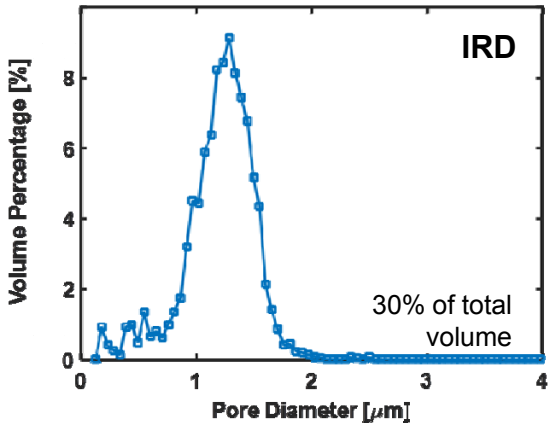




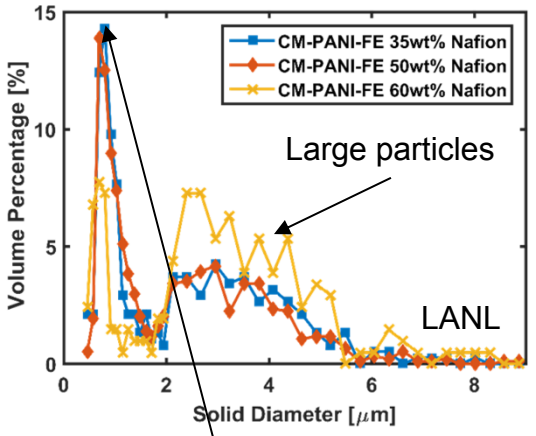
Better Nafion® distribution after following CMU suggestions from model studies

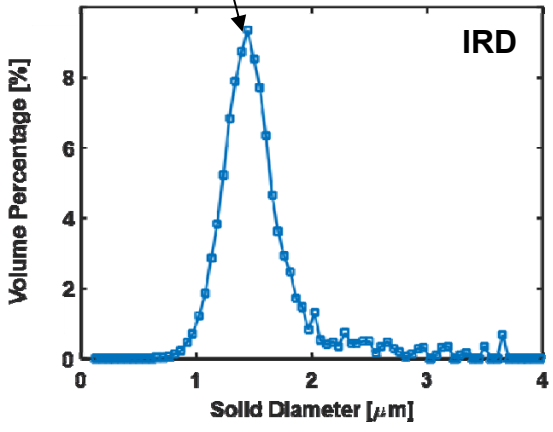
Macropore size distribution





Solids size distribution

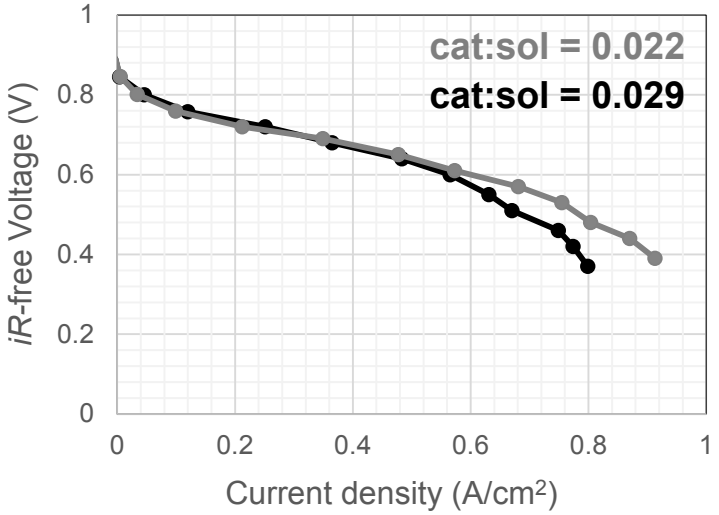




- Reduction of pores larger than 2 μm from improved ink preparation and deposition providing better Nafion® infiltration into smaller pores
- Large particles eliminated in IRD sample; similar small particle size distribution

Microstructural Analysis of Different Catalyst-to-Solvent Ratios

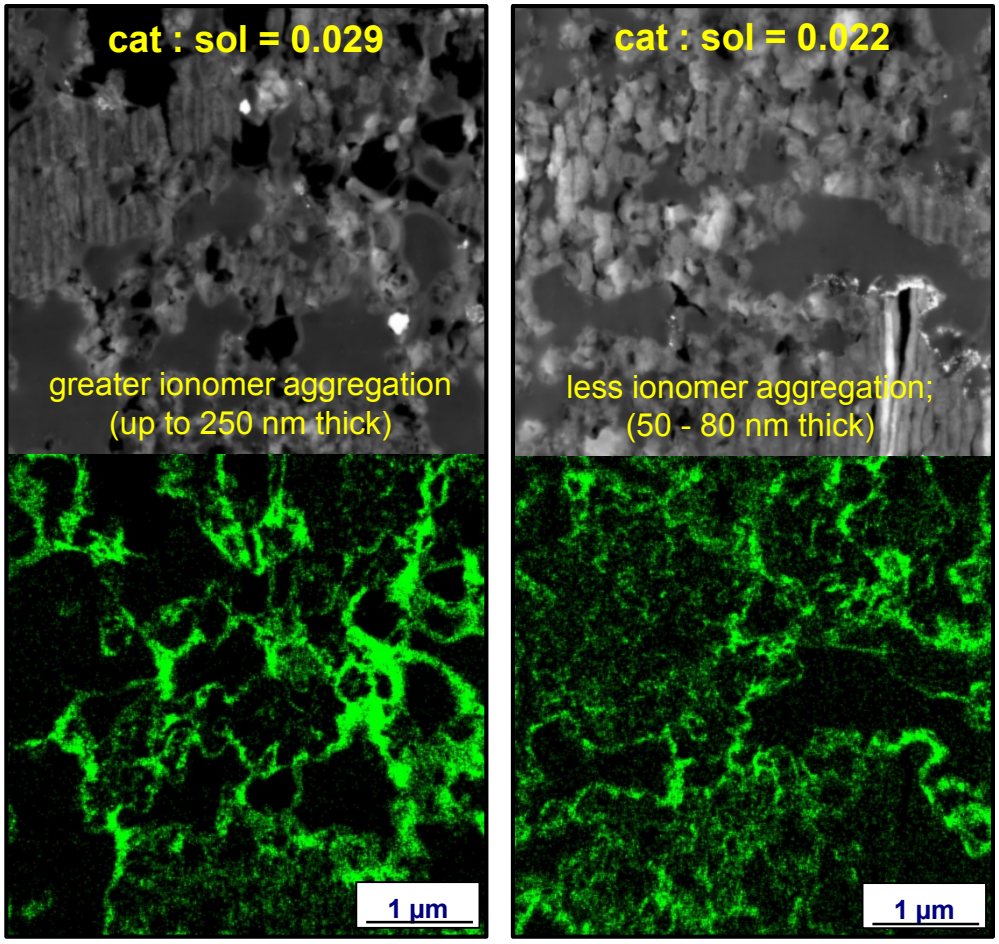
Anode: 0.15 $mg_{Pt}\,cm^{-2}$ Pt/C H_2,1.5 bar H_2 partial pressure; **Cathode:** 3 mg cm^{-2}, 1.5 bar total air pressure; **Cell**: 5 cm^2; 100% RH; 80°C.



Ink particle-size distribution

cat:sol	$d_{(0.1)}$ (µm)	$d_{(0.5)}$ (µm)	$d_{(0.9)}$ (µm)	Average pore size from EM (µm)
0.029	0.70	2.73	4.77	0.16
0.022	0.69	1.91	3.41	0.37

Electron Microscopy Analysis



Highlight: Differences in ionomer distribution are a direct consequence of the "dense" carbon agglomerate size in catalyst layers

Collaborations

- **Seven organizations directly participating in the project (highly complementary skills and capabilities in catalyst development, electrode structure design, materials characterization, MEA fabrication, fuel cell system development and commercialization):**
  - ✓ Los Alamos National Laboratory (direct DOE-EERE contract)
  - ✓ Oak Ridge National Laboratory (direct DOE-EERE contract)
  - ✓ Carnegie Mellon University (subcontract to LANL)
  - ✓ University of Rochester (subcontract to LANL)
  - ✓ University of Waterloo (subcontract to LANL)
  - ✓ IRD Fuel Cells (subcontract to LANL)
  - ✓ General Motors (collaborative research and development agreement, CRADA, with LANL)
- **Selected Organizations not directly participating in the project:**
  - ✓ University at Buffalo (SUNY), Buffalo, New York – novel non-PGM catalysts
  - ✓ Fraunhofer ICT, Pfinztal, Germany – non-PGM catalyst corrosion (DEMS studies)
  - ✓ Pajarito Powder, LLC, Albuquerque, New Mexico – catalyst scale-up and commercialization
  - ✓ Argonne National Laboratory, Lemont, Illinois – hard X-ray studies; high-throughput of catalyst development and characterization
  - ✓ CEA – LITEN/DEHT/SCGE, Grenoble, France – MEA characterization
  - ✓ Strategic Analysis, Arlington, Virginia – non-PGM catalyst cost analysis
  - ✓ Northeastern University, Boston, Massachusetts – ORR mechanism
  - ✓ Stanford University, Palo Alto, California – soft X-ray studies
  - ✓ Chevron Energy Technology Company, Richmond, California – CRADA on non-electrochemical application of non-PGM carbon-based materials

Remaining Challenges and Barriers

- Oxygen reduction reaction activity of non-PGM catalysts in need of further improvement (required to lower cost of stack components)
- Still insufficient long-term stability and performance durability of non-PGM catalysts
- Understanding of the active-site and reaction mechanism to allow bottom-up catalyst design
- Electrode integration for (i) adequate ionic and electronic conductivity in thick catalytic layers and (ii) efficient mass transport to/from the active reaction sites
- MEA design, optimization, fabrication, and scale-up
- Integration with existing automotive fuel cell stack and system technology

Proposed Future Work

Catalyst Development, Electrode Design, Active Site Studies, and Modeling:

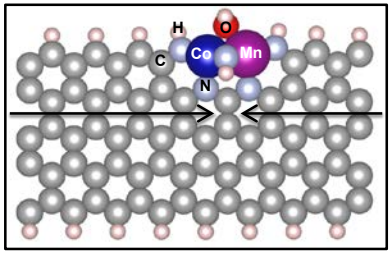
Catalyst/electrode development completed according to schedule on March 31, 2016.

MEA Optimization and Deliverable:

Timeline		
Date	**Action**	**Party**
5/2016	Complete ink and coating optimization studies of catalysts (rheology, ionomer studies, coating and processing, etc.)	IRD & IRD
6/2016	Delivery of fourth 2.5 g batch of catalyst to IRD	LANL
6/2016	Conformational/independent testing of 50 cm^2 MEAs fabricated by IRD	IRD & GM
8/2016	Delivery of 50 cm^2 non-PGM MEA to DOE-designated facility	GM & IRD

Non-PGM Catalyst Development in Near Future:

- Molecular-level dispersion of transition-metal ORR active sites (for activity enhancement) in highly graphitized carbon matrices (for durability enhancement)
- Rational design of catalyst based on the knowledge of ORR active-site(s)
- Improvement in the activity of Fe-free catalysts, *e.g.*, via inducing strain in bimetallic catalysts



- Full utilization of National Laboratory capabilities, in particular through recently established Electrocatalysis Consortium (ElectroCat Electrocatalysis Consortium), part of EERE Energy Materials Network (EMN)

Technology Transfer Activities (since 2015 AMR)

- **Patent license agreement** executed on February 1, 2016 between Los Alamos National Laboratory and Pajarito Powder, LLC for LANL-developed non-PGM ORR catalysts.

> **Pajarito Powder, LLC Announces Precious-Metal-Free Fuel Cell Catalysts Licensing Arrangement with Los Alamos National Laboratory**
>
> **February 27th, 2016 • Posted by PPC** • Permalink
>
> Pajarito Powder, LLC (PPC), manufacturer of advanced Engineered Carbon Supports and catalysts Fuel Cells, has entered into a licensing arrangement with Los Alamos National Laboratory (Los Alamos) to transfer, evaluate and commercialize the world's leading precious-metal-free fuel cell catalysts developed by Piotr Zelenay and Hoon Taek Chung of Materials Synthesis and Integrated Devices at Los Alamos. "This licensing arrangement with Los Alamos nicely enhances Pajarito Powder's intellectual property with regard to platinum-free catalyst development, our core focus", said Thomas J. Stephenson, PPC's CEO and Chairman.
>
> http://pajaritopowder.boomtime.com/pajarito-powder-llc-announces-preciousmetal-free-fuel-cell-catalysts-licensing

- **Patent issued:** H. T. Chung and P. Zelenay; "Non-precious Metal Catalysts Prepared from Precursor Comprising Cyanamide;" U.S. Patent 9,169,140, issued on October 27, 2015.
- **Patent application:** H. T. Chung and P. Zelenay; "Nitrogen-doped carbon adsorbents for removal of sulfur impurities in liquid fuels" (No. S133328/L2015068).
- **National Laboratory Showcase:** T2M event sponsored by FCTO at 228th ECS Meeting in Phoenix, Arizona, October11-16, 2015 – participated in the electrocatalysis part of the event (poster, on-site meetings).
- **Feynman Center for Innovation at LANL:** Actively pursuing non-PGM catalyst portfolio through meetings with potential customers, brochures, quad charts, etc.

Summary

- Improvements to ORR non-PGM catalyst activity in FY16 resulted in a fuel cell voltage of **0.87 V** at the reference current density of 0.044 A cm^{-2} (0.01 V below the intermediate 2018 target of 0.88 V) – nearly **fourfold** increase in activity over the life of this three-year project
- In addition to improvements in ORR activity, catalyst synthesis pursued in FY16 has focused, like never before, on non-PGM catalyst durability. Approaches involved:
  - ✓ *Three catalysts derived from PANI with amine side chains for high active site density*
  - ✓ *Catalysts with Zn-induced microporosity for high activity ($E_{½}$ 0.81 V) and potentially improved durability (thanks to the use of a higher heat-treatment temperature)*
  - ✓ *Homemade "Fe-MOF" catalyst with best durability to date (collaboration with UB)*
  - ✓ *Fe-free non-PGM catalysts with improved ORR activity ($E_{½}$ only 30 mV lower than for Fe-based catalysts, activity likely to improve further based on the modeling study)*
- CO_2 and F^- emissions from non-PGM cathode (Fe-based catalyst) have been found to be very similar to those measured with Pt-based catalysts under the same test conditions.
- Nitrogen found to be associated with iron at ratio of 4:1 on the carbon surface; possibly the first ever direct observation of **FeN_4** (often suggested as the most likely ORR active site)
- Parametric study of cathode performance revealed active site activity/density values and properties of the electrode/ionomer required to meet power density targets
- All project performance measures have been met; final electrode design is nearing completion with the help of microstructural analysis of factors determining electrode performance; project deliverable remains on schedule (summer 2016)

Co-Authors

– **Catalyst research and characterization; project management**

Piotr Zelenay (Project Lead), Hoon Chung, Ling Lin, Edward Holby, Ulises Martinez, Gerie Purdy, Xi Yin

– **Catalyst and electrode characterization**

Karren More (PI), David Cullen

– **Electrode characterization, modeling and design**

Shawn Litster (PI), Siddharth Komini Babu

– **Catalyst characterization**

Michael Neidig (PI), Jeffery Kehl, Jared Kneebone

– **Catalyst development and characterization**

Zhongwei Chen (PI), Ja-Yeon Choi, Xiaogang Fu, Pouyan Zamani

– **MEA design, integration, testing and scale-up**

Madeleine Odgaard (PI), James Brewster, Debbie Schlueter

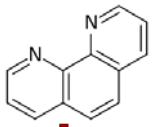
– **Electrode and MEA research; MEA validation**

Joseph Ziegelbauer (PI)

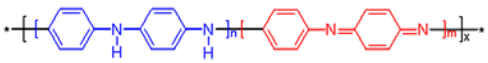
Technical Back-Up Slides

Approach: Dual Nitrogen Precursor Catalysts (Phen+PANI)-Fe-C

Phenanthroline



Polyaniline



Carbon

$FeCl_3$

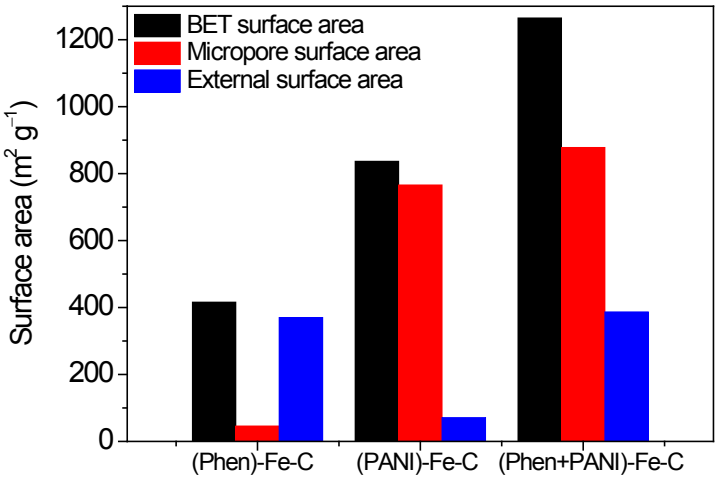
First heat treatment at 900°C in inert atmosphere

0.5 M H_2SO_4 leach at 80-90°C

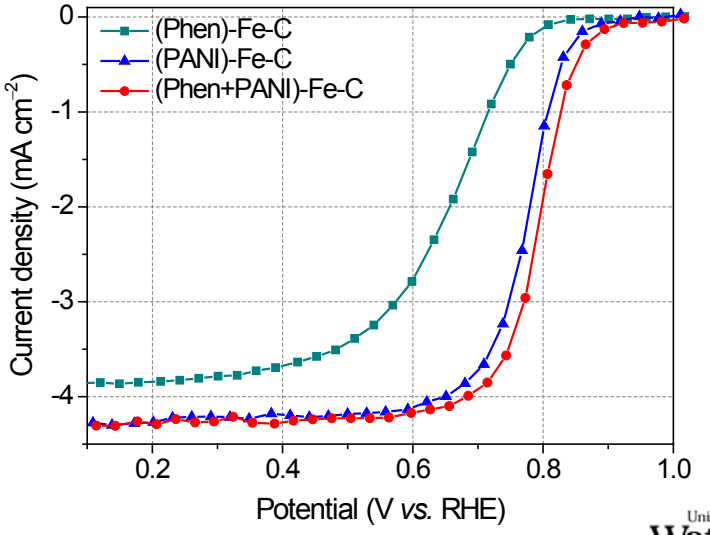
Second heat treatment at 900°C in inert atmosphere

Ammonia treatment at **900°C**

ORR performance evaluation; characterization



RDE: 0.5 M H_2SO_4; 0.6 mg cm^{-2}; 900 rpm; 25°C; RHE reference electrode; graphite counter electrode; steady-state potential program: 30 mV steps, 30 s/step.



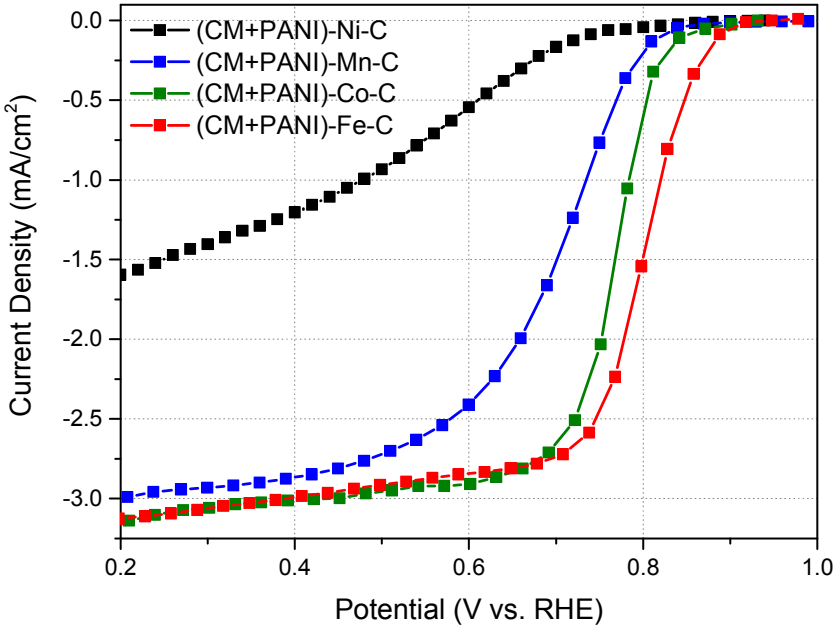
- Impregnation of small phenanthroline molecules within carbon pores, possibly forming active sites inside
- PANI polymerization creates graphitic network defining the macroscale morphology

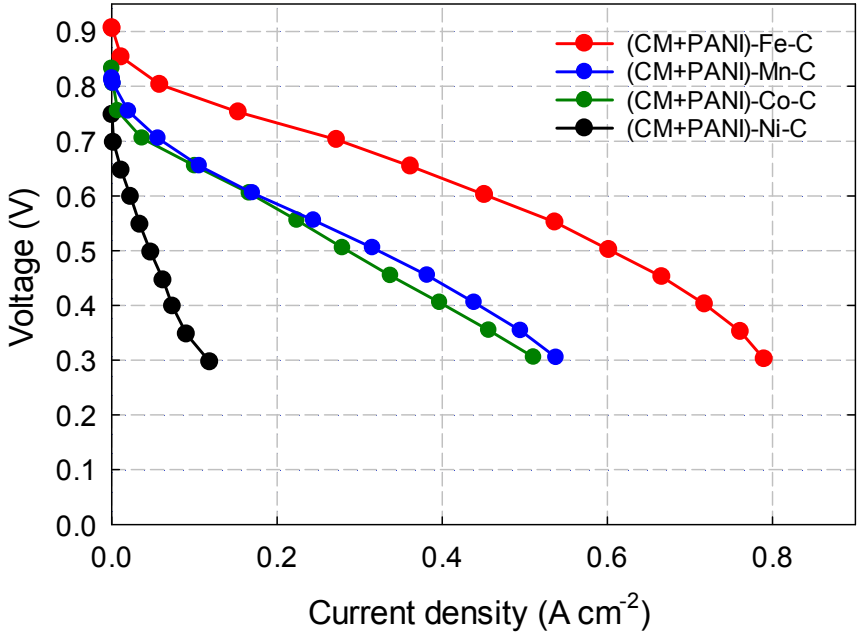
Highlight: Half-wave potential of **0.80 V** achieved with (Phen+PANI)-Fe-C

Electrochemical Activity of (CM+PANI)-*Me*-C Catalysts

ORR: 0.6 mg/cm^2; 0.5 M H_2SO_4; 900 rpm; 25ºC; Ag/AgCl (3 M KCl) reference electrode; graphite counter electrode; steady-state potential program: 30 mV steps, 30 s/step

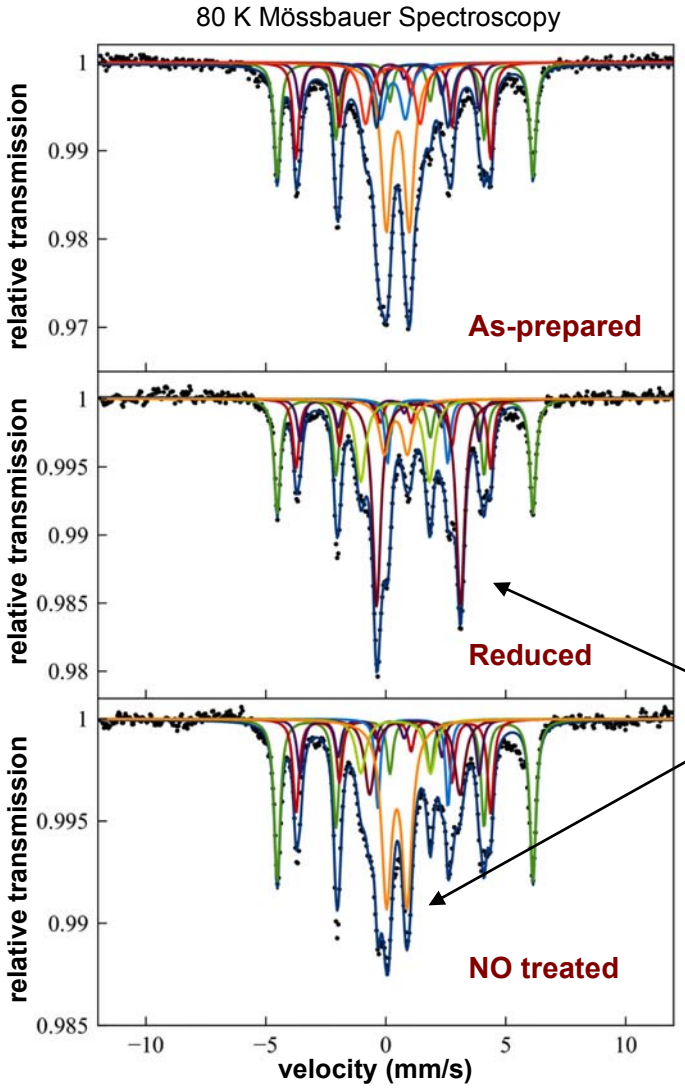
Anode: 0.2 mg_{Pt} cm^{-2} Pt/C H_2, 1.0 bar H_2 partial pressure; **Cathode**: *ca.* 4.0 mg cm^{-2} (CM+PANI)-*Me*-C, 1.0 bar air partial pressure; **Membrane**: Nafion®-211; **Cell size**: 5 cm^2





Improved activity of (CM+PANI)-Co-C catalyst by removal of crystalline Co phases, from 0.72 V to 0.77 V ($E_{½}$) approaching (CM+PANI)-Fe-Co activity

Accomplishment: Synthesis *vs.* Fe Speciation: (PANI+CM)-Fe-C



Key Observations:

- Bulk constitutes a larger amount of the total iron content in (PANI+CM)-Fe-C (~ 1/2) compared to PANI-Fe-C (~ 1/3)
- Bulk iron speciation is more complex in (PANI+CM)-Fe-C
- Reduction and NO treatment effects are observed within the doublet iron species consistent with previous PANI-Fe-C studies

Highlight: Mossbauer parameters of species consumed upon NO treatment are perturbed relative to reactive species in PANI-Fe-C ($\delta/\Delta E_Q$ (mm/s): 1.21/3.76 vs. 1.54/2.72)

Selective Perturbation in Doublet Iron Upon NO Treatment

Key for Future Applications:

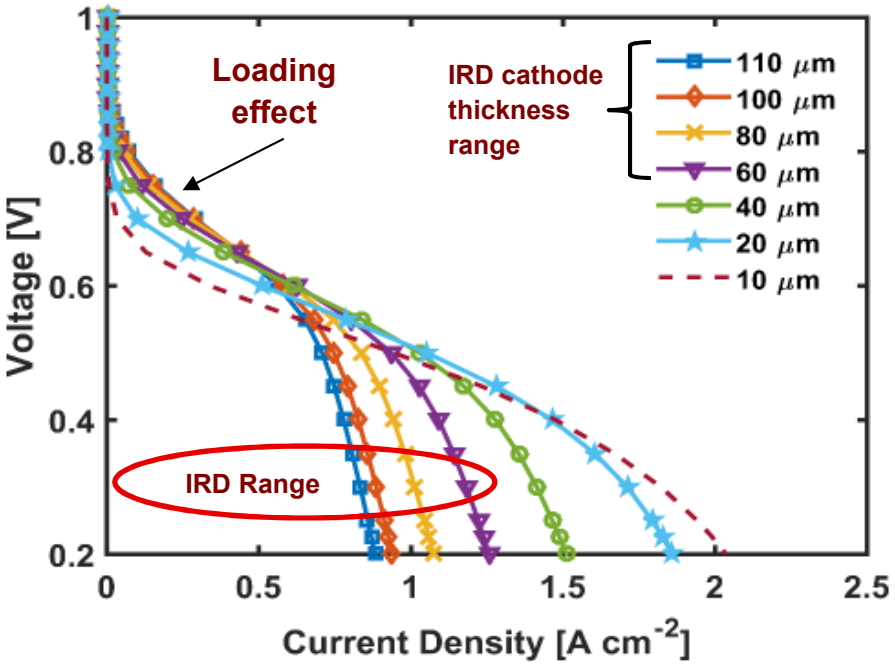
Methodology is general and similar effects are observed in both PANI-Fe-C and (PANI+CM)-Fe-C; Provides a general experimental Approach for quantitative probing of speciation and potential O_2 reactive site identification

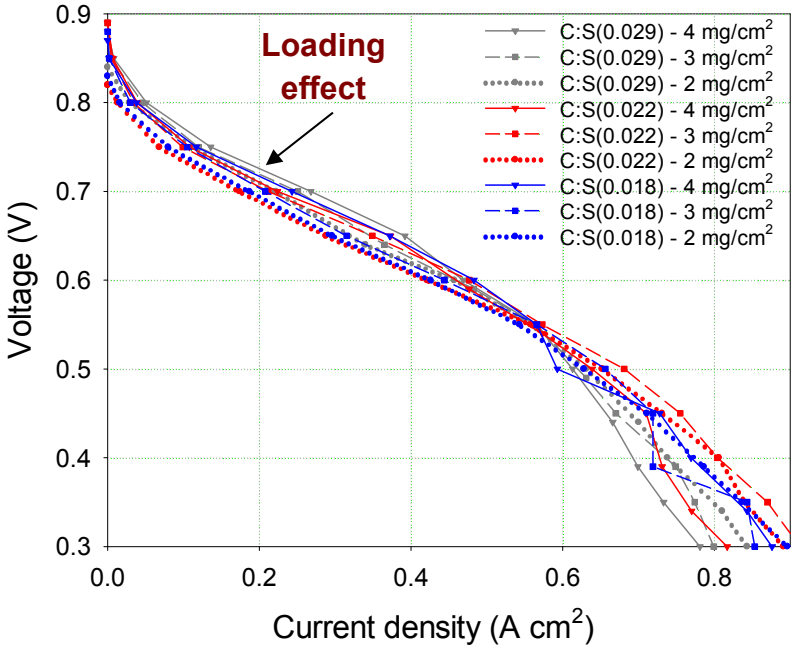
Reactivity Differences in PANI-Fe-C vs. (PANI+CM)-Fe-C can be correlated to a fundamental difference in the nature of the reactive iron species as opposed to a simple quantity of reactive species effects

Comparison between Experimental and Simulated Loading Studies

Simulated fuel cell data

Anode: 0.15 mg_{Pt} cm^{-2} Pt/C H_2, 1.5 bar H_2 partial pressure;
Cathode: Batch #4, 2-4 mg cm^{-2}, 1.5 bar air/O_2 partial pressure;
Cell size: 5 cm^2; 100% RH; 80°C

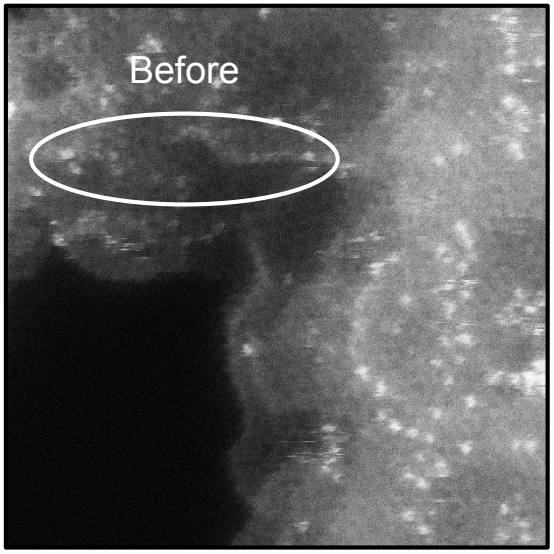


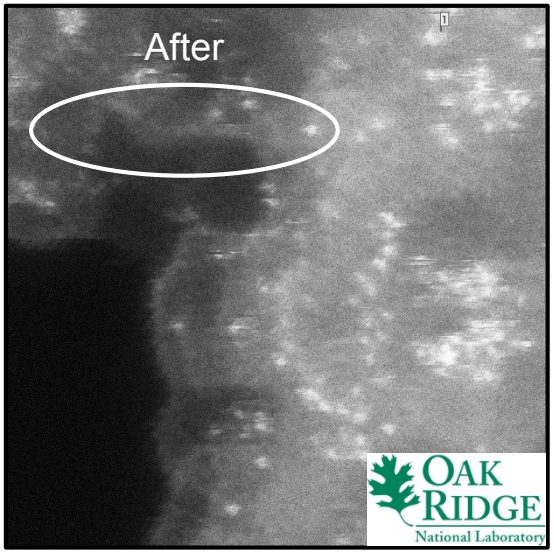


- Good agreement between experimental and simulated loading studies (within experimental variability)
- Low sensitivity to loading (thickness) for experimentally tested 2-4 mg/cm^2 range at voltages > 0.6 V
- **Highlight:** Mass transport benefiting from lower loadings and lower catalyst-to-solvent ratios

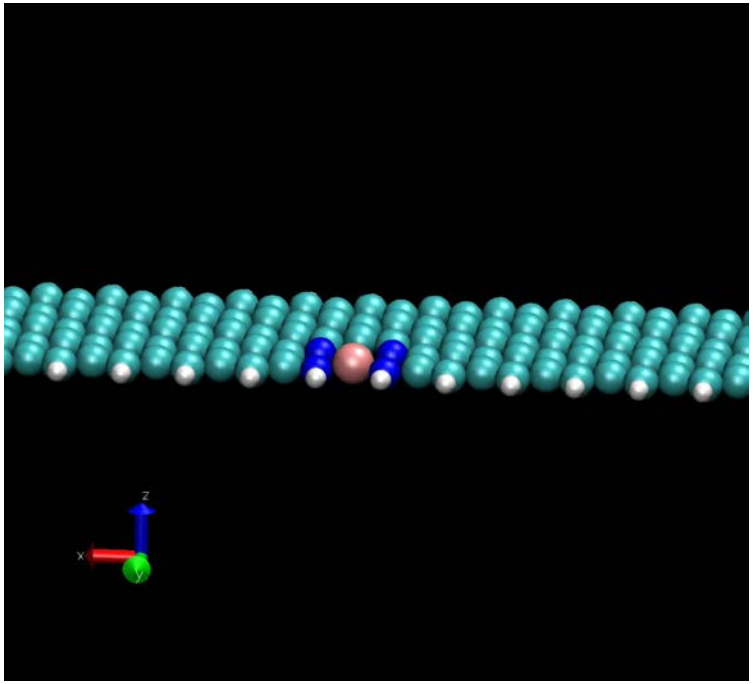
Accomplishment: TEM Beam Damage of Edge Sites

HAADF-STEM (60 kV)





Simulate electron collisions with atoms in proposed non-PGM catalyst active sites using *ab initio* molecular dynamics (AIMD): Elastic collision model for initial velocity vector; 100 fs with 1 fs time steps.



- N atom most susceptible to removal for both FeN_4 edge (124 kV) and bulk (150 kV)
- FeN_4 edge structure more susceptible to beam damage than bulk structures
- **Highlight:** Beam damage model may serve as computational durability descriptor for non-PGM active sites