Development of Novel Non-Pt Group Metal Electrocatalysts for Proton Exchange Membrane Fuel Cell Applications

2015 DOE Hydrogen and Fuel Cell Program Review

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Project ID# FC086

Overview Slide

- **Timeline**:
  - Start date: 8/01/2010
  - End date: 7/31/2015
- **Budget Data**: Total Funding Spent as of 3/31/2014:
- Total Project Value: $ 4,942,301 (Federal), $ 1,437,714 (cost share); Total $ 6,38015
- Cost Share Percentage: 20%
- Total DOE Funds Spent*: $4672,824

* As of 3/31/15

- **Barriers/Targets (Addresses both 'Cost' and 'Durability')**
  - **Key Barriers**: Elevating inherent mass activity (at 0.85 to 0.9 V) and areal activity in Air (0.65 V) to approach DOE FCTO PGM 2020 targets.
  - **Activity Targets**: for Non-PGM catalysts (**BP-1**): Volumetric activity: to exceed 300 A/cm^3 (2015-target) and Areal Activity: 100 mA/cm^2 at 0.8 V 1.5 bar total pressure. (**BP-2**): Areal Activity (Air): 30 mA/cm^2 at 0.8 V (Q2, FY-14) and 1.0 A/cm^2 at 0.4 V (Q5-FY-15) in H_2/Air 2.5 bar total pressure.
  - **Durability Target**: at temperatures ≤ 80°C, Non-pgm catalysts subjected to load cycle testing will achieve a loss of initial catalytic activity of < 60% and less than 30 mV loss in potential at 0.8 A/cm^2.
- **Partners**
  - *Northeastern Univ.*, (Prime) Boston: S. Mukerjee (P.I)
  - *Univ. of New Mexico*, Albuquerque: Prof. P. Atanassov
  - *Michigan State University*: Prof. S. C. Barton
  - *Pajarito Powders*, Albuquerque, NM, Dr. B. Halevi
  - *Nissan Technical Center North America (NTCNA)*: Dr. N. Dale

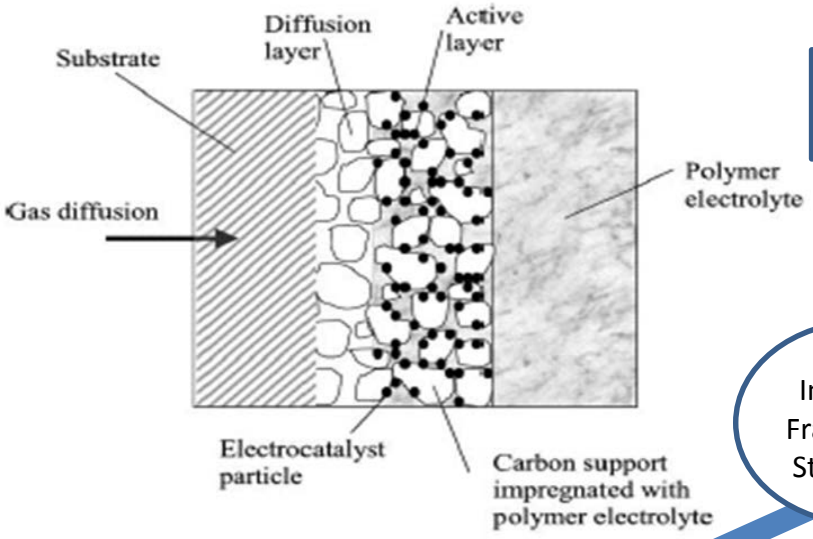
Relevance

- Objectives: To develop new classes of non-PGM electrocatalysts which would meet or exceed 2015 project targets for activity and durability. 2015 Project Activity targets are 100 mA/cm^2 (H_2/O_2, 1.5 bar total pressure) and 30 mA/cm^2 @ 0.8 V and 1 A/cm^2 at 0.4 V (H_2/Air) at 2.5 bar total pressure .
- Relevance to DOE Mission: This will enable decoupling PEM technology from Pt resource availability and lower MEA costs to less than or equal to $ 3/KW. Science of electrocatalysis will be extended from current state of the art supported noble metal catalysts to a wide array of reaction centers.
- Impact
  - Lower MEA cost to less than or equal to $ 3/KW
  - Independence from Pt and other precious metal global availability
  - Greater tolerance to poisons which typically effect Pt & Pt alloys (i.e., sulfur, CO etc.), Hence ability to tolerate H_2 with greater impurity.

Overall Approach

- **Overall technical approach:**
  - **Comprehensive materials development strategy encompassing:**
    - **Novel new reaction Centers for Oxygen Reduction**
      - High Performance Catalysts
      - Tailored Catalysts for Understanding Structure Property Relationships
    - **Controlling Metal support interactions**
      - Efficient mass transport of charged and solute species
    - **Ensuring Stability via careful control of reaction center's electronic structure**
  - **Computing transport and reaction dynamics**
    - Transport modeling in multi-layer structures
  - **Ex Situ XPS and In Situ Synchrotron X-ray Spectroscopy**
    - For elucidating electrocatalytic pathways in complex reaction centers
    - Quantifying degradation with element specificity under *in situ* operating conditions
- **Program Technical Barriers and Approach to Overcome them:**
  - Meeting and Exceeding Program Areal Activity Target of 30 mA/cm^2 @ 0.8 V and 1 A/cm^2 @ 0.4 V, non iR corrected, H_2/Air, 80^{o}C, 2.5 bar total pressure, 100% RH
    - (a) Development of new classes of materials,
    - (b) Redesign of the catalyst support and Electrode Structure for efficient mass transport.
    - (c) Understanding ORR electrocatalysis using a combination of spectroscopy and computation
    - (d) Determining degradation pathways under actual operando conditions.

Approach: Program Management and Implementation



Nano-Engineering of Reaction Centers for Non-PGM Interfaces
Thrust Area 1-Task 1.1-1.2

Metal Inorganic Framework Structures [NEU]

Open Framework Structures [UNM]

Non Metal Polymer Complexes [MSU, NEU, UNM]

Bio-Inspired Non PGM Transition Complexes [NEU]

Designing Interfacial Structures for Enhanced Mass Transport (NEU, MSU)
Thrust Area 2-Task 2.1

Computation (MSU) and Spectroscopy XPS (UNM) and in situ Synchrotron Spectroscopy (NEU)
Thrust Area 4-Task 3.1-3.3

Electrocatalyst Scale up (PPC) and MEA Fabrication (NEU, PPC)-**Task 1.3**

MEA Fabrication, Initial Validation and Single Cell Testing
Thrust Area 3-Task 2.2

Single Cell Validation Tests and Durability Protocol Implementation (NTCNA /LANL) **Thrust Area 5-Task 2.3**

Automotive Test Protocols, Stack Testing and Durability Validation (NTCNA)
Thrust Area 5-Task 2.4

Quarterly Milestones Q3 FY14-Q3 FY15

- Q2 (FY 14): First batch of the scaled up non-pgm catalyst samples (at least 30 g) tested for kinetic reproducibility both intra and inter sample basis with variation of the activity, as measured by RDE, being $\leq \pm 5\%$.

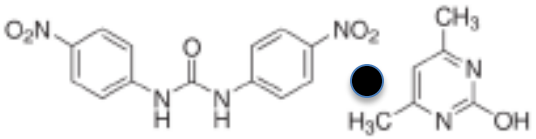
Status: As shown below the project Objectives have been met.

- Q3 (FY 14): Finish both the intra and inter sample analysis of fuel cell data (MEA single cell performance) measured at Nissan Technical Center scheduled for March 2014, confirming a) performance obtained in other laboratories or b) trends identified in other laboratories.
- Q4 (FY 14): Using non-pgm cathode catalysts, demonstrate MEA performance of at least 30 mA/cm2 at 0.8 V in H_2/Air, 2.5 bar total pressure.
- Q1 (FY 15): Non-pgm catalysts subjected to catalyst stability (<10% of initial activity) and load cycle testing will achieve a loss of initial catalytic activity of < 60% and less than 30 mV loss in potential at 0.8 A/cm^2.
- Q2 (FY15): Demonstrate a unified mechanism for ORR wherein the active site and its function are identified for a range of Non-PGM catalysts prepared with different approaches leading to a better fundamental understanding of the requirements for a non-pgm ORR catalyst. A detailed report will be submitted or accepted in a peer reviewed journal.
- Q3 (FY15): With a cathode optimized for non-pgm catalysts, achieve MEA performance of at least 1.0 A/cm^2 at 0.4 V in H_2/Air, 2.5 bar total pressure.

Task 1.1-1.2: Design and Synthesis of Novel Materials for Oxygen Reduction Reaction (ORR) - Advanced Performance Catalysts: Development of Novel MNC Catalysts

Materials Design Strategy: Evolution of Different Approaches in Budget Period 1… Continued

- **Mechano-Chemical Approach (UNM)**



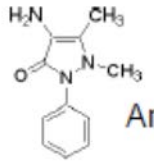
Nicarbazin

Ball milling

+ Fe-Salt+ Silica templated

UNM-CTS

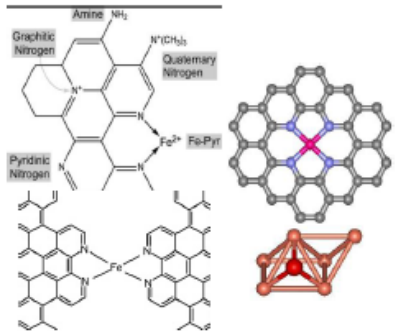
- **N-Chelating Precursor-Metal Salt Approach (UNM, MSU)**



Aminoantipyrine

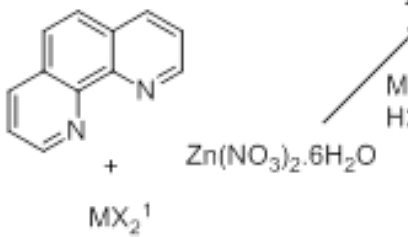
+ Fe-Salt+ Silica templated

Pyrolysis



M-N-C catalyst

- **Metal Organic Framework Approach: (NEU)**



+ $Fe(NO_3)_3$, DMF, 140°C, 120 h

UNM-Fe-MOF

MeOH

rt

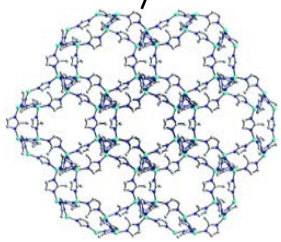
2h

MeOH/ H_2O

$Zn(NO_3)_2.6H_2O$

MOF + Encapsulated N-Precursor and Metal Salt

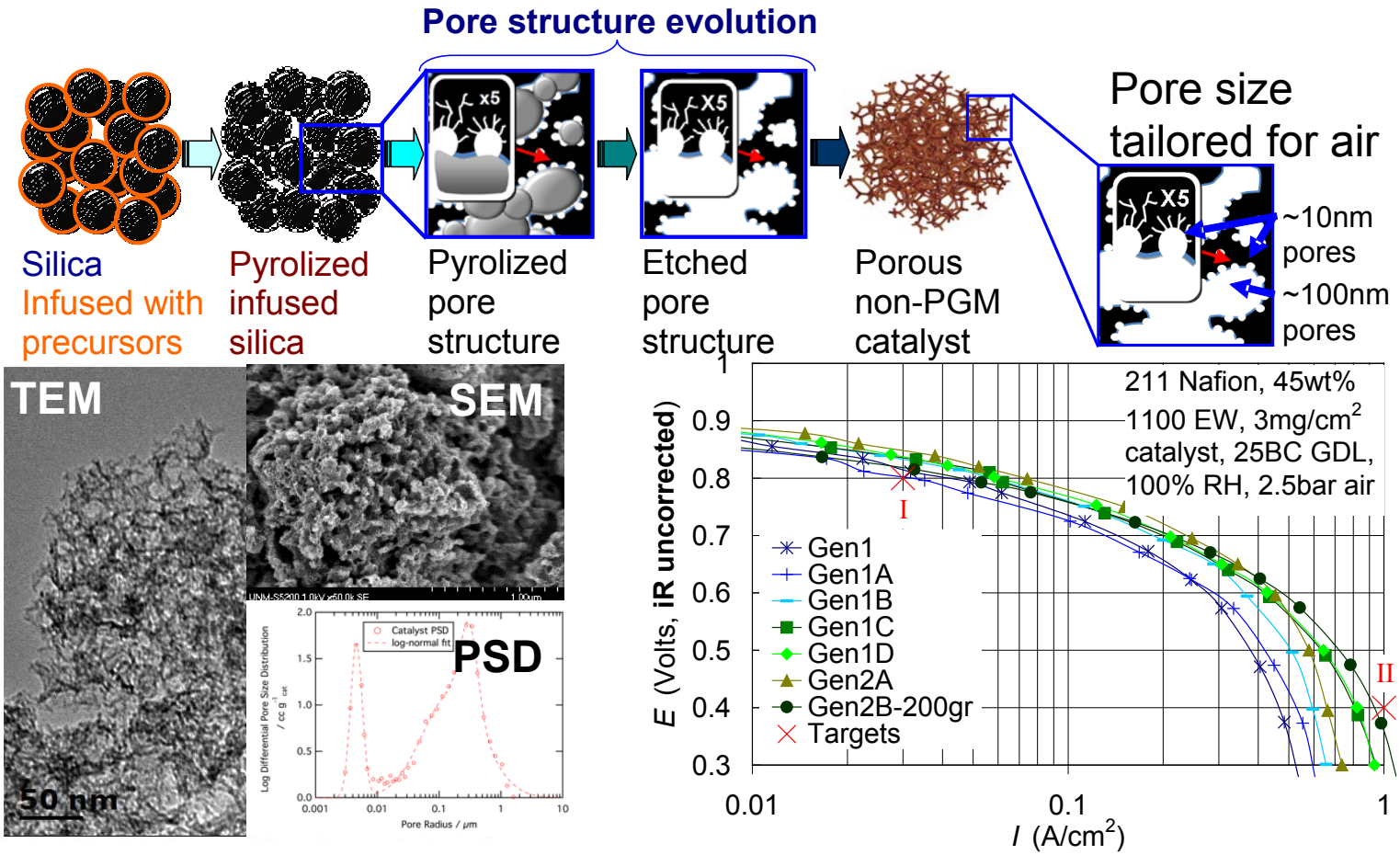
NEU-Fe-MOF



[1] M=Fe, Co; X=$C_2H_3O_2$, Cl

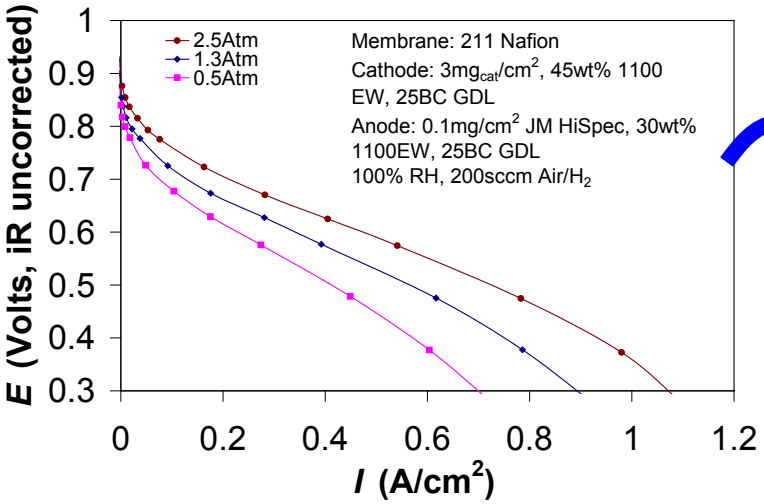
[2] '@' indicates chemical encapsulation of phenanthroline and metal (M-N_4 active site)

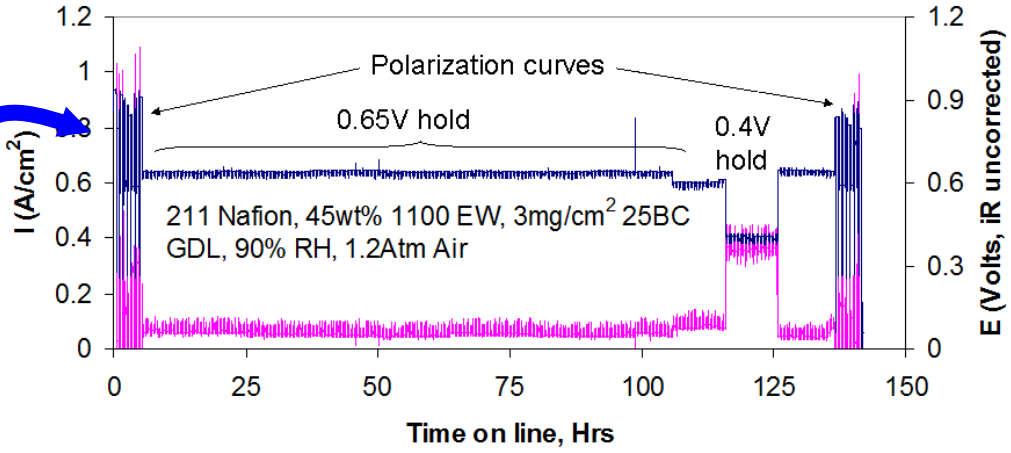
Fe-CTS Modification for Air and Scale Up



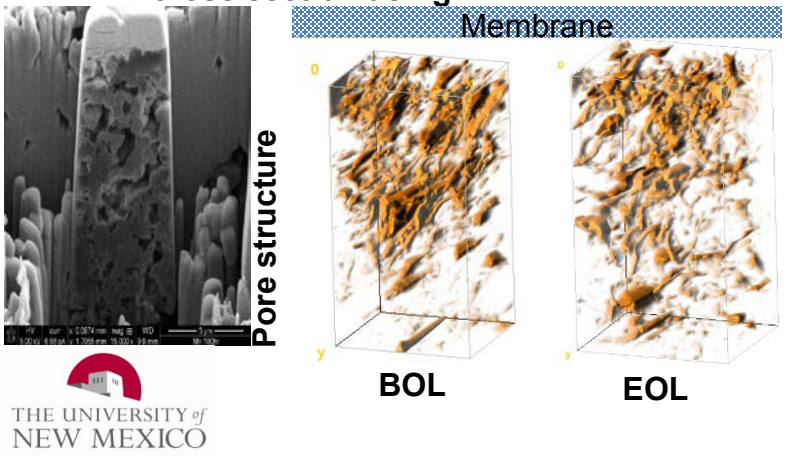
- **UNM SSM method Fe-CTS catalyst porosity modified for air operations and scaled to 200gram per batch**

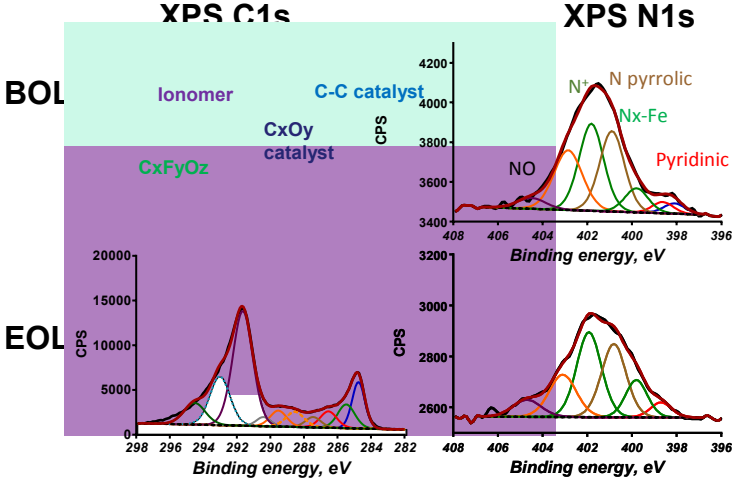
Stability & Degradation Mechanism of Fe-CTS





MEA cross section using FIB-EDX

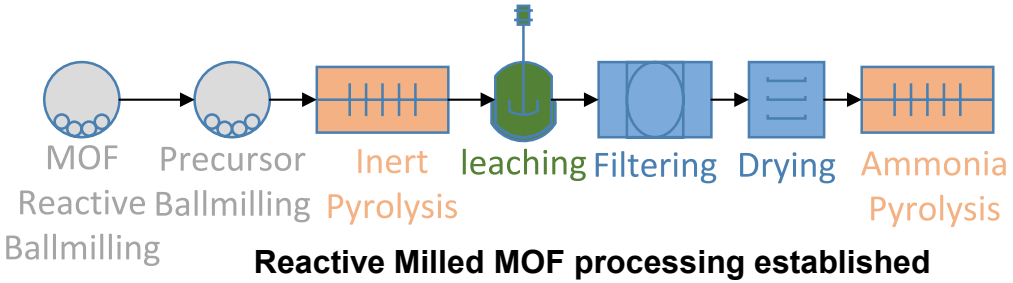




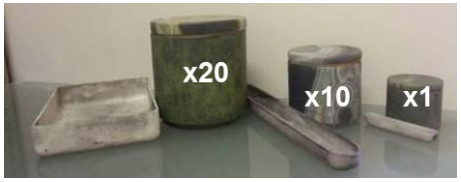
- **Catalyst stable at 0.65V for 100+ hrs**
  - **surface oxidized, some active sites lost, slight collapse of pores and roughening**

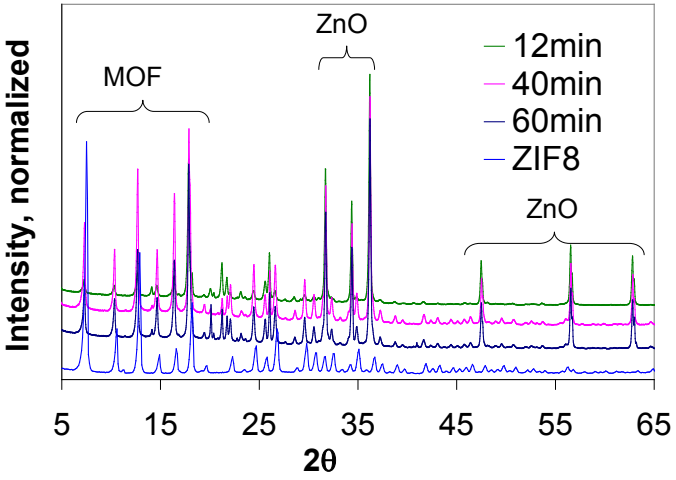
PAJARITO POWDER

Fe-MOF tech Transfer and Scale Up

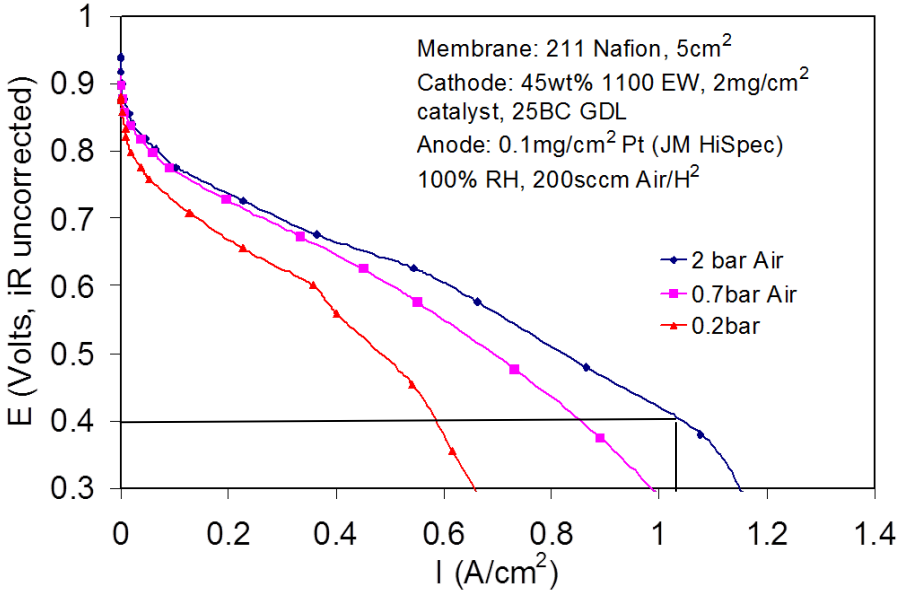


Reactive Milled MOF processing established

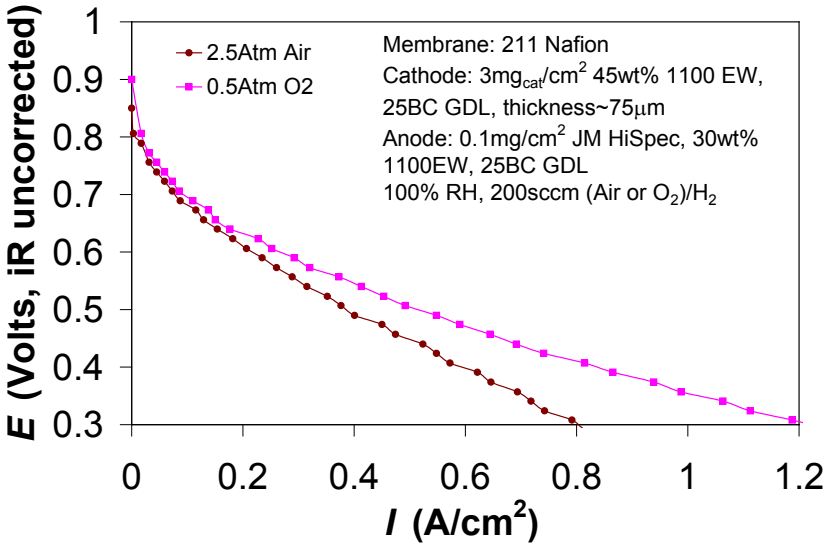




MEA performance of x 5 scale catalyst



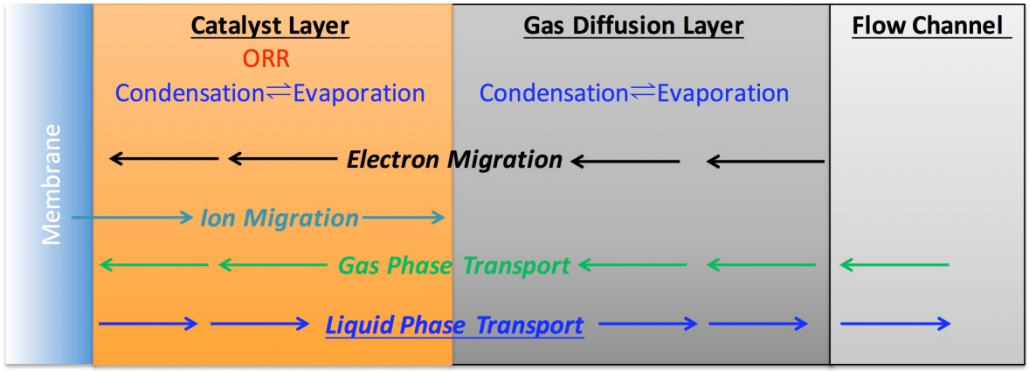
MEA performance of x10 scale catalyst



- **Key process steps and variables established and being adjusted for x20 scale**
- **Promising performance of initial x10 batches established**

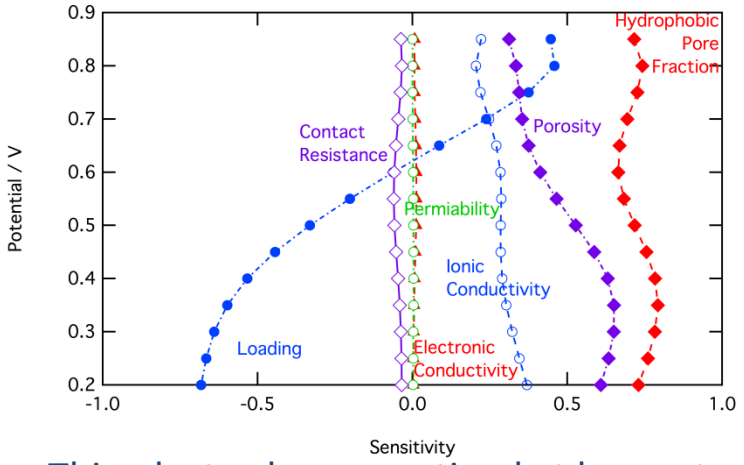
Mass Transport Studies: Modeling and Experiments

- Accounts for **hydrophilicity** and **pore size distribution** in catalyst layer. UNM CTS catalysts

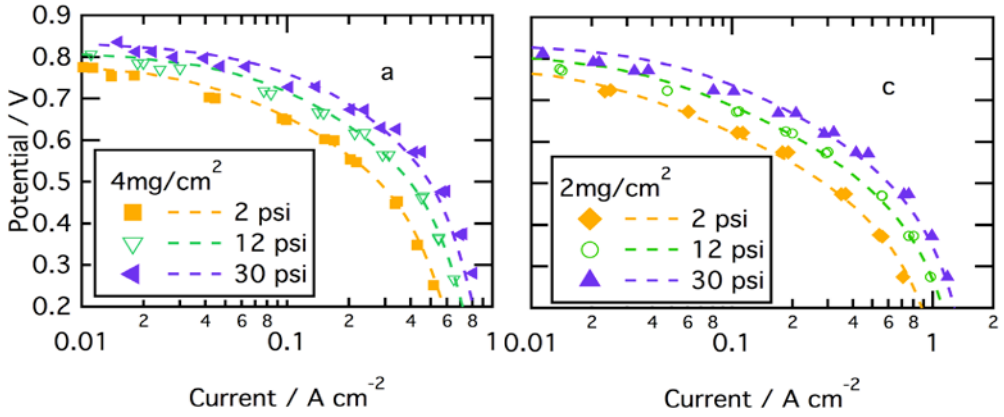


Dominant Parameters:

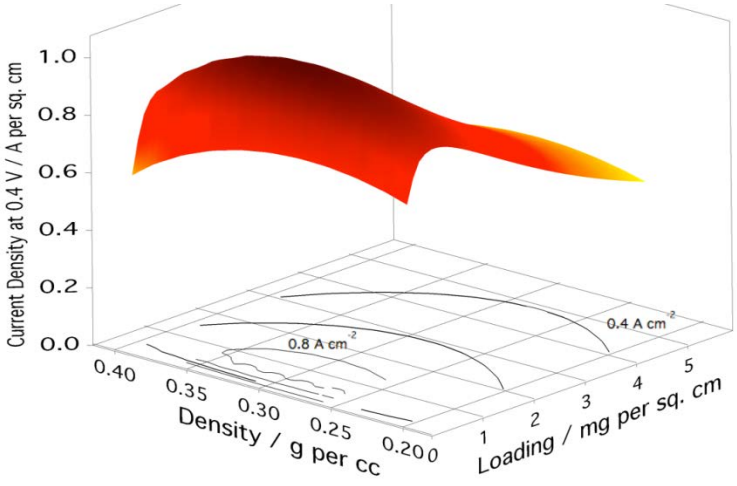
- Hydrophobicity (All Potentials)
- Loading (low potentials)



Fit to PPC MEA Data



Thin electrodes are optimal at low potential.



Temp. 80 C, 25BC GDL, 4mg/cm^2 Catalyst Loading, 45 wt% Nafion®, Cell Area: 5cm^2, membrane: NR211.

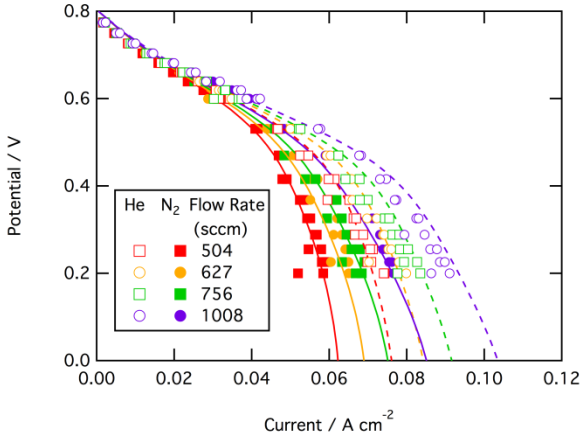
Northeastern University
Center for Renewable Energy Technology

Helox Transport Study

MICHIGAN STATE UNIVERSITY

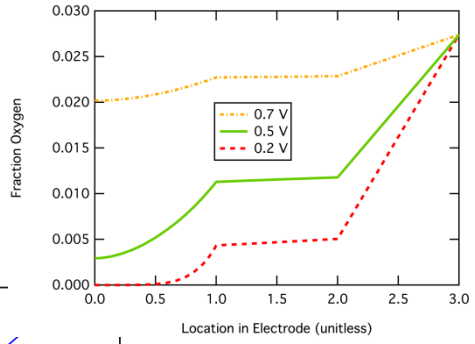
- Study transport in catalyst layer with varying **carrier gas** (He, N_2, Ar) and **diffusivity**.
- O_2 consumption <20%, amenable to **1D model**.
- Transport losses in both **flow channel** and **Catalyst layer.**

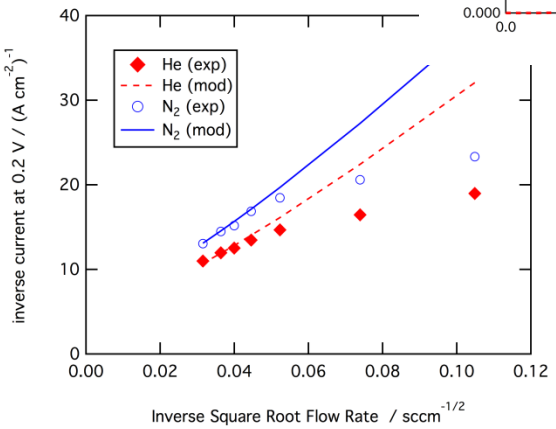
Fit to Experiment (NEU MOF) for two carrier gases



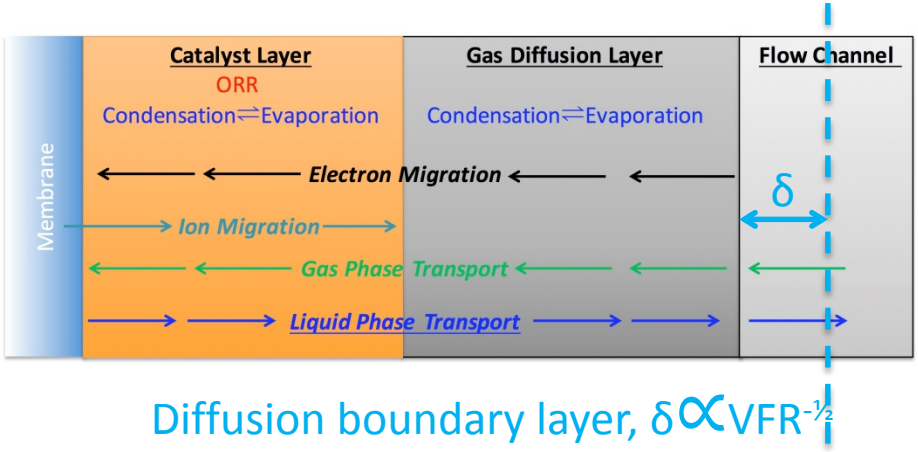
4 % O_2, Temp. 80 C, 25BC GDL, 2.6 mg/cm^2 Catalyst Loading, 45 wt% Nafion, Cell Area: 4.62cm^2

Majority of losses in CL and channel





Channel losses vary as $VFR^{-½}$



Diffusion boundary layer, $\delta \propto VFR^{-½}$

DURABILITY-Fuel Cell Data NEU MOF Catalyst

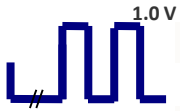
- The stability of NEU-MOF catalyst was evaluated under Nissan load cycling and start-stop cycling protocols

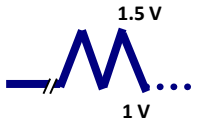
➢ Nissan evaluates catalyst durability using two protocols: load cycling and start-stop cycling to simulate FC stack conditions.

Protocols for Nissan and DOE Durability Working Group

Condition	Nissan Load cycling	Nissan Start-stop cycling
Temperature (°C)	80	80
Gas condition Cathode	N2	N_2
Gas – Anode	H2	H2
Voltage scan (V)	[0.6,1.0]	[1.0, 1.5]
Scan rate (mV/s)	6s/cycle	500
Catalyst loading (mg/cm²)	0.6	
No of cycles	10,000	1000

Load cycling

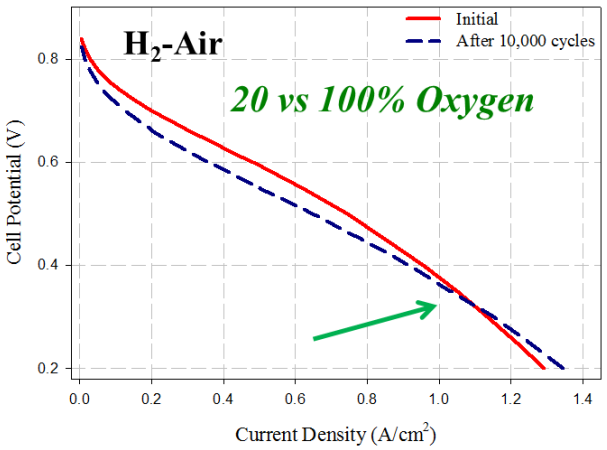


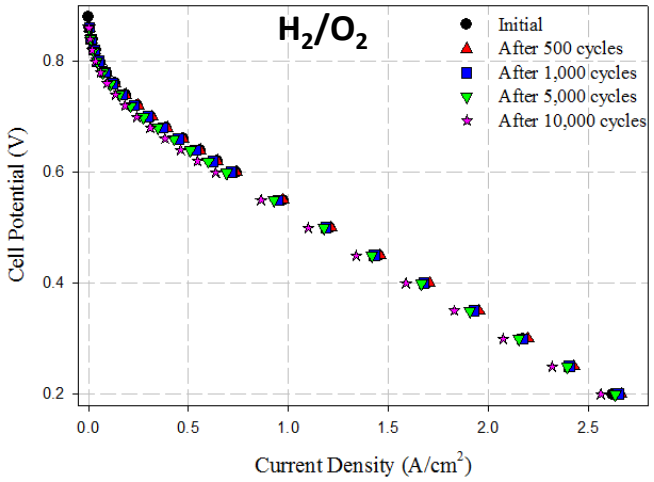


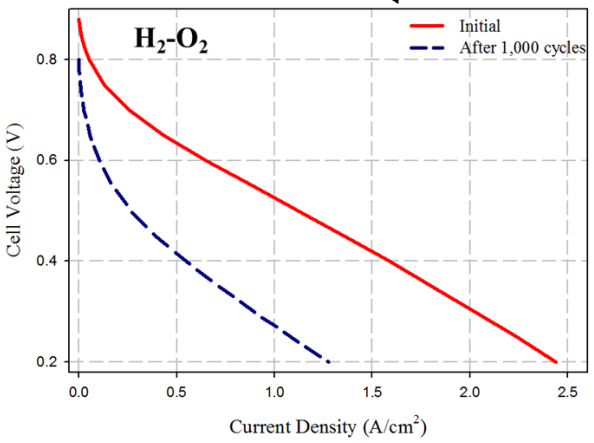
Start-stop cycling

Load Cycling

Start-stop Cycling







- ❑ Minimal change in performance is observed after 10,000 potential cycles (load cycling) from 0.6 to 1.0V. The same durability is observed for 35% and 55% Nafion® loading.
- ❑ The CV profile barely changed after 10,000 potential cycles. This is also observed for the 35% and 55% Nafion® loading MEAs.
- ❑ A similar severe drop in performance is observed for UNM Fe-CTS and traditional Pt on high surface area carbon catalysts.

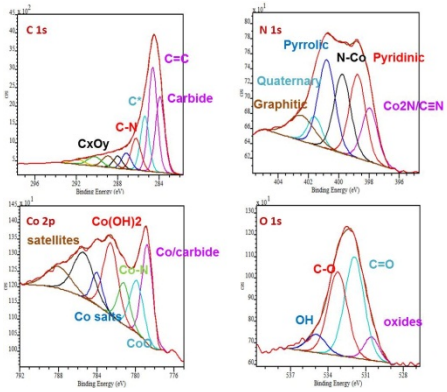
Mechanistic Studies and Spectroscopy

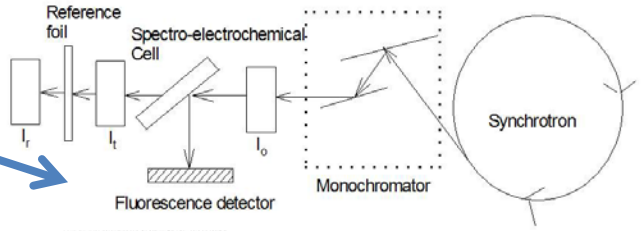
Participating Institutions:

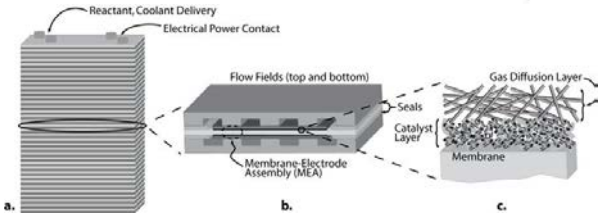
UNM - XPS Studies

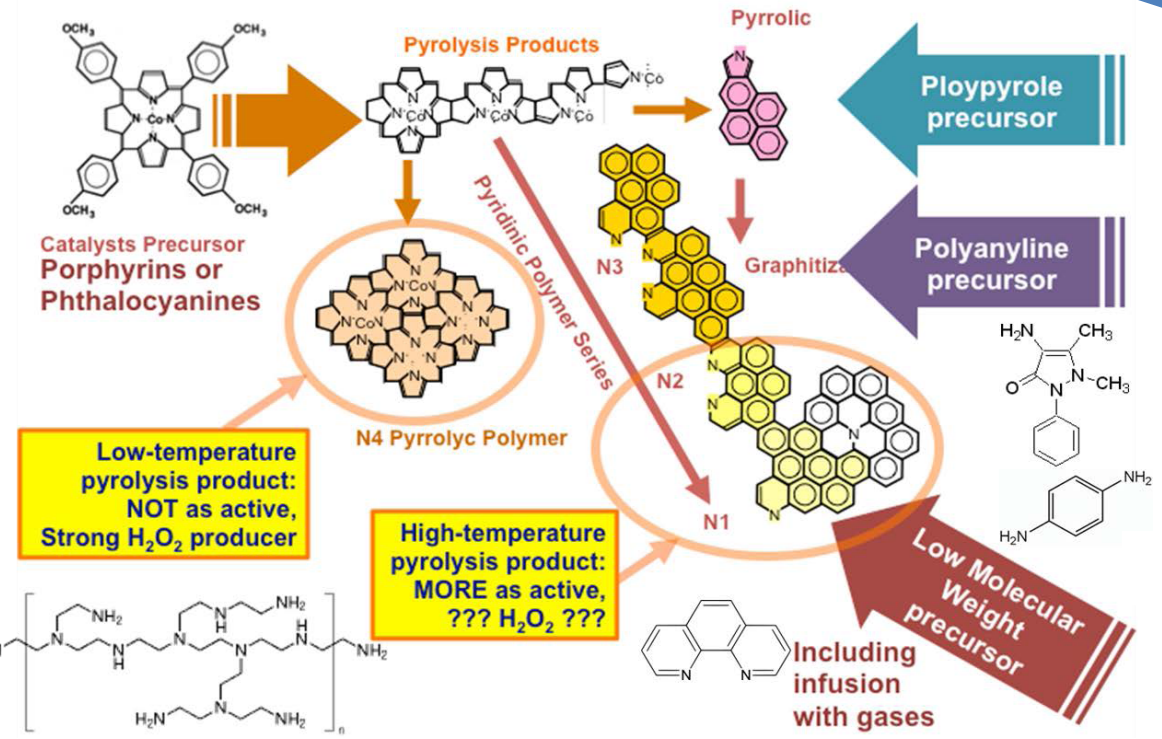
NEU - In situ Spectroscopy with Synchrotron Measurements

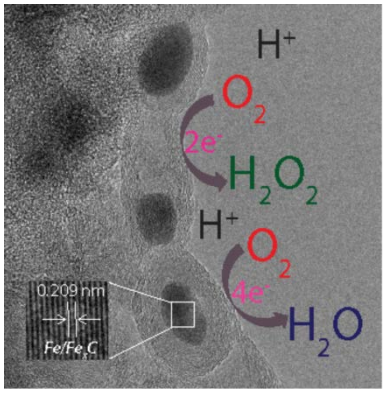
MSU - Macroscopic Modeling











Ambient Pressure XPS – 2.5 nm

Direct evidence of oxygen binding at the FeN_x site

Metal-containing Fe-N-C catalyst

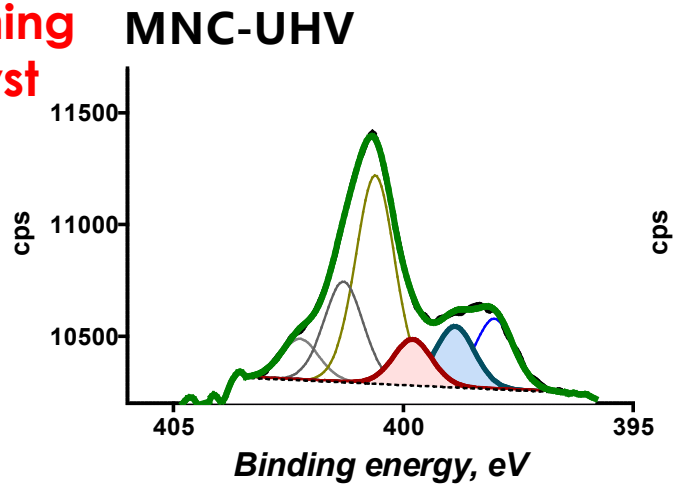
Metal-less N-C catalyst

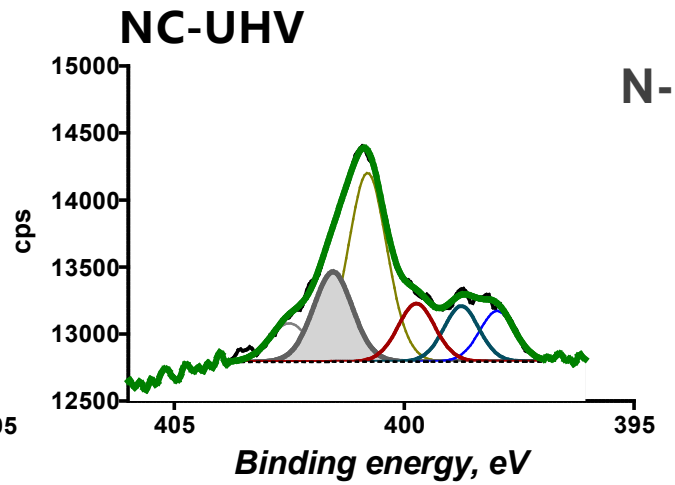
In the case of metal-containing catalysts:

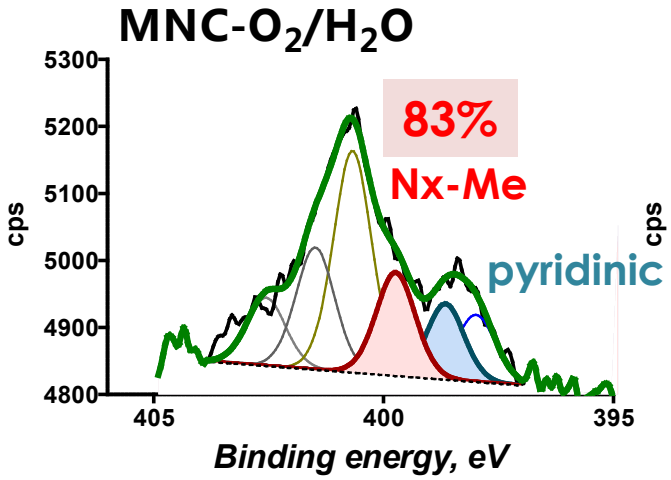
Rearrangement is occurring where Pyridinic N And FeN_x sites contribute.

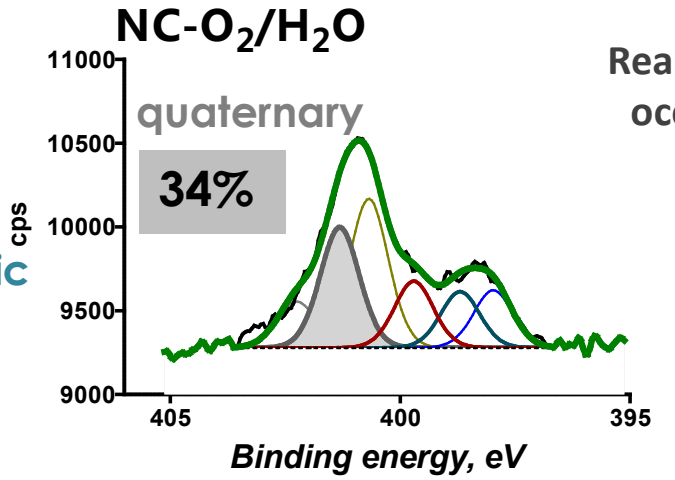
In the case of metal-less catalysts:

Rearrangement is occurring where graphitic and quaternary contribute





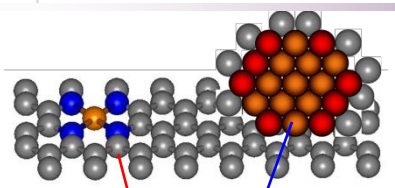


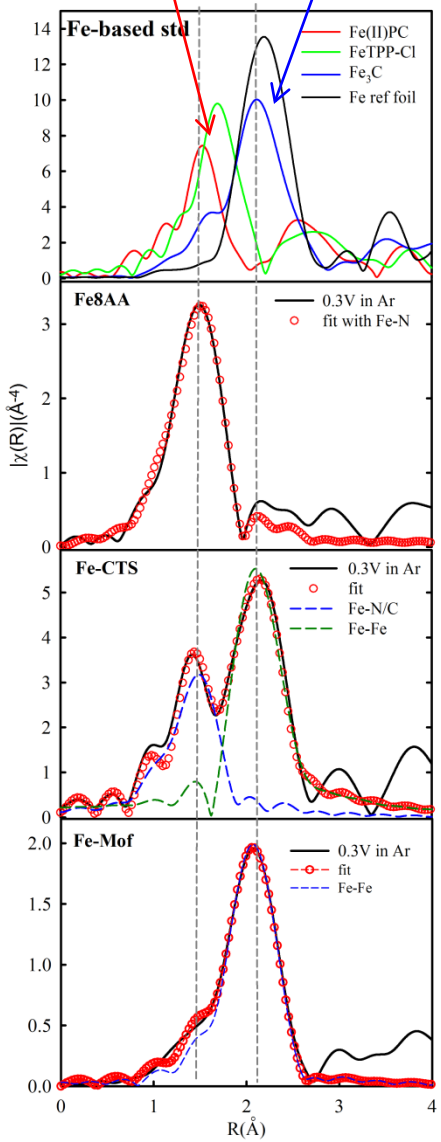


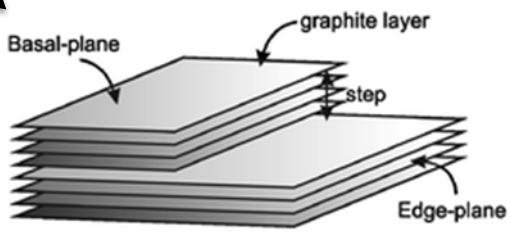
- Rearrangement of Nitrogen spectra due to Oxygen (O_2) binding
- Shifting the position of Nitrogen peak to higher Binding Energies (BE)
- Most prominent effect explicitly associated with FeN_x sites

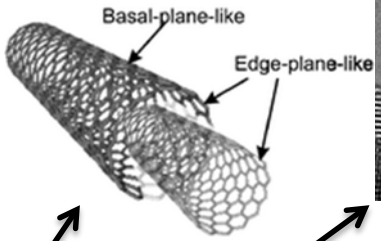
In Situ XAS Studies at the Fe K edge

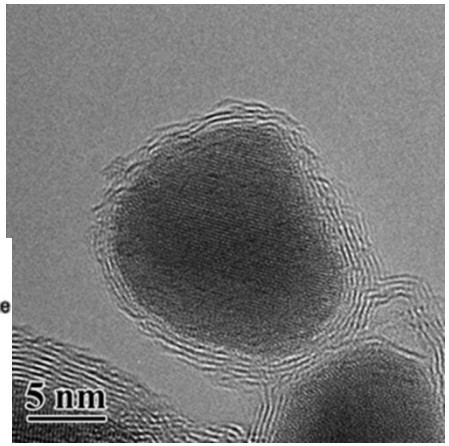
Two major sites identified by *in situ* XAS

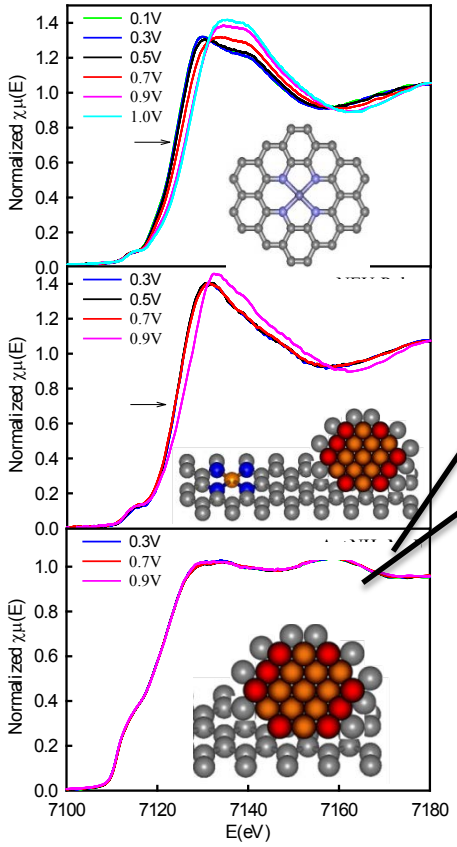










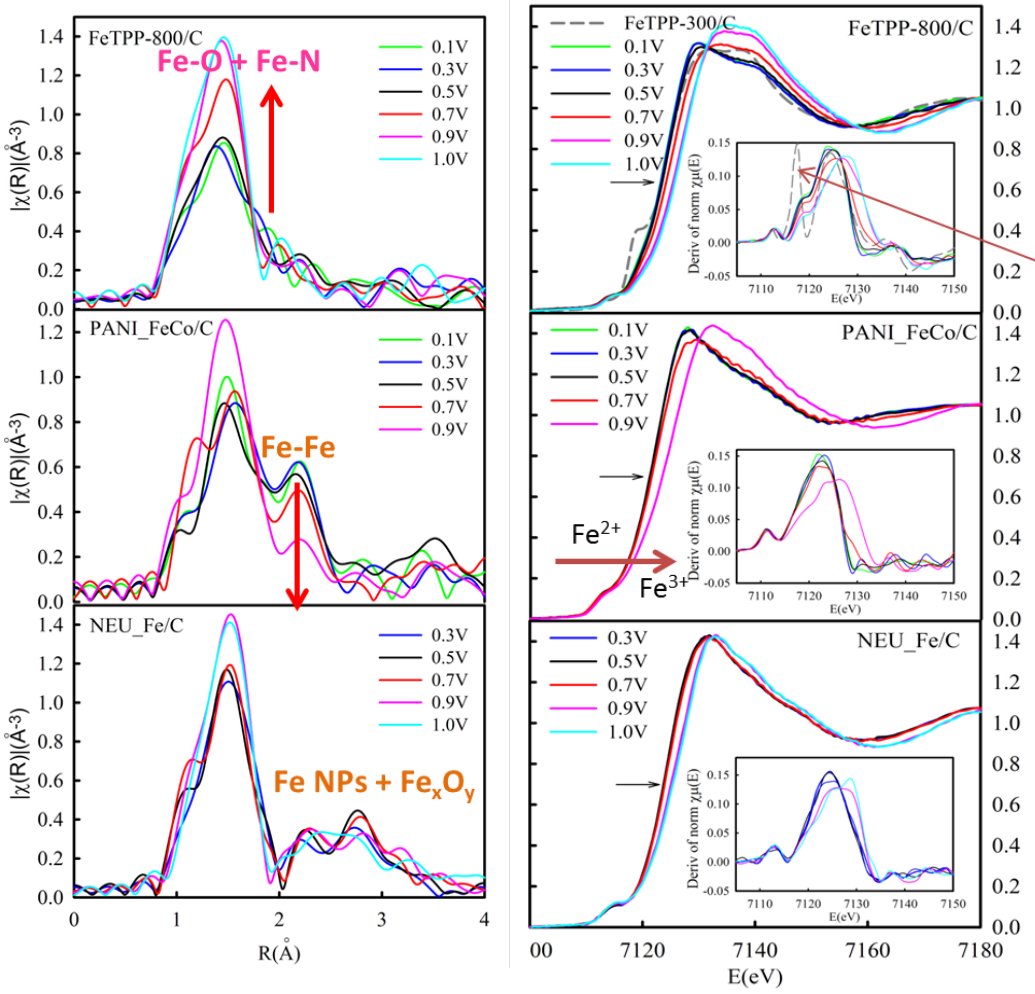


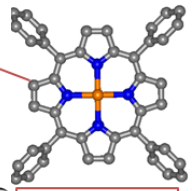
The two major types of sites in heat-treated Fe-N-C catalysts can be clearly distinguished by *in situ* XAS.

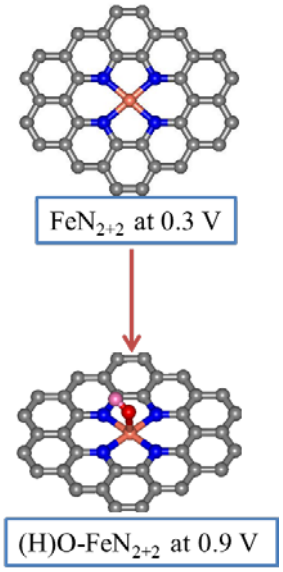
The local geometry, and relative content of each site can be quantitatively determined by EXAFS fitting.

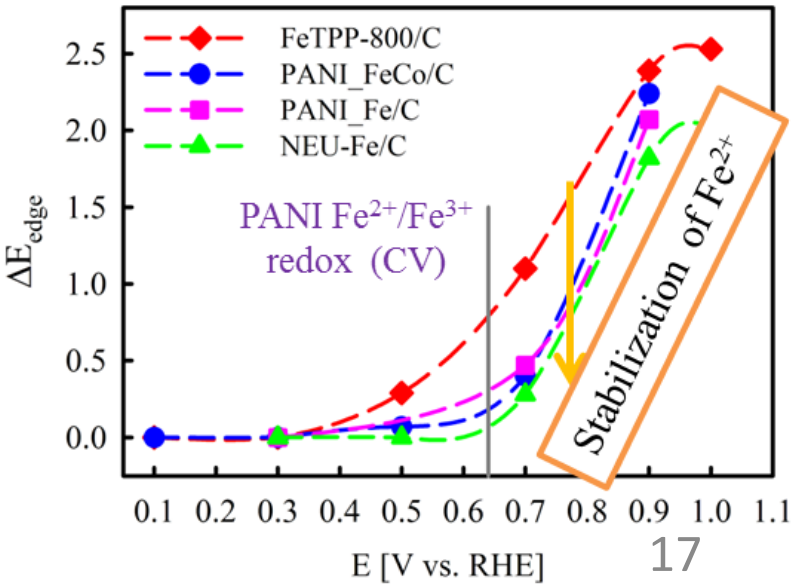
This information facilitates to have controls over the content of the catalysts by controlling the precursors and the preparation procedures.

Mechanistic Studies and Spectroscopy







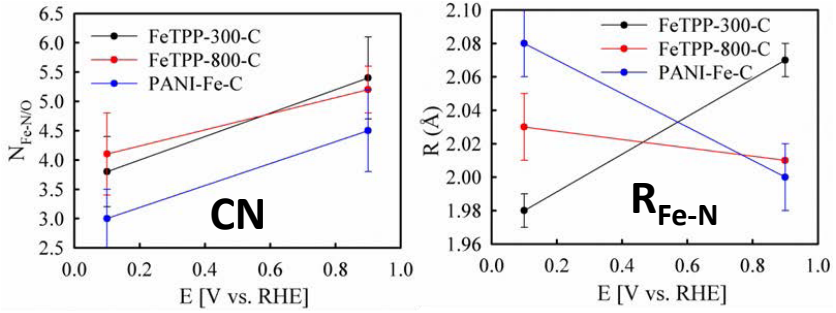


The transition between Fe^{2+} and Fe^{3+} oxidation states is accompanied with the adsorption of OH.

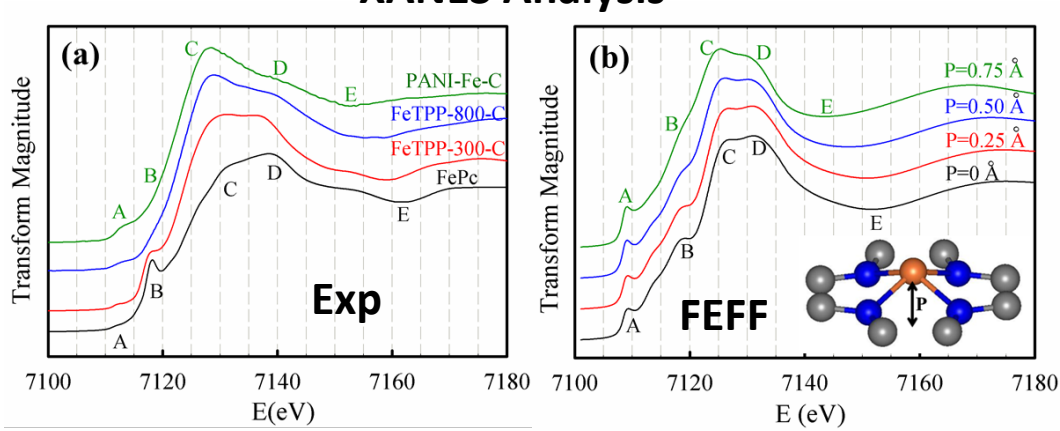
$$N_4\text{-}Fe^{II} + H_2O \rightarrow N_4\text{-}Fe^{III}\text{-}OH + H^+ + e^-$$

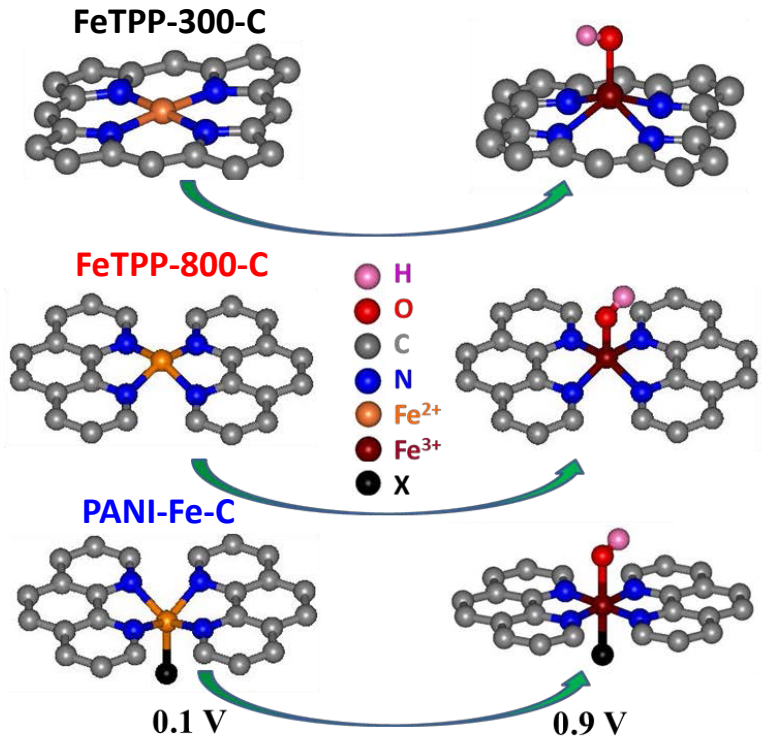
Fe-N Switching behavior

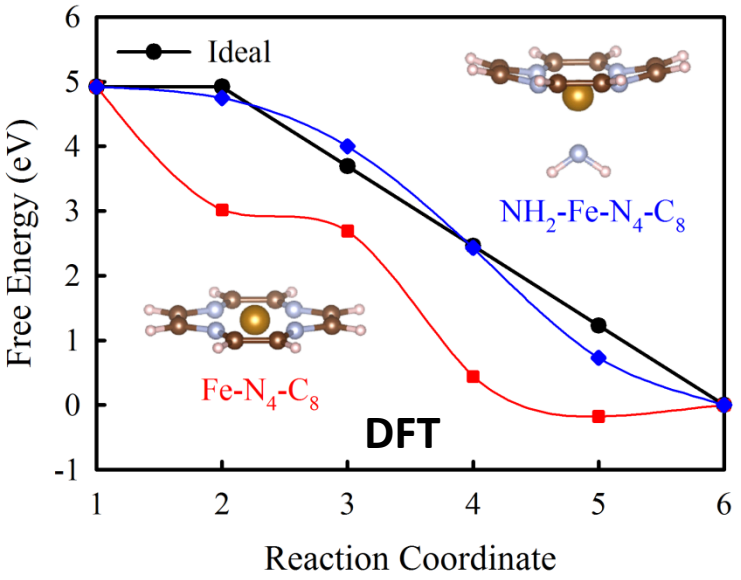
EXAFS Analysis



XANES Analysis



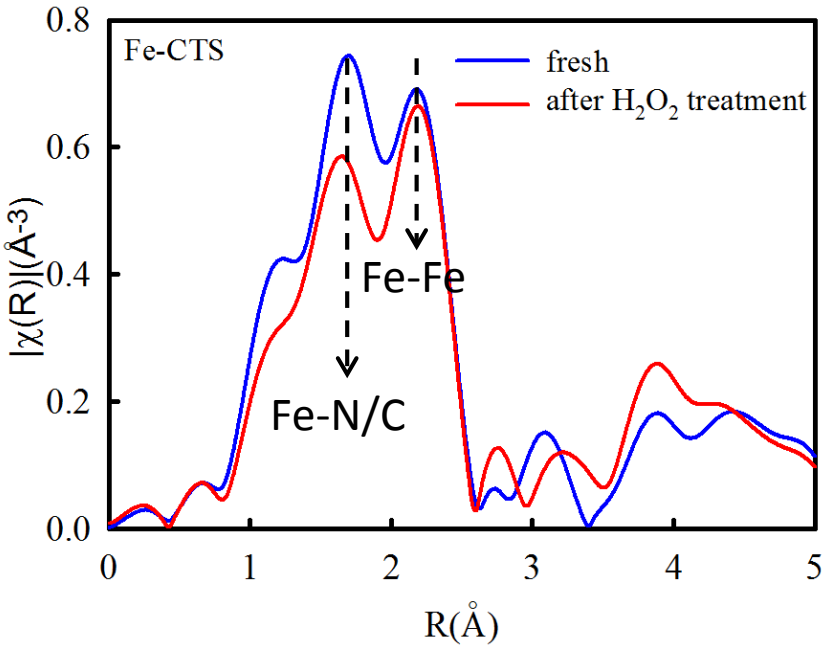


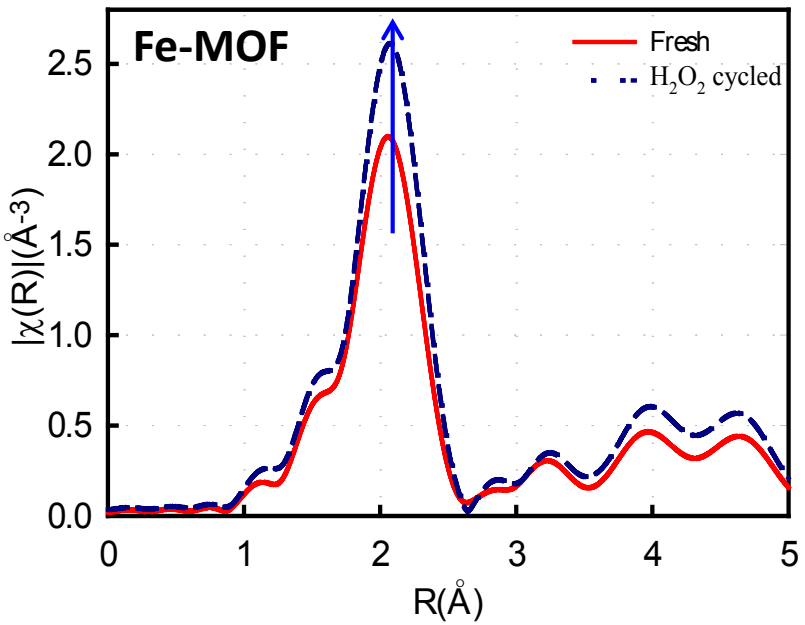


Three dissimilar Fe-N switching behavior found in three different Fe-N_x-C active sites.

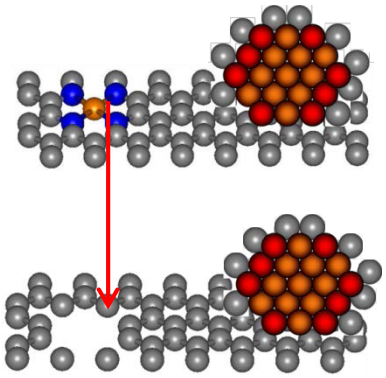
The underlying fifth ligand was confirmed by XAS in combination with FEFF calculations. DFT suggests it drastically increases ORR activity.

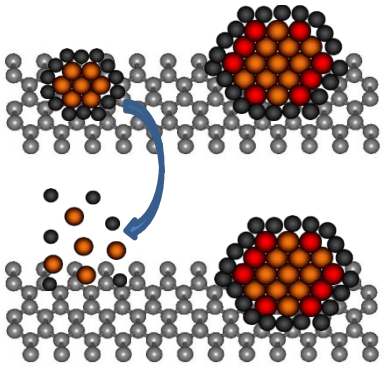
Stability: Peroxide treatment





70 mM H_2O_2 in 0.1 M $HClO_4$ cycled between 0.0 and 1.0V, 250 cycles, 20 mV/s



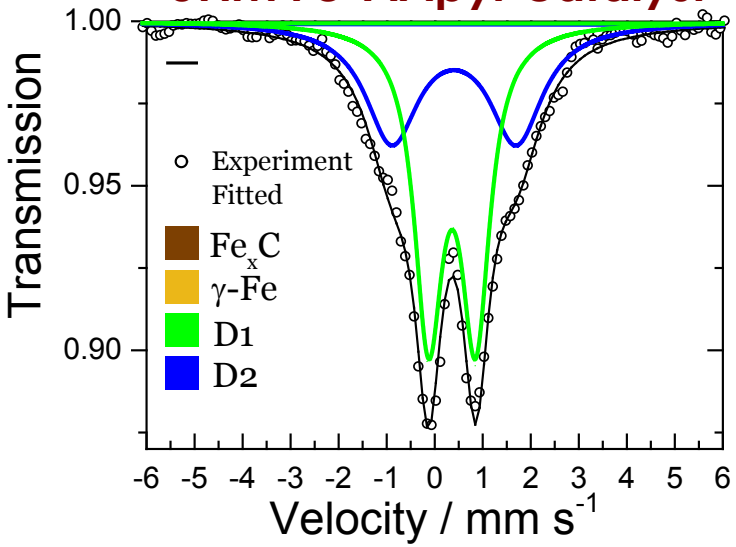


^{57}Fe Mössbauer Spectroscopy

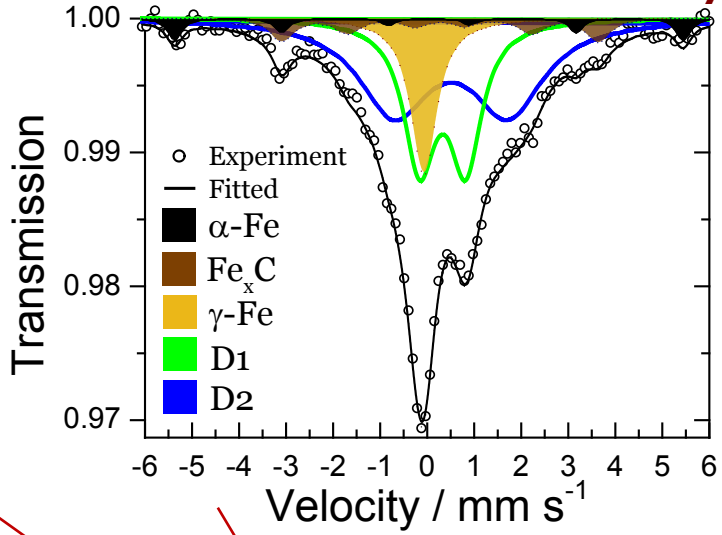
Frederic Jaouen

Spectroscopic observations of the chemical moieties

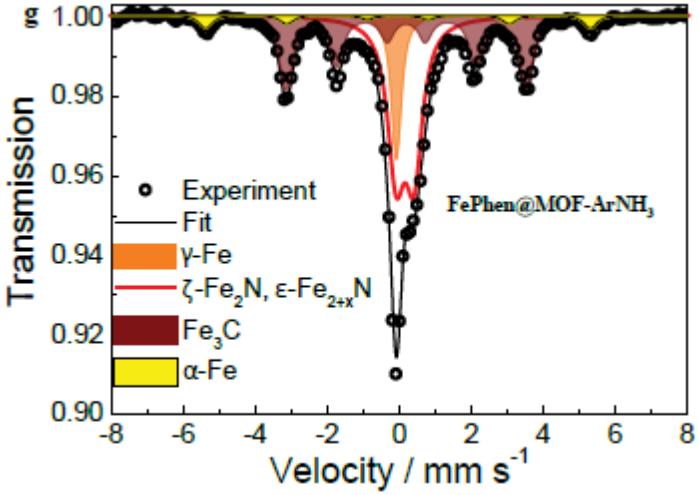
UNM Fe-AApyr catalyst

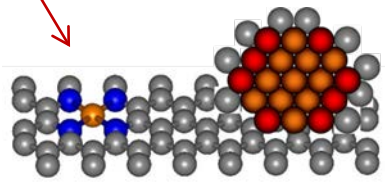


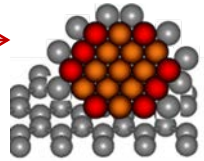
UNM Fe-Nacarbazin catalyst

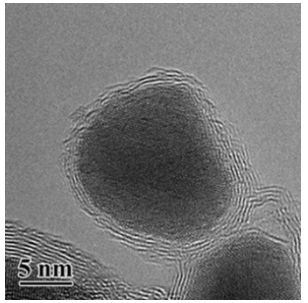


NEU-MOF









Summary Slide

- Task 1.1 Design of Materials as High Performance Catalysts: These have lead to several candidates meeting DOE target of 150-400 A/cm^3 and 100 mA/cm^2 @ 0.8 V (iR free), H_2/O_2 , 1.5 bar total.
- **DOE Go/No Go decision point successfully reached by down-selected UNM catalyst.**
- Task 1.2: Tailored Synthesis for Mechanistic Interpretation. This is progressing in concert with spectroscopy and computation leading to a concerted structure property relationship. This is 90 % complete, MNOF derived material needs further investigation.
- Task 1.3 Catalyst Scale up initiated with Pajarito Powder LLC (Albuquerque, NM), the scale up effort is aiming to exceed the DoE goals by reaching 100 gm batch size at the end of the program with <5% variability (inter and intra batch).
- Task 2.1 Actual fuel cell performance levels with Air, with a target to 30 mA/cm^2 at 0.8 V and 1 A/cm^2 at 0.4 V (non iR corrected) H_2 /Air, 2.5 bar total pressure. Lowering of mass transport in the reaction and electrode structure is our current focus. Q4 and Q5 target for Air operation met successfully.
- Task 2.2 Good catalyst durability has been reported. However pushing the limits of carbon stability causes severe activity decline. This task is 80% complete.
- Task 3. Good synergy has been reported to spectroscopy and computation with first ever report of a concerted understanding of structure property relationship. This task is 90% complete.

Future Activities

- Strategies for MOF derived catalyst scale up to 50 gm batch size with < 5% variability in H_2/Air MEA performance.
- Final validation of MOF derived catalyst at NTCNA for performance and durability.
- Advanced interfacial studies to investigate peroxide initiated free radical formation on various non PGM catalysts
- Advanced electrode and microporous layer design for enhanced mass transport.

Technology Transfer Activities

1. Patents and Provisional Patents Filed:

Publications:

1 Ganesan, S., Leonard, N. & Barton, S. C. Impact of transition metal on nitrogen retention and activity of iron–nitrogen–carbon oxygen reduction catalysts. *Physical Chemistry Chemical Physics* **16**, 4576-4585 (2014).

2 Leonard, N. D. & Barton, S. C. Analysis of Adsorption Effects on a Metal-Nitrogen-Carbon Catalyst Using a Rotating Ring-Disk Study. *Journal of The Electrochemical Society* **161**, H3100-H3105 (2015).

3 Robson, M. H., Artyushkova, K., Patterson, W., Atanassov, P. & Hibbs, M. R. Non-platinum Carbon-Supported Oxygen Reduction Catalyst Ink Evaluation Based on Poly (sulfone) and Poly (phenylene)-Derived Ionomers in Alkaline Media. *Electrocatalysis* **5**, 148-158 (2014).

4 Serov, A., Artyushkova, K., Andersen, N. I., Stariha, S. & Atanassov, P. Original Mechanochemical Synthesis of Non-Platinum Group Metals Oxygen Reduction Reaction Catalysts Assisted by Sacrificial Support Method. *Electrochimica Acta* (2015).

5 Serov, A., Artyushkova, K. & Atanassov, P. Fe-N-C Oxygen Reduction Fuel Cell Catalyst Derived from Carbendazim: Synthesis, Structure, and Reactivity. *Advanced Energy Materials* **4** (2014).

6 Serov, A., Tylus, U., Artyushkova, K., Mukerjee, S. & Atanassov, P. Mechanistic studies of oxygen reduction on Fe-PEI derived non-PGM electrocatalysts. *Applied Catalysis B: Environmental* **150**, 179-186 (2014).

7 Tylus, U. *et al.* Elucidating Oxygen Reduction Active Sites in Pyrolyzed Metal–Nitrogen Coordinated Non-Precious-Metal Electrocatalyst Systems. *The Journal of Physical Chemistry C* **118**, 8999-9008 (2014).

8 Strickland, K., Miner, E., Jia, Q., Tylus, U., Ramaswamy, N., Liang, W., Sougrati, M. T., Jouen, F., and Mukerjee, S., 'Metal Nx Free Electrocatalyst with High Activity for Oxygen Reduction Reaction', Nature Comm., (accepted).

Patents:

1. Patterson, W., Artyushkova, K. D., Halevi, B., Robson, M. H., Serov, A., Walker, C., and Atanassov, P., *'Structured Cathode Catalysts for Fuel Cell Application Derived from Metal-Nitrogen-Carbon Precursors',* (US Patent 20,140,349,843, 2014).
2. A. Serov, Kateryna D. Artyushkova, Barr Halevi, Michael H. Robson, Wendy Patterson and Plamen B. Atanassov "*Cathode Catalysts for Fuel Cell Application Derived from Polymer Precursors*", Appl. Number: 2011-103, Appl. Date: May 9, 2011
3. A. Serov, Kateryna D. Artyushkova, Barr Halevi and Plamen B. Atanassov "*Non-PGM Cathode Catalysts for Fuel Cell Application Derived from Heat Treated Heteroatomic Amines Precursors*", Appl. Number: 2011-107, Appl. Date: May 16, 2011
4. Mukerjee, S., Sgtrickland K., Tylus, Q., '*Non Noble Metal Electrocatalysts for Oxygen Depolarized Cathodes and Their Uses*' PCT/US14/10502.

Technology Transfer Agreements in place with PPC between UNM and NEU groups for scale up.

Collaborations

Partners (this project)

- Northeastern Univ., (Prime) Boston, MA: S. Mukerjee (P.I)
- Univ. of New Mexico, Albuquerque, NM: Prof. P. Atanassov (Univ., subcontractor)
- Michigan State University, East Lansing, MI: Prof. S. Barton (Univ., subcontractor)
- Pajarito powders, Albuquerque, NM: P. Short and B. Halevi (Industry subcontractor)
- Nissan Technical Center North America, Detroit, MI: Dr. N. Dale (Industry, subcontractor)

Other collaborators:

Dr. Piotr Zelenay, Los Alamos National Laboratory

Jean-Pol Dodelet: Canetiq, Canada

Frederic Jouen, University of Montpelier, France

Critical Assumptions and Issues

- XAS data used for building active site models are based on assumptions inherent in the FEFF code. Careful control experiments have been used to validate the reported results.
- All iR corrections performed on fuel cell data was conducted using high frequency resistance measurements at 1 kHz.

Technical Back-Up Slides

MICHIGAN STATE UNIVERSITY

Governing Equations (Electrode-Scale)

B.C. I

$$I_s|_I = 0$$

$$V_e|_I = I_e|_I R_{Mem}$$

$$N_L|_I = I_i|_I \beta F$$

$$N_w|_I = 0$$

Electrolyte Membrane

$$0 = -\kappa_s \nabla^2 V_s + nF r_{ORR}$$

$$0 = -\kappa_e \nabla^2 V_e - nF r_{ORR}$$

$$0 = -\frac{\kappa}{\mu} \nabla^2 P_l + 2 r_{ORR}|_x - r_{evap}|_x$$

$$0 = -\nabla N_w + r_{evap}|_x$$

B.C. II

$$V_s|_{II} = 0$$

$$I_e|_{II} = 0$$

Channel

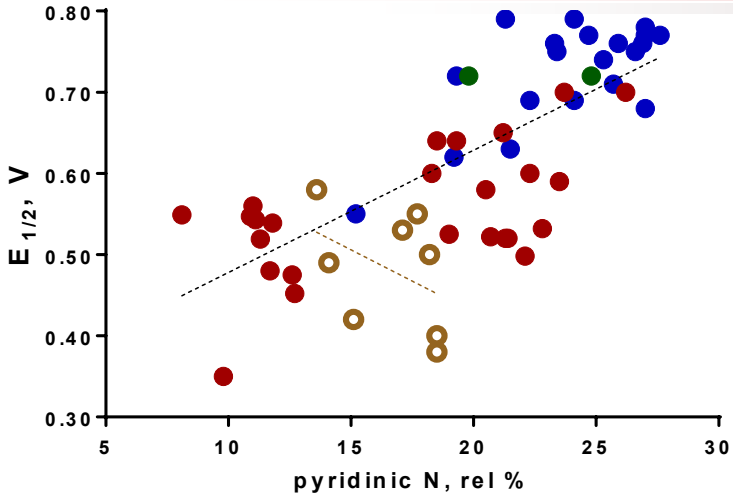
$$P_L|_{II} = P_g$$

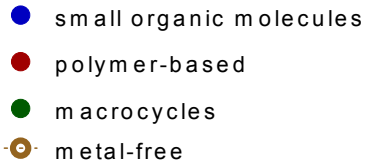
$$x_i|_{II} = x_{i,bulk}$$

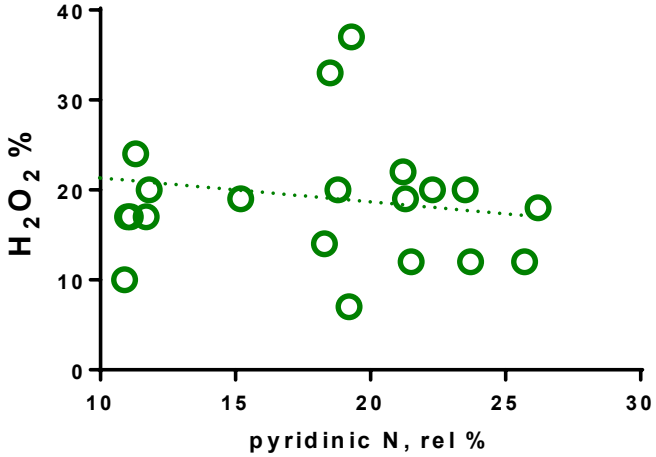
Springer et al. J. Electrochem Soc. 140(12) 1993, Weber et al. J. Electrochem Soc. 151(10) 2004

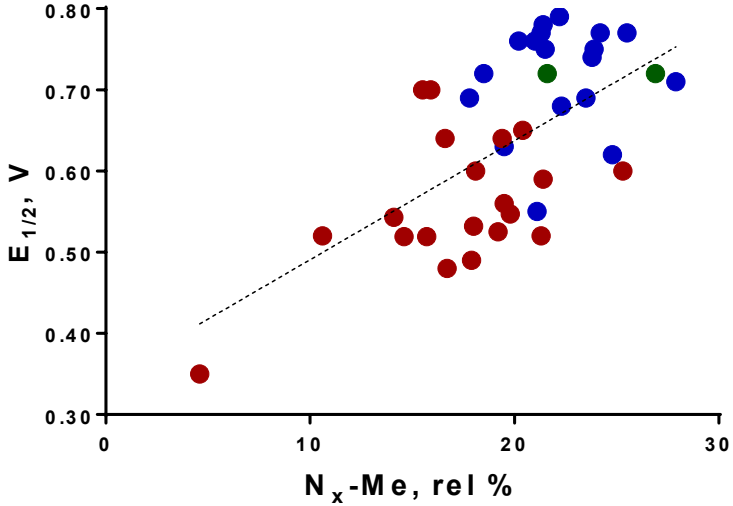
Focusing on the M-N-C Active Sites

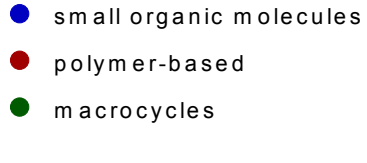
Correlations of catalysts activity with the presence of FeN_x site

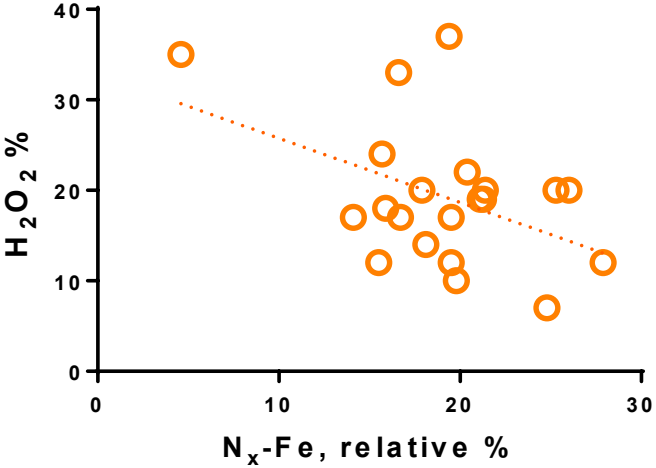








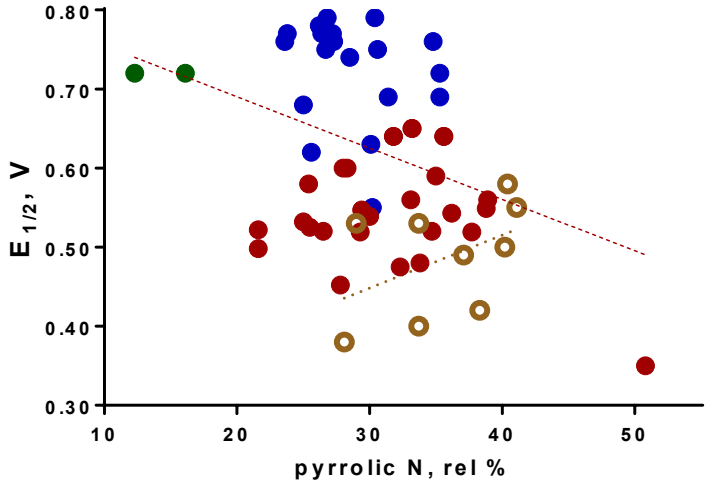


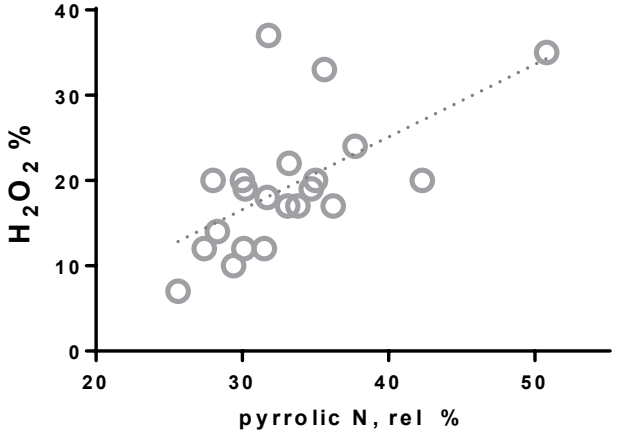


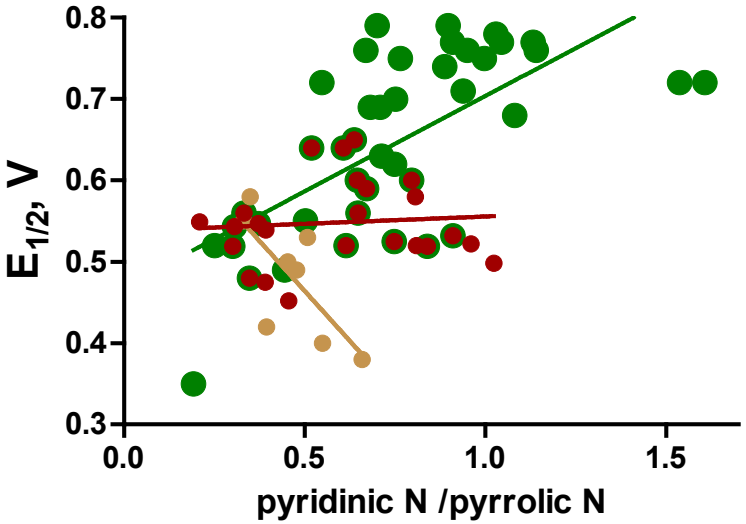
Observation: direct correlation of FeN_x sites and $E_{1/2}$ on one side, and analogous correlation for the pyridinic Nitrogen-containing moieties with $E_{1/2}$

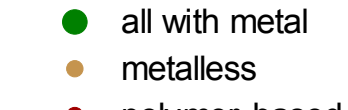
Structure-to-Property Correlations

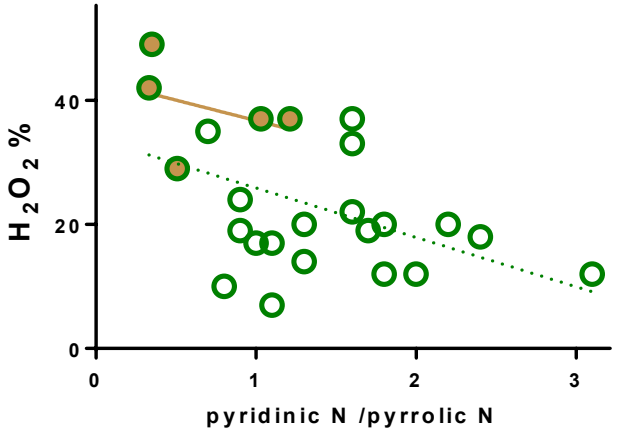
Correlating ORR activity with the ORR mechanism





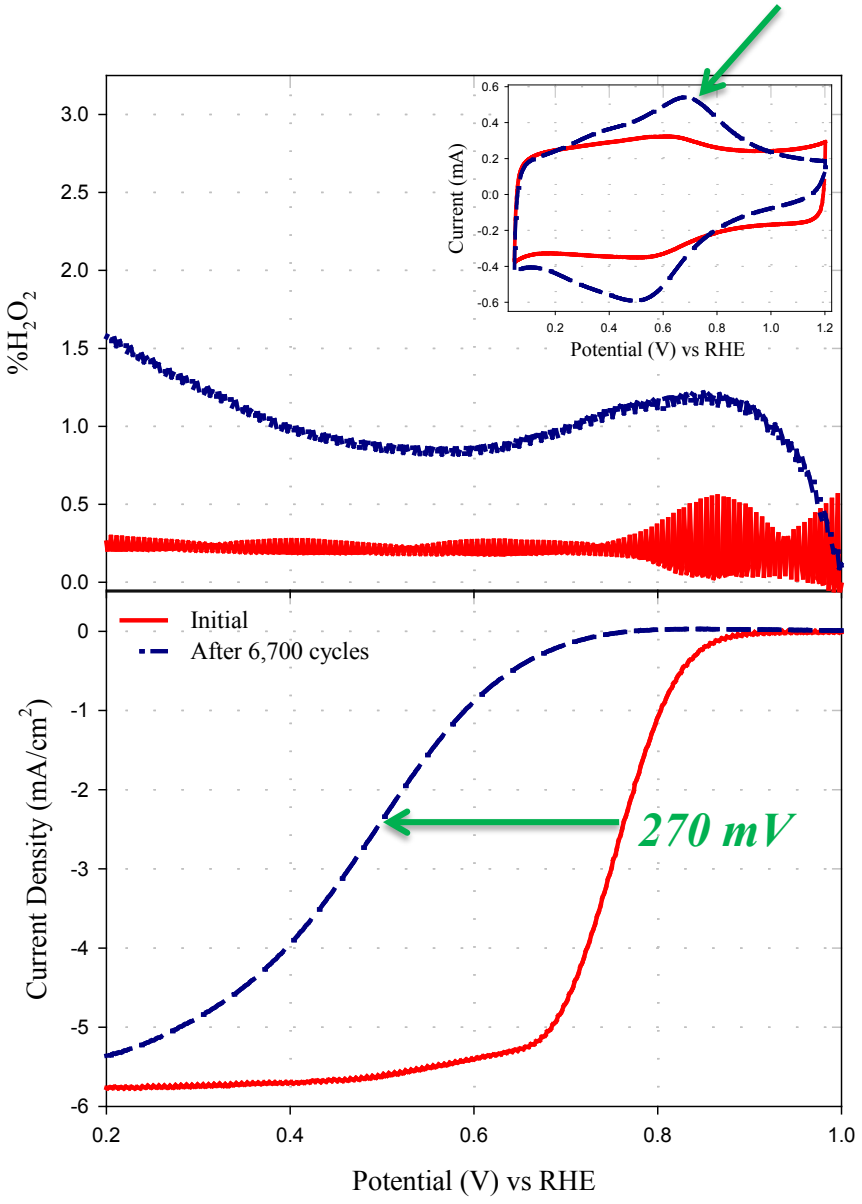


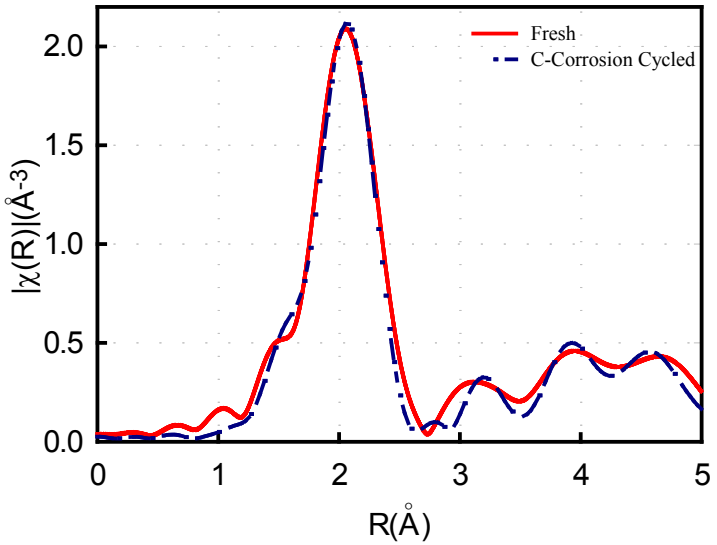


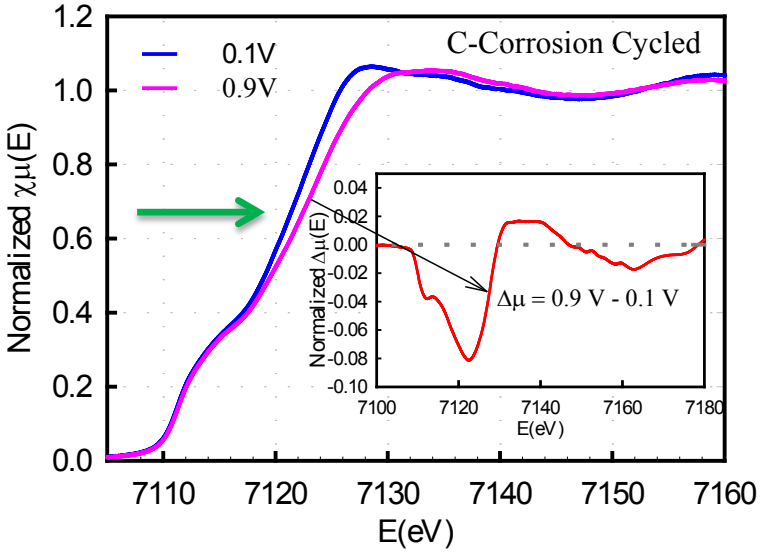


- Pyridinic Nitrogen is a marker for edge plane defects
- Peak due to pyridinic Nitrogen is where disordered FeN_x centers contribute
- In metal-less catalysts (no FeN_x centers) – pyridinic catalyzes $H_2O_2 \rightarrow H_2O$

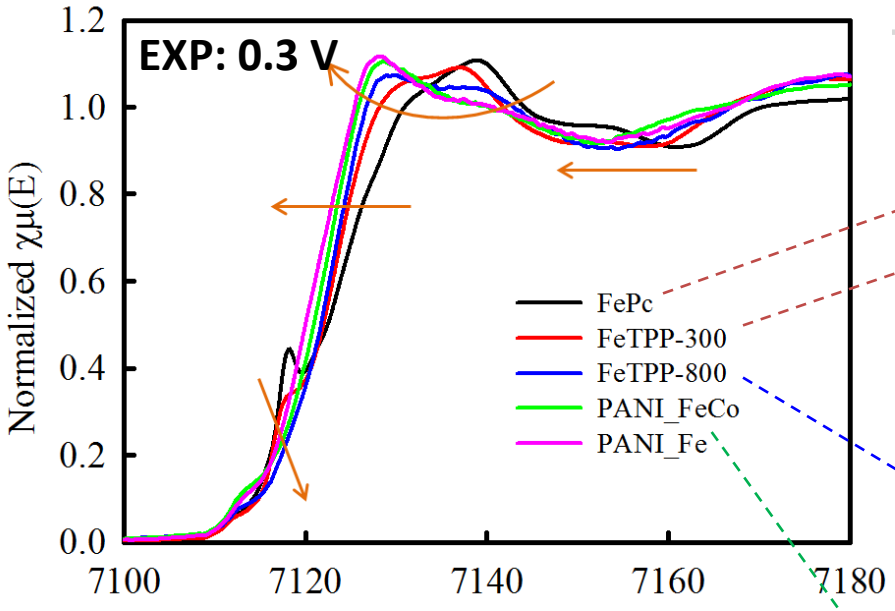
Start/Stop Cycling

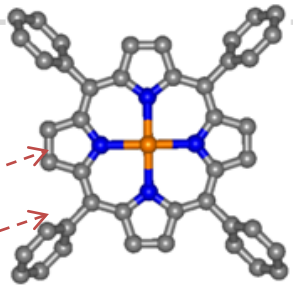




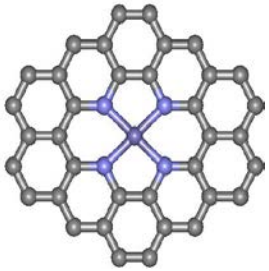


Central Iron displacement as evidenced by XAS + FEFF

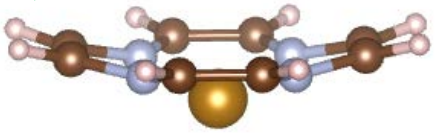




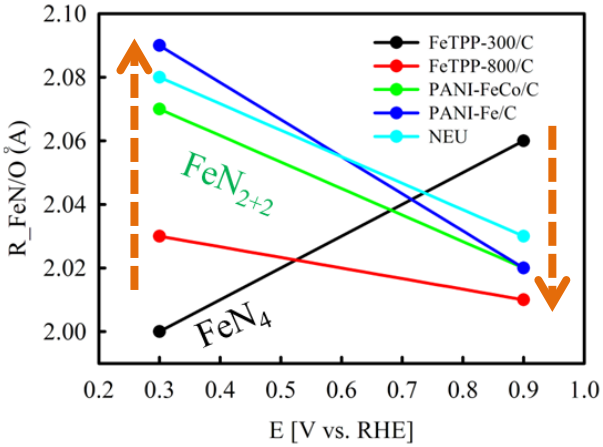
Intact FeN_4



Distorted FeN_{2+2}

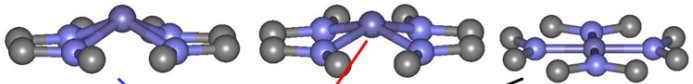


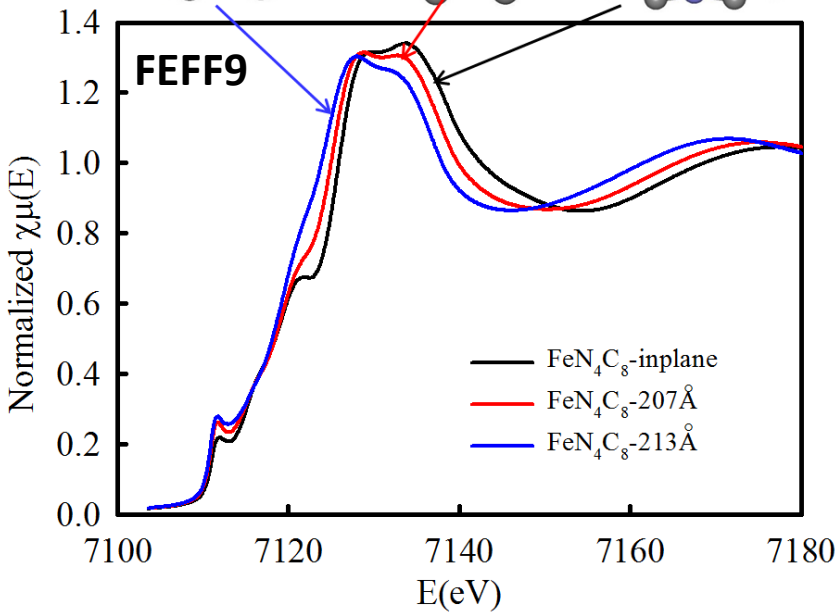
Out-of-plane FeN_{2+2}



Fe displacement trend

FeTPP-300< FeTPP-800<PANI-Fe-based





EXAFS plus FEFF9 calculations give the first evidence of the central iron displacement in the pyrolyzed samples, and samples with bigger displacement appears to show better ORR activity.