

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

**2013 DOE Hydrogen and Fuel Cell Program Review**

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Northeastern University, 360 Huntington Av., Boston, MA 02115**

**May 16<sup>th</sup>, 2013**

Project ID# FC086

# Overview Slide

## ➤ **Timeline:**

- Start date: 8/01/2010
- End date: 7/31/2014
- Percent complete: 60% (18 months remaining)

## ➤ **Budget Data:** \$ 4,942,301 (Federal), \$ 1,437,714 (cost share); Total \$ 6,38015 FY11 funding \$750,000, Planned FY12 funding \$850,000

## ➤ **Barriers/Targets**

- Activity Targets for Non-PGM catalysts: exceed 300 A/cm<sup>3</sup> (2017 Target).
- Durability at temperatures ≤ 80°C; 5000 hrs (2017 Target).

## ➤ **Partners**

- Northeastern Univ., (Prime) Boston: S. Mukerjee (P.I) and S. Smotkin
- Univ. of Tennessee, Knoxville: Prof. T. Zawodzinski
- Univ. of New Mexico, Albuquerque: Prof. P. Atanassov
- Michigan State University: Prof. S. Calabrese Barton
- BASF Fuel Cells, Somerset, NJ: Dr. E. DeCastro
- Pajarito Powders, Albuquerque, NM, Dr. B. Halevi
- Nissan Technical Center North America (NTCNA): Dr. K. Adjemian
- Los Alamos National Lab: Dr. P. Zelenay

# Relevance

- Objectives: This project will develop new classes of non-PGM electrocatalysts which would meet or exceed DOE 2017 targets for activity and durability.
- 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 of Pt & Pt alloys (e.g., sulfur, CO etc.). Hence ability to tolerate H<sub>2</sub> with greater impurity levels.

# 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**
    - Reaction dynamics at complex reaction layer for oxygen and oxide bonding
    - Transport modeling in multi-layer structures
  - **In situ Infrared and 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:**
  - **Current volumetric Power density is  $\sim 150 \text{ A/cm}^3$**
  - **2017 target is  $300 \text{ A/cm}^3$  which requires the following approach to materials development**
    - (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.

*Our approach addresses all these issues for meeting 2017 DOE targets.*

# Milestones and Go/No Go Decisions

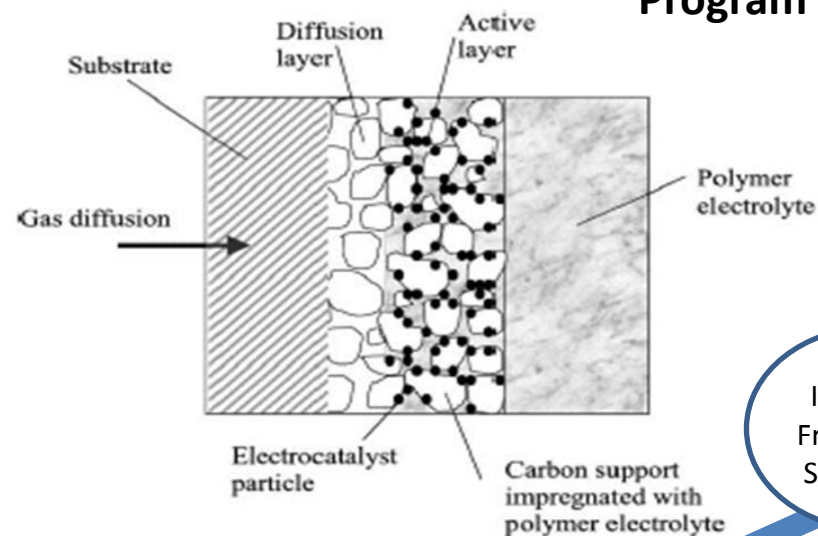
## ➤ Milestones (2012-13)

- Materials Development: Cross Laboratory RDE measurement of ORR activity FY12Q 1-4
- Fuel Cell tests for Volumetric Activity: Meet  $\sim 150\text{-}200\text{ A/cm}^3$  (iR free) at 0.8 V RHE (80°C or below) FY12Q 1-4, FY13Q1: Milestone met
- Meet Durability target based on DOE protocols using RRDE and single cells FY12Q 1-4, FY13Q1: Catalyst durability milestone met
- In situ measurements for degradation and electrocatalytic pathways for ORR FY12Q1-4, FY 13 Q1: Milestone in progress
- Initiation of scale up for select catalysts FY12Q 3-4, FY13Q1: Milestone met
- Connecting computational efforts with characterization results for mechanistic and transport measurements FY12Q 2-4, FY13Q1: Milestone met

## ➤ Go/No Go Decisions (2013)

- Down selected catalysts based on UNM and MSU formulations for validation based on  $150\text{ A/cm}^3$  at 0.8 V (iR free), and  $100\text{ mA/cm}^2$  at 0.8 V iR Free, 1.5 bar pressure.
- Meeting DOE specified catalyst durability criterion.

# Program Structure and Management



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]

Bio-Inspired Non PGM Transition Complexes [UTK]

Computation (UTK, MSU, UNM) and In situ Vibration and Synchrotron Spectroscopy (NEU)  
**Thrust Area 4-Task 3.1-3.3**

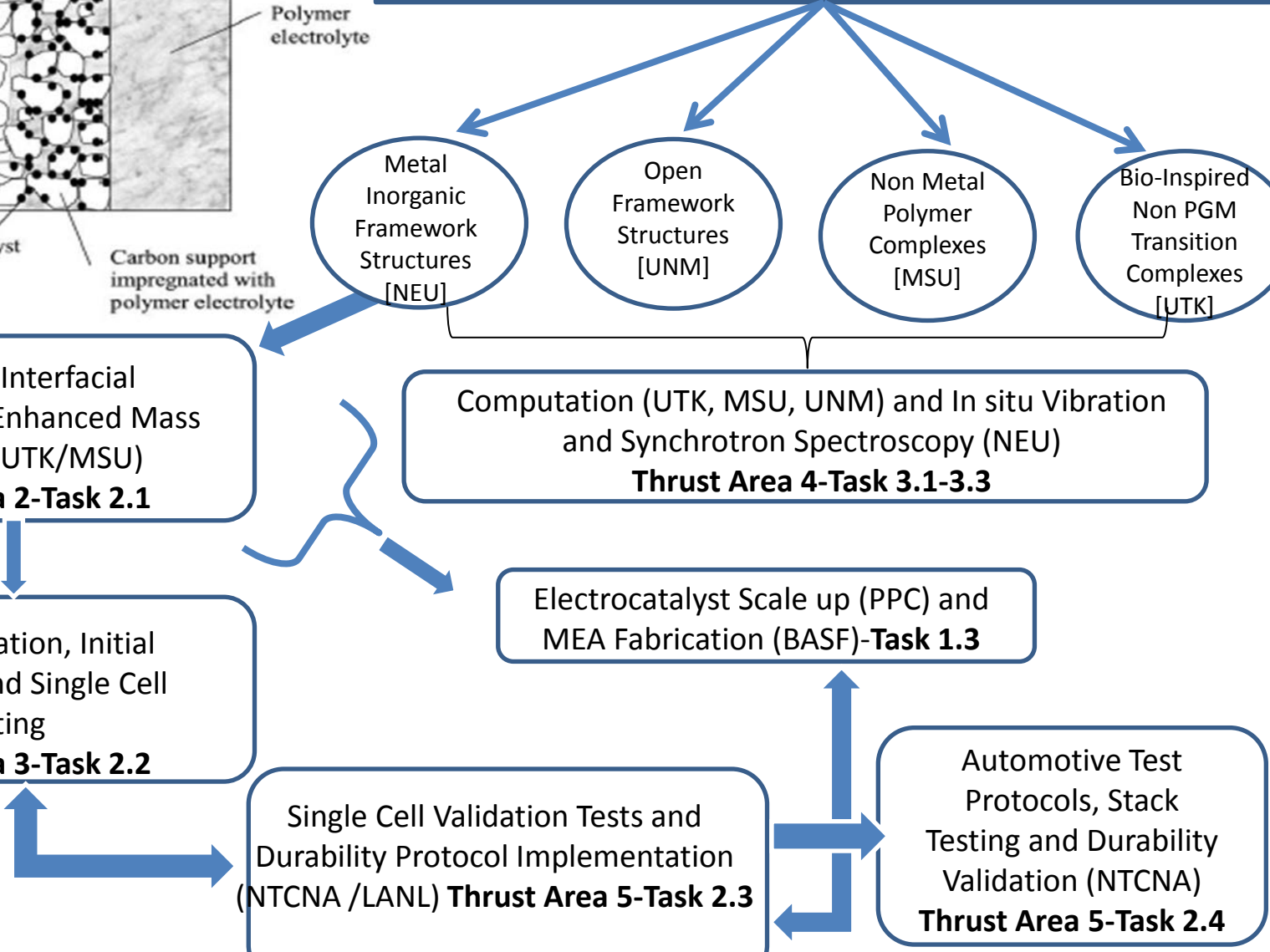
Designing Interfacial Structures for Enhanced Mass Transport (UTK/MSU)  
**Thrust Area 2-Task 2.1**

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

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

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

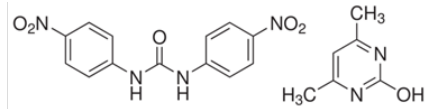
Automotive Test Protocols, Stack Testing and Durability Validation (NTCNA)  
**Thrust Area 5-Task 2.4**



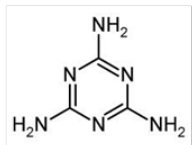
# Task 1.1-1.2: Design and Synthesis of Novel Materials for Oxygen Reduction Reaction (ORR)

## - Advanced Performance Catalysts: Development of Novel MNC Catalysts

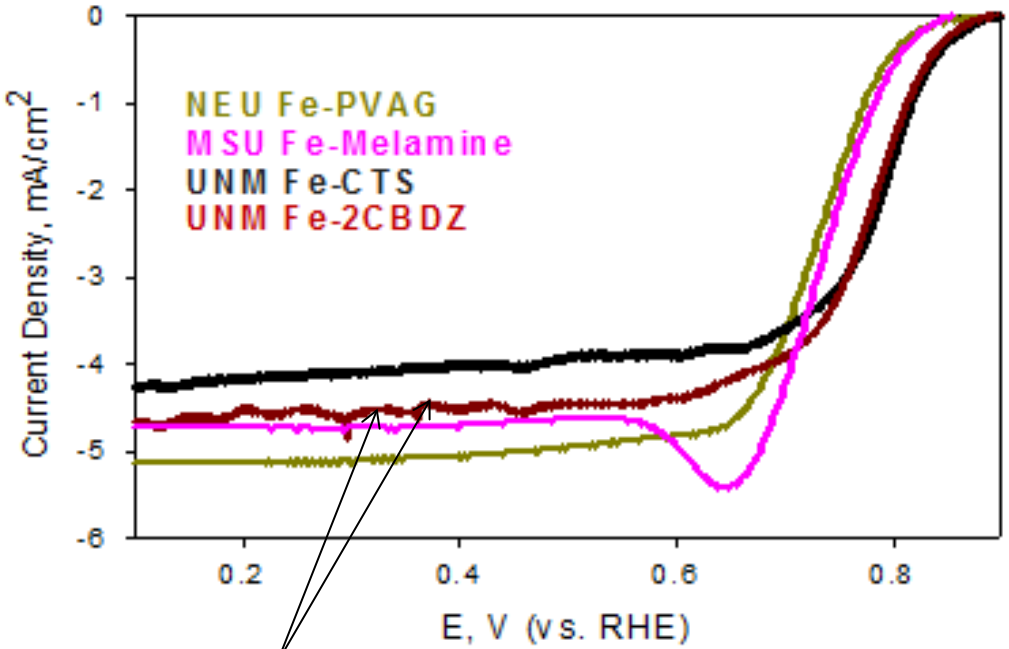
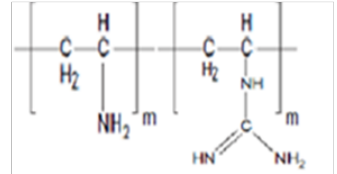
UNM Fe-CTS



MSU Fe-Melamine



NEU Fe-PVAG



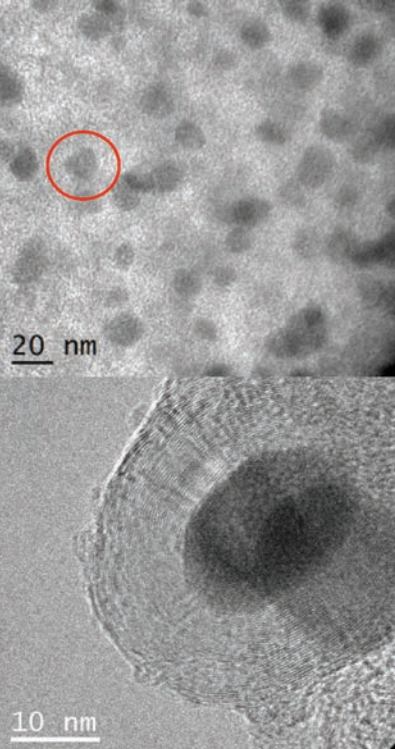
Variations due to differences in catalyst dispersions

Catalyst	$i$ at 0.8 V mA/cm <sup>2</sup>	$E_{1/2}$ [V]	Tafel Slopes (mV/dec)
NEU Fe-PVAG	0.43	0.73	60
MSU Fe-Melamine	0.58	0.74	65
UNM Fe-CTS	1.60	0.80	56
UNM-Fe2CBDZ	1.40	0.79	56

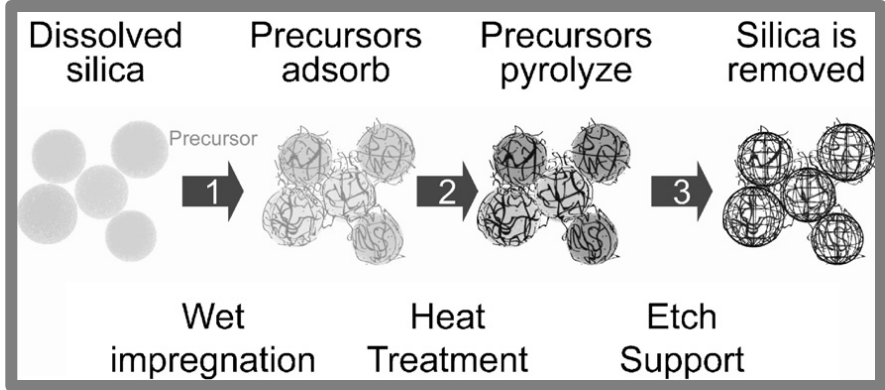
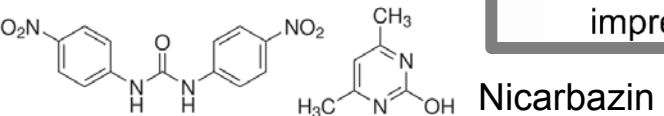
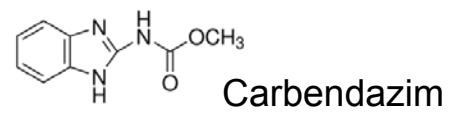
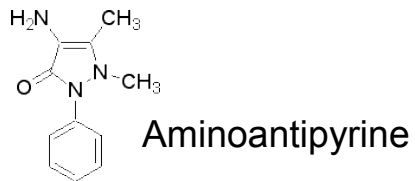
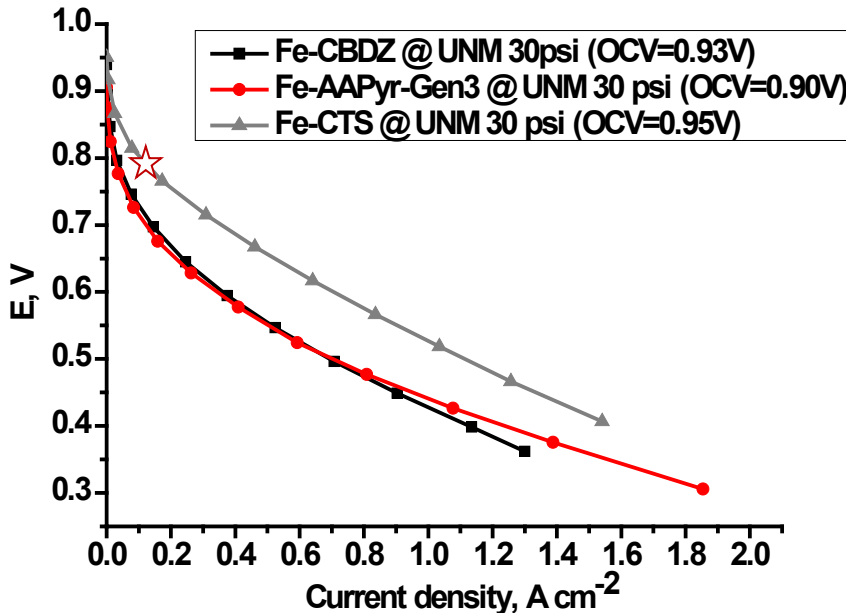
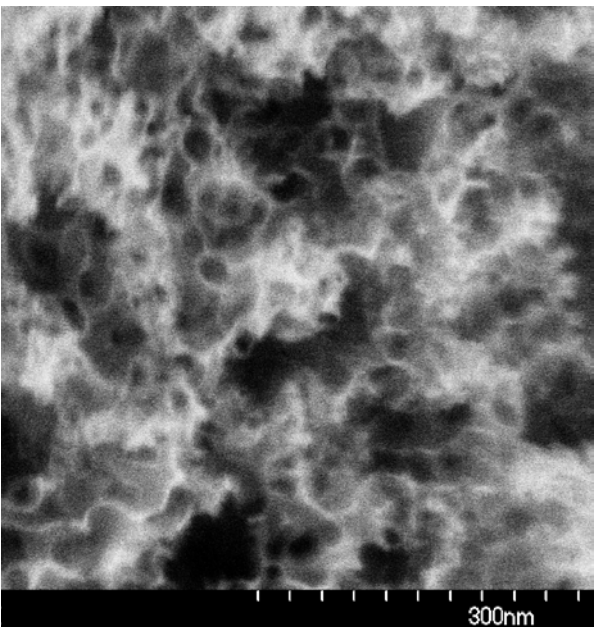
Technical Accomplishment continued....

## Task 2. Design and Synthesis of Novel Materials for Oxygen Reduction Reaction (ORR)

### – Advanced Performance Catalysts: MEA fabrication and Fuel Cell Performance (UNM)



Sacrificial Support Method of catalyst synthesis results in hierarchically-structured morphology



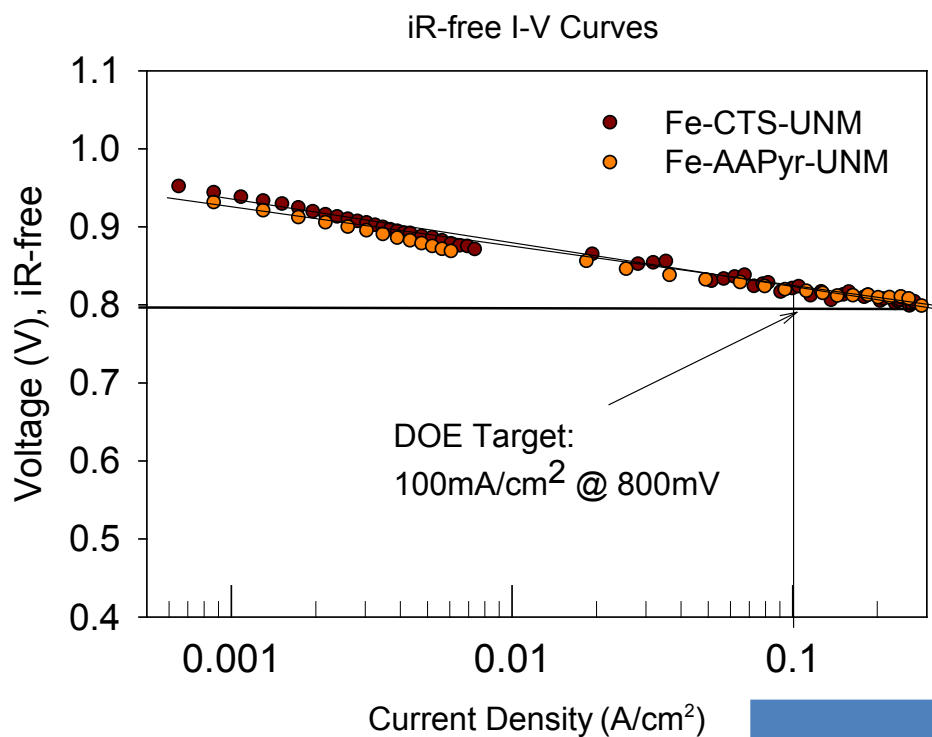
NOT iR-Corrected MEA Test  
 Testing conditions:  
 Humidity: 100%RH;  
 Flow Rate: 100ccm H<sub>2</sub>/O<sub>2</sub>;  
 Backpressure: 30psig;  
 T<sub>cell</sub>=80C;  
 Membrane: 211 Nafion®;  
 Cathode: 4mg cm<sup>-2</sup>



Technical Accomplishment continued....

## Task 2. Design and Synthesis of Novel Materials for Oxygen Reduction Reaction (ORR) - Advanced Performance Catalysts: MEA fabrication and Fuel Cell Performance (UNM)

### MEA Validation Test Performed at NEU



MEA testing conditions: Humidity: 100%RH;  
Flow Rate: 100ccm H<sub>2</sub>/O<sub>2</sub>;  
Backpressure: 28psig/NEU, LANL 13 psig;  
T<sub>cell</sub>=80°C; Membrane: 117 Nafion®; Cathode: 2 mg cm<sup>-2</sup>

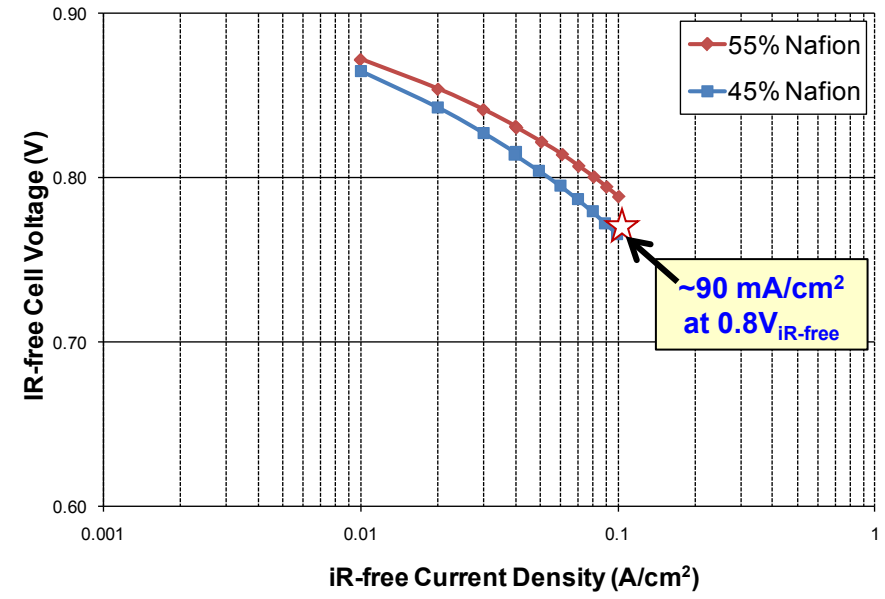
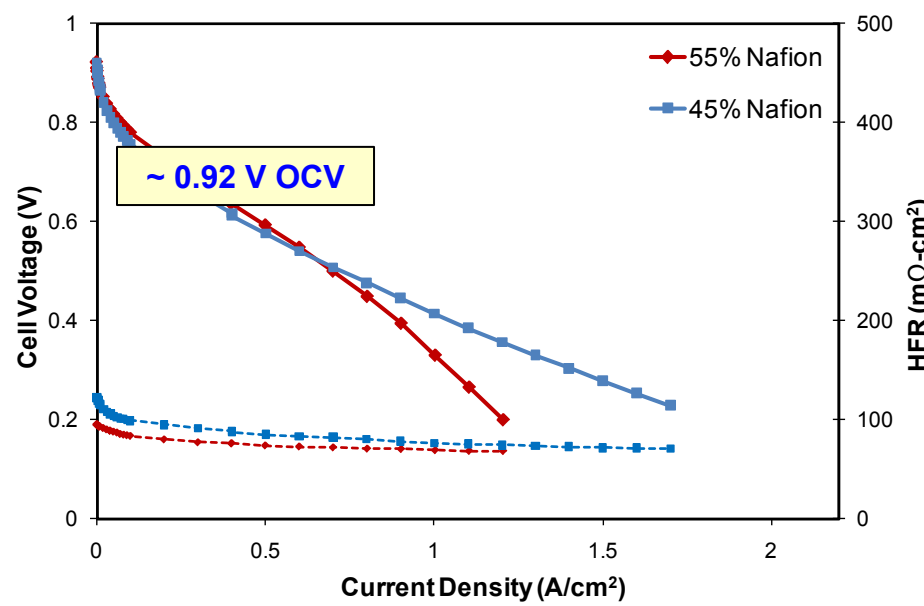
	mV @ 200 A/cm <sup>3</sup>
DOE Target	800
FE-CTS (UMN)	770
Fe-AAPyr (UNM)	740

# Task 2: MEA fabrication and Fuel Cell Performance (UNM)

## UNM Fe-CTS Catalyst – MEA Testing, Nissan Validation Results – iV Performance



**H<sub>2</sub>/O<sub>2</sub> 80°C 100% RH 1.5 bar Total Pressure (DOE standard conditions)**



**Anode: 0.4 mg<sub>Pt</sub>/cm<sup>2</sup>  
Cathode: 4 mg<sub>catalyst</sub>/cm<sup>2</sup>  
Membrane : NR 211**

❑ Increasing the Nafion content from 45% to 55% while keeping the catalyst loading constant at 4 mg/cm<sup>2</sup> improved the activity but mass transport losses increased.



❑ The 55% Nafion sample gave **~90 mA/cm<sup>2</sup> at 0.8V<sub>iR-free</sub>**, very close to the DOE target of 100 mA/cm<sup>2</sup> at 1.5 bar total pressure (0.5 bar<sub>gauge</sub> backpressure).

# Task 2.3: UNM Fe-CTS Catalyst – RDE Durability

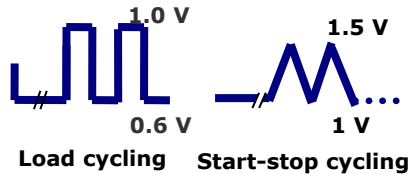
## Durability Protocol Evaluation



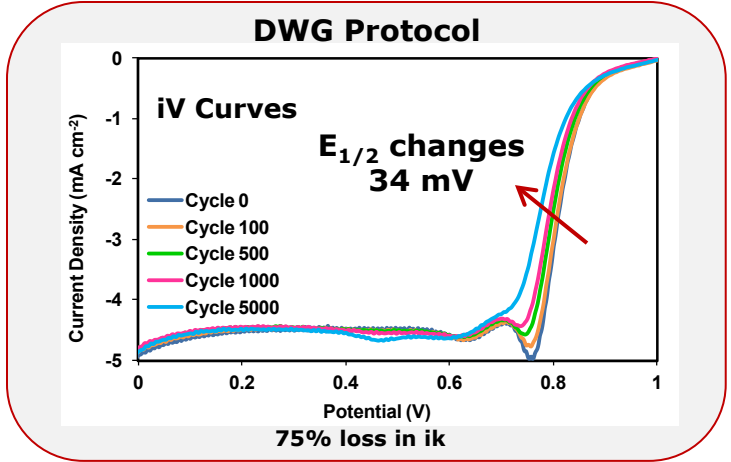
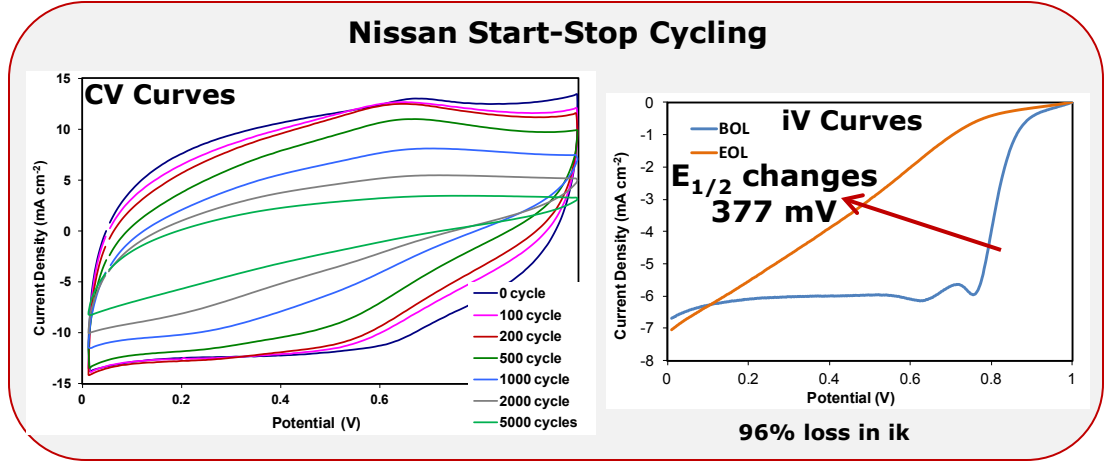
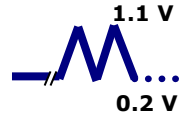
- The stability of Fe-CTS was evaluated under Nissan load cycling and start-stop cycling protocols and DOE Durability Working Group's (DWG) suggested accelerated stress protocol. The kinetic current at 0.8V,  $i_k$  ( $\text{mA cm}^{-2}$ ), was calculated as the index to show the activity loss of the catalyst.

Protocols for Nissan and DOE Durability Working Group			
Condition	Nissan Load cycling	Nissan Start-stop cycling	DWG
Temperature ( $^{\circ}\text{C}$ )	60	60	25
Gas condition	N2	N <sub>2</sub>	O <sub>2</sub>
Rotating (RPM)	0	0	900
Voltage scan (V)	[0.6,1.0]	[1.0, 1.5]	[0.2, 1.1]
Scan rate (mV/s)	6s/cycle	500	50
Experimental time (h)	24	8	42
Electrolyte	0.5M H <sub>2</sub> SO <sub>4</sub>		
Catalyst loading ( $\text{mg/cm}^2$ )	0.6		
No of cycles	10,000	5000	

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



DOE Durability Working Group's suggested protocol to evaluate catalyst durability mechanistically



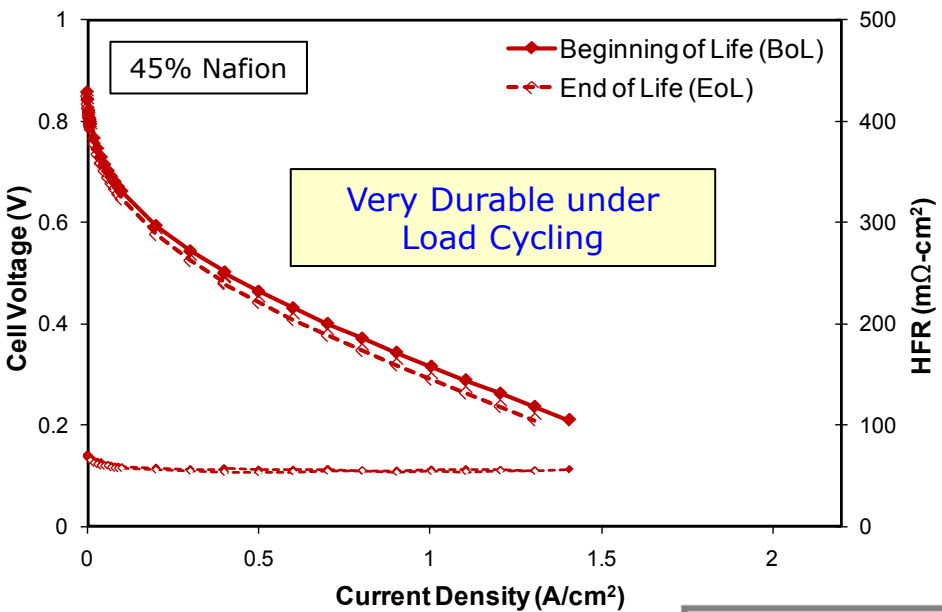
- Fe-CTS is found to be stable under DWG protocol. Nissan start-stop cycling is effective for the evaluation of catalyst durability since the desired effect is achieved in only 8 hours.
- Fe-CTS also showed good stability under Nissan load cycling protocol. No or minimal change observed in CVs after 10,000 potential cycles (not shown here).

# Task 2.3: UNM Fe-CTS Catalyst – MEA Testing

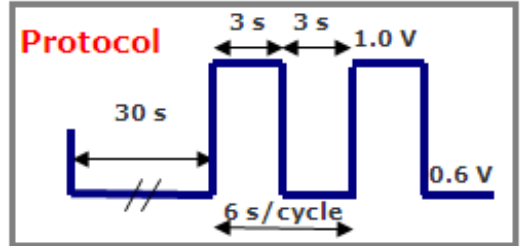
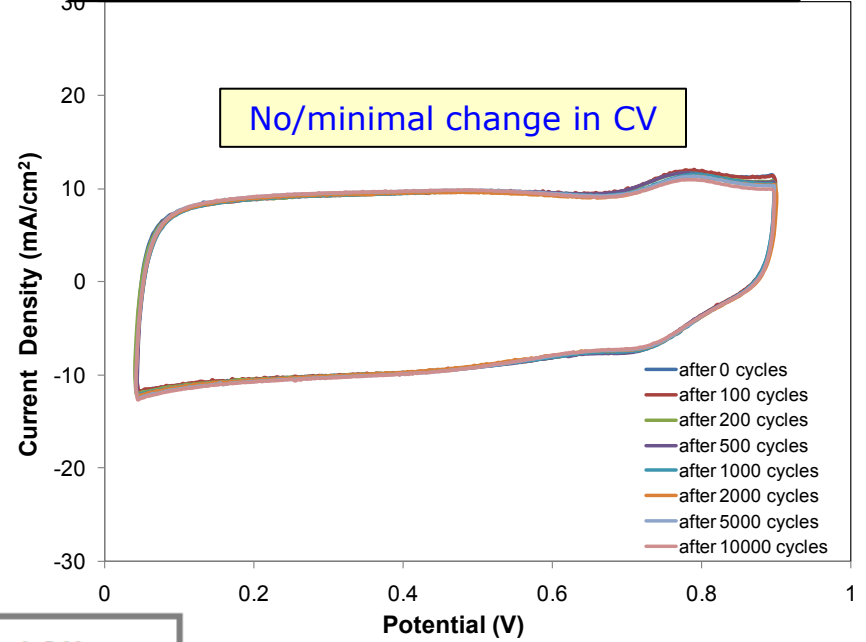
## Durability – Load Cycling (0.6 to 1.0V)



H<sub>2</sub>/O<sub>2</sub> 80°C 100% RH 1.5 bar Total Pressure (DOE standard conditions)



Effect on CV due to load cycling  
0.6 V- 1.0 V, H<sub>2</sub>/N<sub>2</sub>, 80°C 100% RH



- Minimal change in performance is observed after 10,000 potential cycles (load cycling) from 0.6 to 1.0V.
- The CV profile barely changed after 10,000 potential cycles (load-cycling).

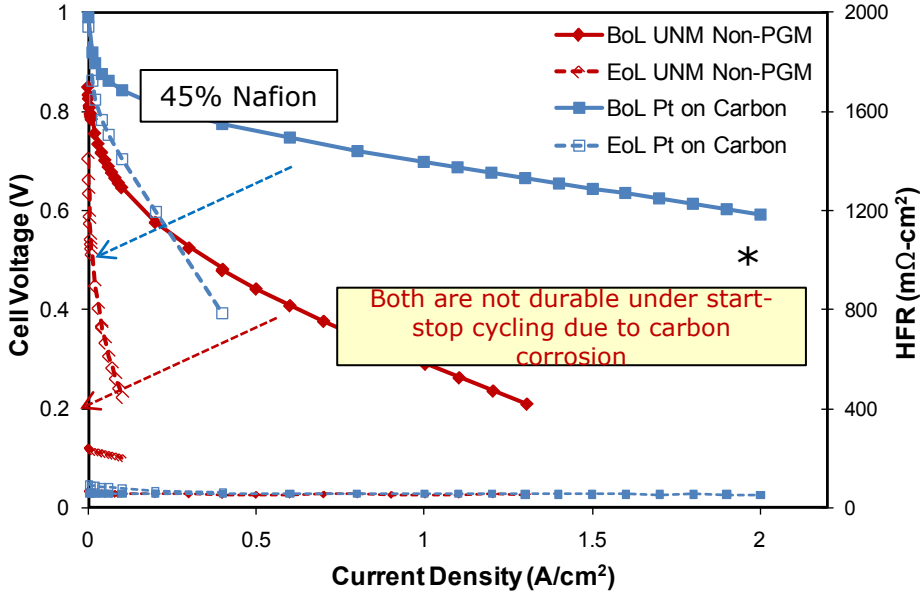


# Task 2.3: UNM Fe-CTS Catalyst – MEA Testing

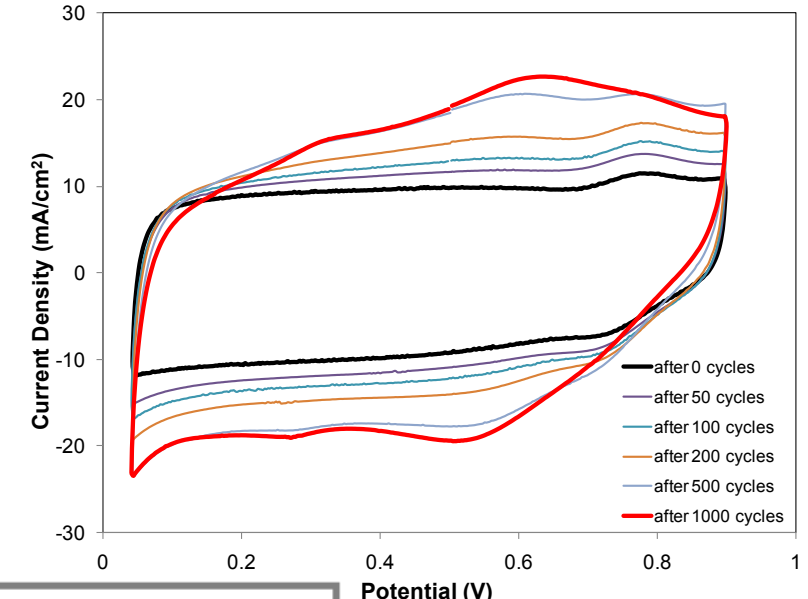
## Durability – Start-Stop Cycling (1 to 1.5V)



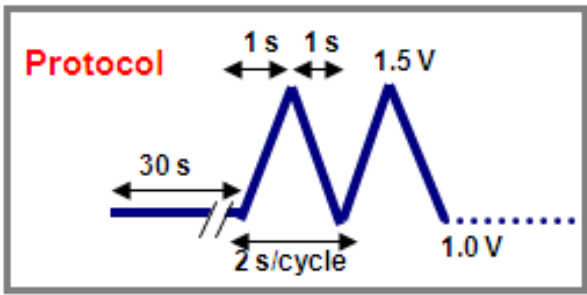
H<sub>2</sub>/O<sub>2</sub> 80 °C 100% RH 1.5 bar Total Pressure (DOE standard conditions)



Effect on CV for Fe-CTS due to start-stop cycling 1.0 V- 1.5 V, H<sub>2</sub>/N<sub>2</sub>, 80 °C 100% RH



\* Pt/C cathode loading = 0.15 mg/cm<sup>2</sup> using a 20% Pt on carbon catalyst



- ❑ A drastic decrease in performance is observed after 1,000 potential cycles (start-stop cycling) from 1.0 to 1.5V. Similar severe drop in performance is also observed for traditional Pt on high surface area carbon catalysts.
- ❑ The CV profile significantly changed after 1,000 potential cycles (start-stop cycling).



Technical Accomplishment continued....

## Task 3. Mechanistic Studies and Spectroscopy

### Participating Institutions:

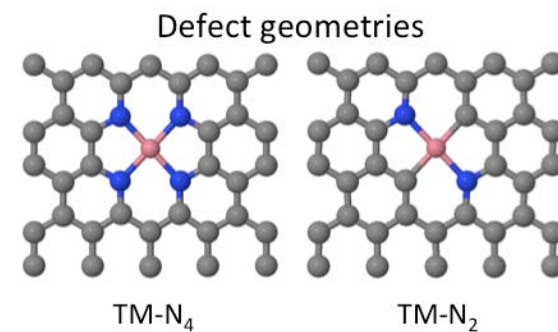
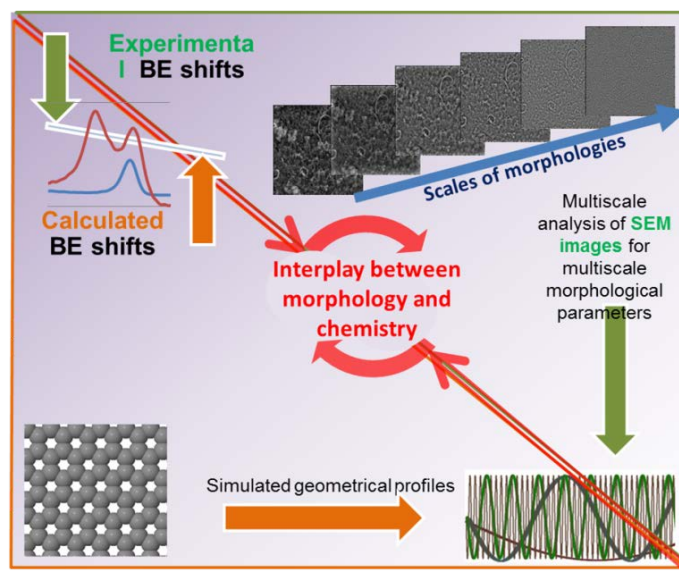
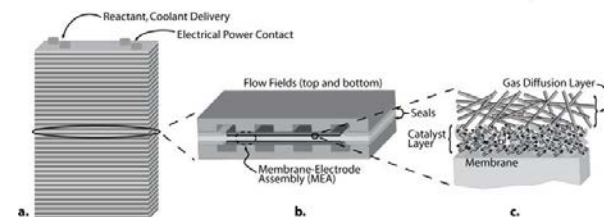
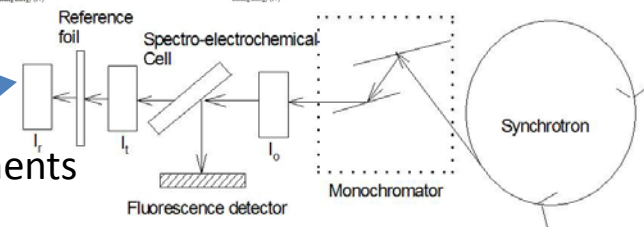
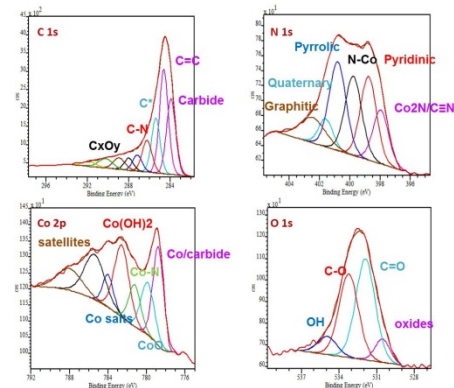
UNM/UTK- DFT Calculations

NEU- In situ Spectroscopy with Synchrotron and Raman Measurements

SMU- Macroscopic Modeling

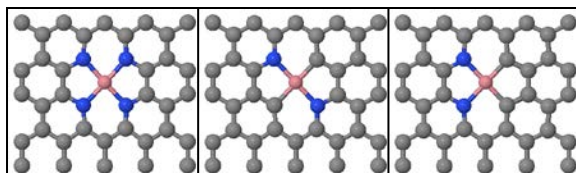
UTK- Molecular Level Computation (Ab-Initio and DFT)

UNM- DFT calculations with XPS and PCA analysis

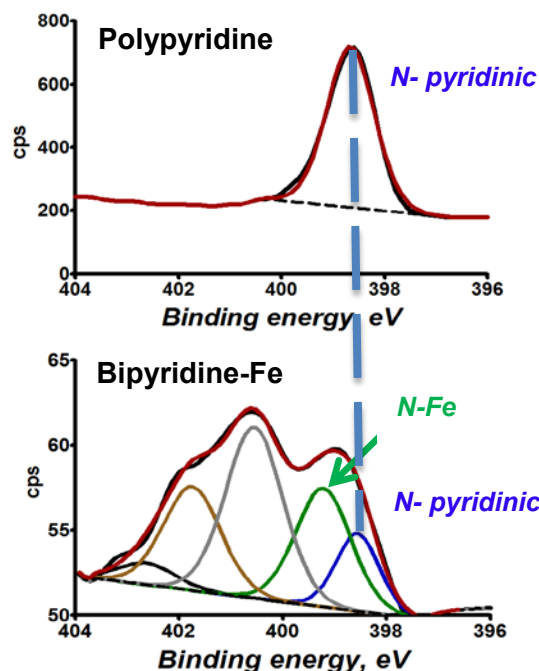


Task 3: Computational & Experimental Methods:  
Synergy between Materials Characterization and Predictive Modeling

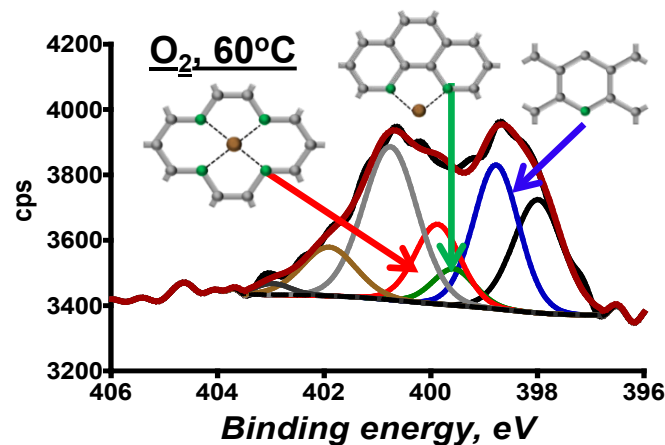
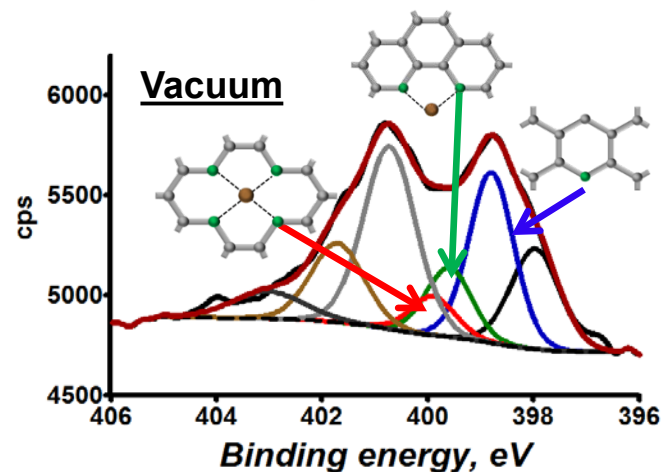
### DFT calculations of XPS binding energy shifts



	Me-N <sub>4</sub>	Me-N <sub>2</sub>	Me-N <sub>2</sub>
theory	+1.1 eV	0.8 eV	1.0 eV
experiment	+0.9-1.1 eV		



### Ambient pressure XPS



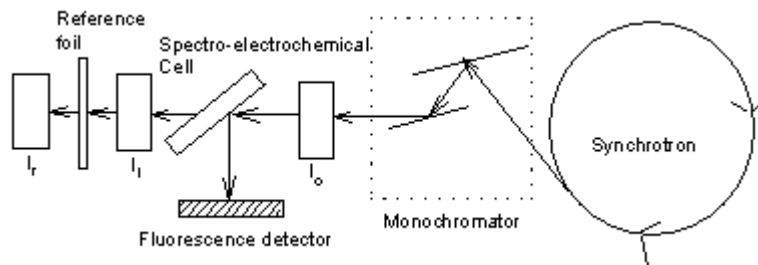
Both Me-N<sub>2</sub> and Me-N<sub>4</sub> centers are present but their relative amount changes upon exposure to oxidizing atmosphere – stabilization of N<sub>4</sub> centers

# Task 3. Mechanistic Studies and Spectroscopy

## X-ray absorption spectroscopy an element specific, core level spectroscopy

### Synchrotron Advantages

- High Intensity
- Broad Spectral Range
- High Polarization
- Flux > 10<sup>10</sup> photons/s
- Natural Collimation



EXAFS, single backscatter

### Physical Basis

Determination of short range atomic order (bond distance, coordination number, Debye Waller factor etc.,)

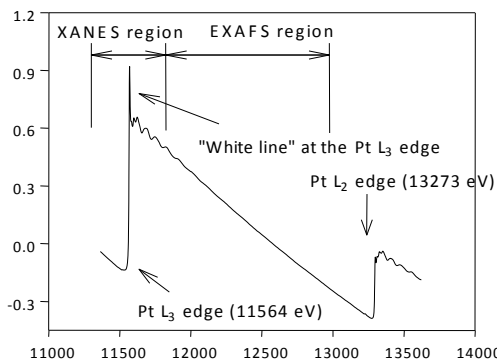
### XANES, multiple scattering

#### Physical Basis

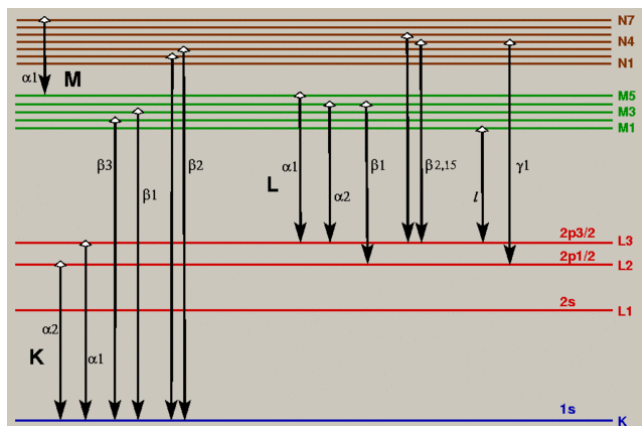
- Determination of oxidation state and coordination symmetry
- Electronic Structure
- Extent of Corrosion

$$E_{\text{photoelectron}} = E_{\text{xray}} - E_0$$

$$\mu x = \ln(I_0/I_t)$$



- N** – Coordination Number
- R** – Interatomic Distance (Å)
- σ<sup>2</sup>** – MSRD (Debye-Waller)
- f(k)** – Amplitude
- δ(k)** – Phase



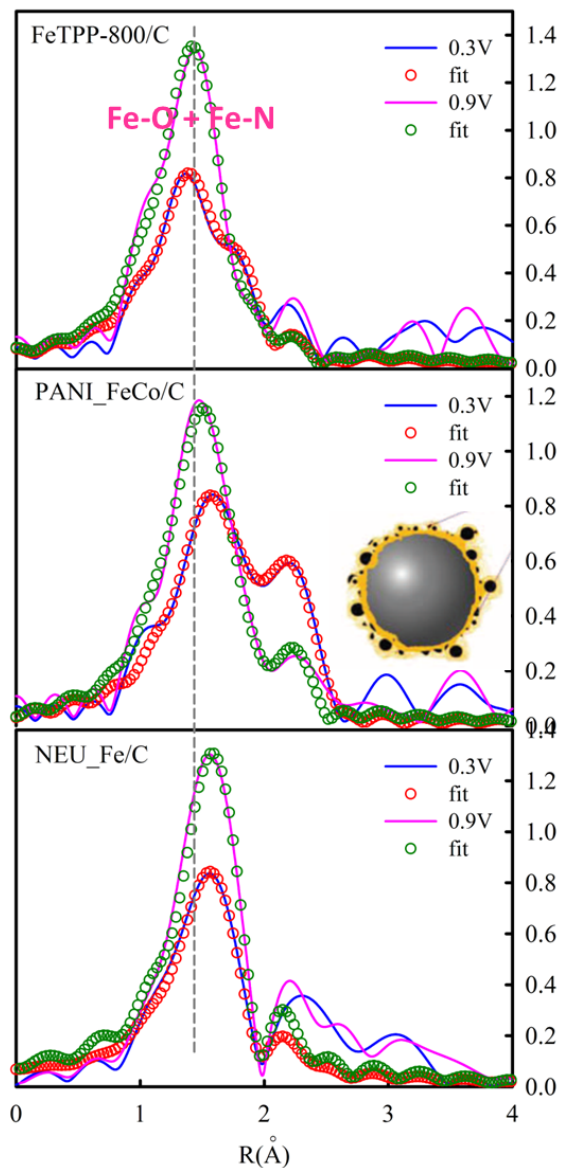
### Detection:

- State-of-the-art 13 element Ge array detector
- Gas ionization chambers
- Photomultiplier tubes
- 14K Cryostat

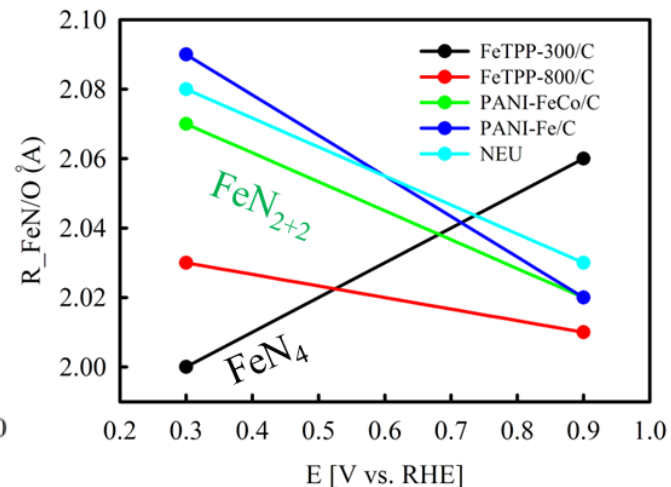
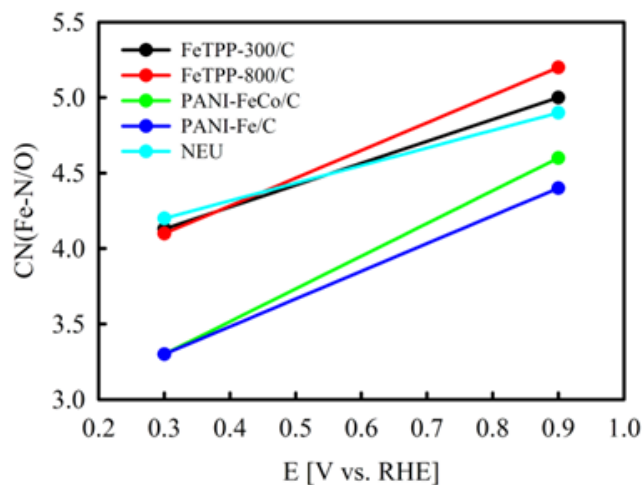
$$E_{\text{xray}} = \frac{hc}{\lambda}$$



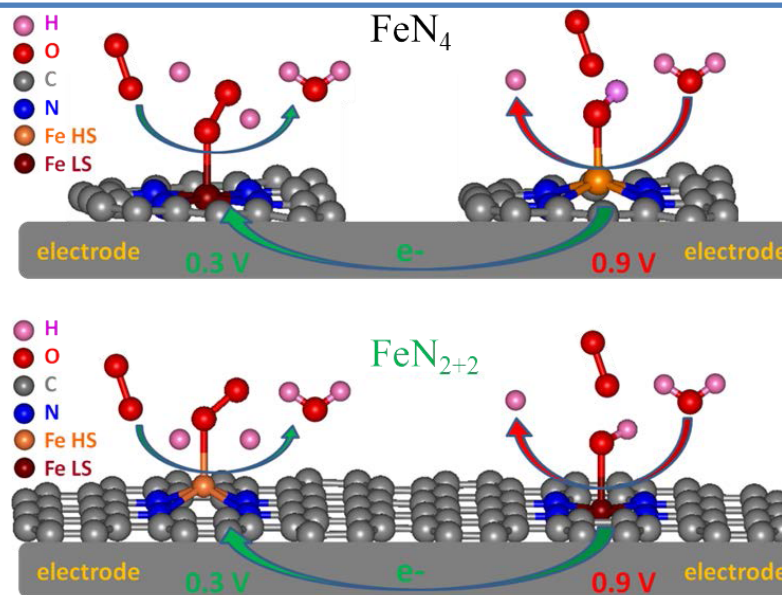
## Task 3. Mechanistic Studies and Spectroscopy



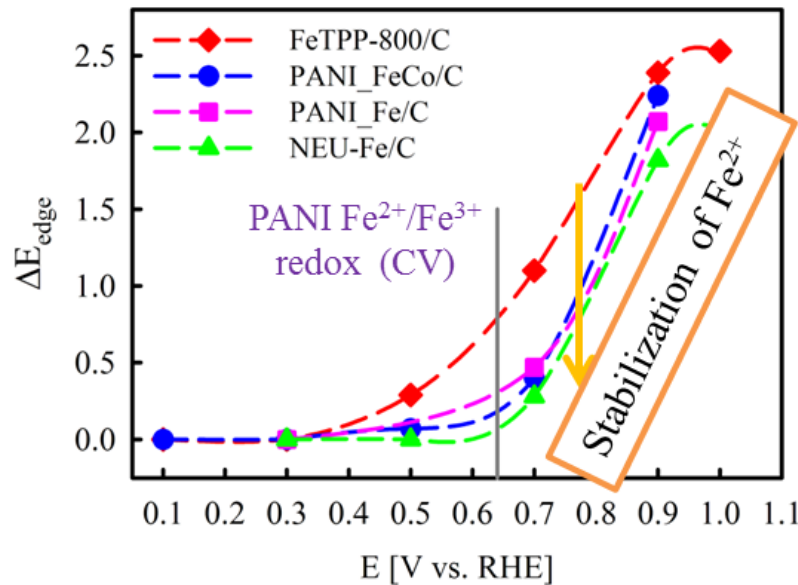
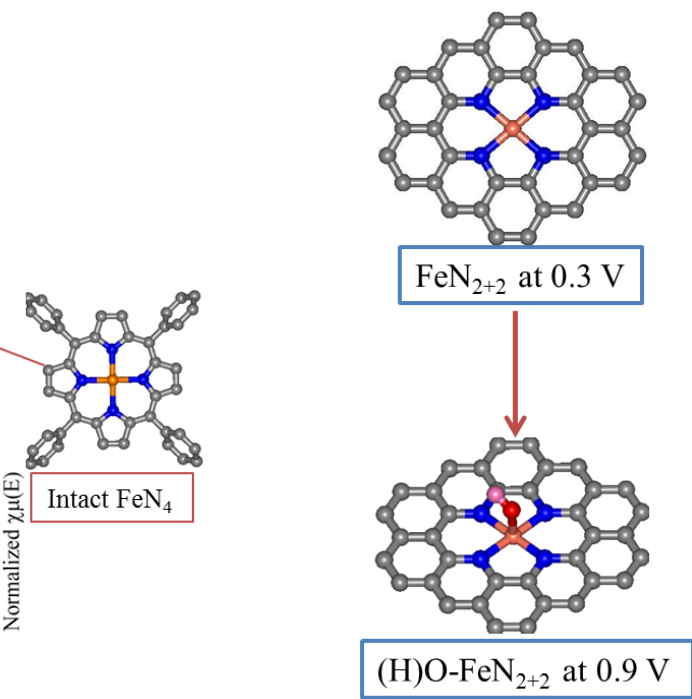
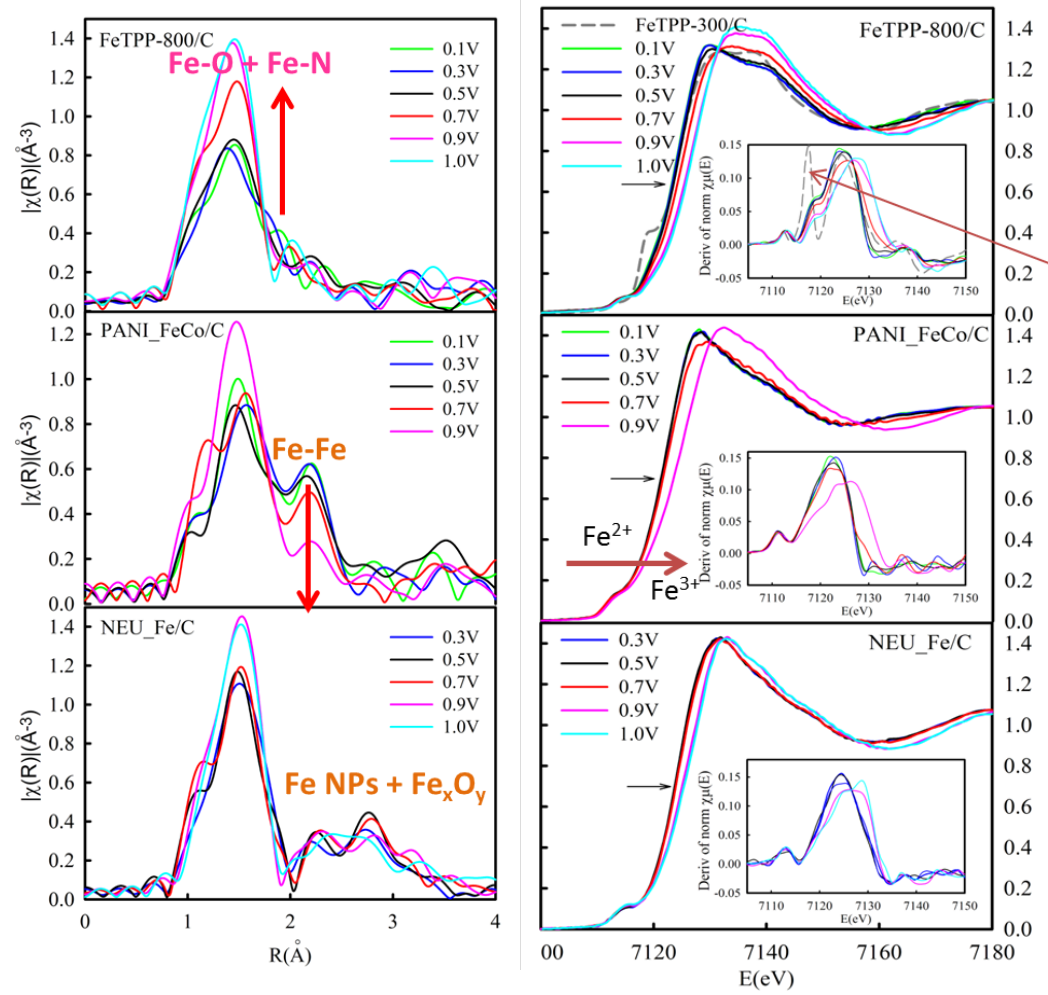
(2011); G. Wu, et al.



The Fe-N bond length/spin switching behavior of  $\text{Fe-N}_{2+2}$  is opposite to that of  $\text{Fe-N}_4$ . This is the origin of the enhanced ORR activity.



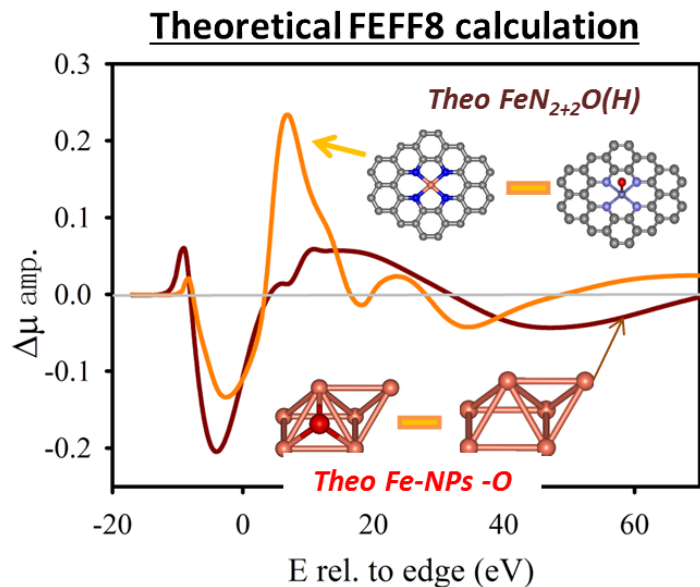
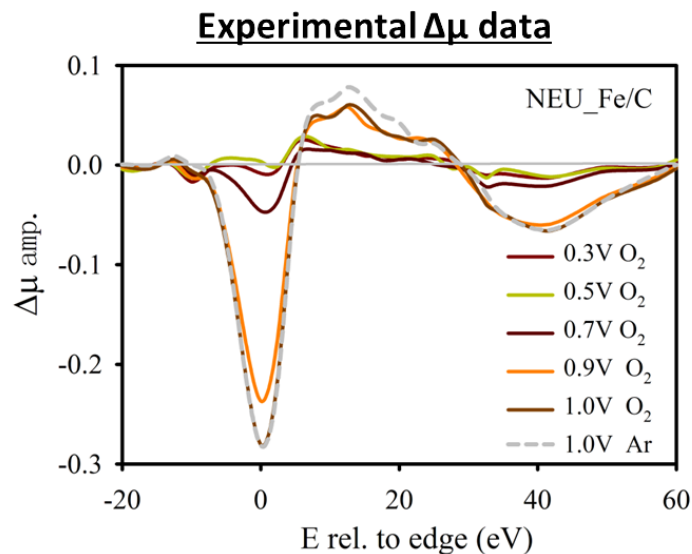
### Task 3. Mechanistic Studies and Spectroscopy



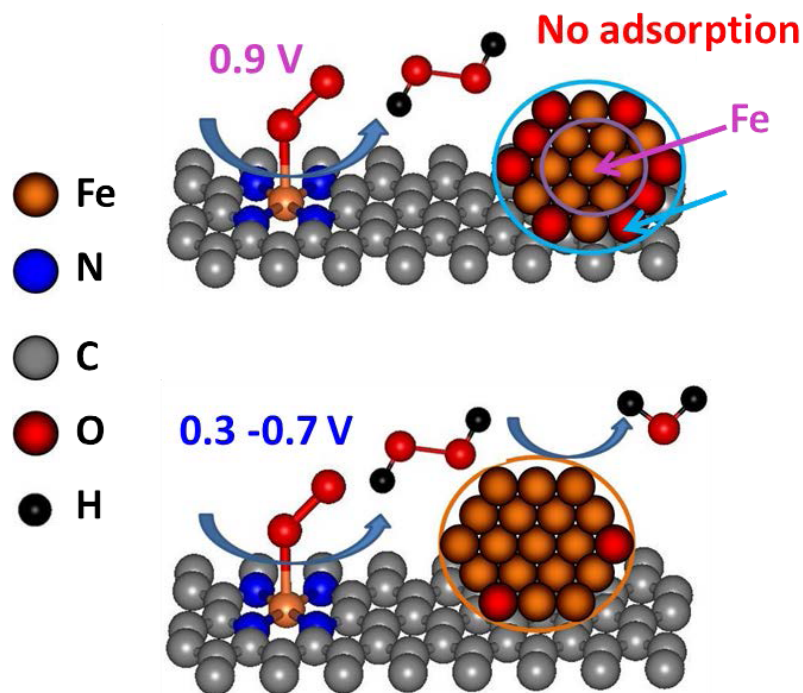
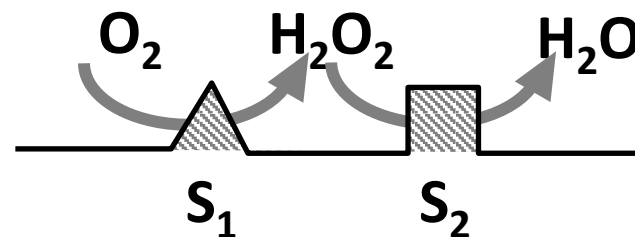
The transition between Fe<sup>2+</sup> and Fe<sup>3+</sup> oxidation states is accompanied with the adsorption of OH.  

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

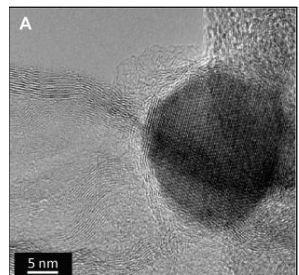
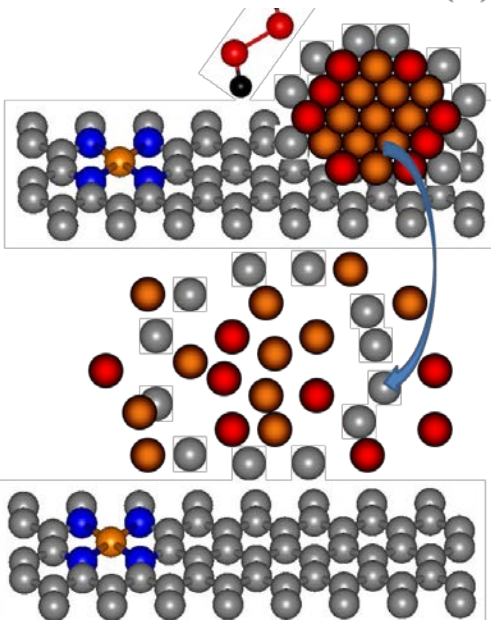
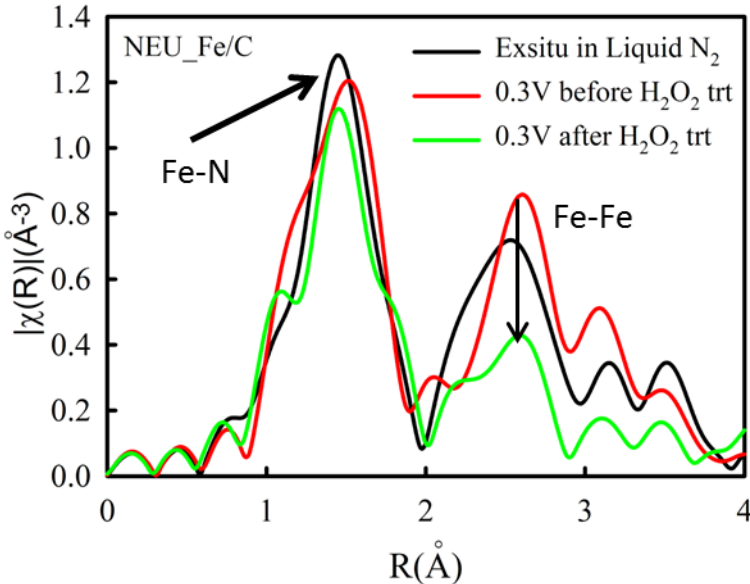
## Task 3. Mechanistic Studies and Spectroscopy



**Dual site consequential:  
2 x 2e- bifunctional mechanism**

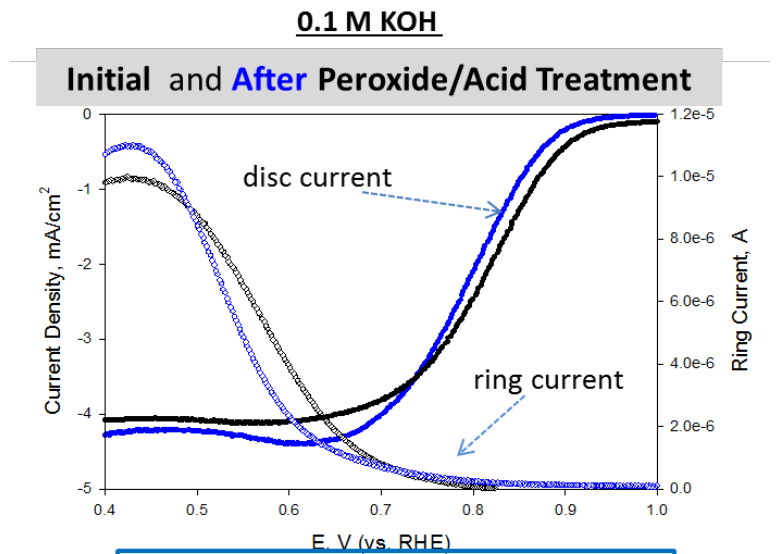
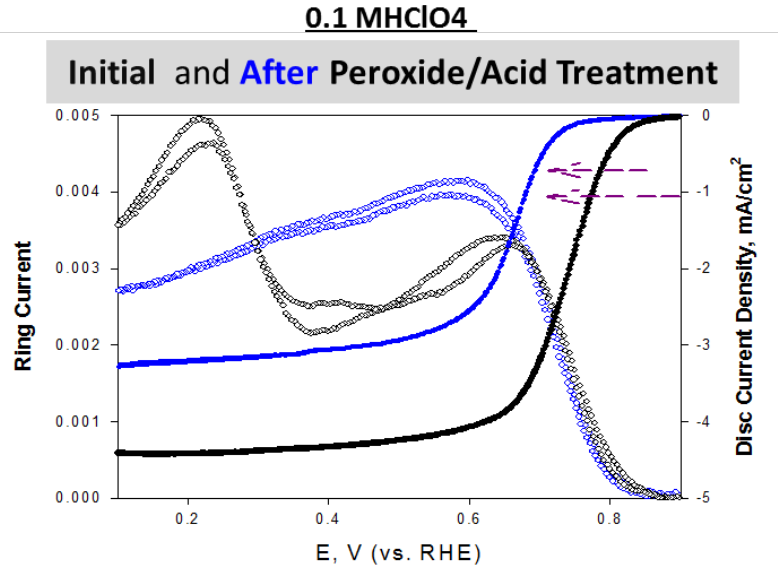


### Task 3. Mechanistic Studies and Spectroscopy



*Sci. (2011); G. Wu, et al.*

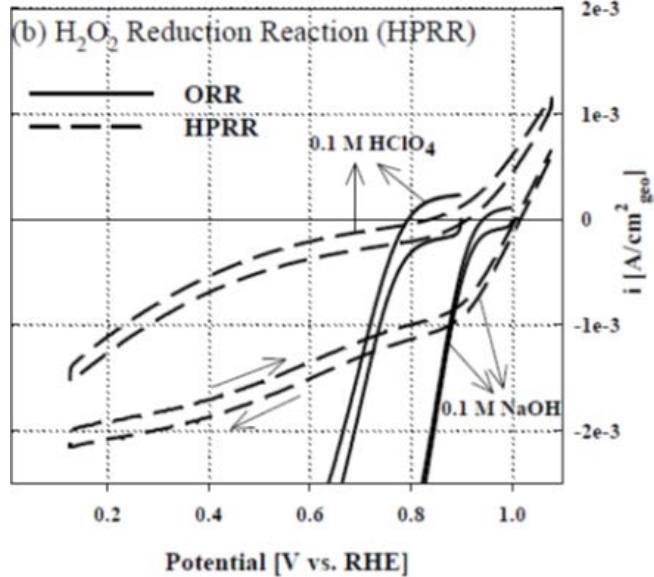
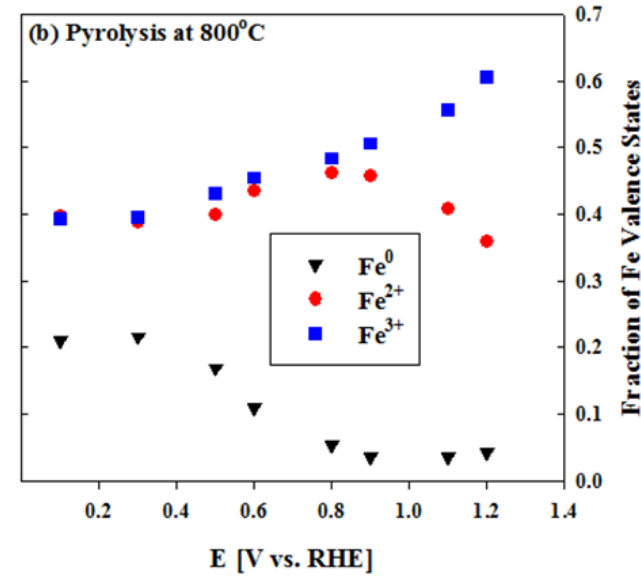
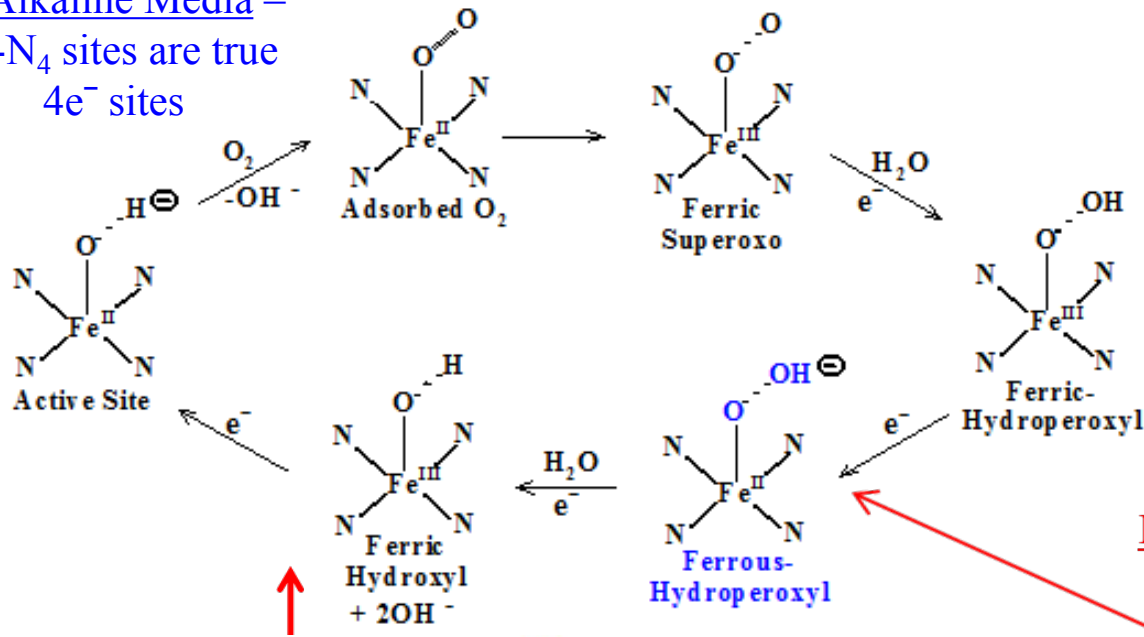
Peroxide attacks the graphene sheets that protect Fe/FeO<sub>x</sub> NPs.



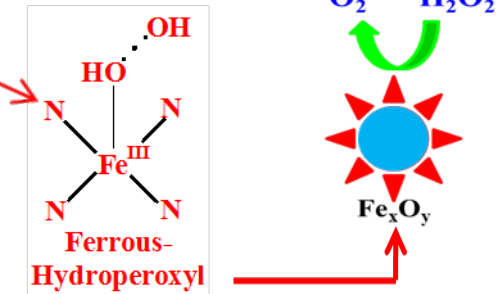
Fe-N<sub>4</sub> sufficient for both O<sub>2</sub> and H<sub>2</sub>O<sub>2</sub> reduction in alkaline

**Task 3-2. Mechanistic Studies and Spectroscopy**

In Alkaline Media –  
Fe-N<sub>4</sub> sites are true  
4e<sup>-</sup> sites



In Acidic Media

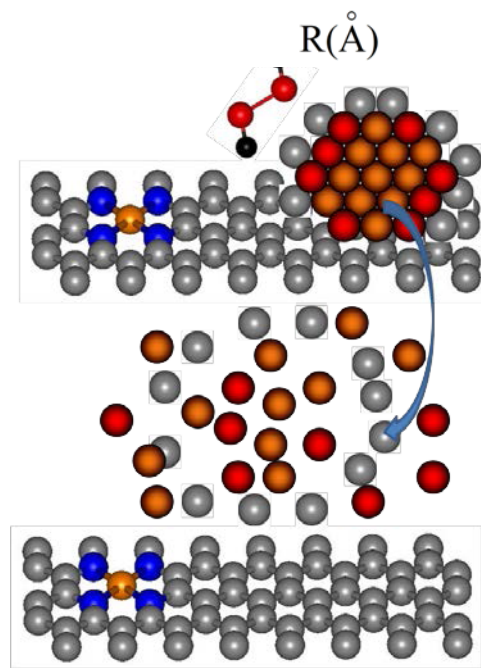
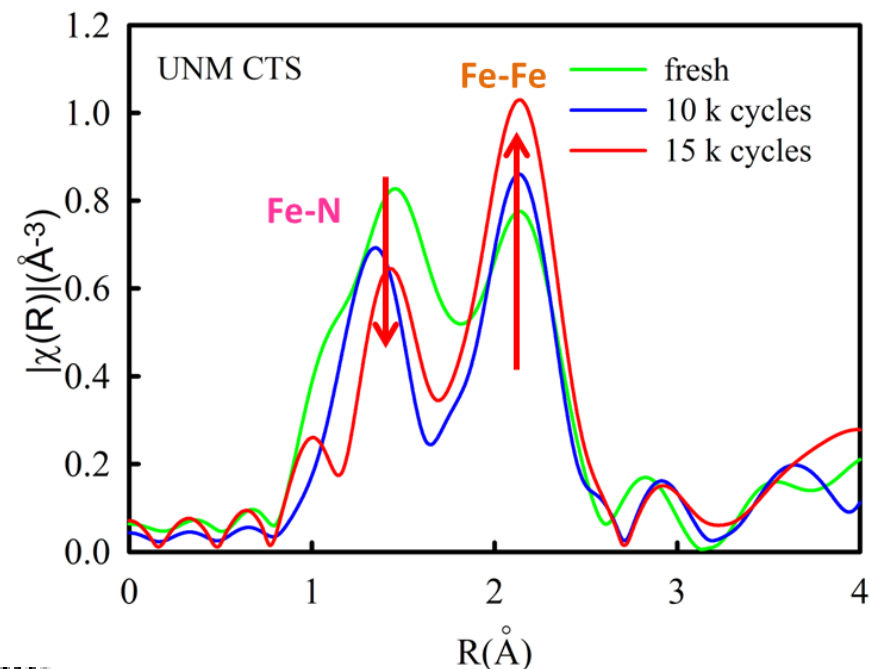
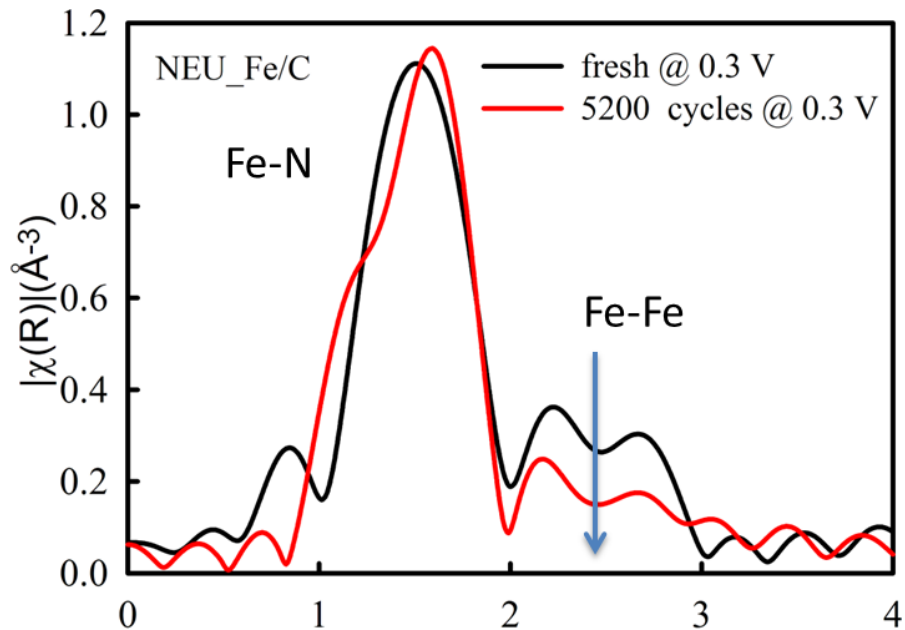


Frumkin-type electrostatic double-layer effect  
stabilizes peroxide intermediate in alkaline medium

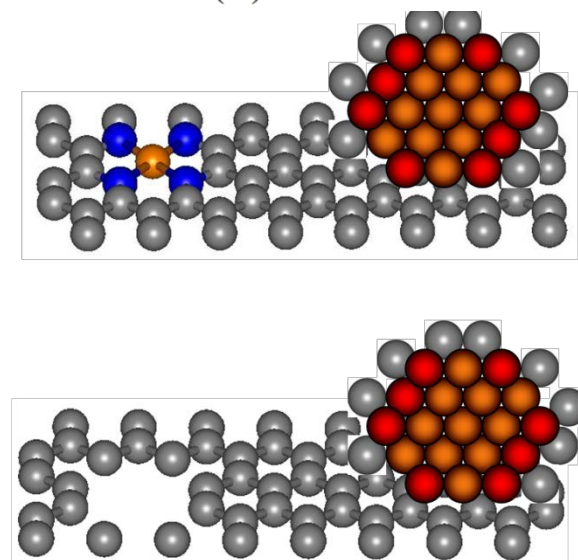
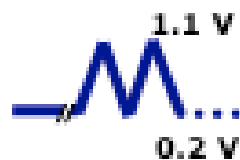
Fe-N<sub>4</sub> sites  
predominantly yield  
peroxide in acidic  
media

Technical Accomplishment continued....

### Task 3: Degradation Mechanism



▶ DOE Durability Working Group's suggested protocol to evaluate catalyst durability mechanistically



## Task 3: Computational Methods

➤ two different approaches have been utilized

- 1. Periodic System (~ 30 atoms) with plane wave basis sets**
- 2. Molecular Systems (~ 30 atoms) with local Gaussian basis sets**

### ***Similarities:***

- both based on Kohn Sham density functional theory (DFT)
- both have established predictive capabilities
- both are independent and complementary to experiment
- neither can determine with certainty the structure of pyrolyzed material

### ***Differences:***

- Approach 1 models the system in the gas phase only
- Approach 1 simulates extended systems through periodic boundary conditions
- Approach 2 includes an implicit solvent (i.e., medium) in the calculations
- Approach 2 is limited to molecular (i.e., isolated) systems

# Task 3: Computation and Simulation: Stability of Graphitic TM-N<sub>x</sub> Defects

## Details:

- 3-d periodic (vacuum thickness 14 Å)
- All-electron like PAW potentials.
- GGA.
- Spin-polarized.

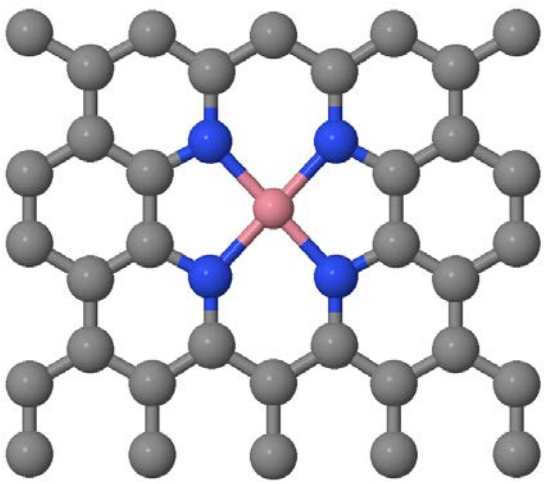


Model system:

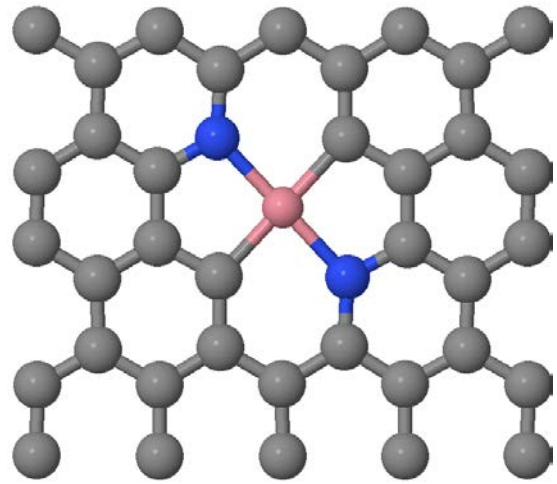
- Carbon support.
- Periodic structure.
- High defect density.

**Simulated region.**  
+ 2-d periodicity  
= extended surface.

## Defect geometries



TM-N<sub>4</sub>



TM-N<sub>2</sub>

Insight:

- Graphitic TM-N<sub>4</sub> defects are expected to be stable to higher voltages.
- Could contribute to the initial decrease of ORR catalytic activity.
- TM-N<sub>4</sub> prime defect motif for ORR activity.

2e process:  $U_{crit} = E_{formation}/2$

	Periodic	
U <sub>crit</sub> (V)	N <sub>2</sub>	N <sub>4</sub>
Fe	0.3	1.55
Co	0.5	1.78
Ni	0.6	1.73



## Task 3: Computations on Molecular Systems-Binding Energies

MN<sub>2</sub>

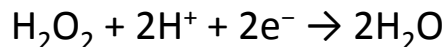
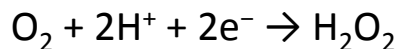
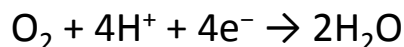
M	Species				
	O <sub>2</sub>	H <sub>2</sub> O	H <sub>2</sub> O <sub>2</sub>	OH <sup>-</sup>	OOH <sup>-</sup>
Cu(II)	-0.08	-0.35	-0.09	-1.67	-1.40
Fe(II)	-0.90	-0.88	-3.28 <sup>Δ</sup>	-2.21	-3.12 <sup>Δ</sup>
Fe(III)	-0.96	-1.11	-0.71	-2.97	-2.89
Co(II)	-1.05	-0.99	-1.03	-2.59	-2.49
Ni(II)	-0.65	-0.87	-0.83	-2.43	-2.39

MN<sub>4</sub>

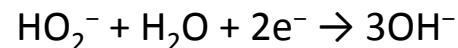
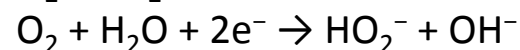
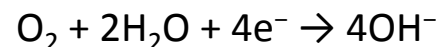
M	Species				
	O <sub>2</sub>	H <sub>2</sub> O	H <sub>2</sub> O <sub>2</sub>	OH <sup>-</sup>	OOH <sup>-</sup>
Cu(II)	0.32	-0.09	-0.13 <sup>*</sup>	0.05 <sup>*</sup>	-0.07 <sup>*</sup>
Fe(II)	-1.13	-0.18	-1.08	-1.21	-1.32
Fe(III)	-0.26	0.00	-0.44	-2.16	-2.20
Co(II)	-0.96	-0.08	-0.20 <sup>*</sup>	-0.27	-0.29
Ni(II)	-0.27	-0.19	-0.19 <sup>*</sup>	-1.95 <sup>◇</sup>	-0.69 <sup>◇</sup>

Energy in eV

### ORR Acidic Medium



### ORR Basic Medium



<sup>Δ</sup>: -H<sub>2</sub>O<sub>2</sub> breaks into 2 -OH radicals and -OOH breaks into -O and OH<sup>-</sup>, respectively

<sup>◇</sup>: calculations based on OH and OOH radicals not anions

<sup>\*</sup>: intermediate species dissociates from the catalyst surface due to weak binding energies

Becke-Perdew functional  
Standard triple- $\zeta$  basis sets  
COSMO solvation model



# Collaborations

## **Partners (this project)**

- Northeastern Univ., (Prime) Boston: S. Mukerjee (P.I) and S. Smotkin
- Univ. of Tennessee, Knoxville: Prof. T. Zawodzinski (Univ., subcontractor)
- Univ. of New Mexico, Albuquerque: Prof. P. Atanassov (Univ., subcontractor)
- Michigan State University: Prof. S. Barton (Univ., subcontractor)
- BASF Fuel Cells, Somerset, NJ: Dr. E. DeCastro (Industry, subcontractor)
- Pajarito powders, Albuquerque, NM: Paul Short and Bar Halevi (Industry subcontractor)
- Nissan Technical Center North America: Dr. K. Adjemian (Industry, subcontractor)
- Los Alamos National Lab: Dr. P. Zelenay (Federal Lab., subcontractor)

## **Other collaborators:**

Jean-Pol Dodelet: Canetiq, Canada (Non funded collaborator)

## Proposed Future Work (2013-, Budget Period 1)

- Final Selection of materials using RRDE & single cell polarization measurements (FY13Q1-Q4).
- Focus on improved mass transport in gas diffusion medium. Novel approaches to electrode preparation, additives for improved oxygen solubility and fabrication of MEAs (FY13Q2-Q4)
- Modeling of mass transport in electrode layers to be in sync with design of electrode structures (layer by layer approach) (FY13Q3-Q4)
- Elucidation of electrocatalytic pathways using spectroscopy and computation leading to first mechanistic interpretation (FY12Q1-4, FY13, Q1).

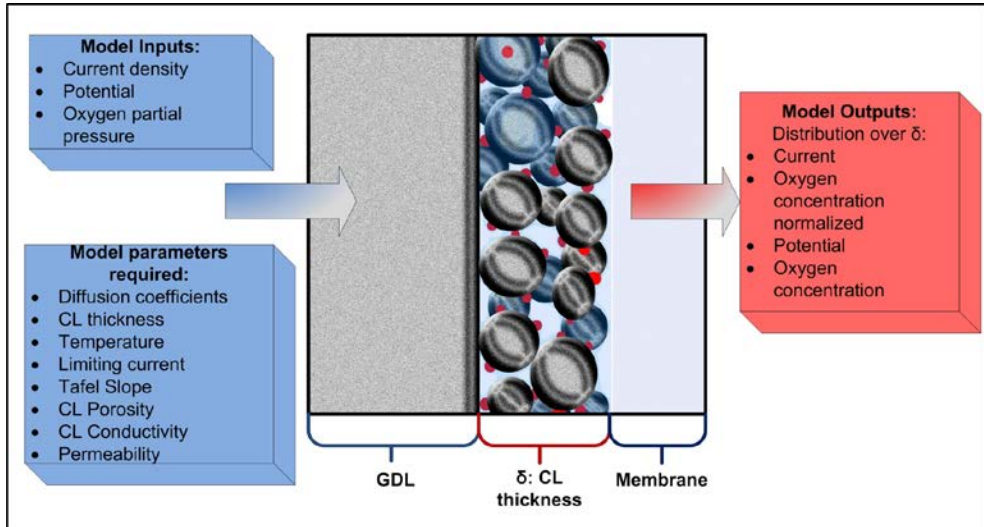
## Summary Slide

- Task 1.1 Design of Materials as High Performance Catalysts: These have lead to several candidates meeting DOE target of 150-200 A/cm<sup>3</sup> (iR free) at 0.8 V vs. RHE. This is 70 % complete considering DOE 2017 target of 300 A/cm<sup>3</sup> .
- 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 80 % complete, needing further confirmation and validation.
- Task 1.3 Catalyst Scale up initiated with Pajarito Powder LLC (Albuquerque, NM), this is expected to be 40 % complete at the end of the first funding period.
- Task 2.1 Translation of volumetric activity to actual fuel cell performance levels, with a target to 100 mA/cm<sup>2</sup> at 0.8 V (iR Free). Lowering of mass transport in the reaction and electrode structure is our current focus. This is 50% complete and forms the bulk of the future effort.
- Task 2.2 Good catalyst durability has been reported. However pushing the limits of carbon stability causes severe activity decline. This task is 70% 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 70% complete.

# Technical Back-Up Slides

# Task 2: Modeling Reaction and Gas Diffusion Layers for Enhanced Air Performance (UTK)

## Modeling Catalyst Layer Performance



### Special features of our approach

1. The model is modular; we can insert collaborators' experimentally derived kinetic models (S. C.-Barton)
2. The model also includes physics for single-site trapping to capture the 'molecular' nature of the active site
3. Experimental inputs (measured pore size distributions, for example) are readily included.
4. 'Fitting' exercises closely couple to experiments that provide many points in key regions; multiple polarization curves are simultaneously fit for more meaningful output.



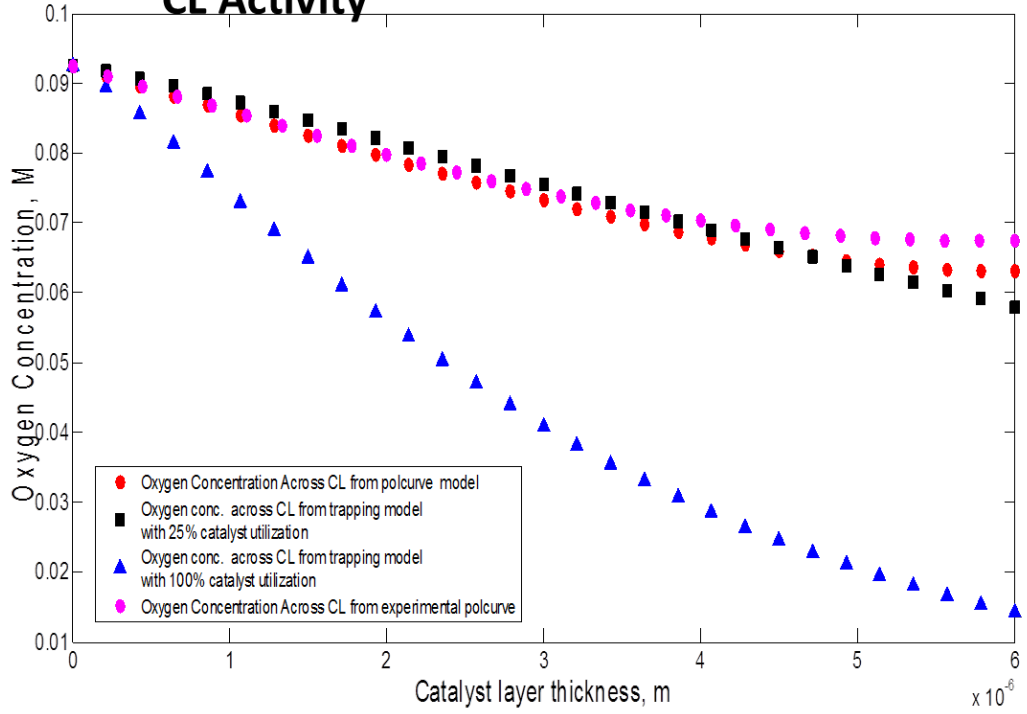
```

    graph TD
      A[Model Description] --> B[Input fitpolcurve]
      B --> C["i, V, p(O2) from experiments"]
      C --> D[Initial values and parameters processing]
      D --> E["T, C(O2), Diffusion coefficients, metal loading, OCV, porosity, permeability"]
      E --> F[Kinetics]
      F --> G["i,V corrected, CL resistance calculation(A-2 Springer), CL active area(A-3 Springer) and ilim calculation(A-4)"]
      G --> H[Reaction-Diffusion coupling]
      H --> I["Diffusion correction C(O2) correction with trapping modeling (C(O2) as a 3D function of the catalyst loading on the CL)"]
      I --> J[Output]
      J --> K["imodeled, Vmodeled C(O2)-corrected, Diffusion coefficient"]
  
```

# Task 2: Modeling Reaction and Gas Diffusion Layers for Enhanced Air Performance (UTK)

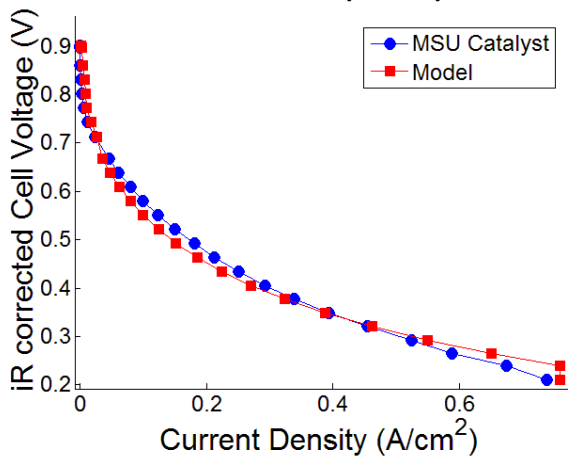
## Modeling Catalyst Layer Performance II

### Use of 'Trapping' Model to Describe CL Activity

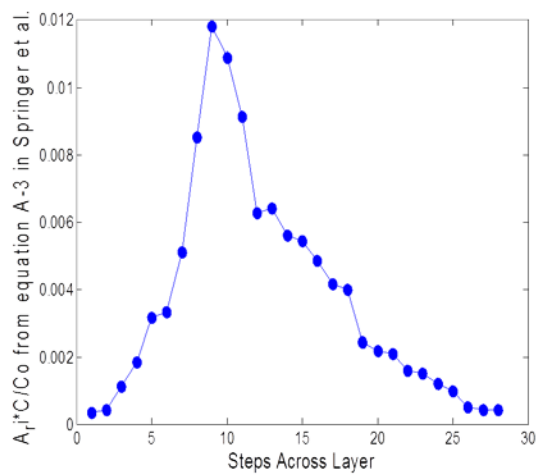


$$C_{O_2} = C_o \exp(C_{traps}^{2/5} \cdot t^{3/5})$$

$$t = \text{distance}^2 / D$$



### Catalyst Utilization as a Function of Position



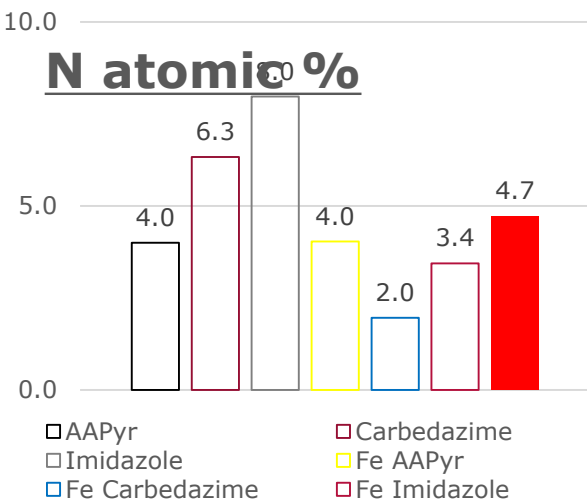
- Presently, we receive data in the form of single polarization curves. In the future, we will fit families of curves with varying oxygen mole fraction and so on.
- Single-site trapping model has been developed and is used to fit oxygen concentration profiles.



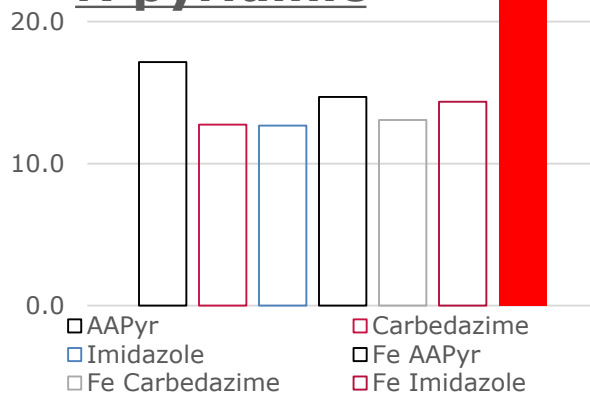
# Task 3. Mechanistic Studies and Spectroscopy

## - XPS Speciation of UNM catalysts obtained by SSM method

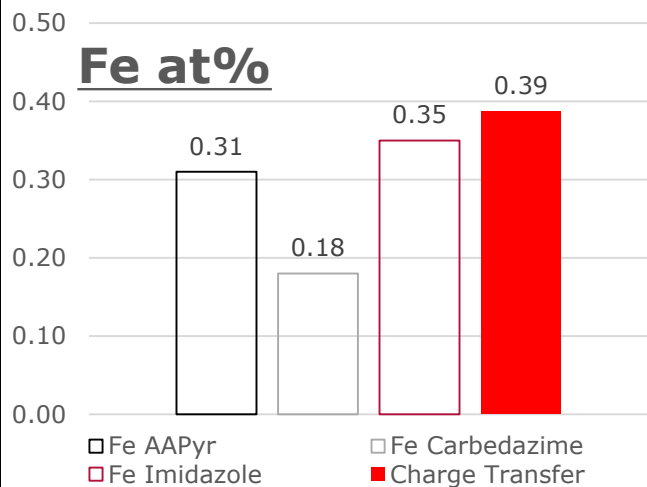
### N atomic %



### N pyridinic



### Fe at%

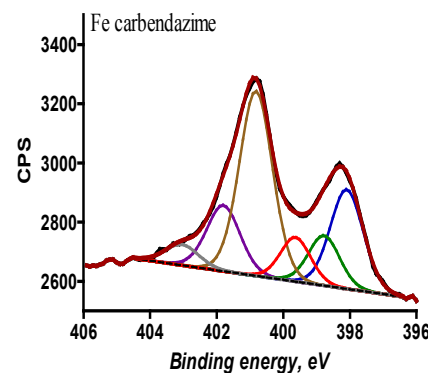
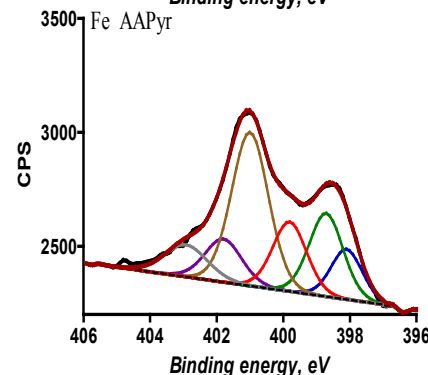
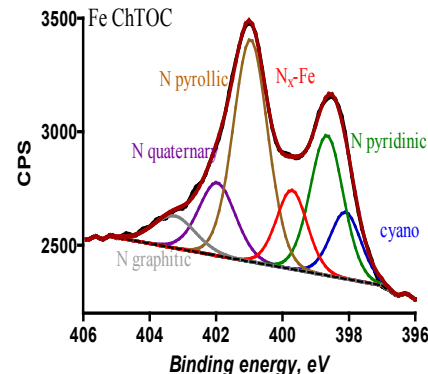


	Fe %	Fe-N %	Fe <sub>3</sub> O <sub>4</sub> %	FeO %	Fe <sub>2</sub> O <sub>3</sub> %
Fe Carbedazime	6.2	25.3	26.0	22.7	19.8
Fe Imidazole	3.9	21.4	26.3	26.5	21.9
Fe AAPyr	4.4	20.1	29.6	27.8	18.2
Charge Transfer	5.6	14.4	27.1	33.3	19.5

Amount of N and pyridinic N is very similar to that from other Me-NC electrocatalysts – slightly more.

Amount of metallic Fe is also at the same level.

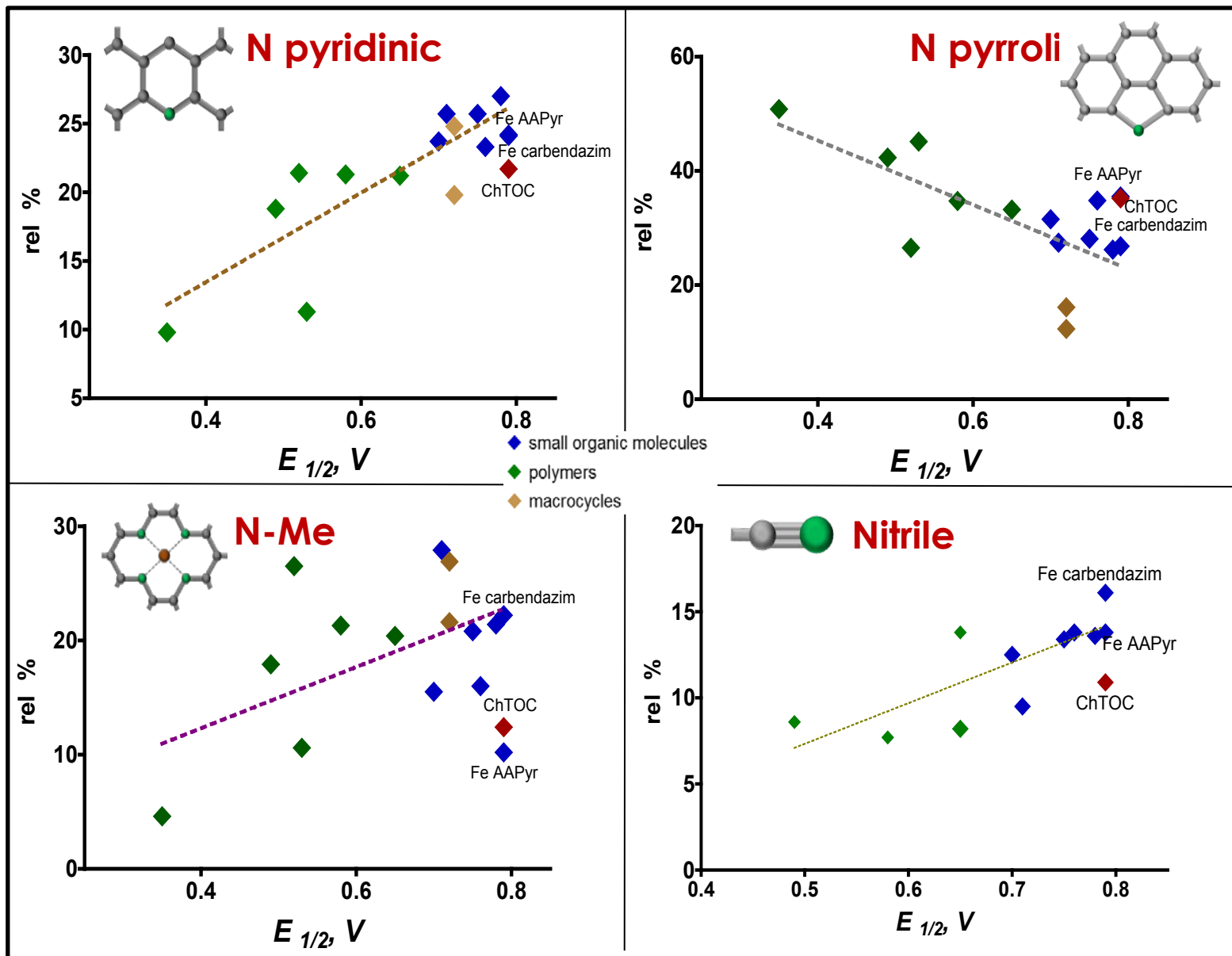
There is even more oxides and less Fe-N detected for ChTOC sample

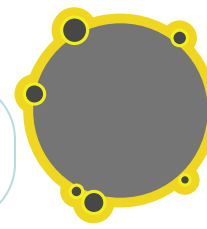




# Task 3. Mechanistic Studies and Spectroscopy

## - Correlation of activity and N-moieties in UNM catalysts





## Scale-up Development

- 5+gram per batch (240CC)
- SOP established
- High Pressure Pyrolysis
  - Quartz ampoule scale-up
    - Direct scale-up: **No go**
  - Knife-Edge/Metal gasket
    - Scalable, expensive seal
    - 700+ psi maintained: **Go**
  - Crushed gasket
    - Scalable, inexpensive seal
    - 700+ psi reached but not-maintained: **Go**

