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

2012 DOE Hydrogen and Fuel Cell Program Review

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May 15th, 2012

Project ID# FC086

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Overview Slide

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

- **Budget Data**: Total $ 6,38015
- $ 5,342,301 (Federal, including $400K to LANL)
- $ 1,437,714 (cost share)
- DOE FY11 funding $750,000, Planned FY12 funding $1050,000

- **Barriers**
  - Activity Targets for Non PGM catalysts: exceed 130 A/cm^3 (2010) and 300 A/cm^3 (2015).
  - Durability at temperatures ≤ 80°C, 2000 hrs (2010); 5000 hrs (2015)
- **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. Barton
  - *BASF Fuel Cells*, Somerset, NJ: Dr. E. DeCastro
  - *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 2015 targets for activity and durability. 2010 Activity targets for DOE are 130 A/cm^2 and 2015 activity targets are 300 A/cm^2.
- 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 (i.e., sulfur, CO etc.), Hence ability to tolerate H_2 with greater impurity.

Overall Approach

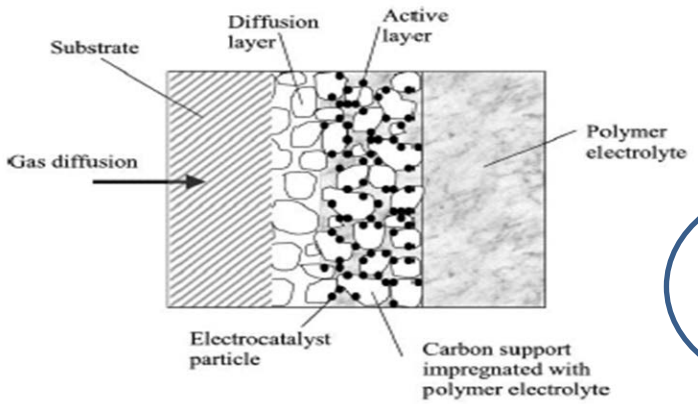
- **Overall technical approach:**
  - **Comprehensive materials development strategy encompassing:**
    - **Novel new reaction Centers for Oxygen Reduction**
      - High Performance Catalysts
      - Tailored Catalysts for Understanding Structure Property Relationships
    - **Controlling Metal support 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**
    - 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 ~ 150 A/cm^3 which is close to 2010 DOE target. 2015 target is 300 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 2015 DOE target.

Milestones and Go/No Go Decisions

- **Milestones (2012)**
  - Materials Development: Cross Laboratory RDE measurement of ORR activity FY12Q 1-4
  - Fuel Cell tests for Volumetric Activity: Meet ~ 150-200 A/cm^3 (iR free) at 0.8 V RHE (80°C or below) FY12Q 1-4
  - Meet Durability target based on DOE protocols using RRDE and single cells FY12Q 1-4
  - In situ measurements for degradation and electrocatalytic pathways for ORR FY12Q1-4
  - Initiation of scale up for select catalysts FY12Q 3-4
  - Connecting computational efforts with characterization results for mechanistic and transport measurements FY12Q 2-4
- **Go/No Go Decisions (2013)**
  - Materials Screening based on above mentioned benchmark (FY12Q2) and decision on materials choice for further development will be based on project's target of 150 A/cm^3 at 0.8 V (iR free), or 100 mA/cm^2 at 0.8 V iR Free.
  - Meeting DOE specified catalyst durability criterion.
  - Computation and Spectroscopic approach to determine oxygen reduction electrocatalysis from the perspective of active site and operating conditions (FY12Q 1-4).

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]

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

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

Electrocatalyst Scale up and MEA Fabrication (BASF)-**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**

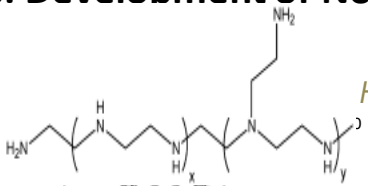
Automotive Test Protocols, Stack Testing and Durability Validation (NTCNA)
Thrust Area 5-Task 2.4

Task 1. **Design and Synthesis of Novel Materials for Oxygen Reduction Reaction (ORR)**

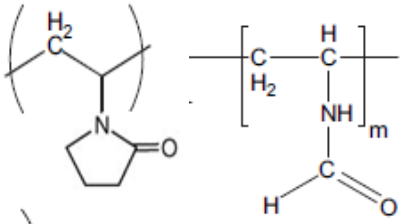
– **Advanced Performance Catalysts: Development of Novel MNC Catalysts (NEU)**

Polymer-Metal Composites

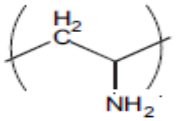
- Poly(ethyleneimine)-Metal networks (NEUPEI)



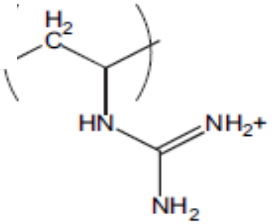
- Poly(N-vinylamides), and derivatives
  - Poly-N-vinyl pyrrolydone (NEU PVP)
  - Poly-N-vinyl formamide(NEU PVF)



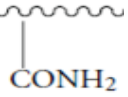
  - Poly-N-vinyl amine (PVA)



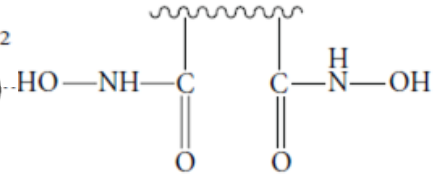
  - Poly-N-vinyl guanidine (PVAG & PVG)



- Poly(acrylamides), and derivatives
  - Polyacrylamide (PAA

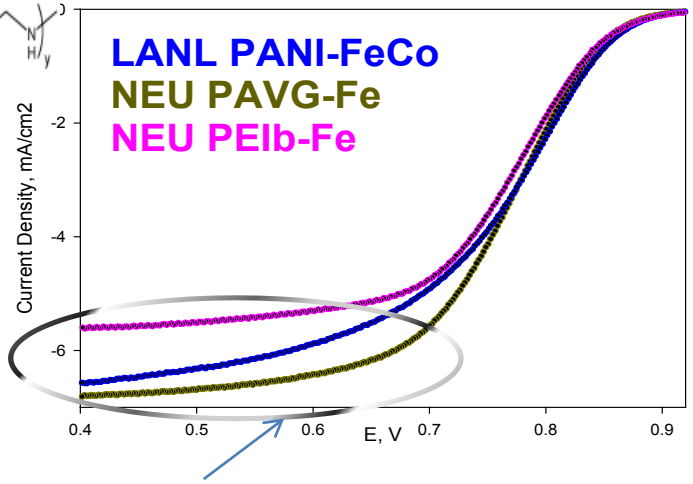


  - Polyhydroxamic acid/salt (PHA)



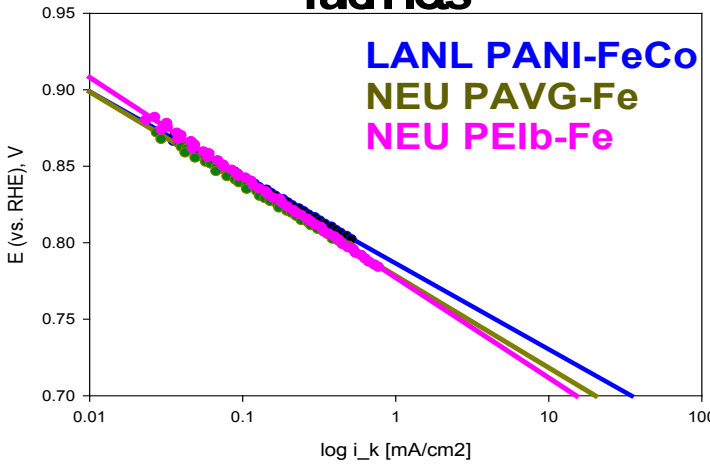
ORR Polarization Curves

HClO4, ref: RHE, 0.6mg/cm² on 0.247cm² GC, RT, 1600rpm



Variations in kinetic currents due to differences in active sites availability

Tafel Plots



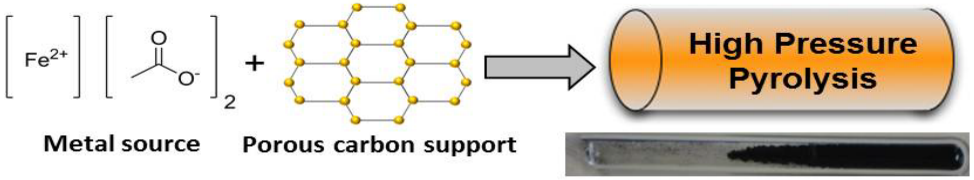
	I at 0.8[V] [mA/cm²]	$E_{½}$ [V]	Tafel Slops, [mV/dec]
LANL PANIFeCo	2.3	0.77	56
NEU PVAGFe	2.2	0.77	60
NEU PEIbFe	1.87	0.77	65

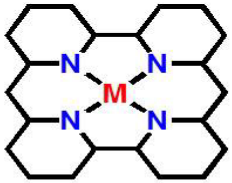
Technical Accomplishment continued….

Task 1. Design and Synthesis of Novel Materials for Oxygen Reduction Reaction (ORR)

– Advanced Performance Catalysts: Development of Novel MNC Catalysts (MSU)

Approach

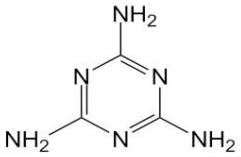




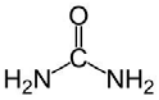
Metal-functionalized pyridinic carbon (Proposed catalytic site)

\+

N precursor

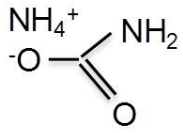


Melamine (N/C – 2.0)



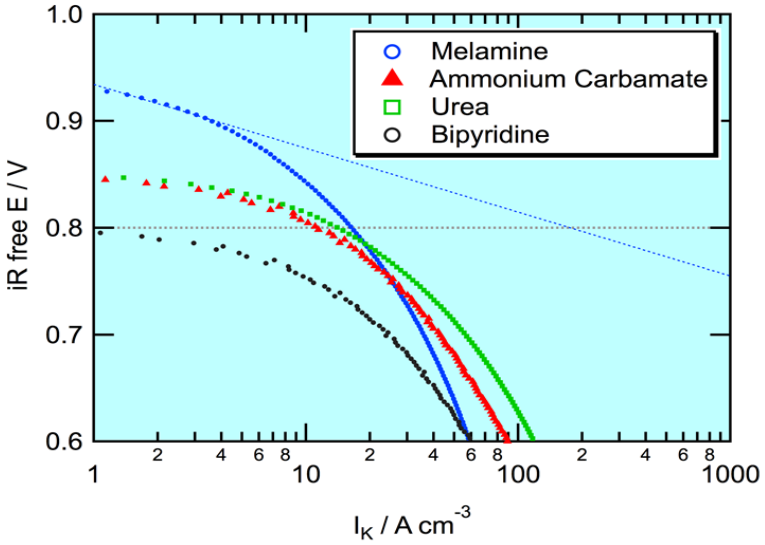
Urea

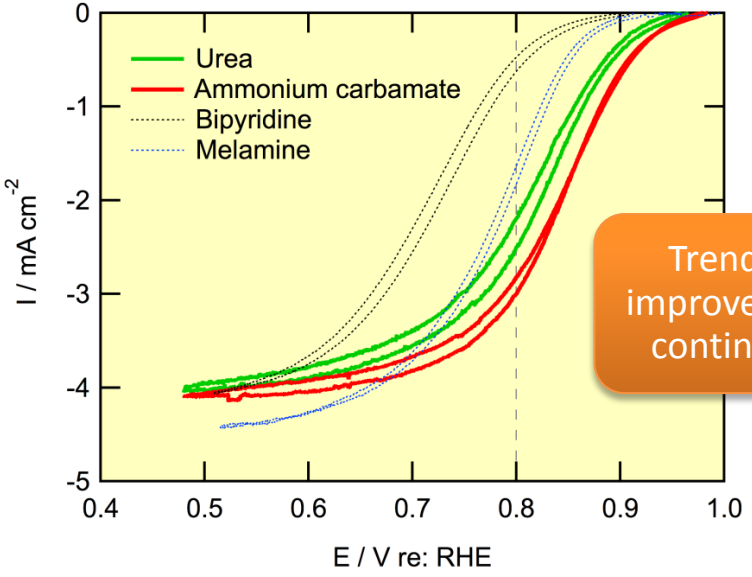
$NH_2CONH_2 \rightarrow NH_3+HCNO$
$HCNO+H_2O \rightarrow NH_3+CO_2$



Ammonium carbamate

$NH_4COONH_2 \rightarrow 2NH_3+CO_2$





Trend of improvement continues.

Nitrogen Precursor	Volumetric Activity (A/cm³ @ 0.8 V)	
	Observed	Extrapolated
Bipyrindine	—	—
Melamine	16	**176 ± 39**
Urea	14	131 ± 45
Ammonium Carbamate	11	132 ± 25

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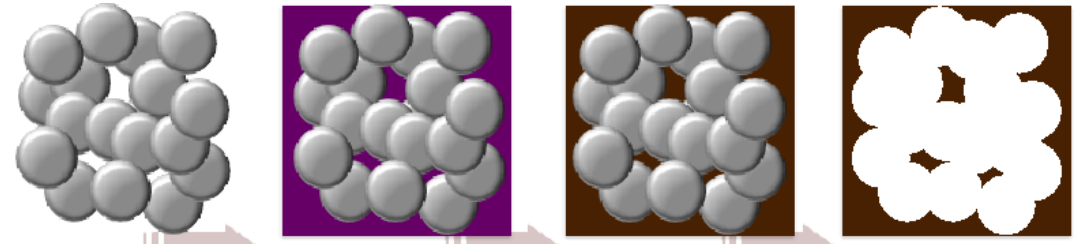
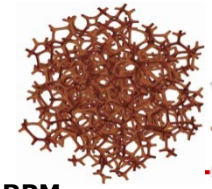
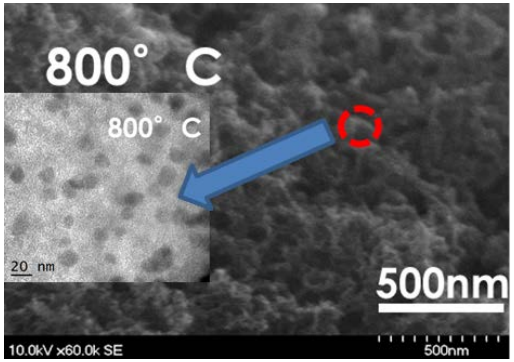
Task 1. Design and Synthesis of Novel Materials for Oxygen Reduction Reaction (ORR)

- Advanced Performance Catalysts: Development of Novel Open Framework Templated Structures (UNM)



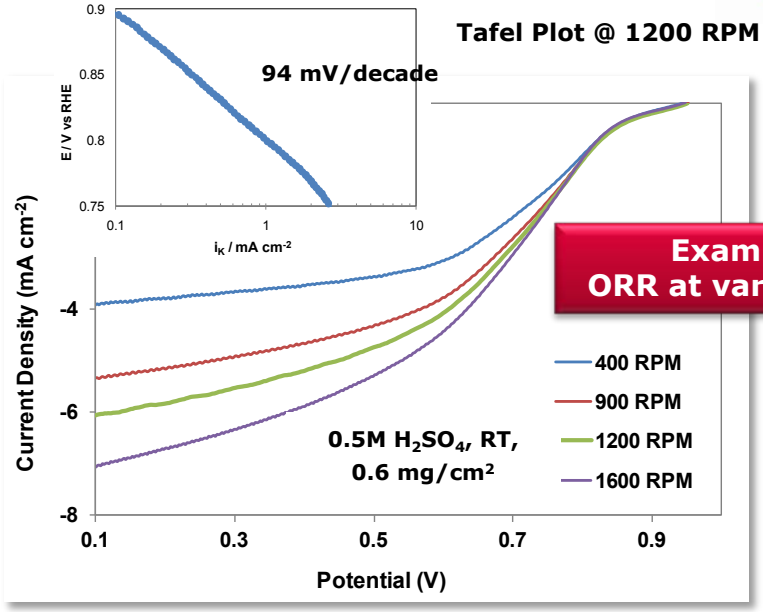


Templated -supported Non-PGM Catalyst



UNM Fe-8AAPyr Catalyst – ORR study using RDE and RRDE

Tafel Plot @ 1200 RPM



Example: ORR at various RPM

- **UNM catalyst Fe-8AAPyr demonstrated high onset potentials and current densities at 0.8V**

Example data at 1200 RPM

Onset Potential, mV	Current density at 0.8 V, mA/cm²	Tafel Slope, mV/decade
950	1.87	94

Zero Emission

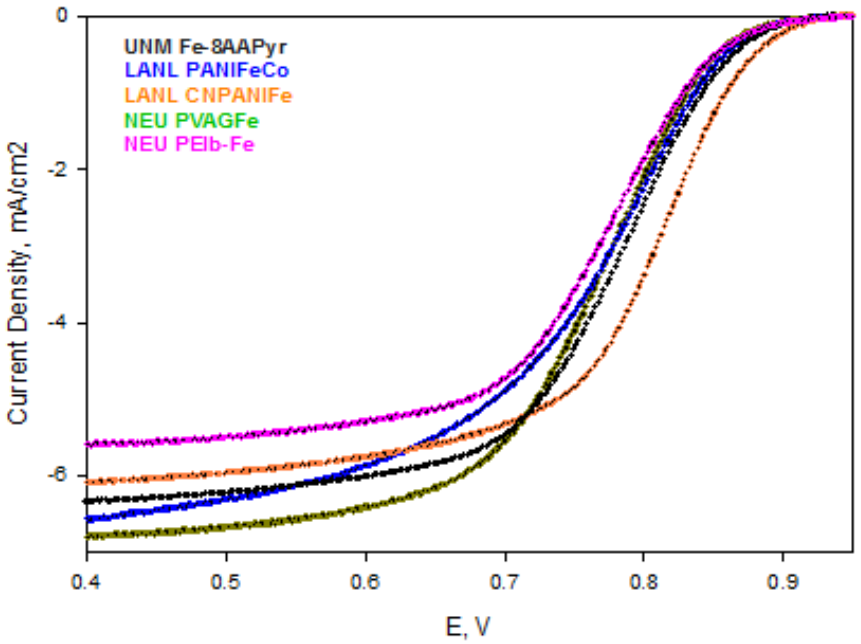
Technical Accomplishment continued….

Task 1. **Design & Synthesis of Novel Materials for Oxygen Reduction Reaction (ORR)**

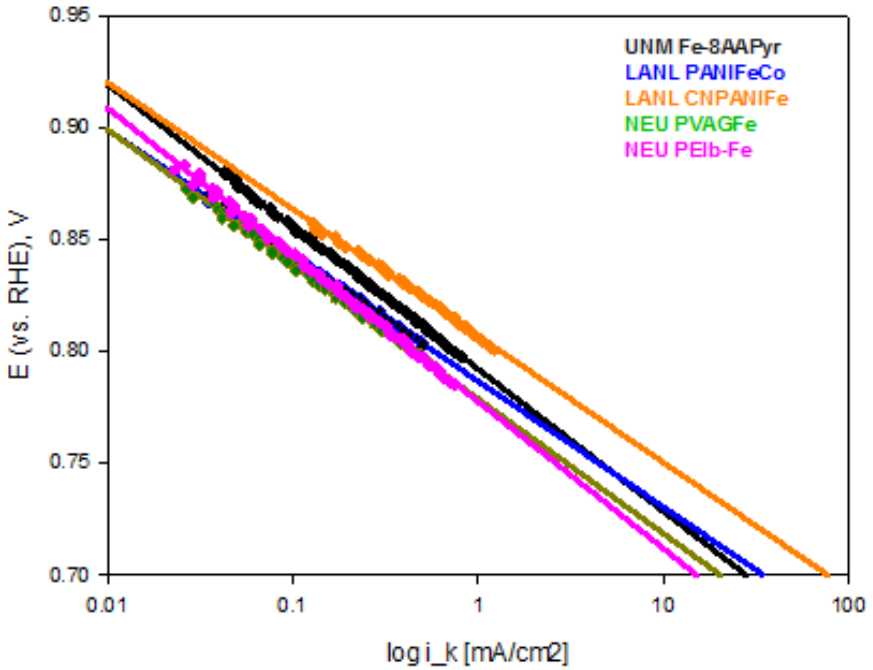
Cross Laboratory Performance Comparison

0.1M HClO4, Ref. RHE, 0.6mg/cm² on 0.247cm² GC, RT, 1600rpm

ORR Polarization Curves



Tafel Slopes



	I at 0.8[V] [mA/cm²]	E ½ [V]	Tafel Slopes, [mV/dec]
UNM Fe-AAPyr	2.5	0.78	63
LANL PANIFeCo	2.3	0.77	56
LANL 2	3.4	0.80	56
NEU PVAGFe	2.2	0.77	60
NEU PEIbFe	1.87	0.77	65

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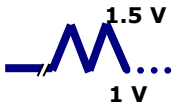
Task 2. Testing and Durability Measurements (MSU/NTCNA)

MSU-Melamine based non-PGM catalyst-Post durability performance recovery

- **Tests were done to recover the performance of MSU's melamine based MNC catalyst post-durability tests**
  - **In-situ test results for the same have been shared during DOE AMR 2011 and ECS 220th***

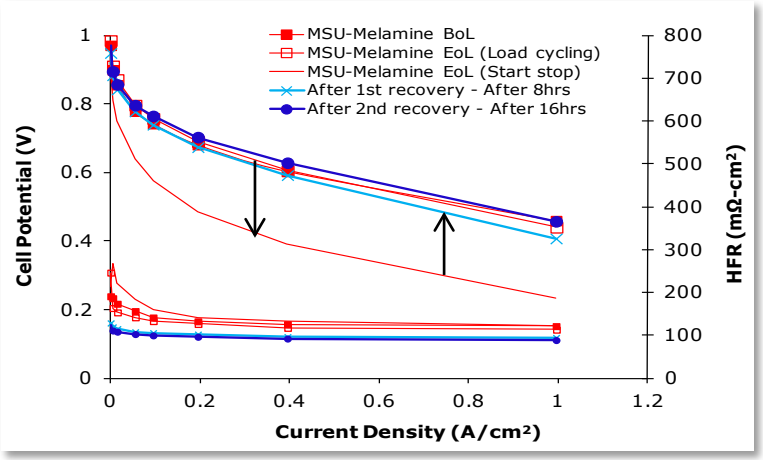
✓ **During the End of Life (EoL) iV performance check (after Start-Stop test), an increase in OCV values was observed**

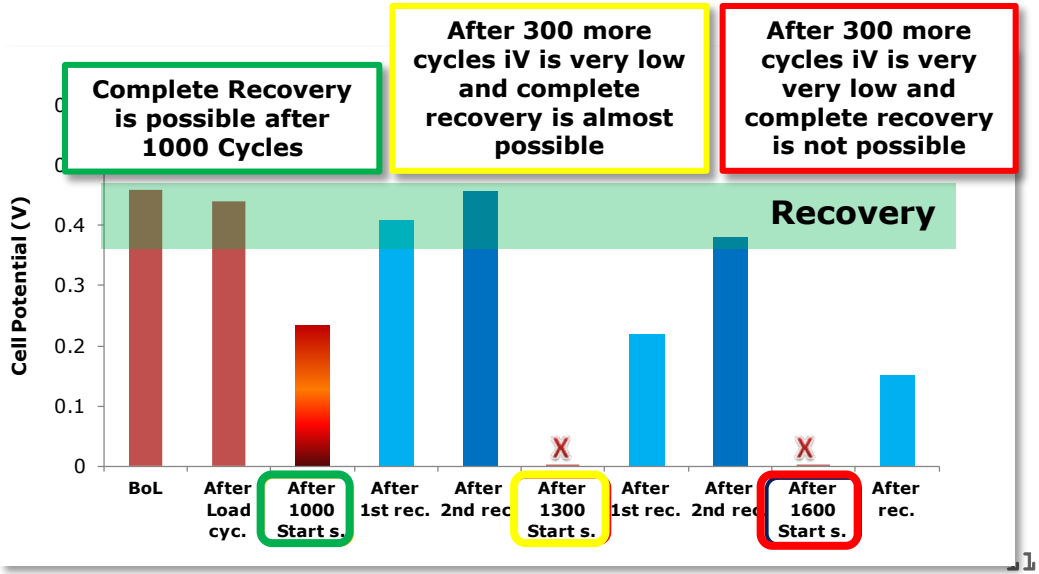
Nissan Start-stop Protocol (1000 cycles std)



✓ **Additional experiments (Post Mortem Conditioning) were performed to further investigate this phenomena and to explore an effect of surface oxide removal on partial performance recovery**

✓ **Complete recovery was observed after 1000 & 1300 cycles however after 1600 total cycling, MSU catalyst may reach the "not recoverable point" this is the point where there might not be enough active carbon left in order to be an effective ORR catalyst**





Zero Emission

* ECS Transactions, 41(1), p2289 (2011)

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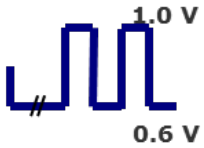
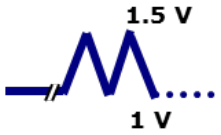
Task 2. Testing and Durability Measurements (UNM/NTCNA)

UNM Fe-8AAPyr Catalyst –RDE Durability (Durability Protocol Evaluation)

- The stability of the catalyst was evaluated under Nissan load cycling and start-stop cycling protocols and DOE Durability Working Group's (DDWG) suggested accelerated stress protocol. The volumetric activity, i_V (A/cm^3), was calculated as the index to present the activity loss of the catalyst in cycles.



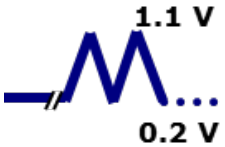
Load cycling



Start-stop cycling

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

- **DOE Durability Work** Group suggested Protocol evaluates catalyst durability mechanistically for catalyst morphology



Condition	Nissan Load cycling	Nissan Start-stop cycling	DDWG
Temperature (°C)	60	60	25
Gas condition	N2	N_2	O_2
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_2SO_4		
Catalyst loading (mg/cm^2)	0.6		
No of cycles	5000		

Zero Emission

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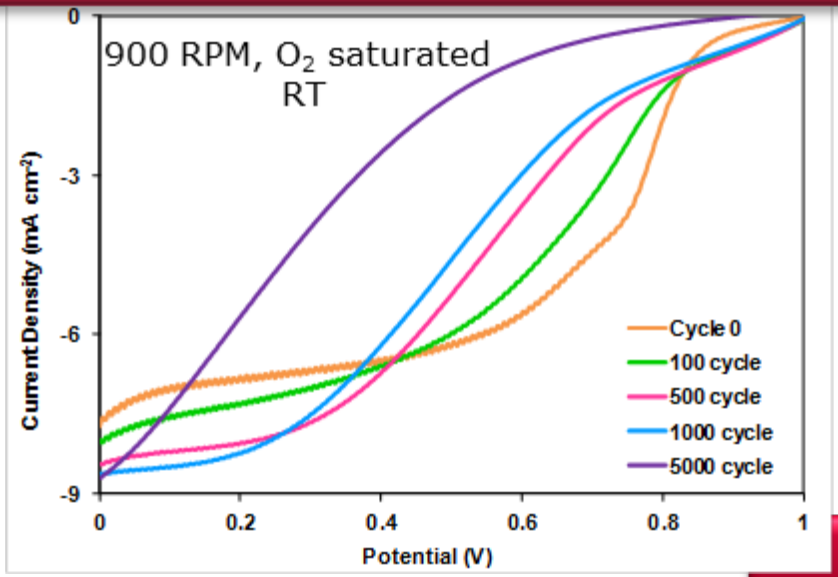
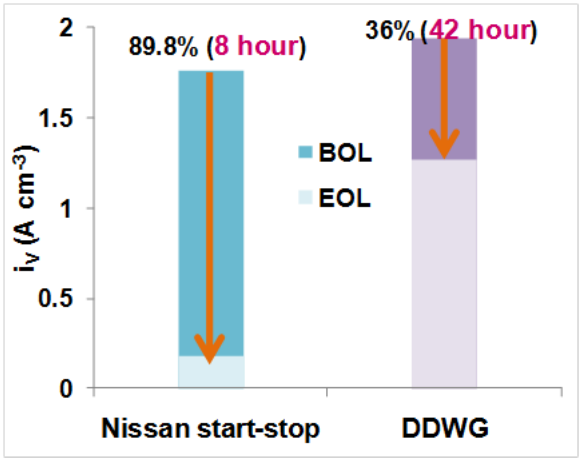
Task 2. Testing and Durability Measurements (UNM/NTCNA)

UNM Fe-8AAPyr Catalyst –RDE Durability (Durability Protocol Evaluation)

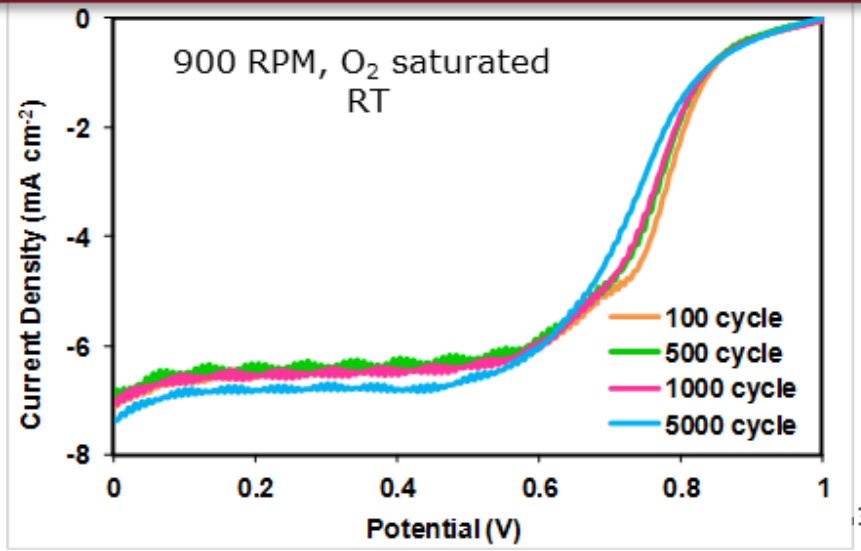
Effect of Nissan start-stop Protocol on iV



- non-PGM catalysts tested thus far at Nissan exhibit very good durability under Nissan's load cycling protocol [0.6, 1.0] i.e. no-effect (not shown)
- Nissan start-stop cycling protocol is very effective for the evaluation of non-PGM catalyst durability; especially for more practical stack applications i.e. major effect in 8 hours



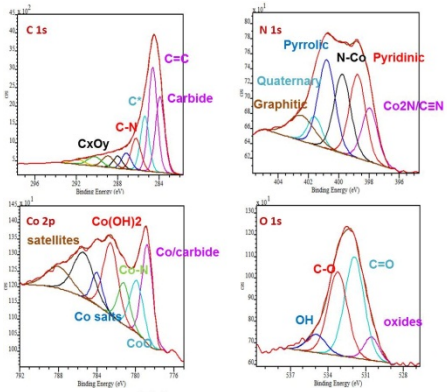
Effect of DDWG Protocol on iV



Zero Emission

Technical Accomplishment continued….

Task 3. Mechanistic Studies and Spectroscopy



Participating Institutions:

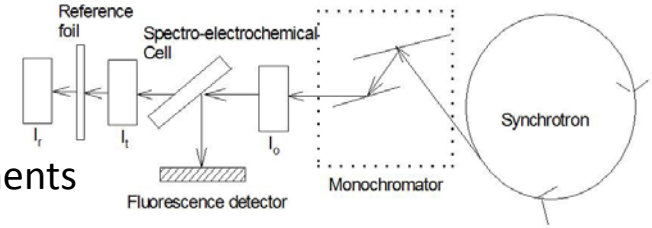
UNM- Ex situ Studies with XPS and PCA analysis

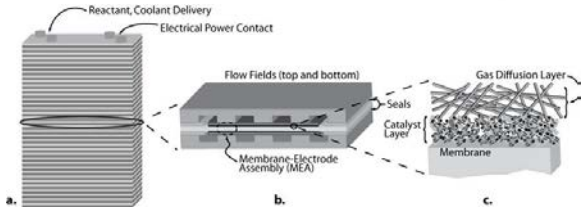
NEU- In situ Spectroscopy with Synchrotron and Raman Measurements

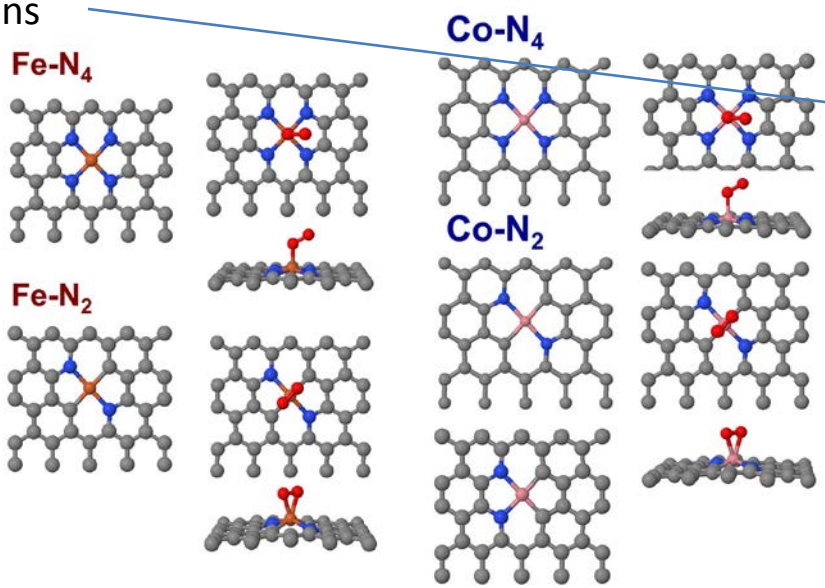
SMU- Macroscopic Modeling

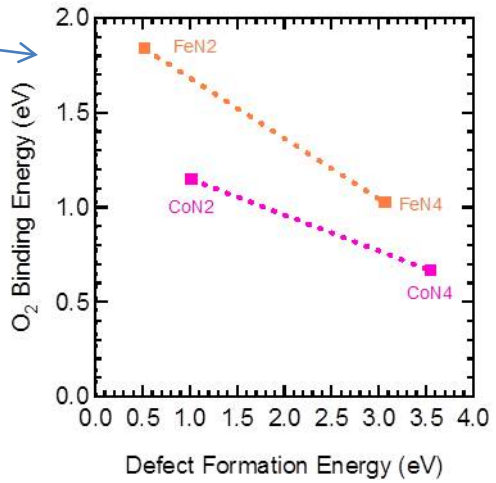
UTK- Molecular Level Computation (Ab-Initio and DFT)

UNM- DFT Calculations







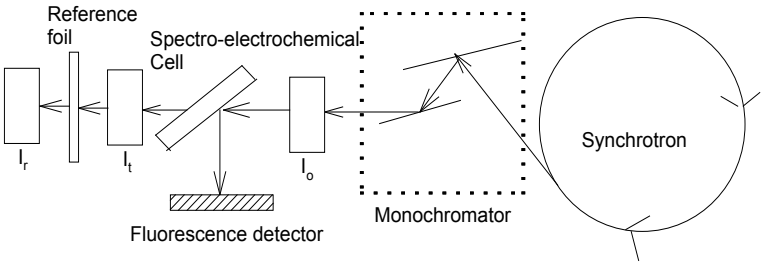


Task 3. Mechanistic Studies and Spectroscopy

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

Synchrotron Advantages

- ***High Intensity***
- ***Broad Spectral Range***
- ***High Polarization***
- ***Flux > 10^{10} photons/s***
- ***Natural Collimation***



EXAFS, single backscatter

Physical Basis

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

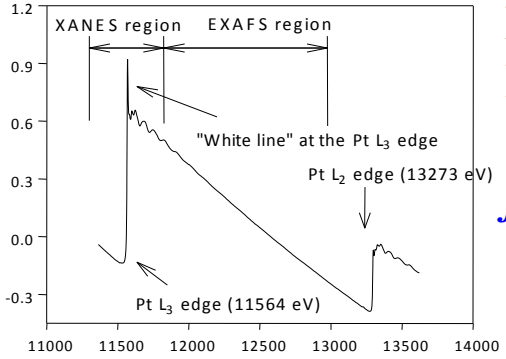
$$E_{photoelectron} = E_{xray} - E_0$$

XANES, multiple scattering

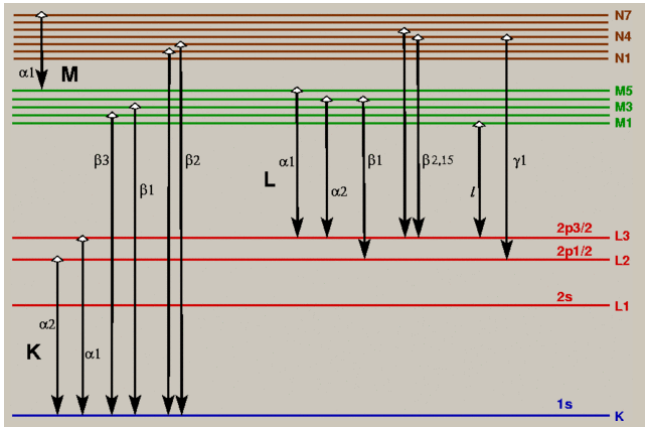
Physical Basis

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

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



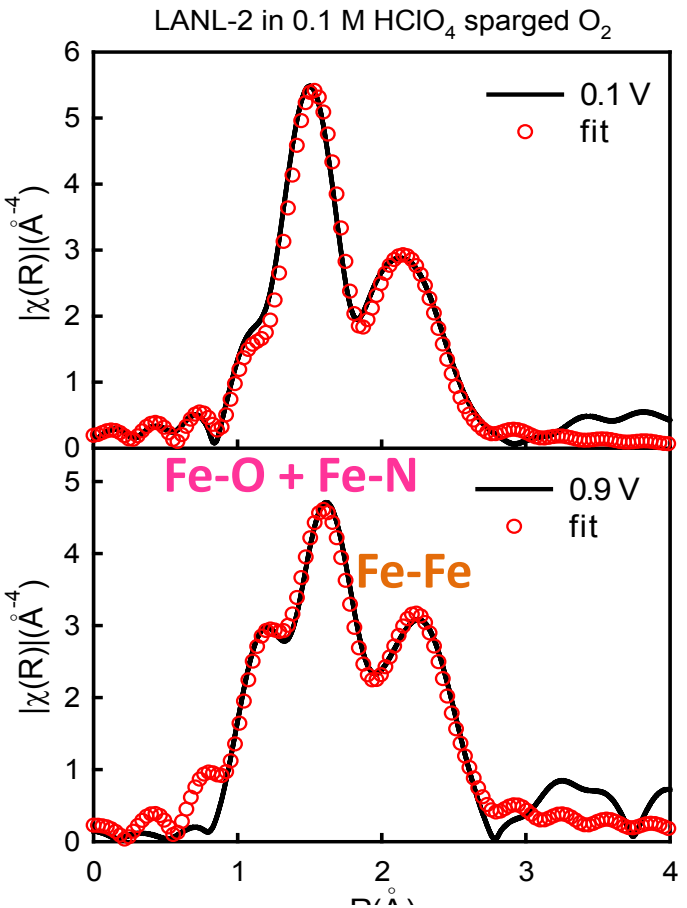
N – Coordination Number
R – Interatomic Distance (Å)
σ^2 – MSRD (Debye-Waller)
***f*(k)** – Amplitude
δ(k) – Phase

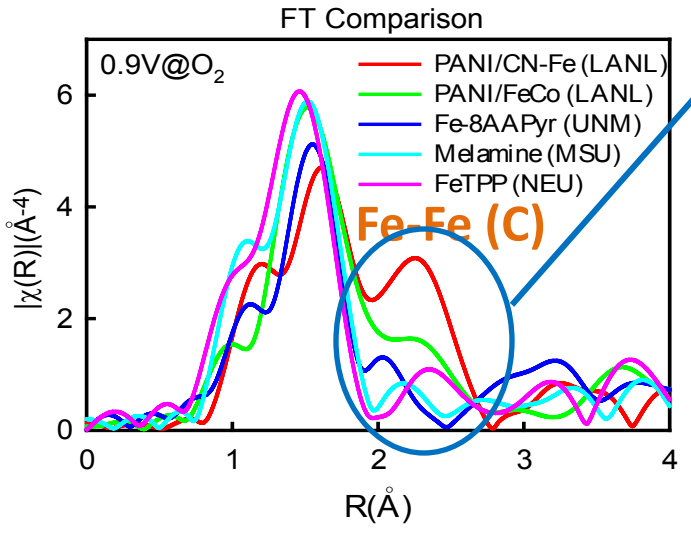


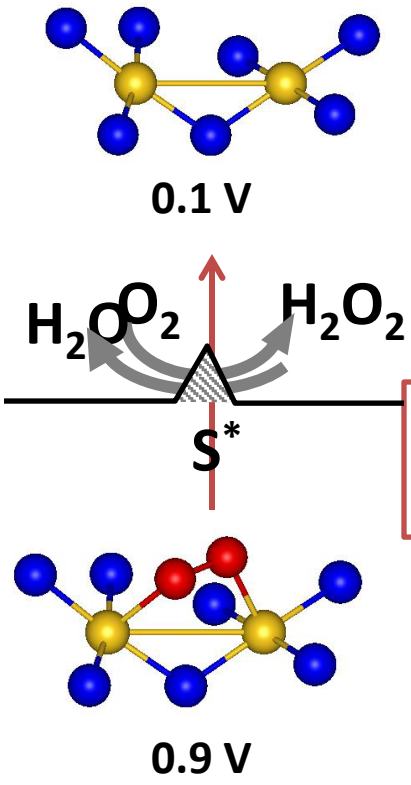
$$E_{xray} = \frac{hc}{\lambda}$$

Detection:

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







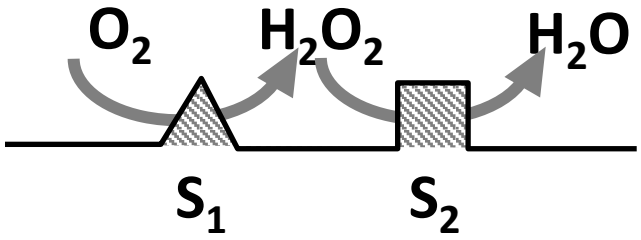
Under O_2		FeN	FeFe	FeO
CN	0.1V	4.1±0.4	1.4±0.3	0
	0.9V	4.5±1.0	1.2±0.3	1.3±0.4
R (Å)		2.01±0.01	2.54±0.01	1.84±0.02

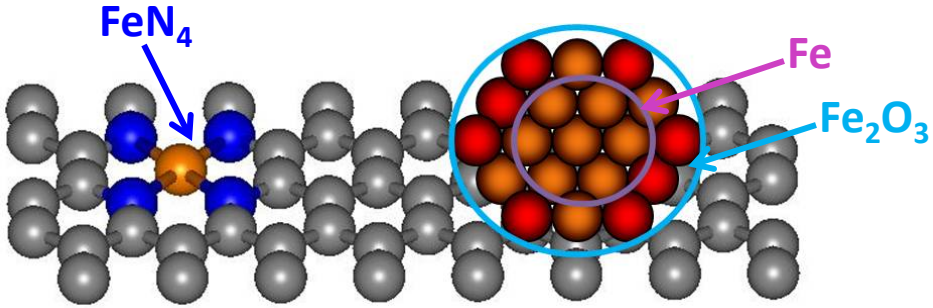
This distance suggests the formation of the bridged structure, which favors the release of H_2O_2 and the 4-electron reduction pathway.*

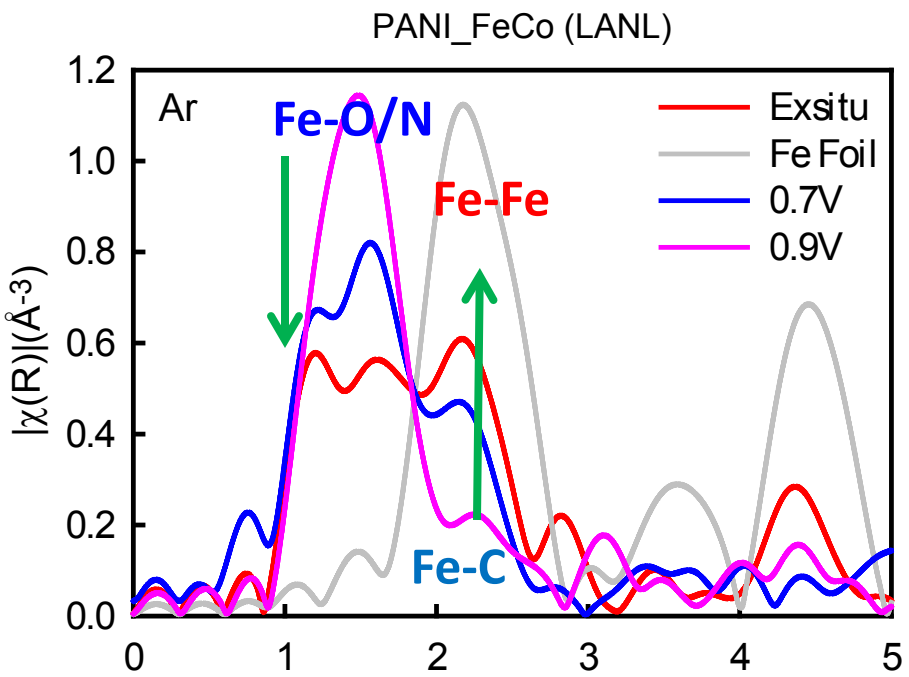
*Jungwon Hwang, et al., Science 287, 122 (2000)

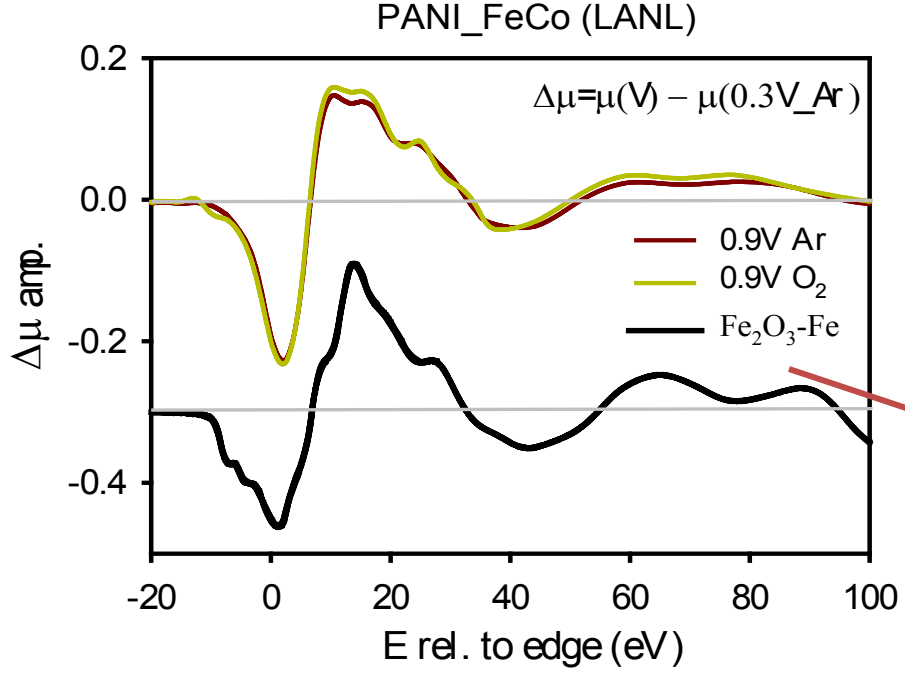
Lack of the Fe-Fe bond at 0.9 V of other samples suggest the bifunctional mechanism.

Dual site consequential: 2 x 2e- bifunctional Mech



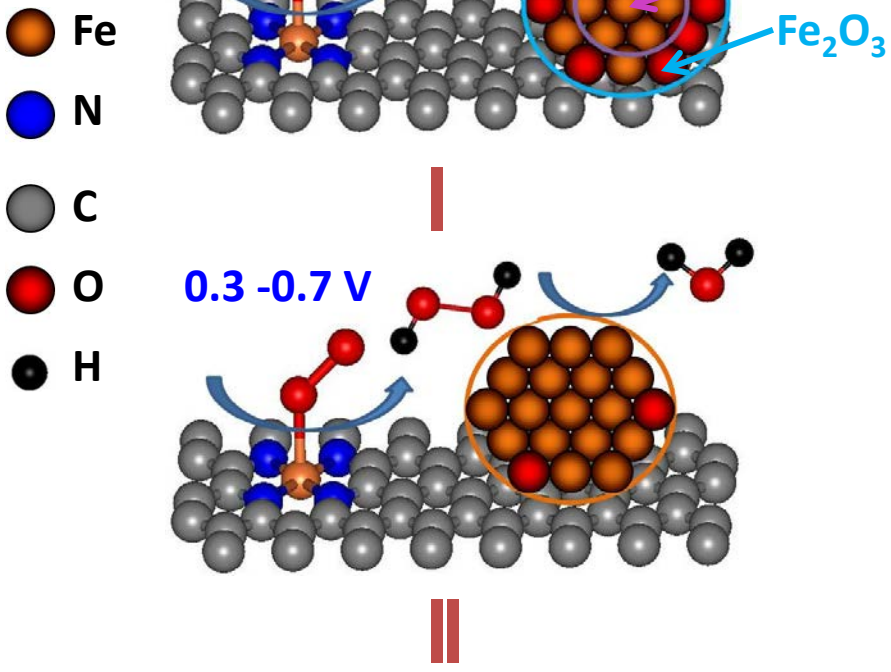






Proposed mechanism

Dual site consequential:
2 x 2e- bifunctional mechanism

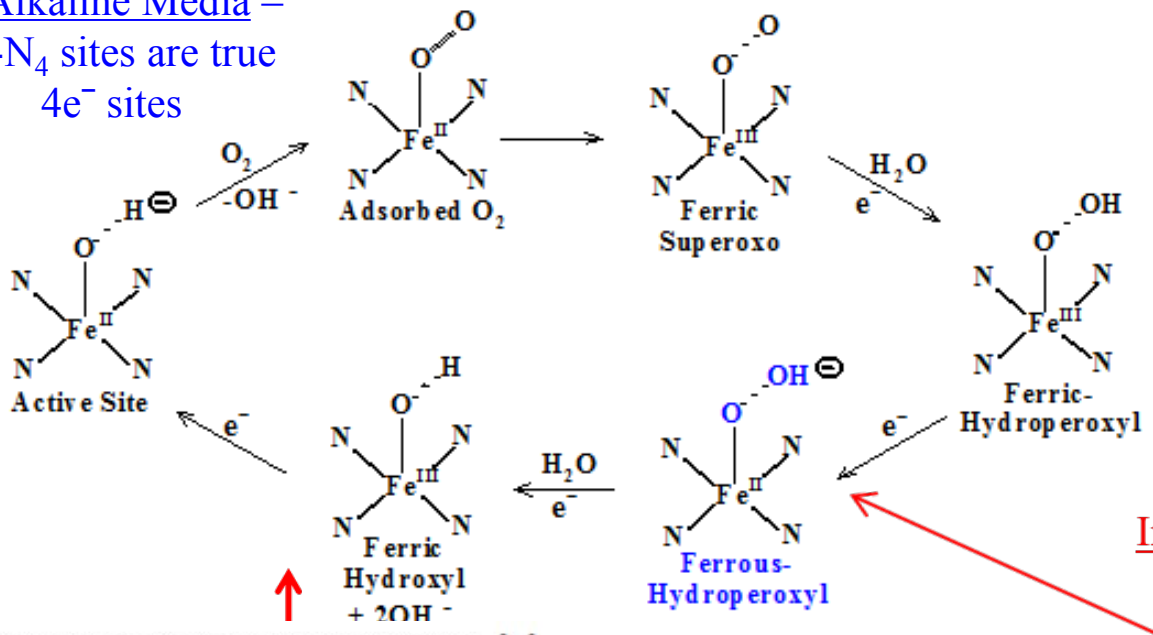


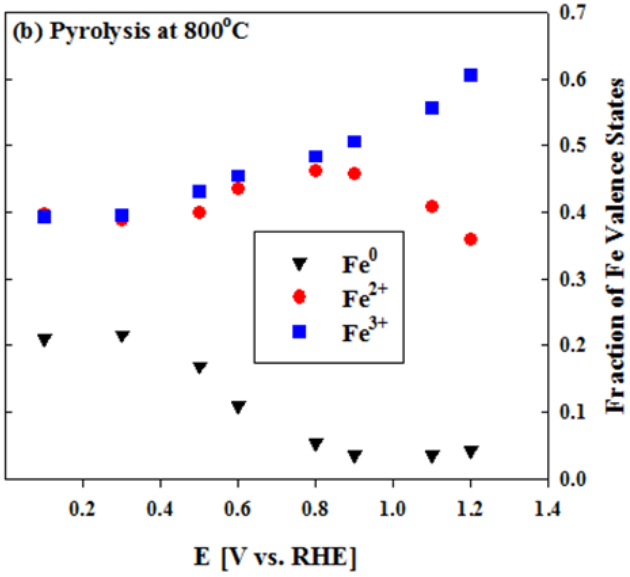
$$\Delta\mu = \mu(0.9\,V) - \mu(0.3\,V)$$
$$= (FeN_4 + Fe_2O_3) - (FeN_4 + Fe)$$
$$= Fe_2O_3 - Fe$$

Oxygen Reduction Mechanism on Fe-N_4 Sites

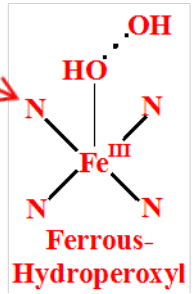
Task 3-2. Mechanistic Studies and Spectroscopy

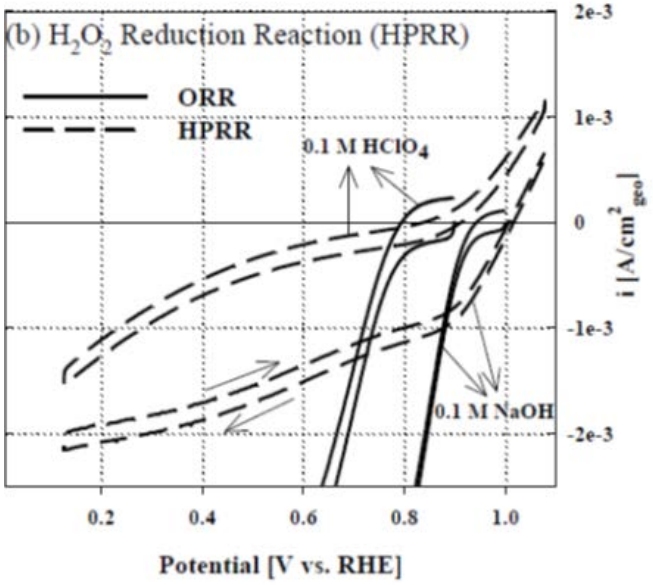
In Alkaline Media – Fe-N_4 sites are true $4e^-$ sites





In Acidic Media





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

Fe-N_4 sites predominantly yield peroxide in acidic media

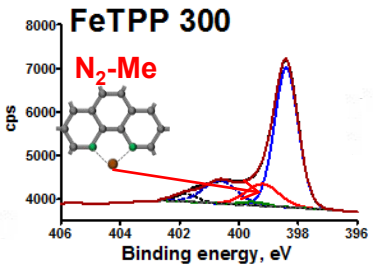
THE UNIVERSITY of NEW MEXICO

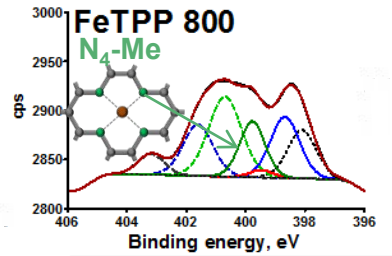
Task 3-2. Mechanistic Studies and Spectroscopy: N speciation from XPS

DFT calculations of N 1s BEs

N pyrrolic reference	Me-N_4	Me-N_2
398.2	+1.1 eV	0.8 eV

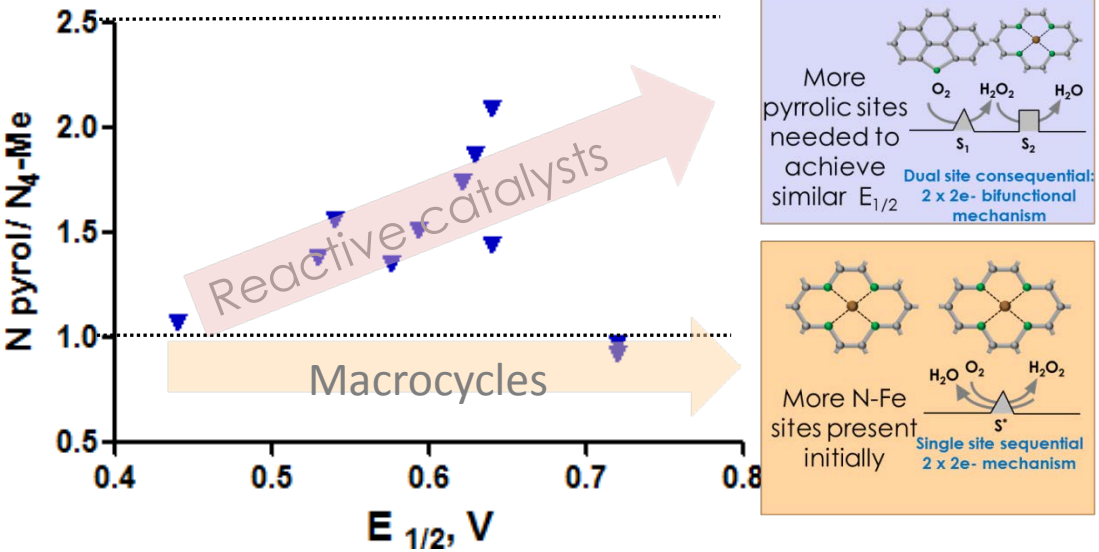
N 1s spectra

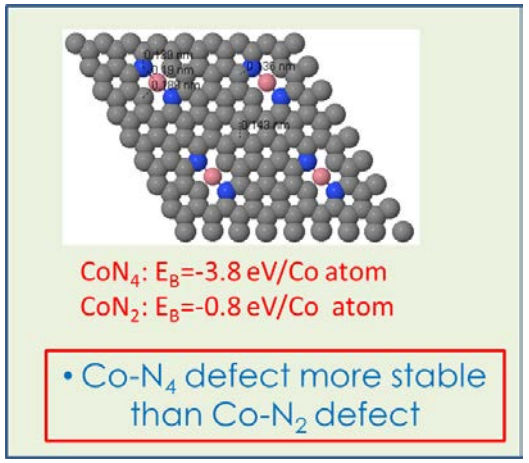




Me-N_4/ Me-N_2

	300°C	800°C
FeTTP	*0.1*	*4.4*
PVP Fe	*0.9*	*4.4*
PEI Fe	*1.1*	*4.5*





-Fe-N_4 are dominant at higher temperatures of pyrolysis
- Two competing 2x2e- mechanism are confirmed
- Macrocycles behave differently from reactive samples

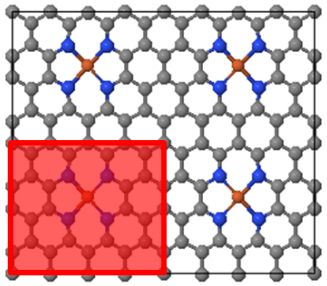
Task 3-3: Computational Studies: DFT studies using extended surfaces

Universal:

Applies to any (co-existing) phases:
solid, liquid and gaseous.
Applies to 0-, 1-, 2-, and 3-d materials.
Applies to heterogeneous bond environments:
Ionic, covalent and metallic bonding.
Applies to complex materials.

- ***Predictive:***
  Independent of experiment.
  Synergy with experiment.

Model system:
- Carbon support.
- Periodic structure.
- High defect density.

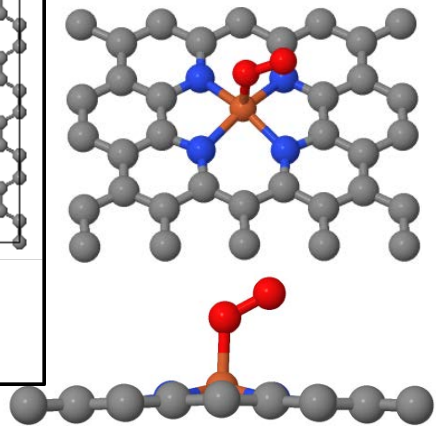


Simulated region.
+ 2-d periodicity
=extended surface.

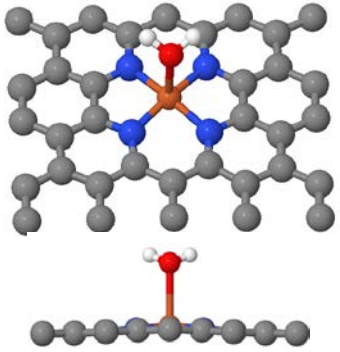
O_2 and H_2O on Fe-N_4

Extended Surfaces

O_2



H_2O



White=H
Grey=C
Blue=N
Red=O
Pink=Co
Brown=Fe

- **Strong interaction with O_2.**
- **Weak interaction with H_2O.**

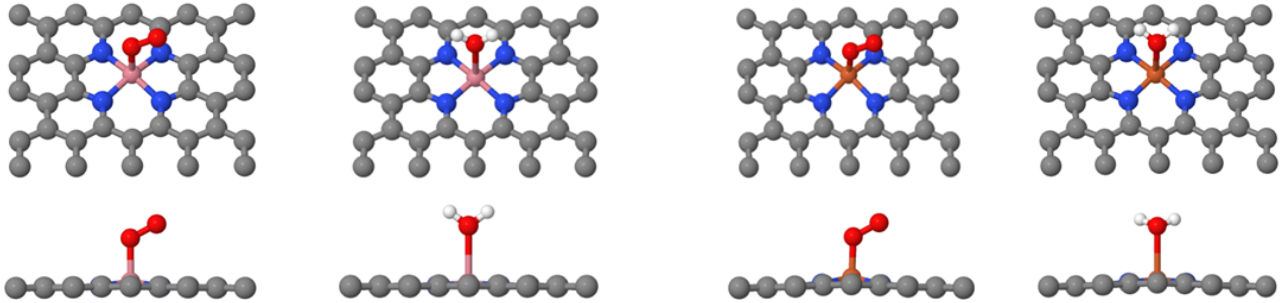
Binding energy (BE) in eV.

Defect	O_2	H_2O
Fe-N_4	-0.97	-0.18

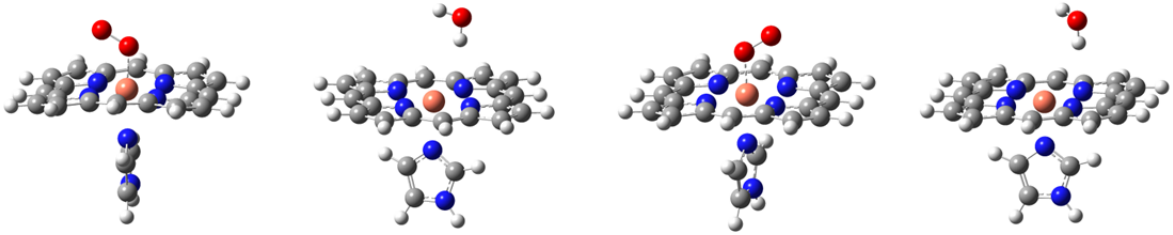
Task 3-3. Computational Studies: Comparison of cluster and extended system DFT approaches

O_2 and H_2O Interactions with M-N_4 (M = Co and Fe)

Extended Surface



Cluster Approach



O_2/Co(II)-N_4 H_2O/Co(II)-N_4 O_2/Fe(II)-N_4 H_2O/Fe(II)-N_4

White=H
Grey=C
Blue=N
Red=O
Brown=M

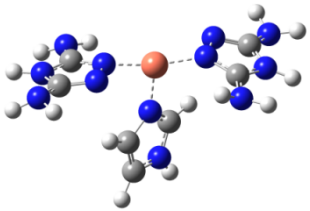
	BE (eV)	Co-N_4	Fe-N_4
Ext.	O_2	-0.67	-0.97
Ext.	H_2O	+0.1	-0.18
Cl.	O_2	-0.96	-1.13
Cl.	H_2O	-0.08	-0.18
Ext. extended surface; Cl. cluster approach			

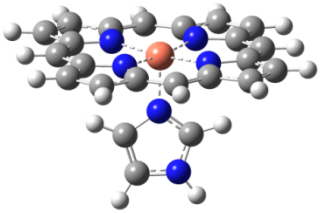
➔ **Results are consistent**

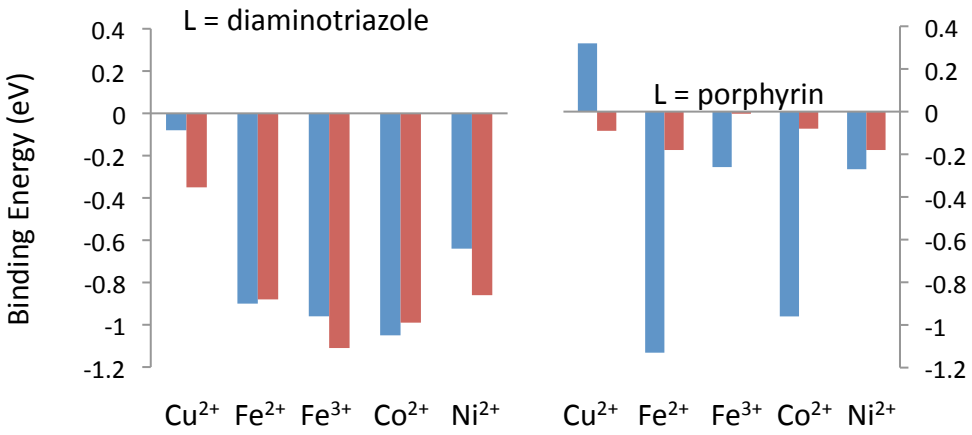
Technical Accomplishment continued…

Task 3-3: Computational Studies: Calculation of O_2 and H_2O Binding to complexed TM Sites

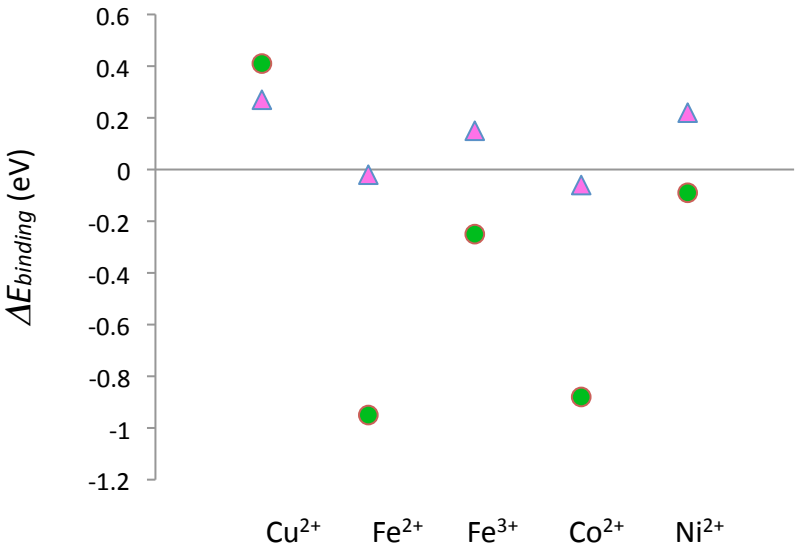
Catalysts under investigation consist of M where M = Cu^{2+}, Fe^{2+}, Fe^{3+}, Ni^{2+}, and Co^{2+}; and L where L = diaminotriazole (M-N_2) or porphyrin (M-N_4). Support is simulated by an imidazole molecule.







Blue: O_2 Red: H_2O



▲ = diaminotriazole ● = porphyrin

$$\Delta E_{binding} = E_{O_2} - E_{H_2O}$$

Density Functional Theory (DFT) calculations based on Becke-Perdew exchange-correlation functional and standard triple-ζ basis sets for all atoms, using the Amsterdam Density Functional (ADF) program.

Scientific Computing & Modelling

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)
- Nissan Technical Center North America: Dr. K. Adjemian (Industry, subcontractor)
- Los Alamos National Lab: Dr. P. Zelenay (Federal Lab., subcontractor)

Other collaborators:

(1) Jean Paul Dodelet: CNRS, Canada (Non funded collaborator)

Proposed Future Work (2012-13, Budget Period 1)

- Final Selection of materials using RRDE & single cell polarization measurements (FY12Q1-Q2).
- Focus on improved mass transport in gas diffusion medium. Novel approaches to electrode preparation, additives for improved oxygen solubility and fabrication of MEAs (FY12Q2-Q4)
- Modeling of mass transport in electrode layers to be in sync with design of electrode structures (layer by layer approach) (FY12Q3-Q4)
- Elucidation of electrocatalytic pathways using spectroscopy and computation leading to first mechanistic interpretation (FY12Q1-4).

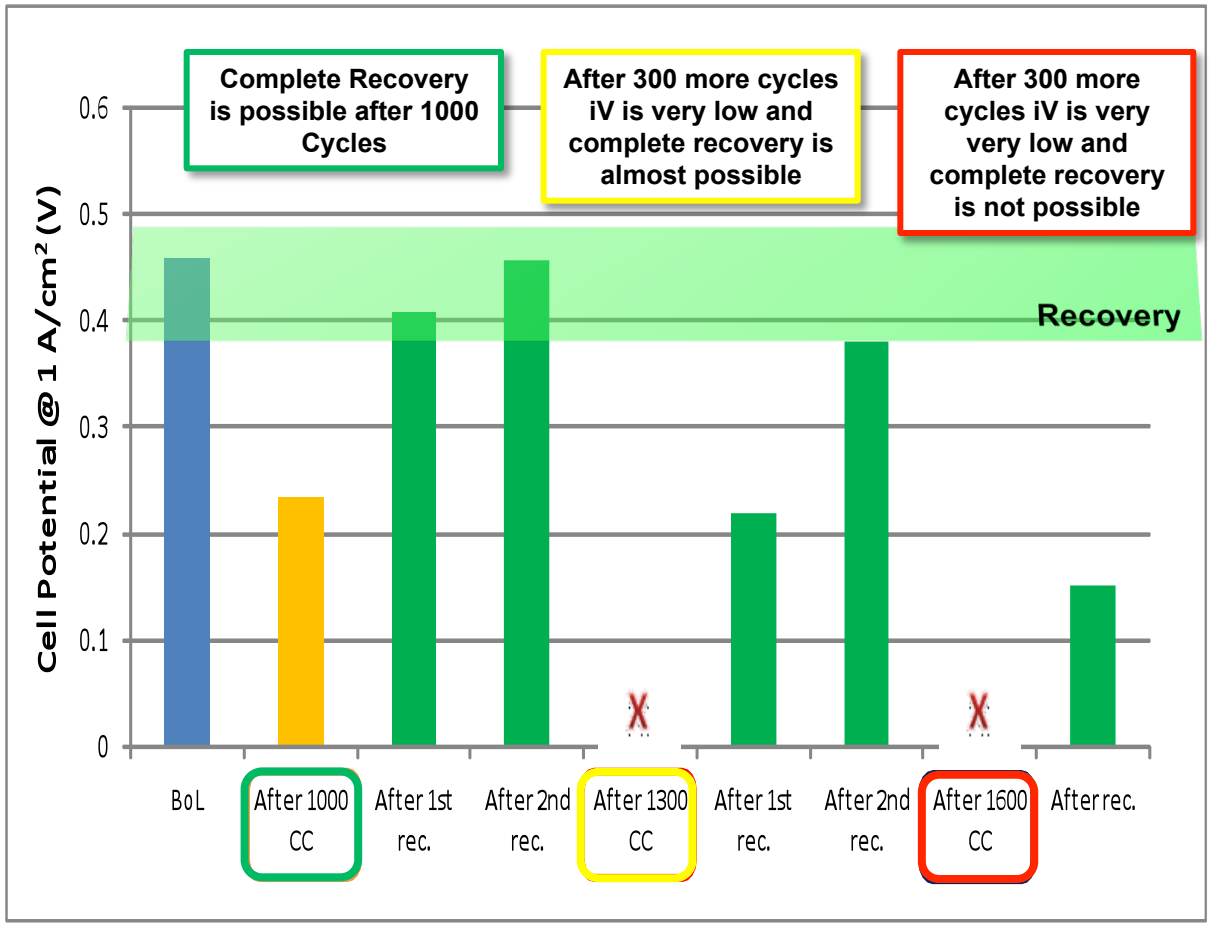
Summary Slide

- Task 1.1 Design of Materials as High Performance Catalysts: These have lead to several candidates meeting current DOE target of 150-200 A/cm^3 (iR free) at 0.8 V vs. RHE. This is 70 % complete considering DOE target of 300 A/cm^3 .
- 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 70 % complete, needing further confirmation and validation.
- Task 1.3 Catalyst Scale up initiated with BASF, 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^2 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.
- Task2.2 Good catalyst durability has been reported. However pushing the limits of carbon stability causes severe activity decline. Some of these are however recoverable. This task is 50% 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 60 % complete.

Technical Back-Up Slides

1. MSU Melamine MNC Catalyst - Recovery

Effects on iV: Additional Cycle/Recovery



Post Mortem Conditioning

1000 Carbon corrosion cycling

↓

Recovery Conditioning

H_2/O_2, 100%, 0.5 nlpm, 10 A, 16 hrs,

↓

+300 Carbon corrosion cycling

↓

Recovery Conditioning

H_2/O_2, 100%, 0.5 nlpm, 10A, 16 hrs,

↓

+300 Carbon corrosion cycling

↓

Recovery Conditioning

H_2/O_2, 100%, 0.5 nlpm, 10A, 20 hrs,

Zero Emission

1. MSU Melamine MNC Catalyst - Recovery

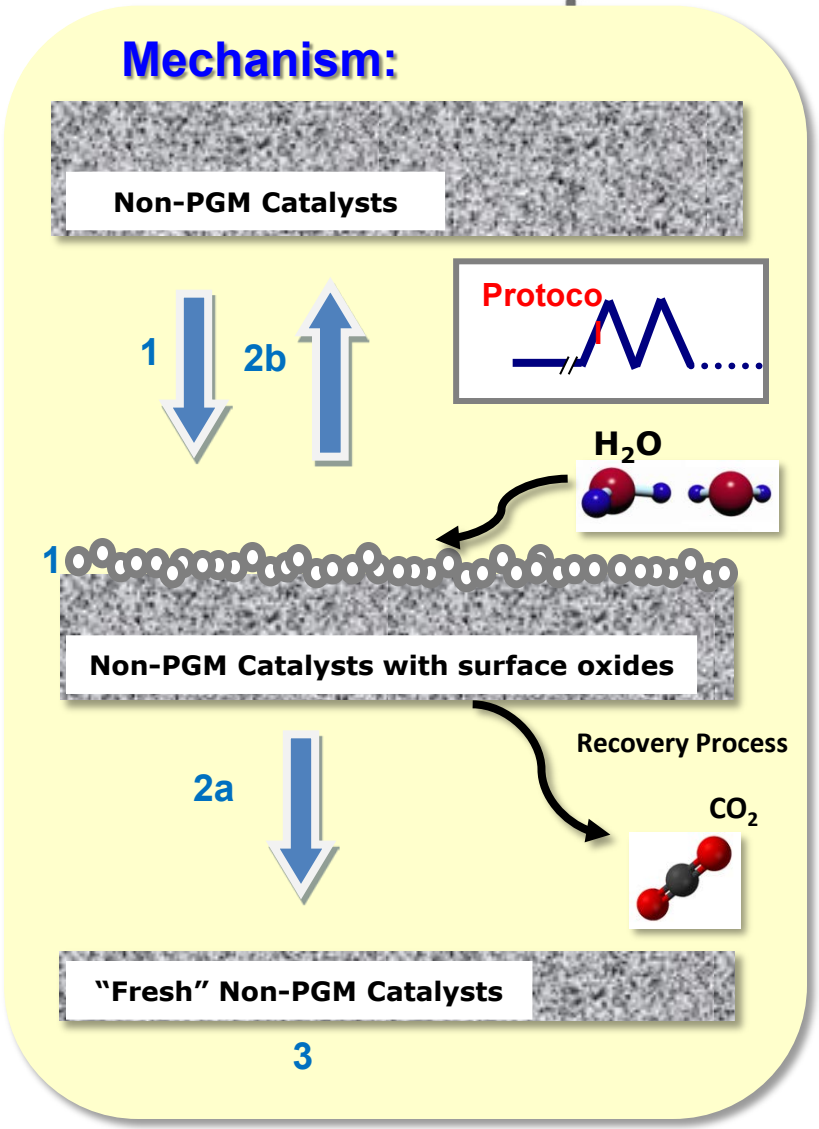
Proposed Mechanism*

1.) During carbon corrosion cycling, surface oxides are formed.

2.) During the recovery process, it is assumed that the created surface oxides on the catalyst surface are removed.
The mechanism for surface oxide removal is some combination of the a) complete oxidization of the surface oxide to CO_2 and / or b) their reduction back to the original catalyst structure or possibly some modified version of it.

3.) After 1600 total cycling, MSU catalyst may reach the "not recoverable point". This is the point where there might not be enough active carbon left in order to be an effective ORR catalyst

❖ Additional work required to verify CO_2 generation during recovery conditioning & reproduction of phenomena



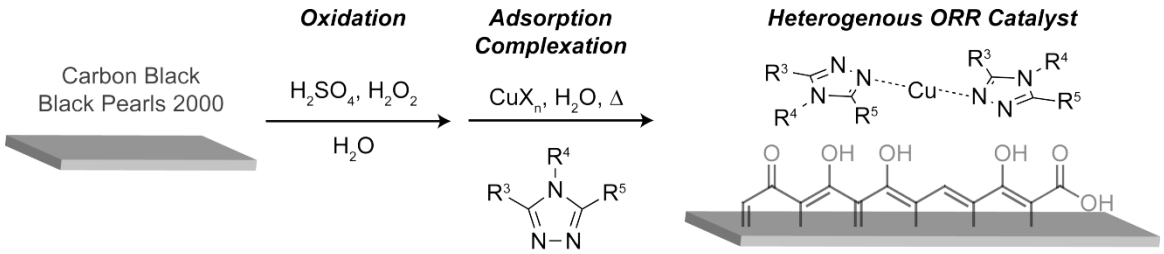
Zero Emission

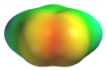
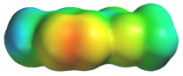
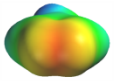
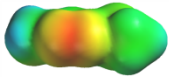
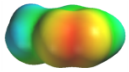
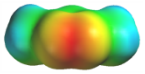
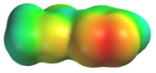
* ECS Transactions, 41(1), p2289 (2011)

Task 1. **Design and Synthesis of Novel Materials for Oxygen Reduction Reaction (ORR)**

Designed Structures for Probing Structure Property Relationships (UTK):

- Rationale: understand how we can 'tune' N properties for better catalysis
- Experimental Approach (initial): Study a series of substituted triazoles with different substituents to tune nitrogen basicity



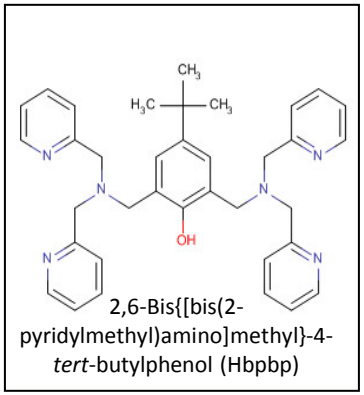
	R^3	R^4	R^5	e⁻ density (N)	$\Delta E_{1/2}$ (V)		R^3	R^4	R^5	e⁻ density (N)	$\Delta E_{1/2}$ (V)
	H	H	H	0	0		NH_2	H	CO_2Me	–	24
	H	NH_2	H	0	-52.5		NH_2	H	SMe	+	61
	NH_2	H	H	+	130		NH_2	H	NH_2	+	37
	CO_2Me	H	H	–	98						

Main Conclusion: electron withdrawing substituents are good

Task 1: Design and Synthesis of Novel Materials for Oxygen Reduction Reaction (ORR)

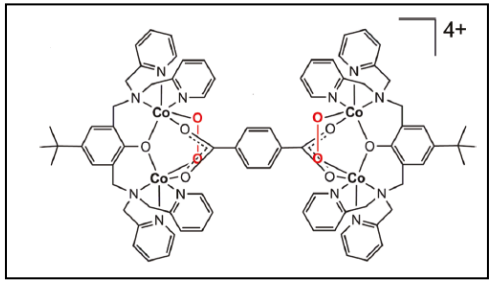
- **Designed Structures for Probing Structure Property Relationships (NEU)**
  - **Bidentate and tetradentate systems**
  - **Abbreviated Metal Organic Framework Systems**

Bidentate

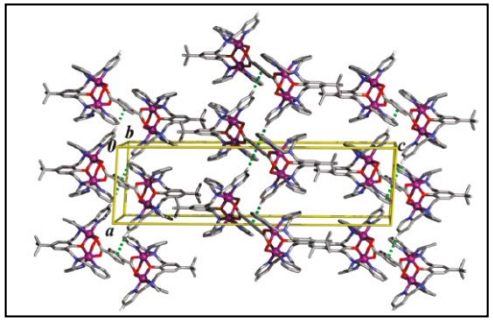


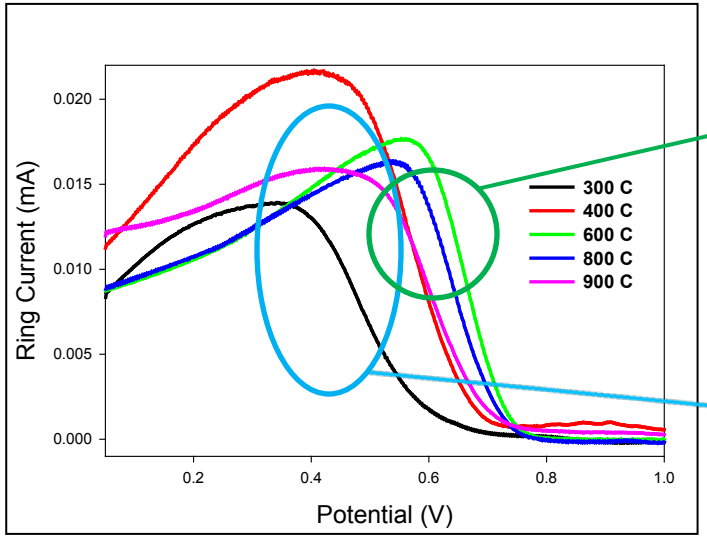
2,6-Bis{[bis(2-pyridylmethyl)amino]methyl}-4-*tert*-butylphenol (Hbpbp)

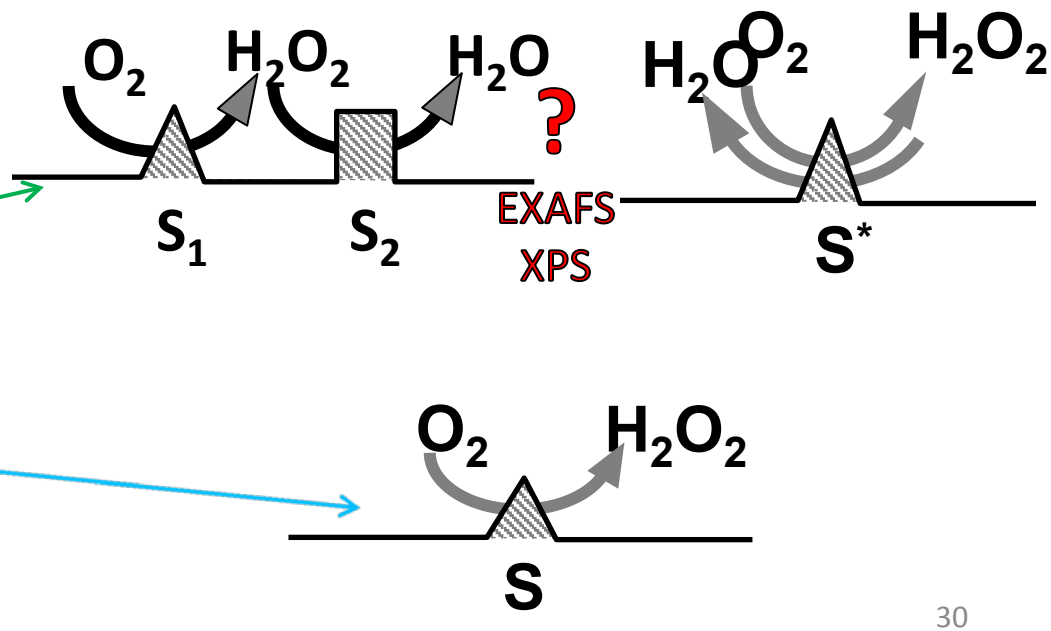
Tetradentate



Coordinated Packing-Chains







P.D.Southon, D.J.Price, *et. al.*, JACS, **2011**, 133, 10885-10891.

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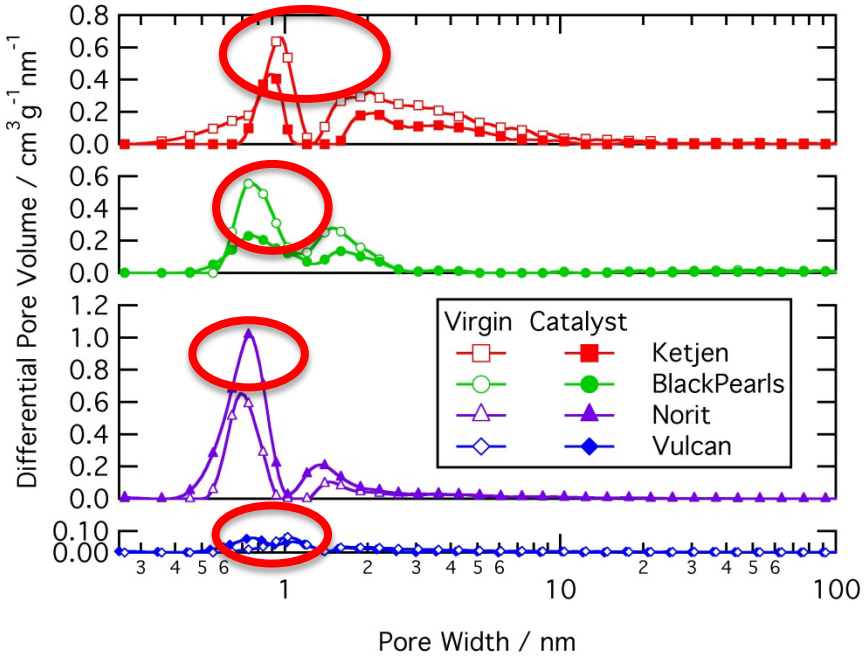
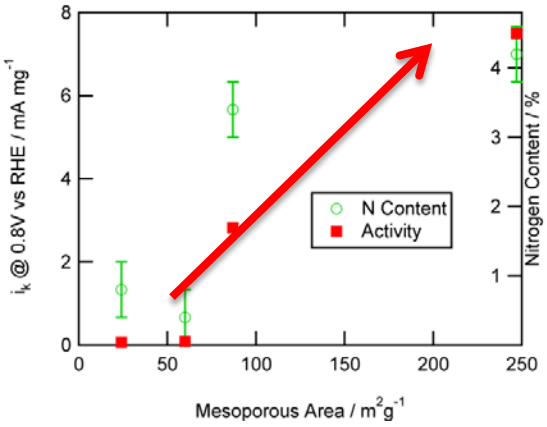
Task 2. Testing and Durability Measurements (MSU/NTCNA)

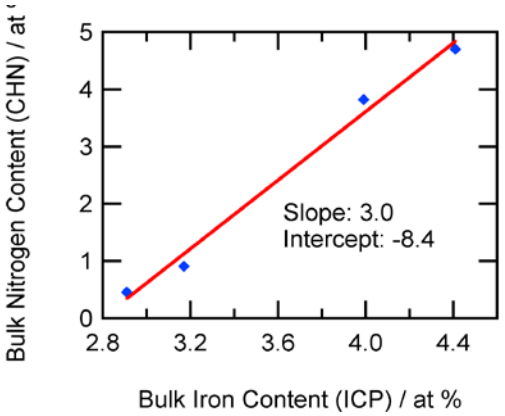
Electrode Structure: Impact of Mesoporosity On Activity

Catalyst activity (Melamine) using various carbon support materials.





as mesoporosity increases, so does catalytic activity and nitrogen adsorption



With increasing nitrogen adsorption, there is also increasing iron content for samples with varying carbon supports

Conclusions:

- Mesoporosity (circled) strongly impacts activity.
- Mesoporosity also plays a roll in nitrogen adsorption
- Iron and nitrogen retention go together

Zero Emission