Saving the Fuel Cell Dream: Making Non Noble Metal Electrocatalysts a Reality?

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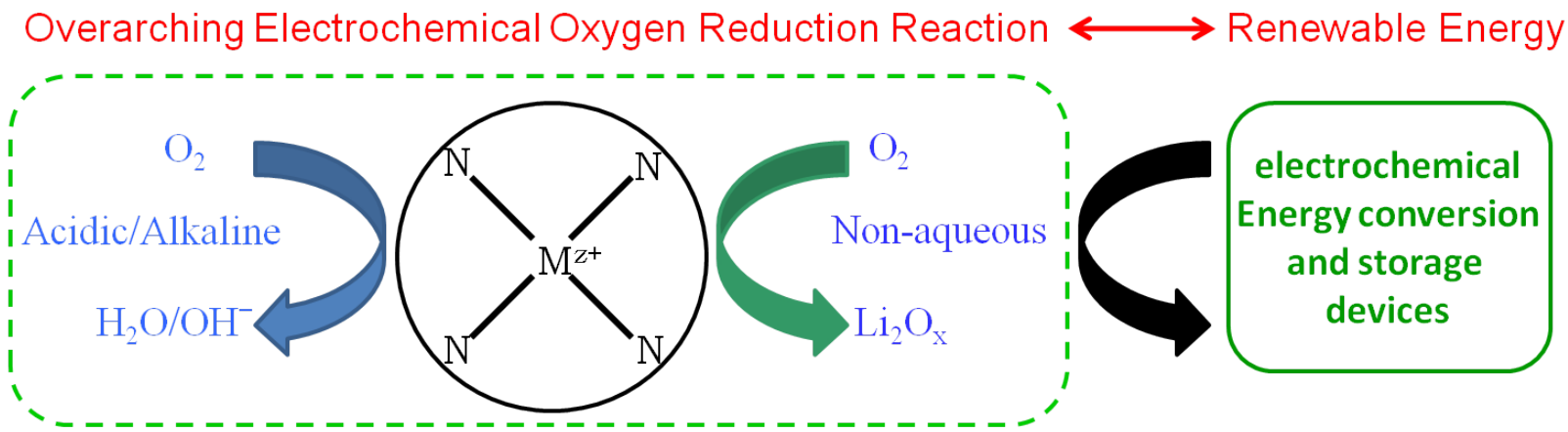


Need to Replace Pt and Pt Alloys

Analysis:

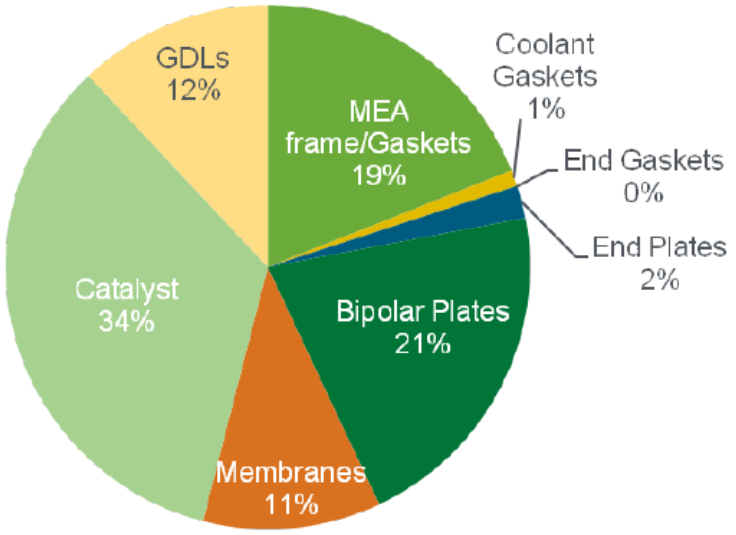
- Scaled to high-volume production of 500,000 units/year
- Assumed Pt cost of $1100/oz

Challenges:

- Platinum cost representing ~34% of total stack cost
- Catalyst durability in need of improvement

James *et al.*, DTI, Inc., 2010 DOE Hydrogen Program Review, Washington, DC, June 9, 2010

Polymer Electrolyte Fuel Cell Stack Cost ($26/kW)

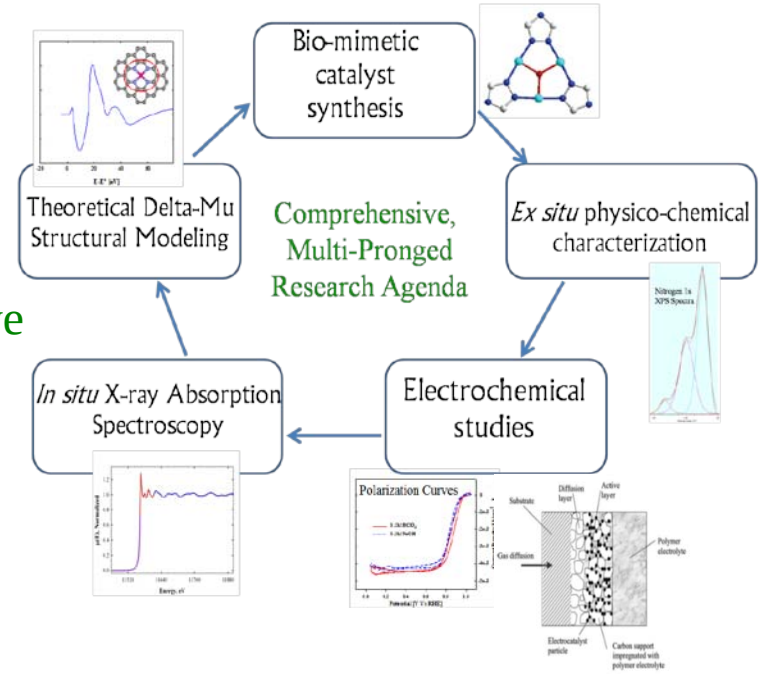


Main strategies to address catalyst cost challenge:

- Reduction in the platinum group metal (PGM) content
- Improvements to Pt catalyst utilization and durability
- Pt alloy catalysts with comparable performance to Pt but costing less
- Non-precious metal catalysts with improved performance and durability

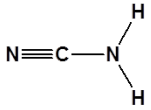
Outline:

- State of the art performance for Non PGM catalysts
- How close are we to Pt ?
- Are these Durable ?
- Literature Review on Metal-free versus M-N_x Active Sites
- Some Mechanistic Principles
- Fundamental understanding using Model Systems
  - Metal-Porphyrin Precursor
  - Cross Laboratory Comparative Study
  - Acid versus Alkaline Perspective
  - Nature of the Active Site
- Knowledge beyond the nature of the active site: Volcano vs. Redox Potentials??

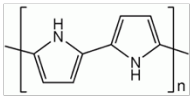


Representative LANL Approach:

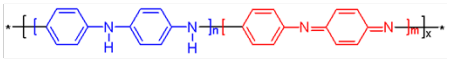
Cyanamide



Polypyrrole



Polyaniline



Carbon support

Transition metal

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

0.5 M H_2SO_4 leach at 80-90°C

Second heat treatment at 900°C in inert atmosphere

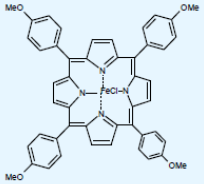
ORR performance evaluation; characterization

INRS-Dodelet Group: Pior Approach

Fe precursor +

- Fe salt
- Fe complex

like porphyrin



Cl-FeTMPP

N precursor +

- NH_3
- CH_3CN
- Fe complex
  like porphyrin
- N-polymer
  like PAN, polypyrrole, polyaniline

C support +

- Carbon black
- Activated carbon
- Ball-milled graphite
- Carbon nanotubes

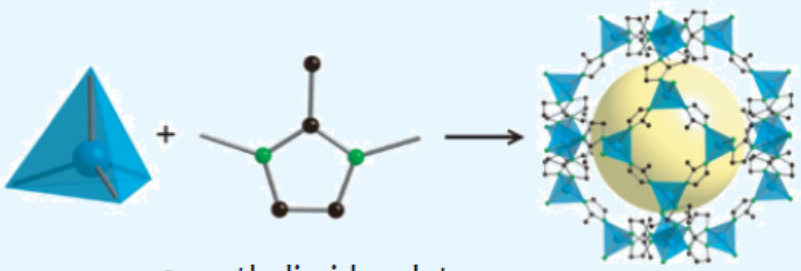
Pyrolysis step

- 500-1100°C

Our choices:

Method:	Wet Impregnation
Fe precursor:	$Fe^{II}Ac$ (ferrous acetate)
N precursor :	NH_3 (ammonia)
C support:	Various carbon supports
Pyrolysis step:	900 to 1000°C

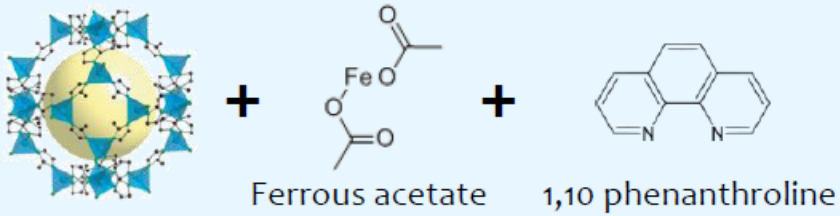
Current INRS-Canetique Approach:



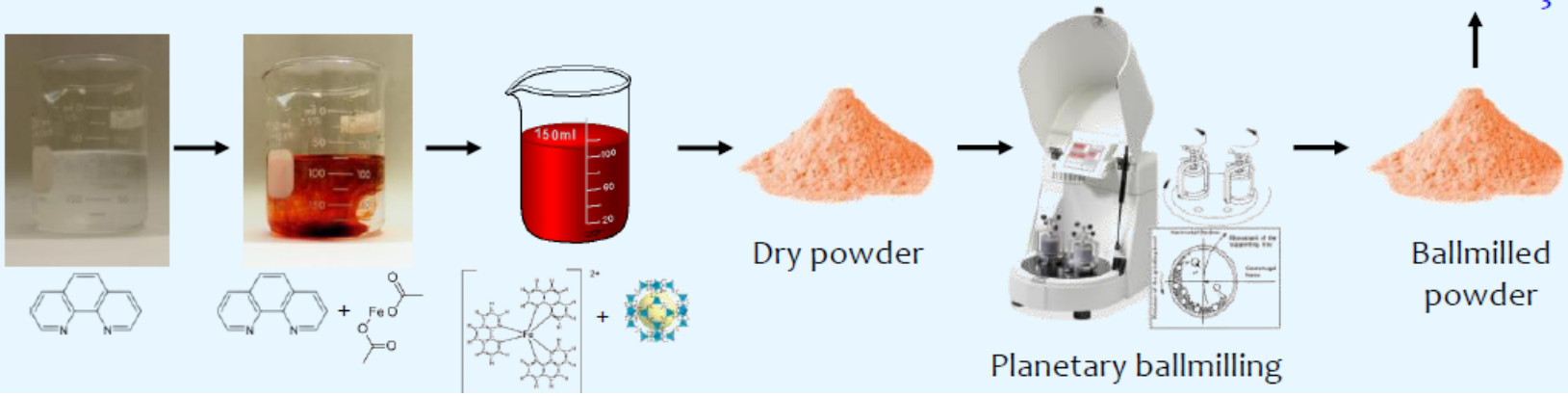
ZIF-8 is a commercial zeolitic imidazolate framework
Surface area ~ 2000 m^2/g
Pore diameter (yellow sphere) = 1.16 nm
Thermally stable up to ~ 500°C in N_2
Chemically stable in air at room temp.

K. S. Park et al. ...O. M. Yaghi, PNAS 103, 10186-10191 (2006)

We replaced the highly microporous carbon support with ZIF-8

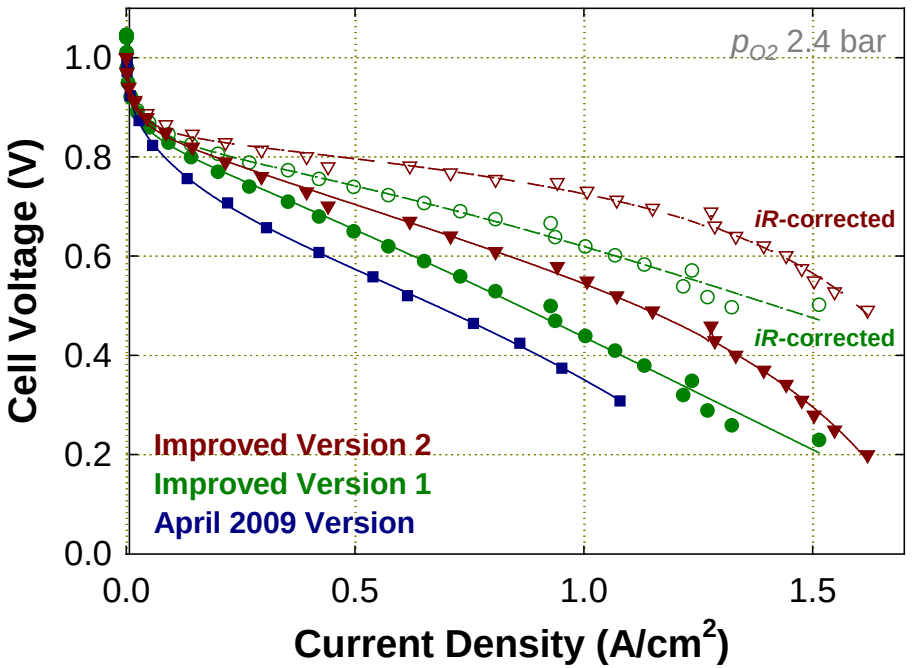


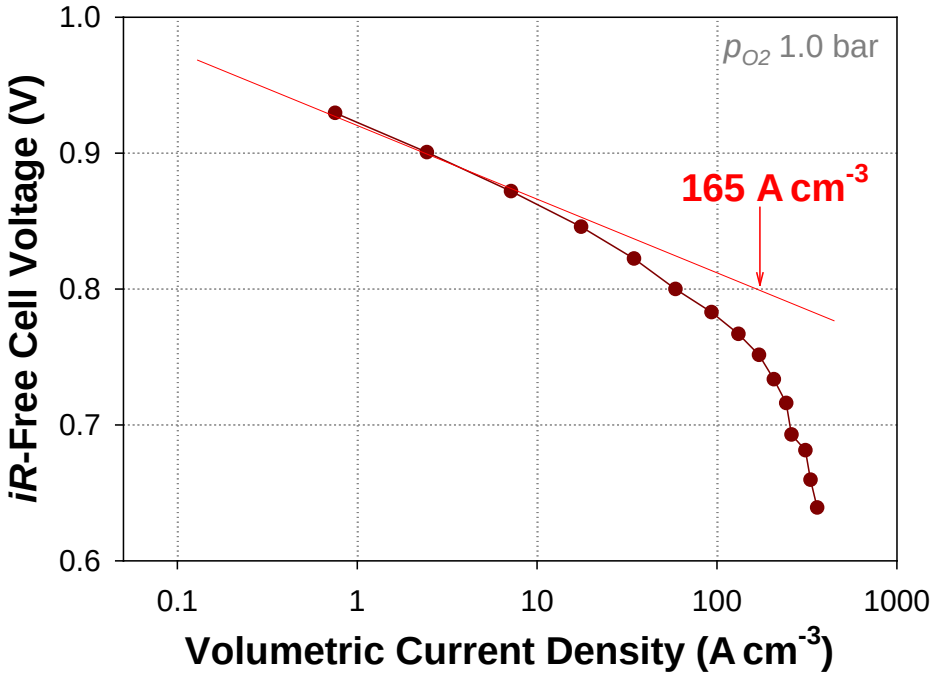
Ferrous acetate 1,10 phenanthroline



Cyanamide-Fe-C Catalyst: Performance-LANL

Anode: *0.25 mg cm^{-2} Pt (E-TEK);* ***Cathode:*** *~3.5 mg cm^{-2} CM-Fe-C;* ***Membrane:*** *Nafion® 117* ***Cell:*** *80°C*

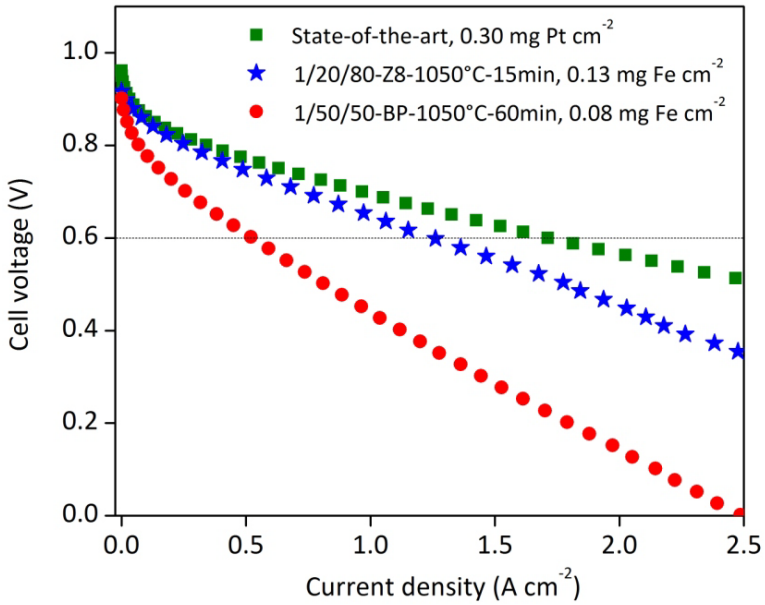


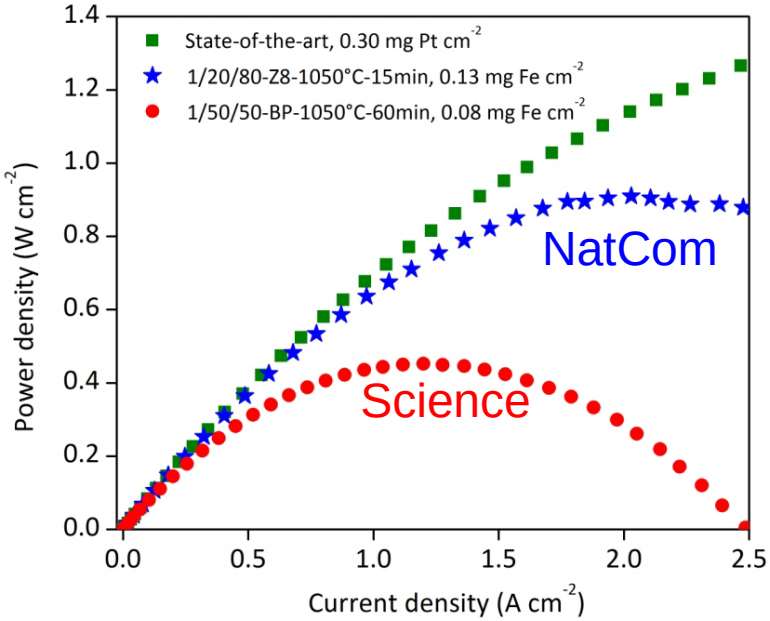


- **Version 1** achieved with change in the carbon support and adjustment of precursor ratios
- **Version 2** generated by including additional sulfur-containing precursor

0.39 A cm^{-2}	–	measured per MEA surface area at 0.80 V (*iR*-corrected)
60 A cm^{-3}	–	measured per electrode volume at 0.80 V (*iR*-corrected)
165 A cm^{-3}	–	extrapolated per electrode volume at 0.80 V (*iR*-corrected)

Best catalyst in 2011 (INRS-NatComm)



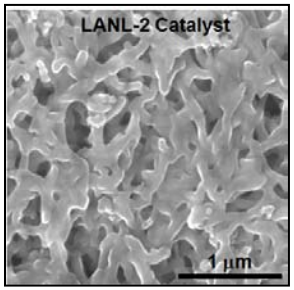


1. Impregnation on Basolite Z1200 (80%wt) with phenanthroline (20%wt) and iron acetate (1%wt Fe)
2. Ball-milling of the precursor
3. First pyrolysis at 1050C under Ar, 60 min
4. Second pyrolysisat 950C under NH3, to obtain final mass loss of 90%wt after the two pyrolysis

Fuel cell tests at 80°C, H_2/O_2, fully humidified, Nafion NRE211
≈ 4 mg / cm^2 of NatCom Catalyst
or of Science catalyst
Back Pressure: 100 kPa
(200 kPa total with atmospheric pressure)

E. Proietti, F. Jaouen, M. Lefèvre, N. Larouche, J. Tian, J. Herranz, and J.P. Dodelet, *Nature Communications*, **2**, 416 (2011)

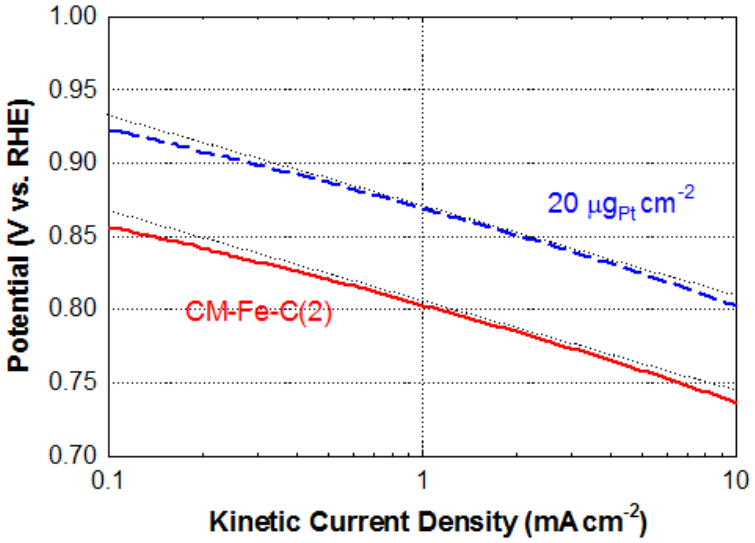
How Far are We From Pt: Not too far I imagine

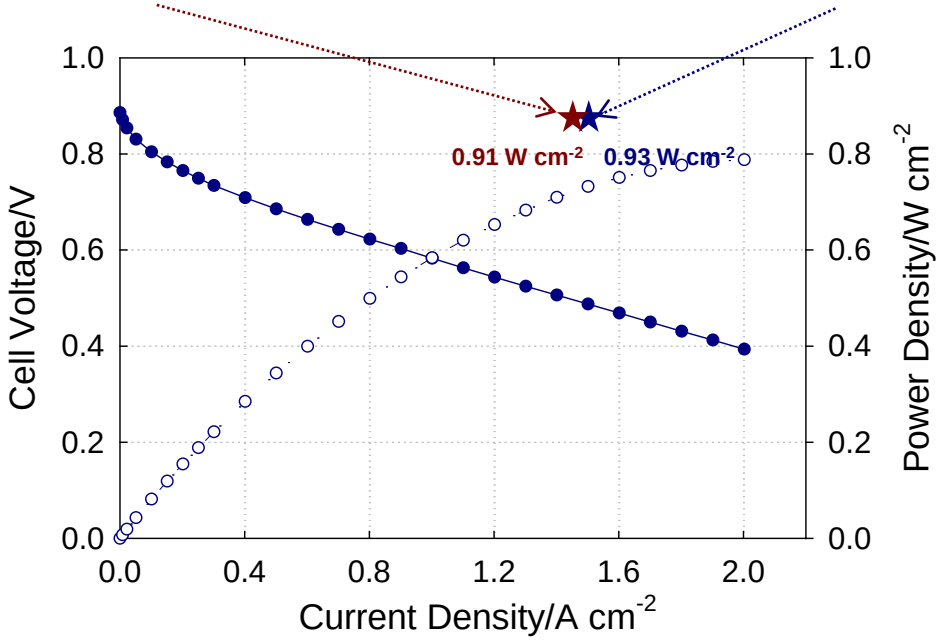


Anode: 0.5 mg cm^{-2} Pt (E-TEK) 1 bar(applied) H_2 200 sccm; Cathode: ~3.5 mg cm^{-2} 1 bar(applied) O_2 200 sccm; Membrane: Nafion® 212; Cell: 80 ℃

*Proietti et. al., Nat. Commun. **2**, 416 (2011): Membrane: Nafion®211; cathode: 3.9 mg cm^{-2}*

"LANL-2" after correction for membrane thickness difference





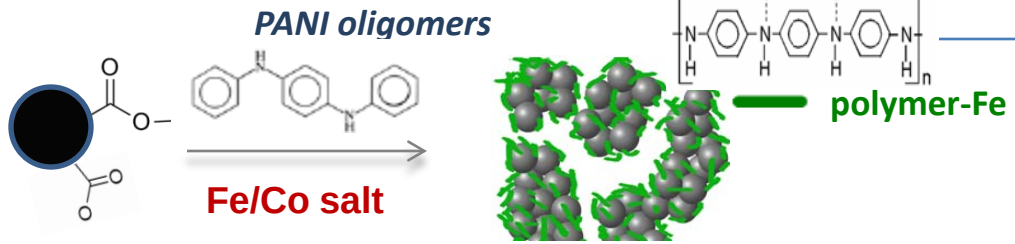
- ~70 mV difference in $E_{1/2}$ between CM-Fe-C catalyst and Pt reference catalyst (20 μg$_{Pt}$ cm^{-2})
- H_2O_2 generation: ~1%
- Tafel slope of CM-Fe-C catalyst in RDE testing: ~61 mV/dec

- High power density of 0.80 W cm^{-2} at 0.40 V recorded
- Power density measured comparable to that published by Proietti *et al.* (after a membrane-thickness correction)

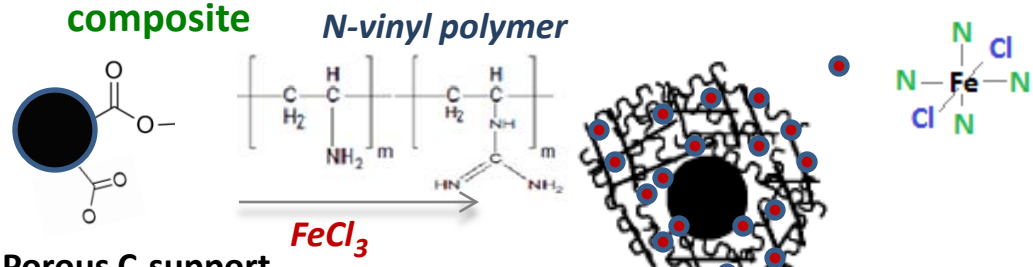
"LANL2" Catalyst with Improved Oxygen Mass Transport

Other MNC Electrocatalysts: Various Synthesis pathways

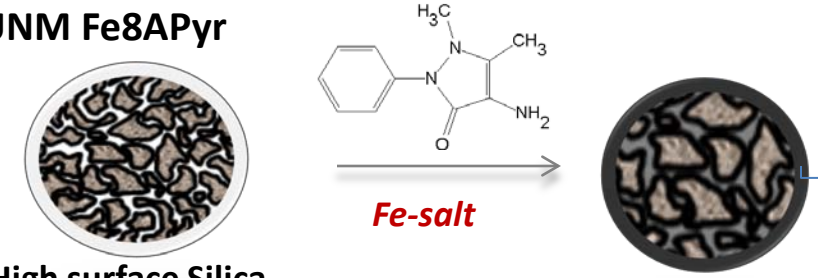
❖ **LANL FeCo**



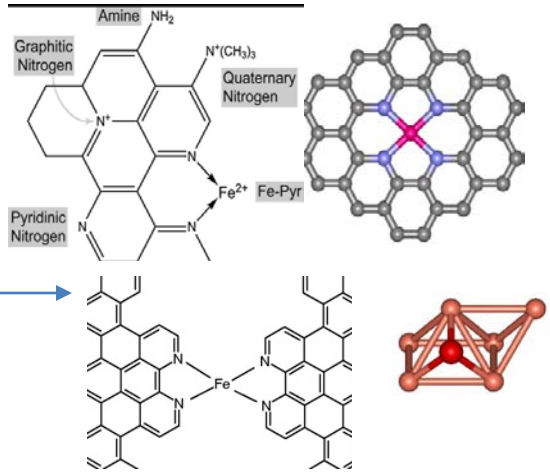
❖ **NEU Fe-Vinyl composite**



❖ **UNM Fe8APyr**



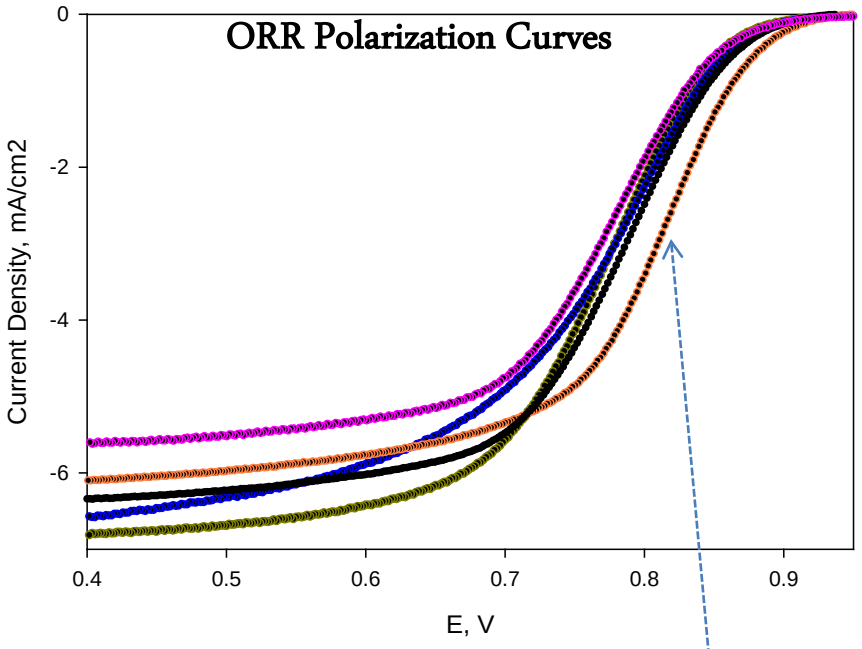
High temp. Pyrolysis 700-1000C

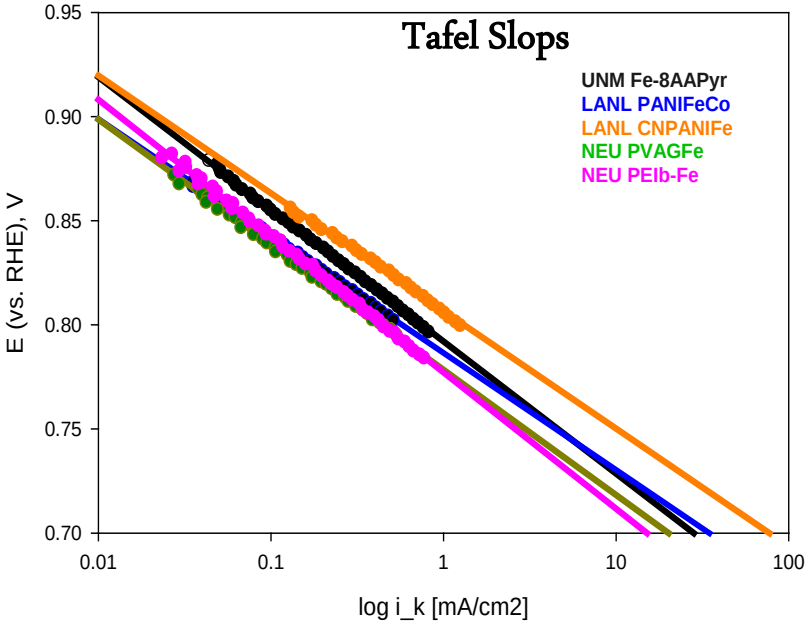


M-N-C catalyst

Comparative ORR activity of MNC catalysts –RRDE testing (NEU)

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

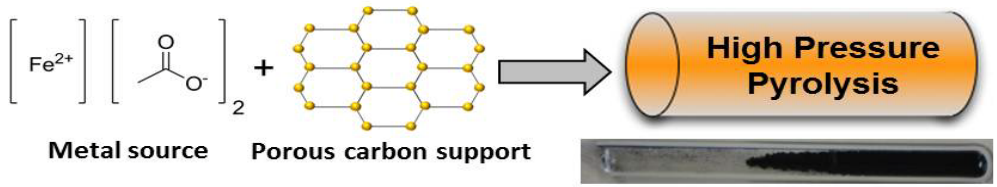




	I at 0.8[V] [mA/cm²]	$E_{½}$ [V]	Tafel Slops, [mV/dec]
UNM Fe-AAPyr	2.5	0.78	63
PANIFeCo	2.3	0.77	56
LANL-2	3.4	0.80	56
PVAGFe	2.2	0.77	60
PEIbFe	1.87	0.77	65

Highest ORR onset potential observed

What about Durability



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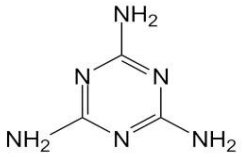
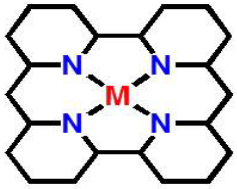
N precurs



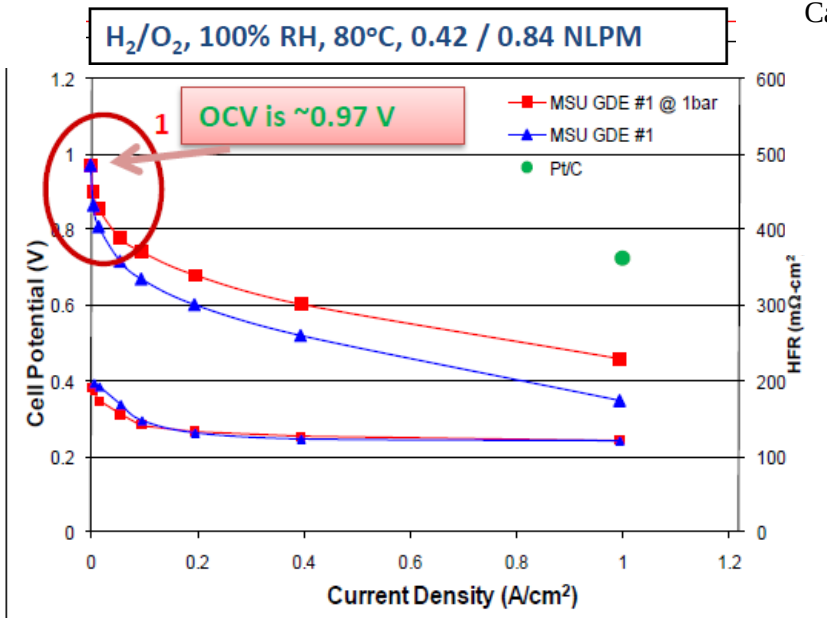
Melamine (N/C – 2.0)



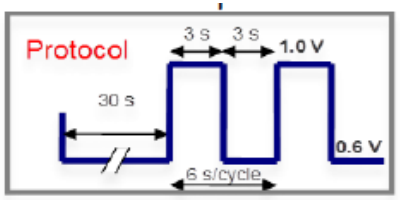
Metal-functionalized pyridinic carbon (Proposed catalytic site)

- GDEs were prepared for Melamine based catalyst using NTCNA spray system.
- MEAs were prepared with NRE211as the electrolyte and JMFC GDE anodes.

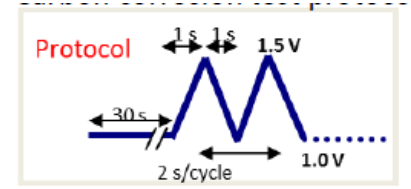
Fuel Cell data –Nissan Tech. Center

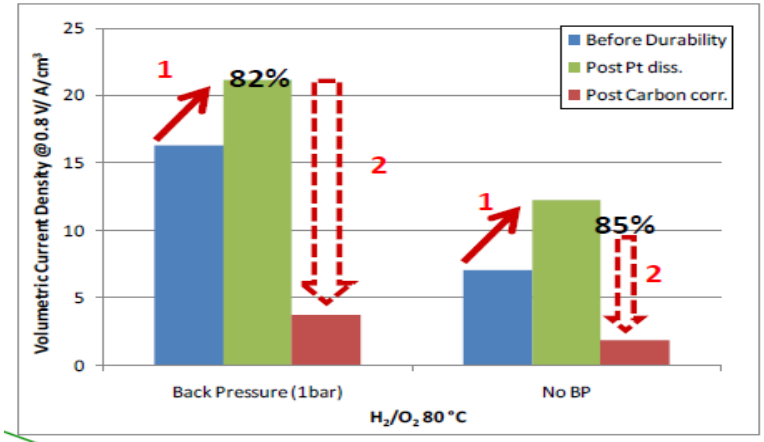


Catalyst durability test protocol



Carbon corrosion test protocol





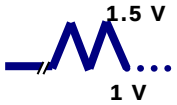
Testing and Durability Measurements (MSU / NTCNA)

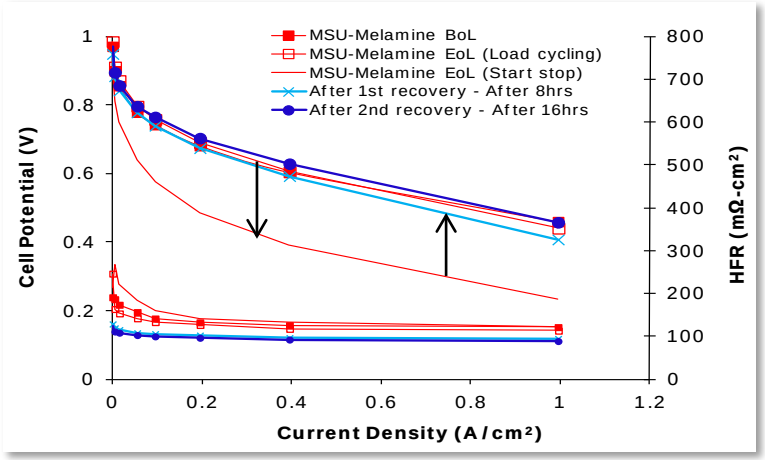
MSU-Melamine based non-PGM catalyst-Post durability performance recovery

- 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

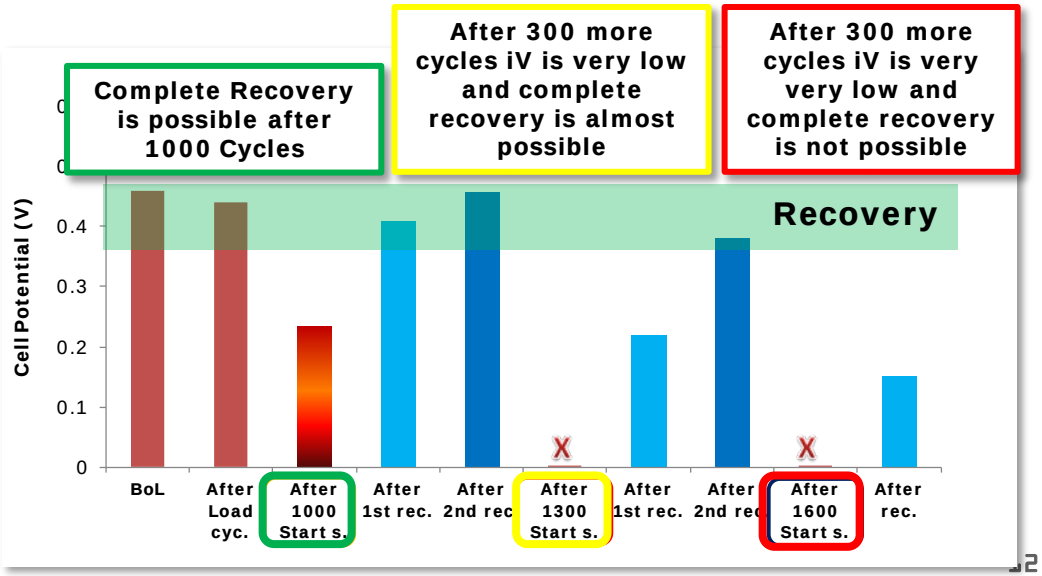
Nissan Start-stop Protocol (1000 cycles std)





✓ 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

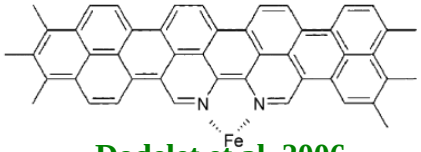
* ECS Transactions, 41(1), p2289 (2011)

Active Site Models in the Literature for Non-PGM Catalysts

NUCRET

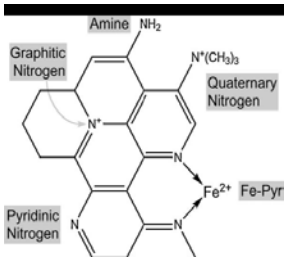
Active sites structure derived from experimental studies

Fe– N2C



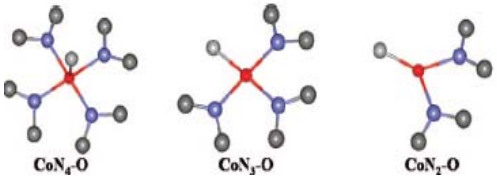
Dodelet et al, 2006

Fe-N_2 on the edge of graphene crystallite

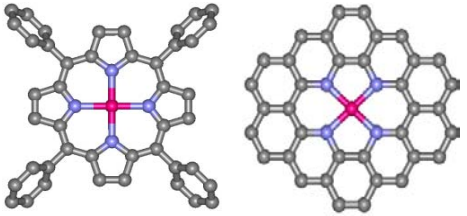


Graphitic, Pyridinic, Pyrrolic forms of Nitrogen present

Artyushkova et al, 2007

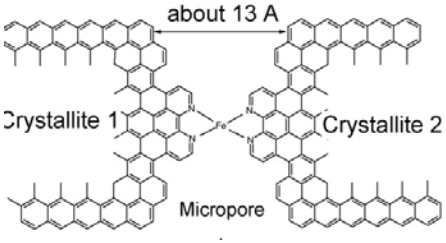


Mukerjee et al, 2008



Ramaswamy et al, 2012

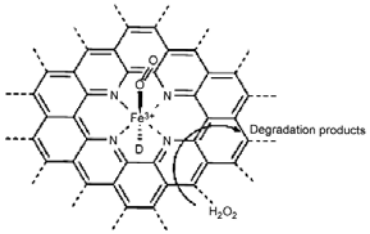
In-situ XAS: From porphyrin to Fe-N4-C in defective pockets of graphitic surface



Dodelet et al, 2009

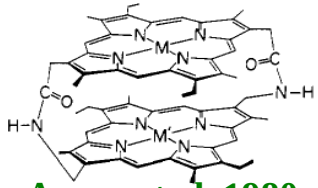
MeN_4/C species embedded in carbon micropores

Fe– N2+2



Shulenburg et al, 2003

Face-to-face porphyrins
Ideal for dirrect 4e ORR

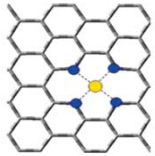


Anson et al, 1980

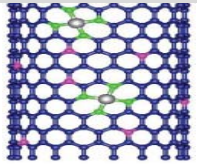
Theoretical Studies DTF calculations

- Metal coordination to nitrogen required for high activity
- Strong correlation between N-pyridinic and ORR activity

- M-N4 defect – energetically favorable over metal-less defects (DFT calculations)
- Pyridinic configurations are energetically preferred over pyrrolic



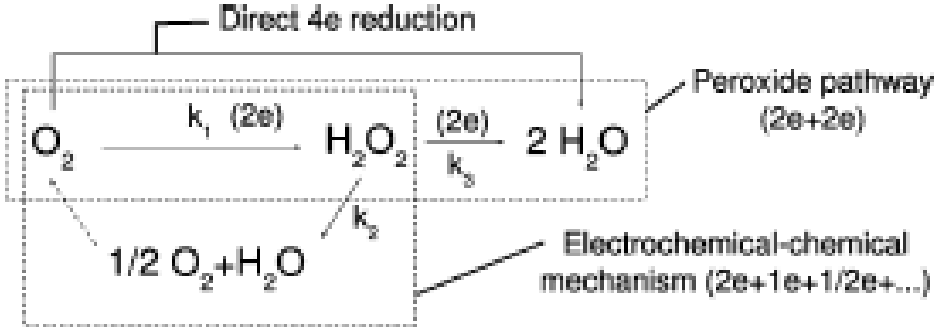
Titov et al, 2009



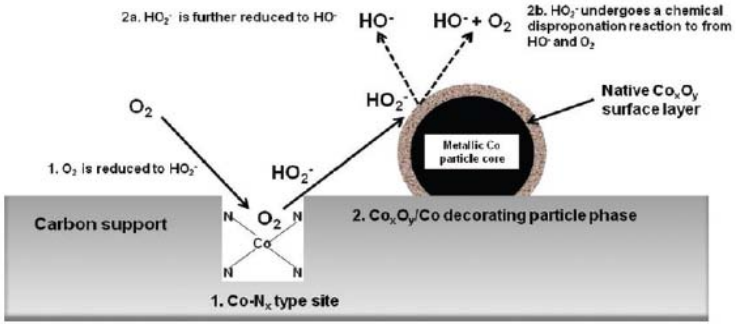
Kim et al, 2011

Mechanistic Pathways in the Literature for Non-PGM Catalysts

Direct 4e or 2x2e ORR mechanism ?

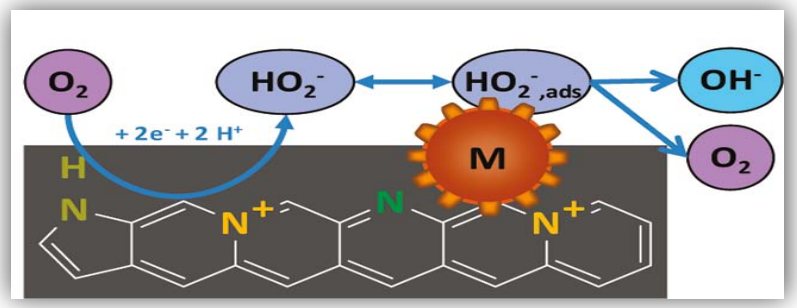


Bi-functional Theory: Metal-N_x



Atanassov et al, 2010

Bi-functional Theory: Metal-free active sites



Stevenson et al, 2011

- ➢ 2e Oxygen reduction to HO_2^- at primary active site - Metal-N4, and
- ➢ Further electrochemical reduction of HO_2^- to H_2O at Metal/Metal Oxide and/or chemical decomposition

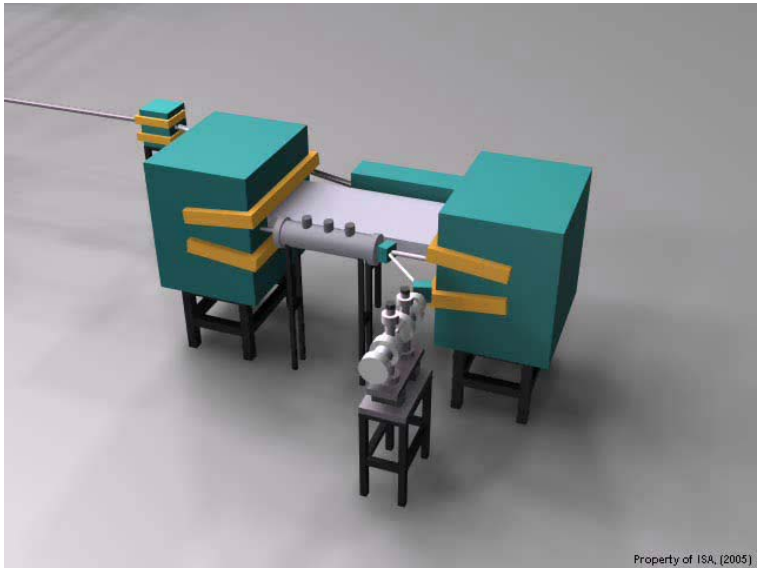
❖ Metal-Free centers as primary active sites:
2e O_2 reduction to HO_2^-, and
❖Adsorption of HO_2^- on Metal/Metal-oxide, and further 2e reduction of HO_2^- to H_2O, and/or heterogenous decomposition to H_2O and O_2

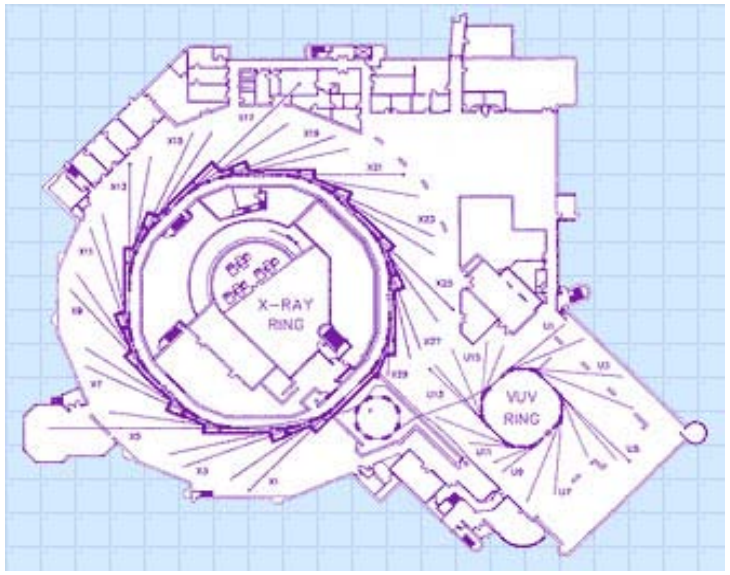
In-situ XAS/ Electrochemical studies

- ➢ Metal-N_x centers sufficient for overall 4e ORR in alkaline media:
  - ❖2e O_2 reduction to HO_2^-, and further 2e conversion to H_2O at the same Metal-N_4
- ➢ In acid, Metal-N_4 not able to perform the HO_2^- reduction. Secondary active site needed

Ramaswamy et al, 2012

Synchrotron Spectroscopy



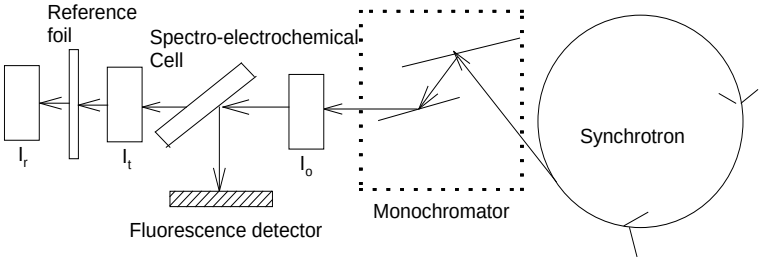


X-ray absorption spectroscopy

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.*,)

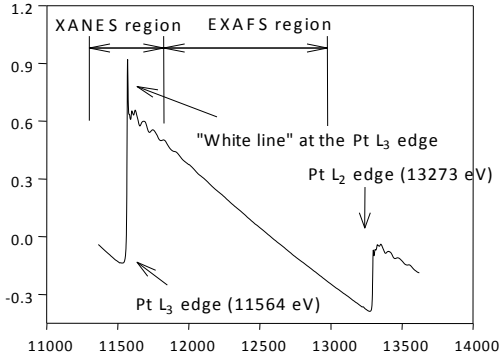
$$E_{photoelectron} = E_{xray} - E_0$$

XANES, multiple scattering

Physical Basis

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

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



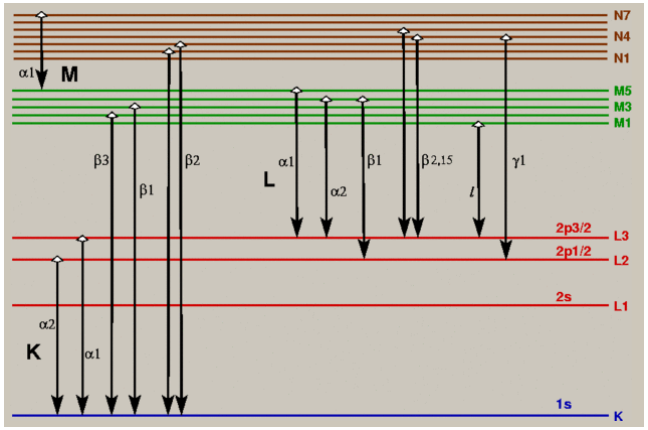
N – Coordination Number

R – Interatomic Distance (Å)

σ^2 – MSRD (Debye-Waller)

***f*(k)** – Amplitude

δ(k) – Phase

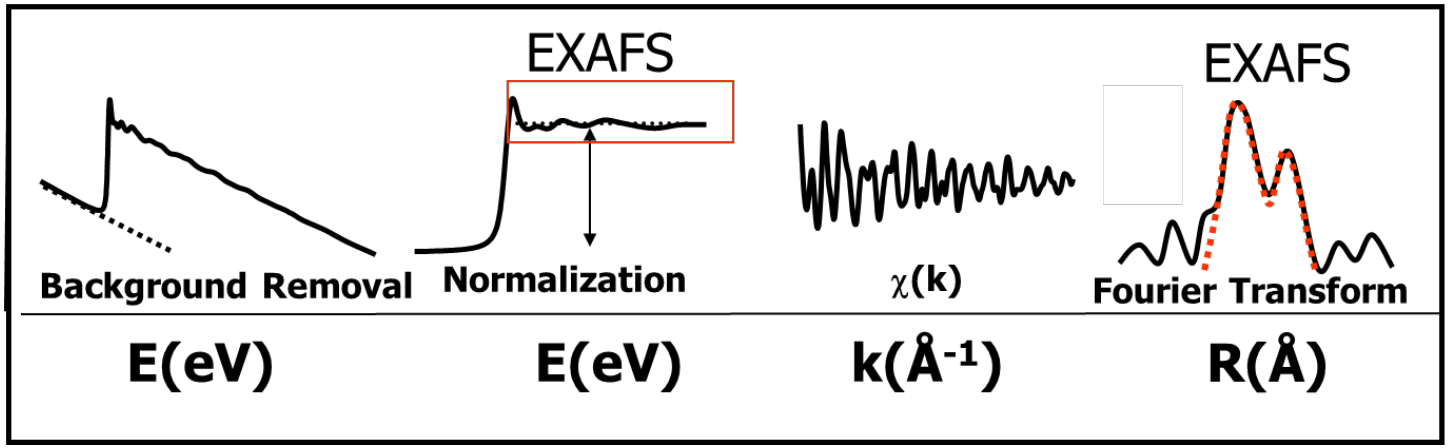


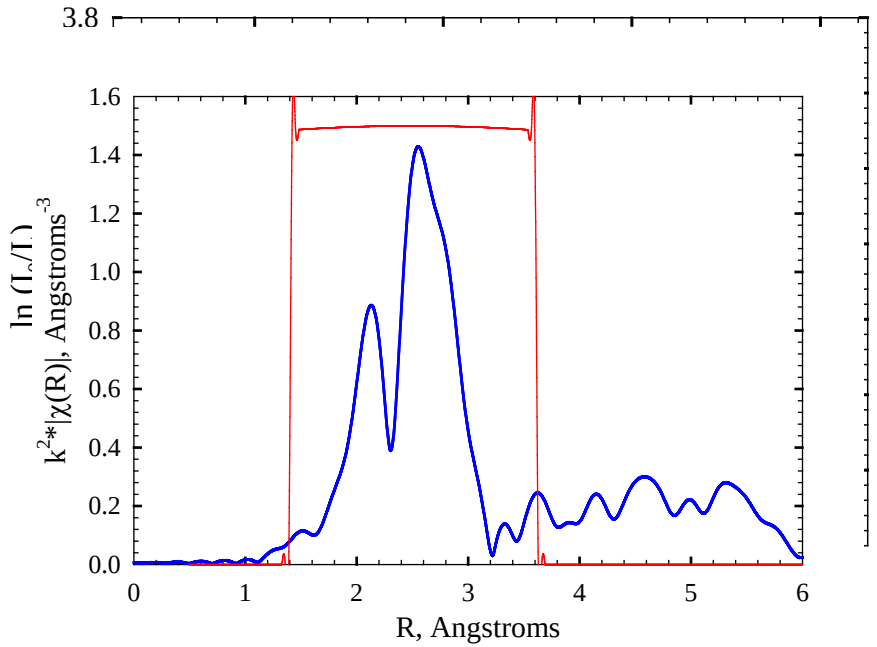
$$E_{xray} = \frac{hc}{\lambda}$$

Detection:

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

Data analysis 1: EXAFS





$$k = \sqrt{\frac{2m_e(E - E_0)}{\hbar^2}}$$

$$\chi(k) = \sum_j \frac{N_j f_j(k) e^{-2k^2\sigma_j^2}}{kR_j^2} \sin[2kR_j + \delta_j(k)]$$

$$\chi(R) = \frac{1}{\sqrt{2\pi}} \int_{k_{min}}^{k_{max}} k^n \chi(k) e^{i2kR} dk$$

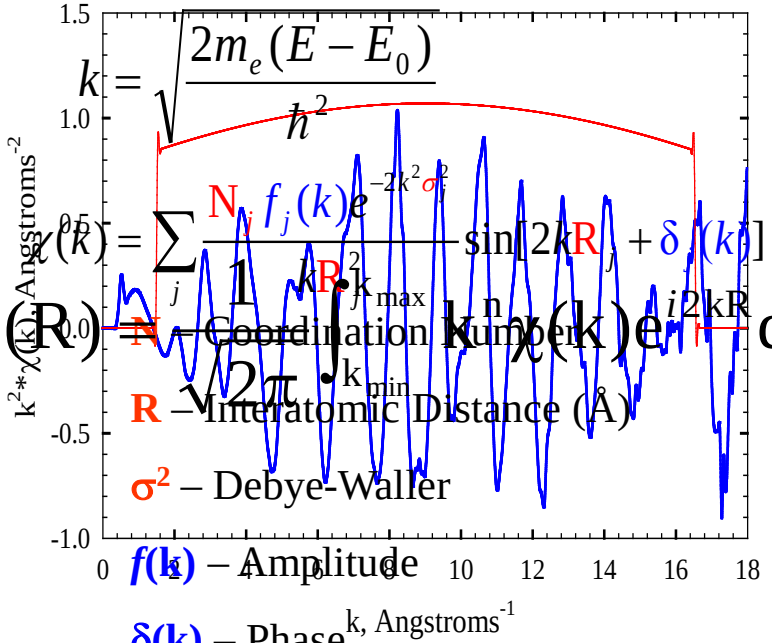
N – Coordination Number

R – Interatomic Distance (Å)

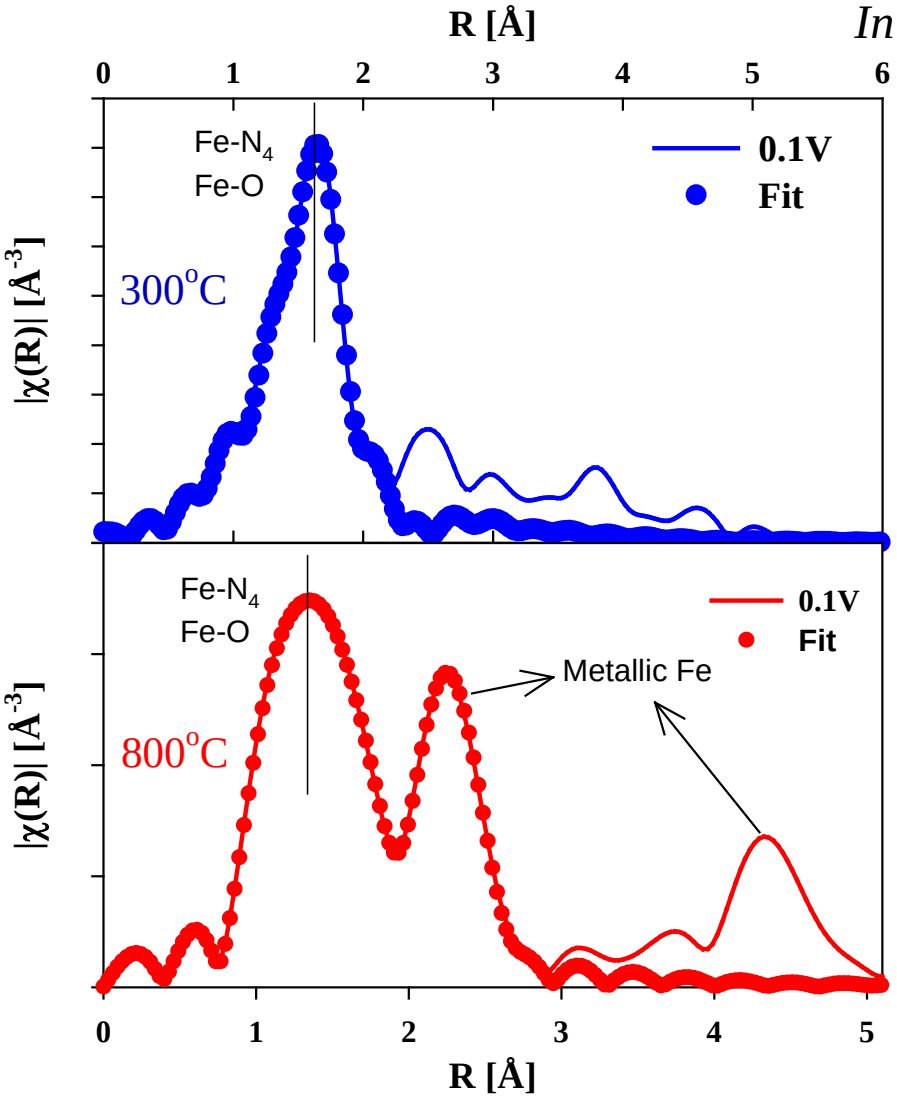
σ^2 – Debye-Waller

***f*(k)** – Amplitude

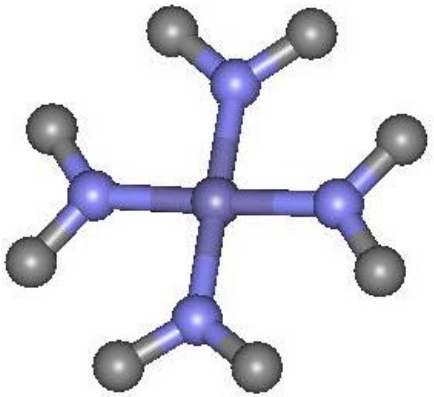
δ(k) – Phase



In situ Extended X-ray Absorption – Fe-N_x Short Range Structure



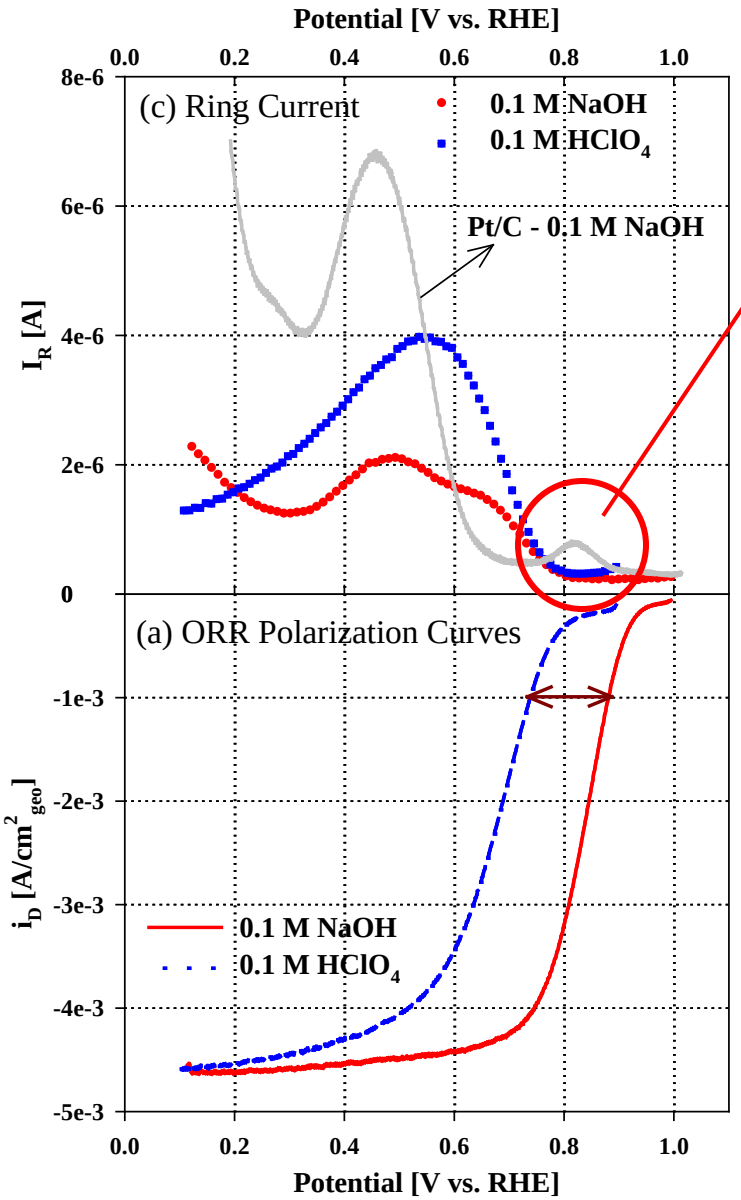
In situ 0.1M NaOH electrolyte @ 0.1 V vs. RHE



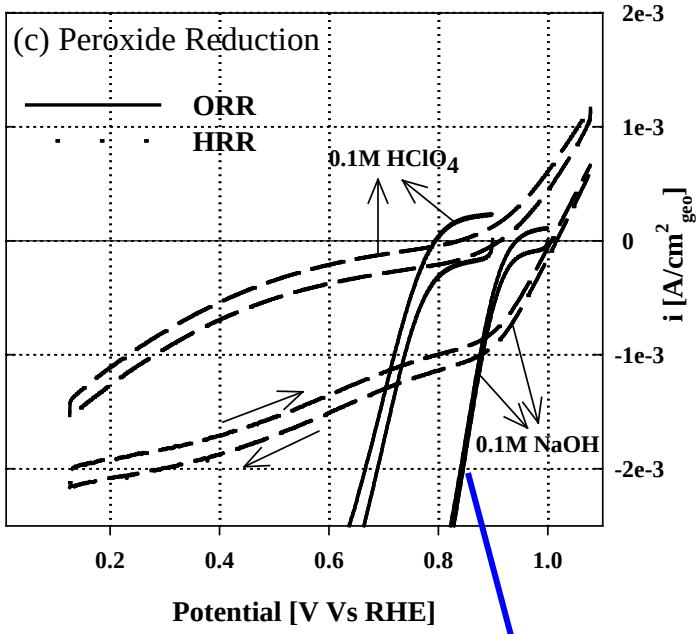
	Fe-N Coordination Number	Fe-N Bond Length [Å]
300°C	**4.00**	1.996
800°C	**4.00**	1.976

O_2 Reduction Activity – Acid versus Alkaline Perspective

Iron-Porphyrin/Carbon
Pyrolyzed – 800°C
100 µg/cm² Loading

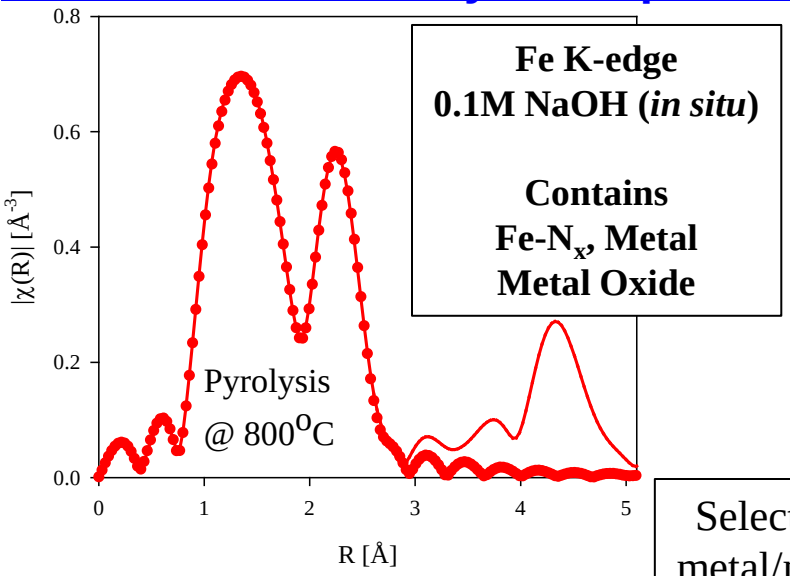


No Outer-Sphere Process on Pyrolyzed Fe-Porphyrin

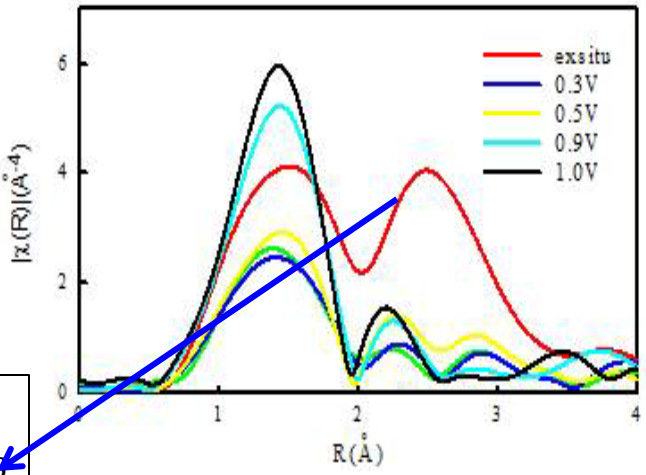


Peroxide intermediate is more stable on the active site in alkaline media

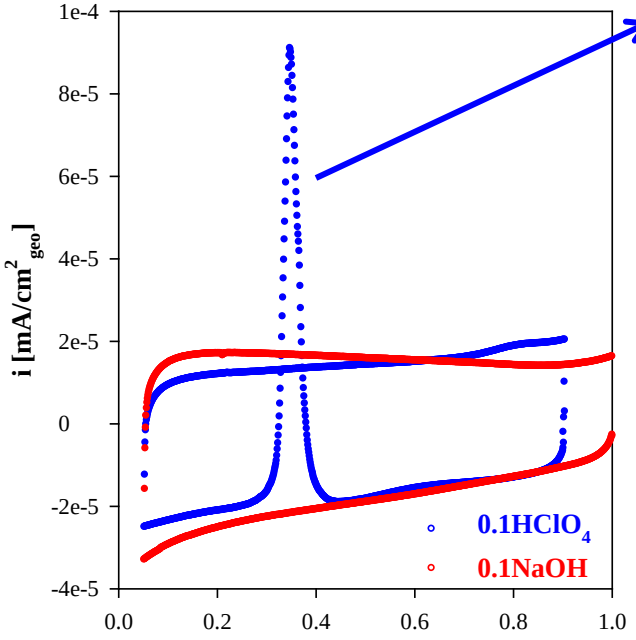
Insitu Extended X-ray Absorption – Fe-N_x Short Range Structure



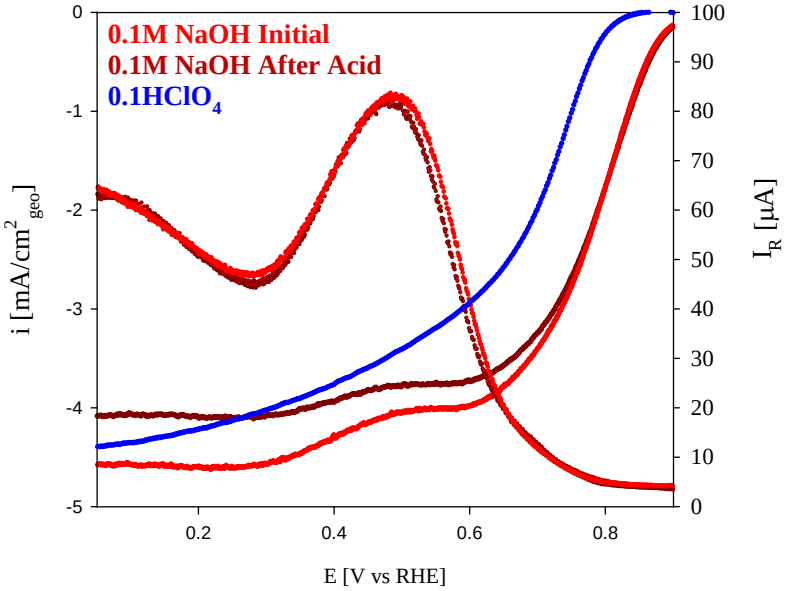
Fe-Porphyrin HT800°C
In situ 0.1M $HClO_4$ electrolyte



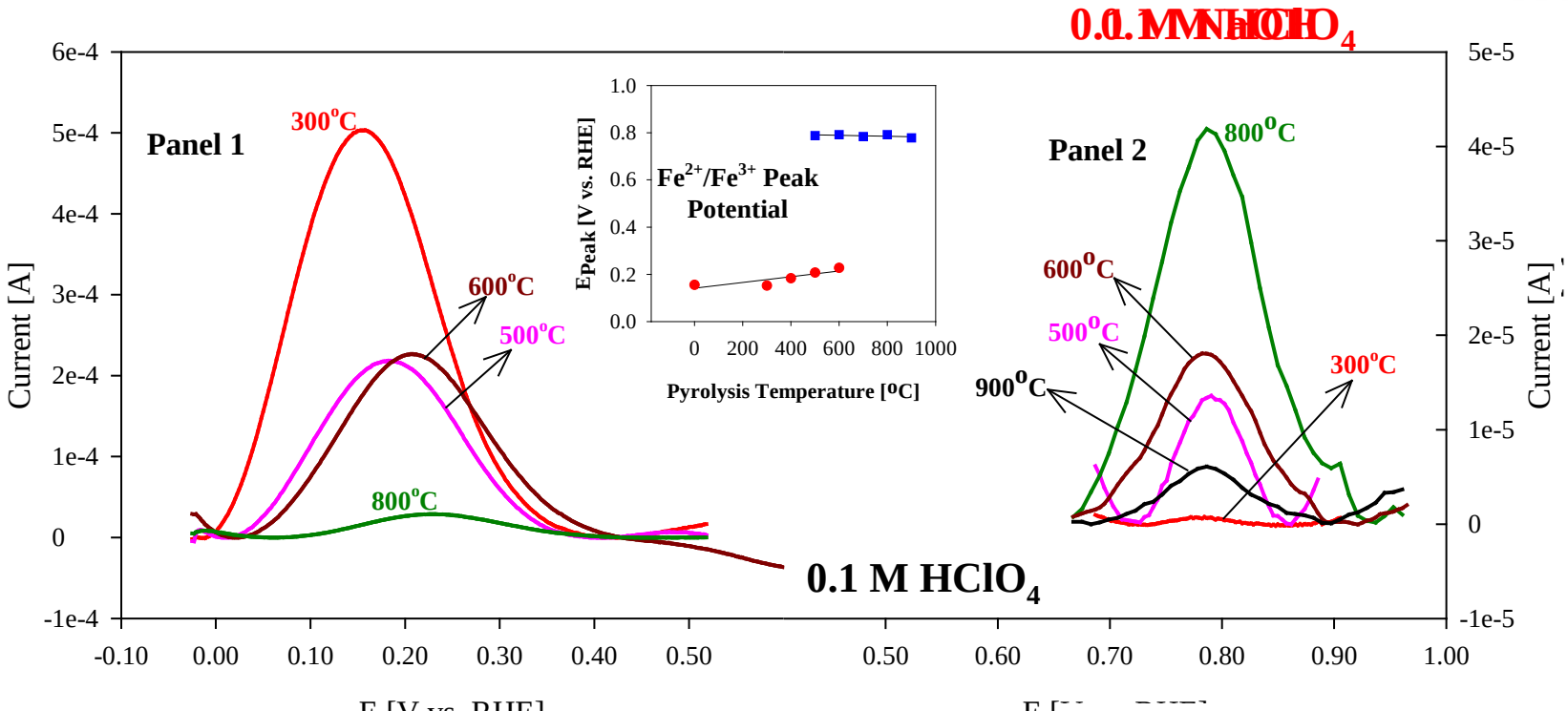
Selective dissolution of metal/metal oxide clusters in acidic media confirmed by EXAFS



No Loss in activity after removal of metal/metal oxide clusters

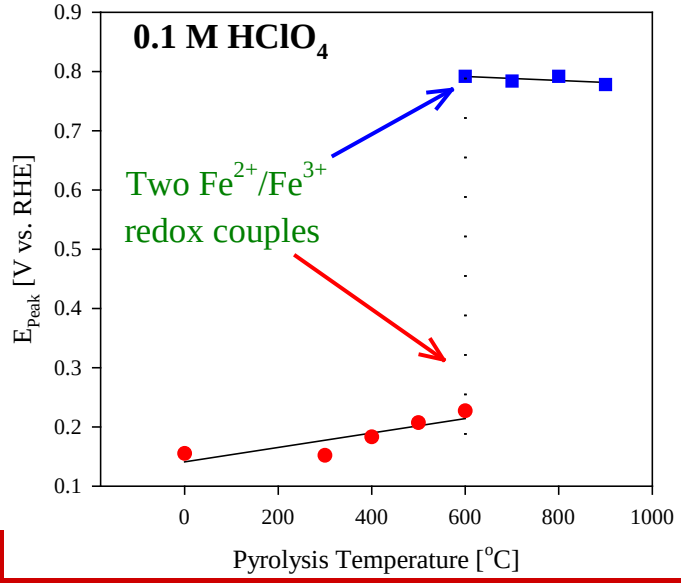


Pyrolyzed Fe-Porphyrin on Carbon – Square wave Voltammetry



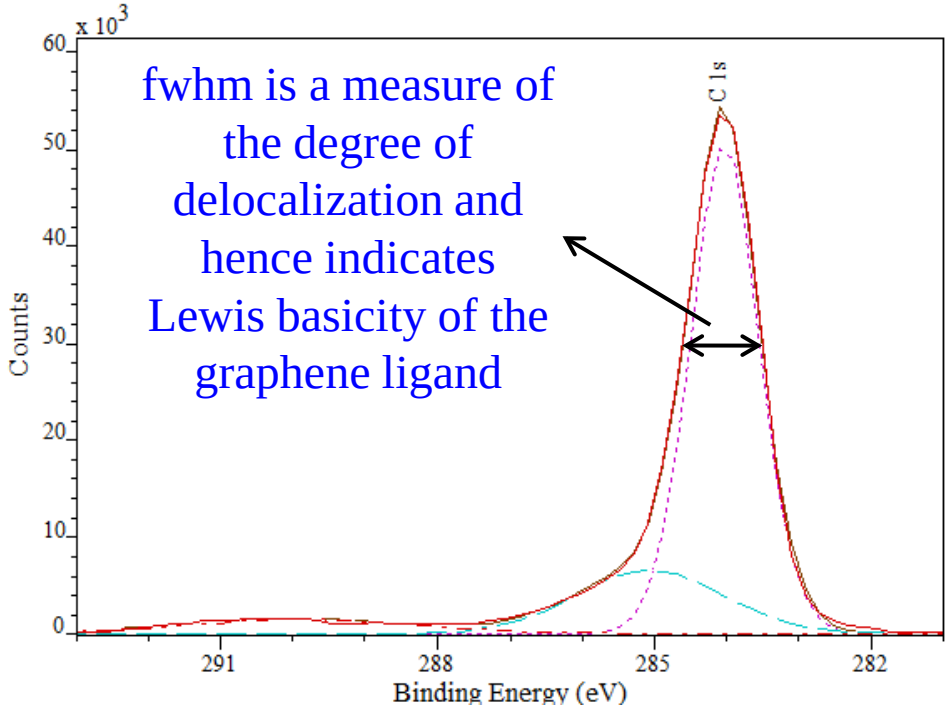
In acidic media:

Dramatic anodic shift in the Fe^{2+}/Fe^{3+} to 0.85V redox potential upon pyrolysis at 600°C

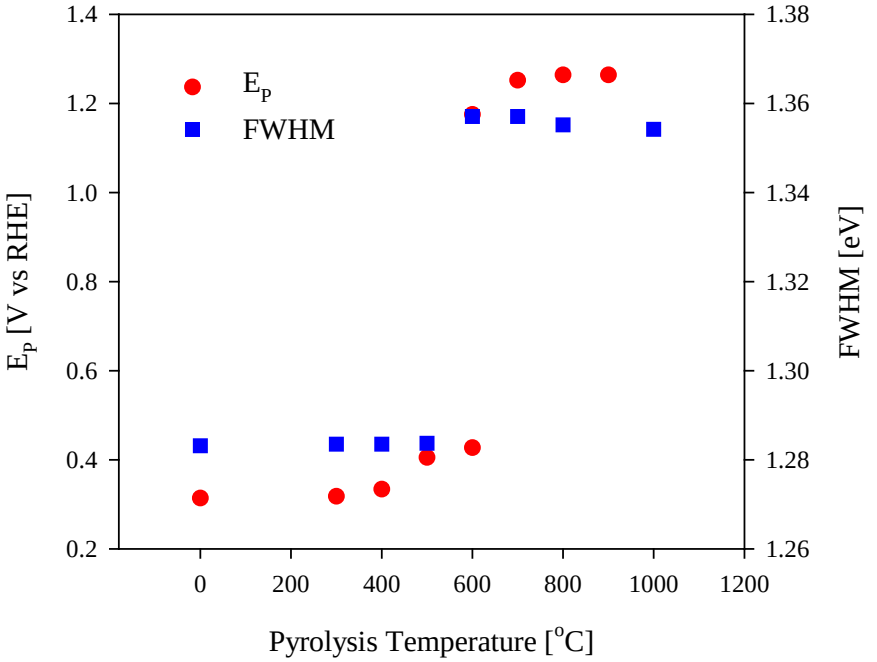


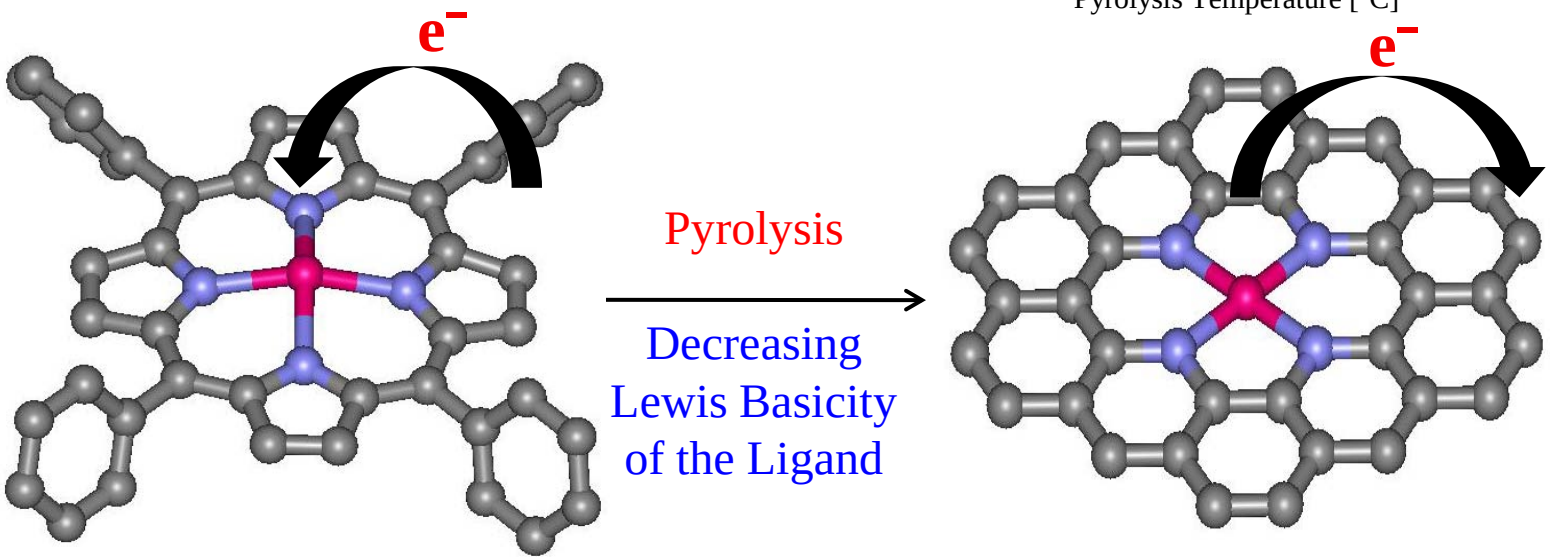
- In acidic media redox potential shifts only to 0.8 V
- Its one reason for higher overpotential in acidic media

Effect of Lewis Basicity of Ligand on Redox Potential



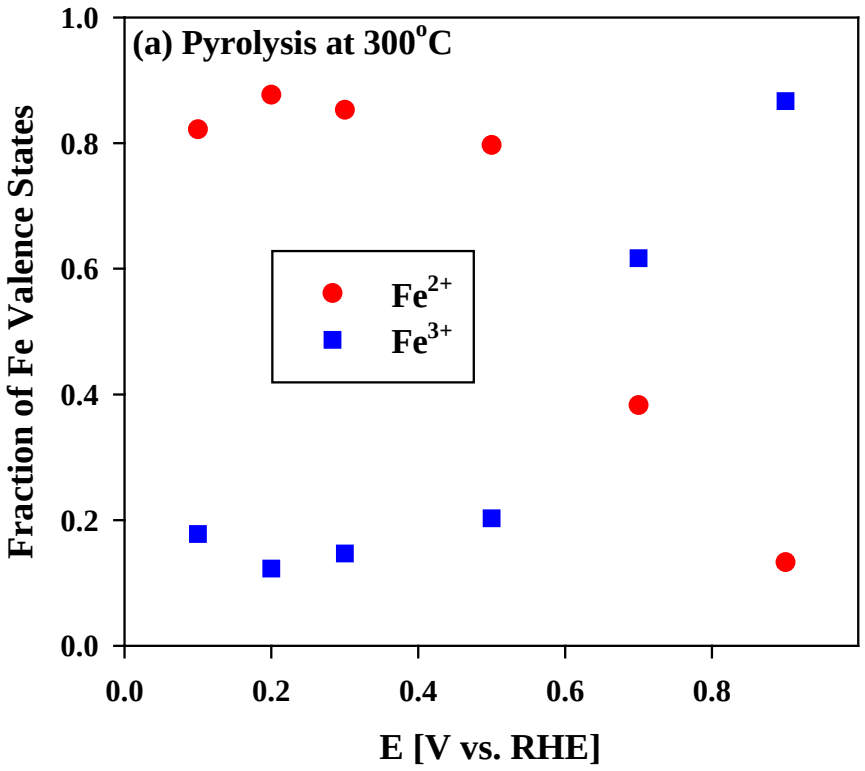
fwhm is a measure of the degree of delocalization and hence indicates Lewis basicity of the graphene ligand

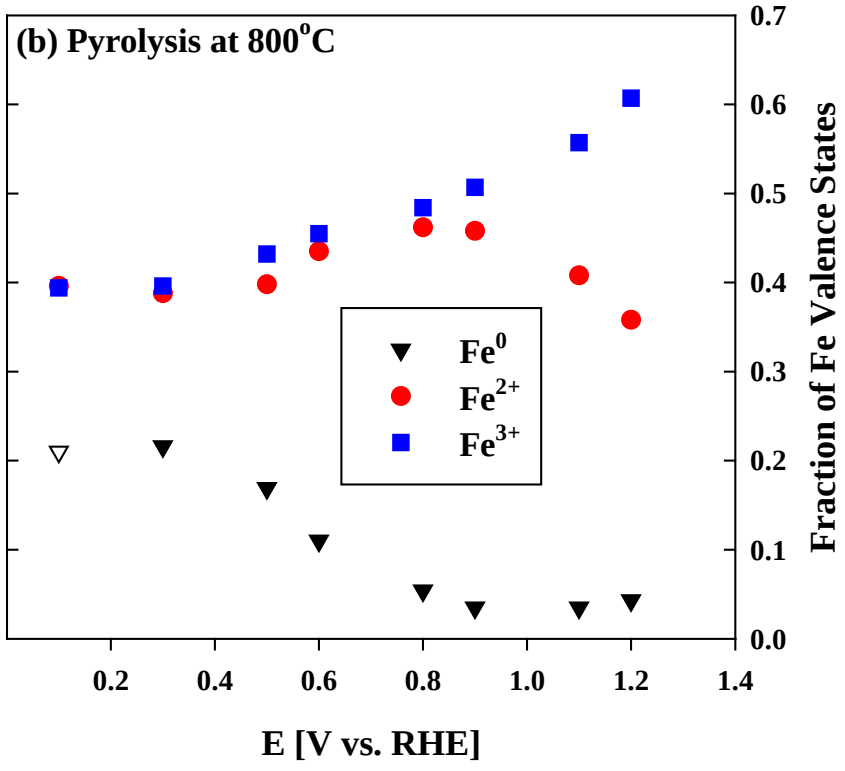




FeTPP/BPC – Efforts to Understand ORR Mechanism

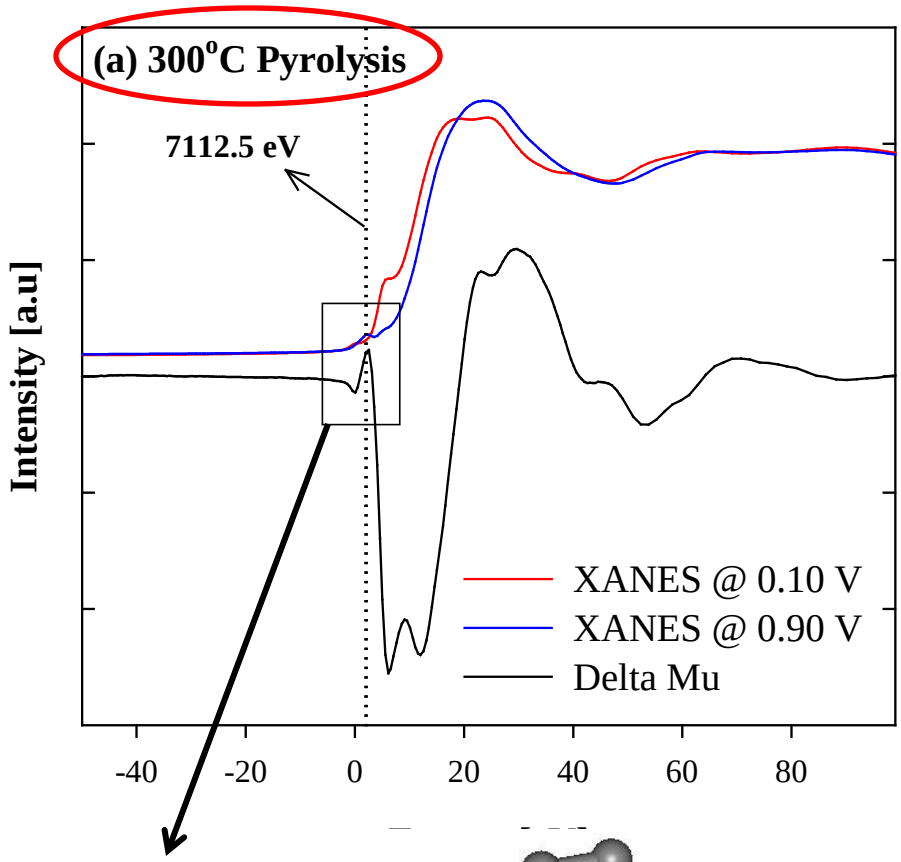
Linear Combination Fitting Analysis of various oxidation states of Fe under insitu conditions



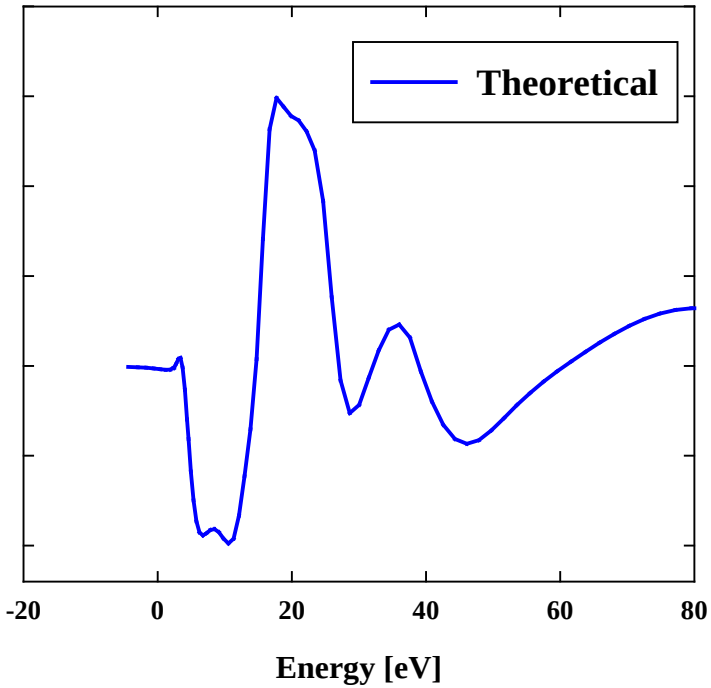


- After 800°C pyrolysis, XANES indicates the shift in $Fe^{2+/3+}$ transition to higher potentials

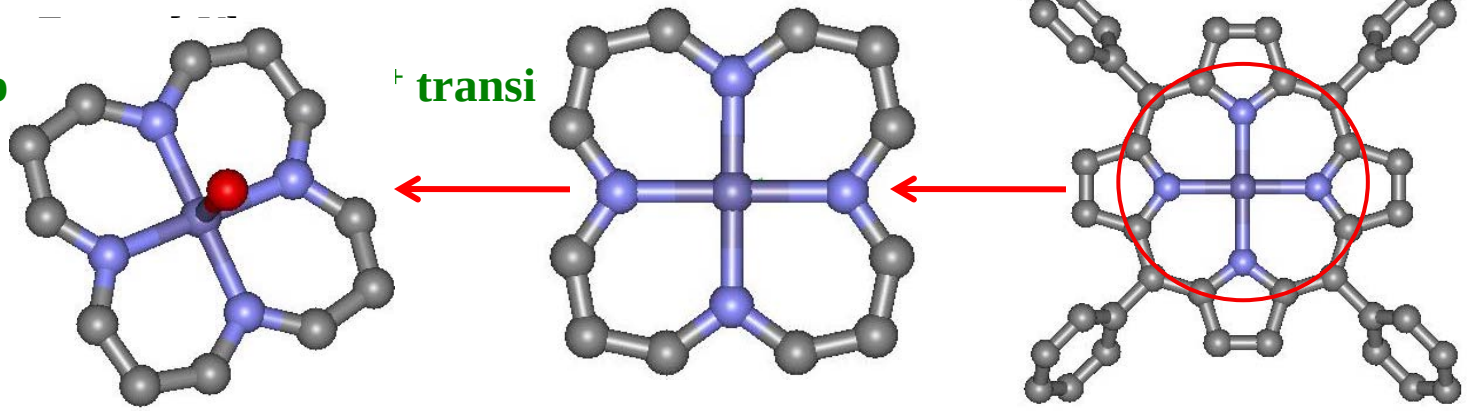
Delta Mu - Identification of Active Site & Oxygen Adsorption Mode



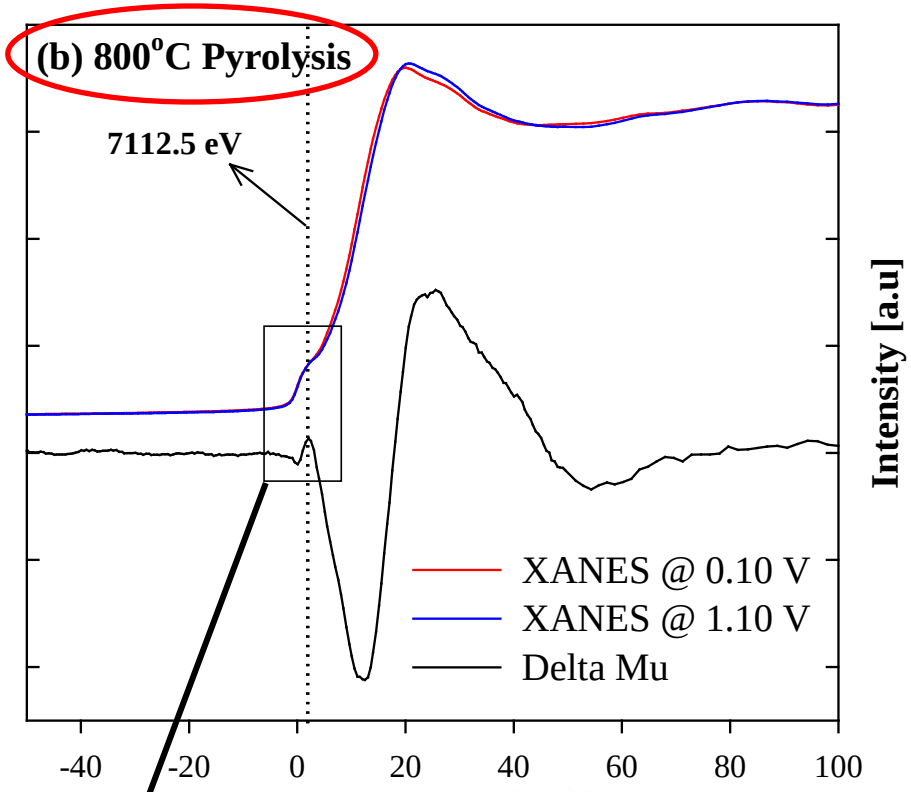
XANES simulation using FEFF

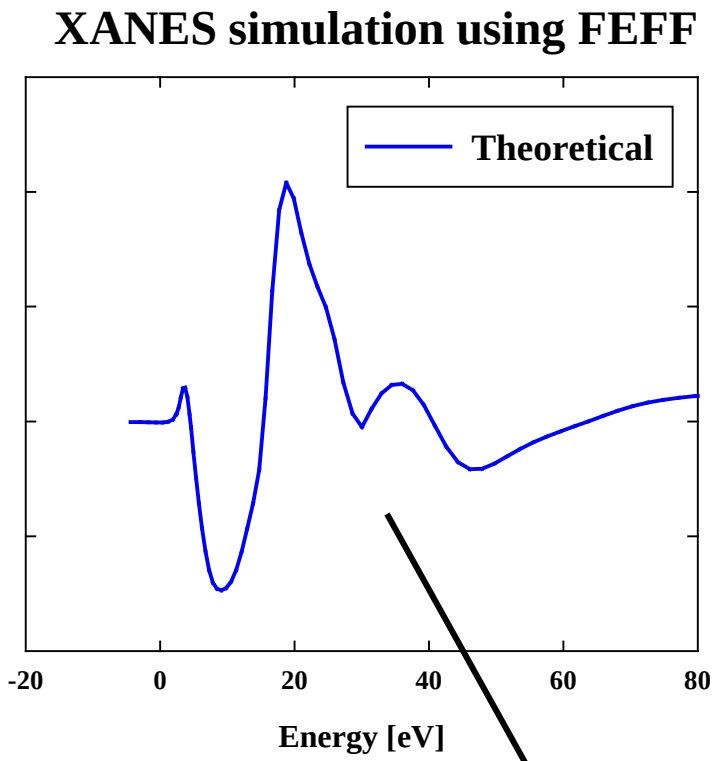


Delta Mu of Fe/N/C pyrolysis FeN_4 structure is preserved in the macrocyclic cavity



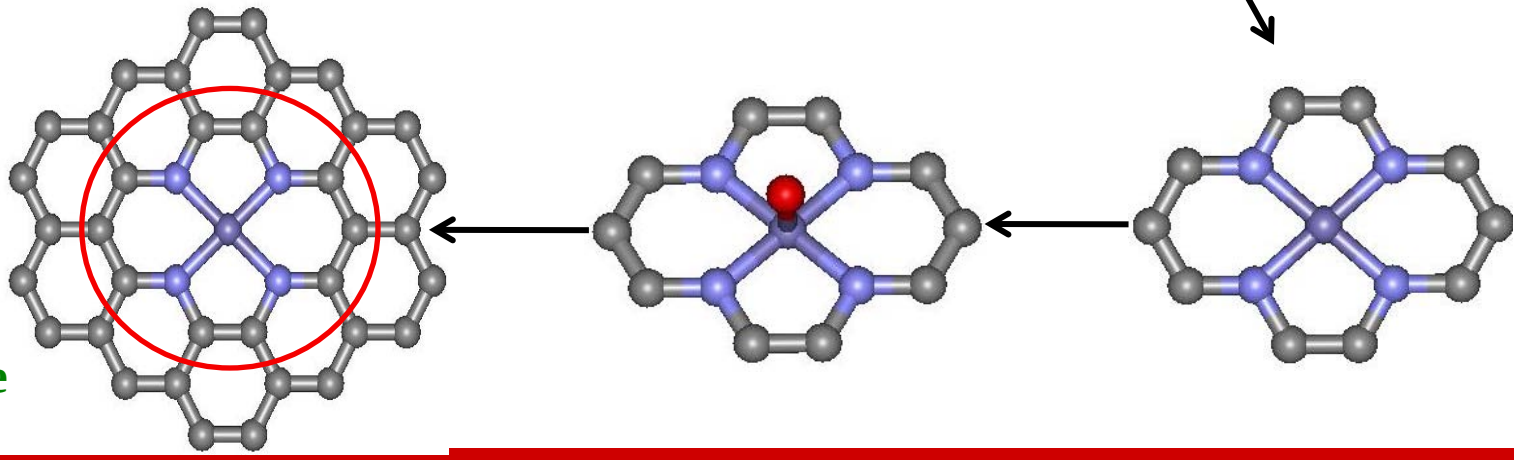
Delta Mu - Identification of Active Site & Oxygen Adsorption Mode



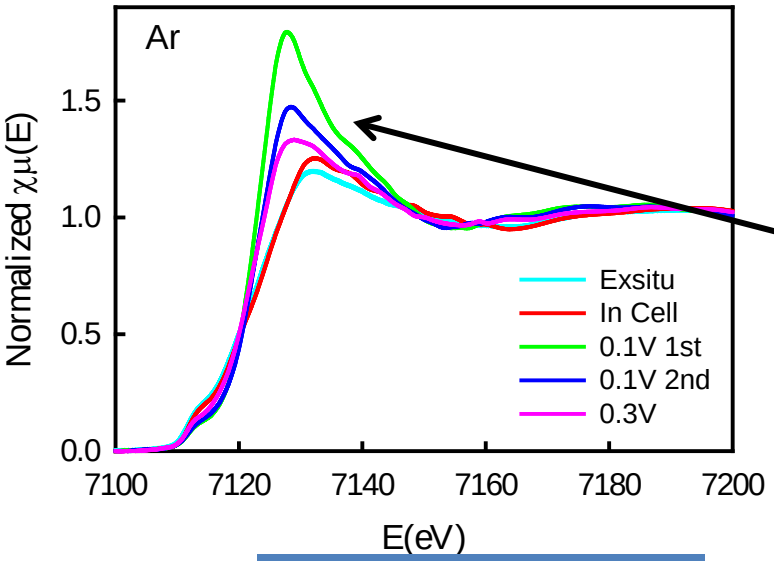


After 800°C pyrolysis active site is reminiscent of divacant defective regions on graphite

Fingerprint for Fe still ol

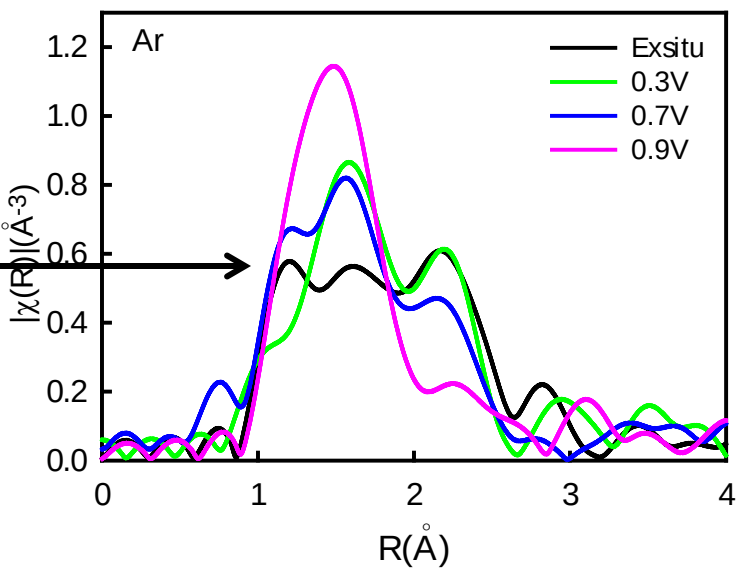


PANI_FeCo (LANL)

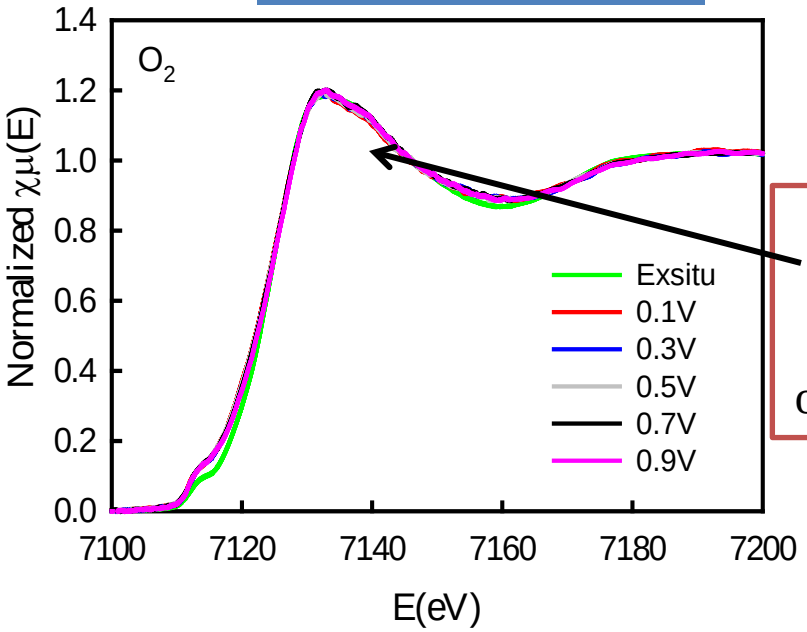


PANI/FeCo has Multi-Component nature.

LANL PANI/FeCo

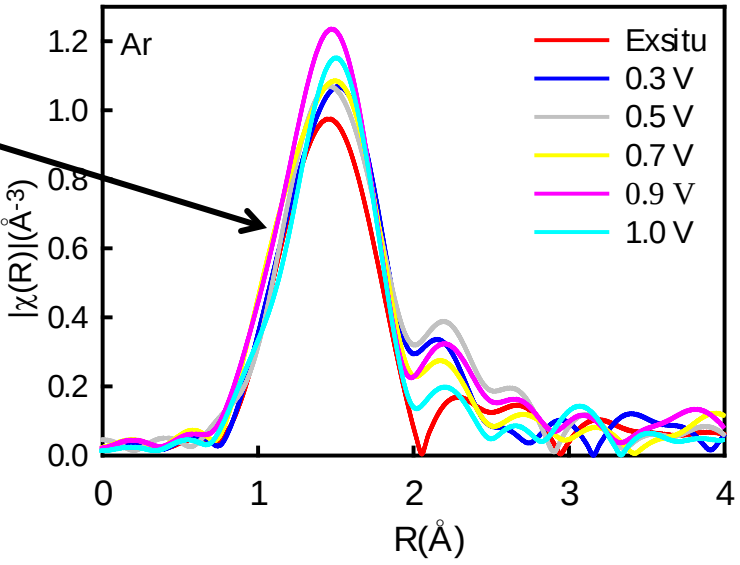


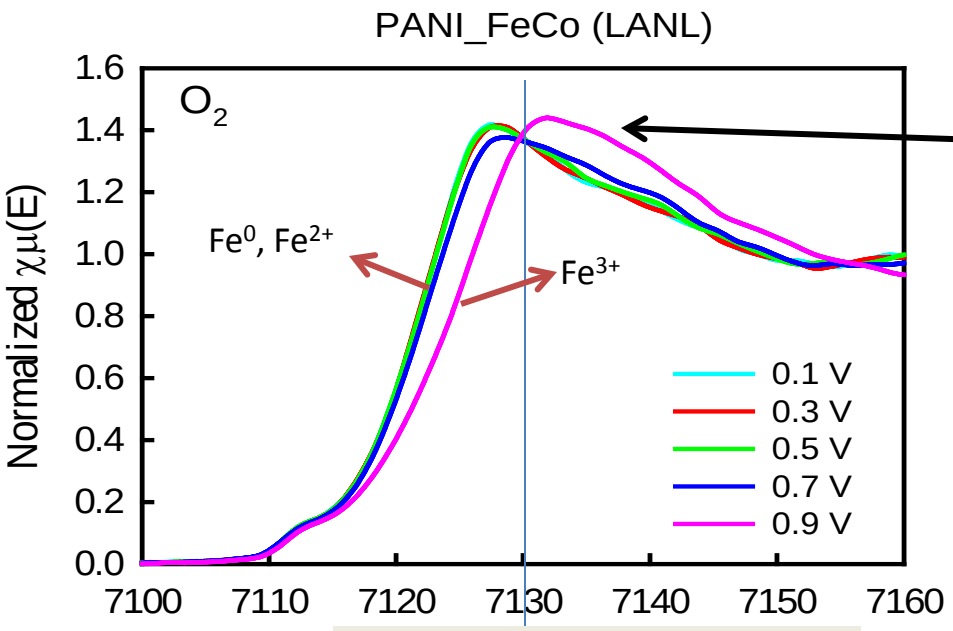
LANL-2



LANL-2 appears to be dominated by one component.

LANL-2



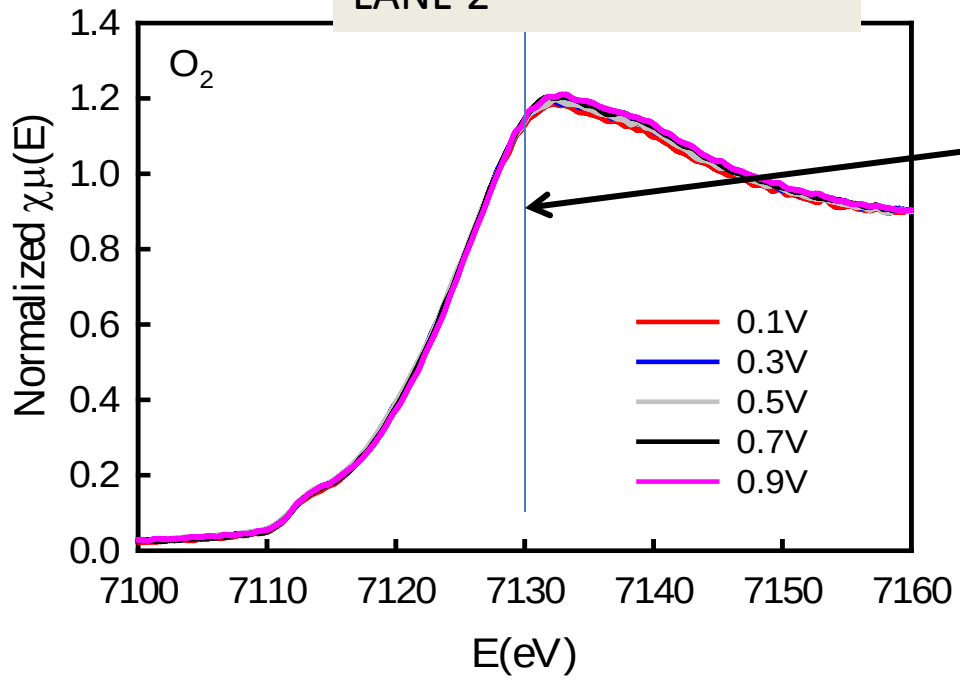


A significant shift at 0.9 V

LCF	Fe	FeO	Fe_2O_3
exsitu	40%	0	22%
0.3 V	19%	23%	17%
0.9 V	5%	5%	37%

A large amount of Fe NPs initially.

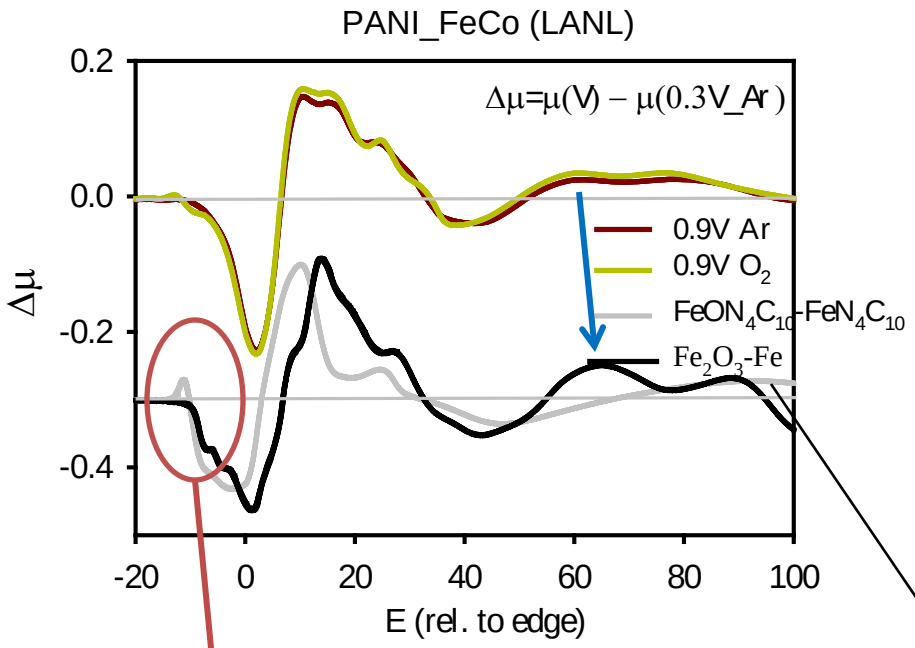
LANL-2

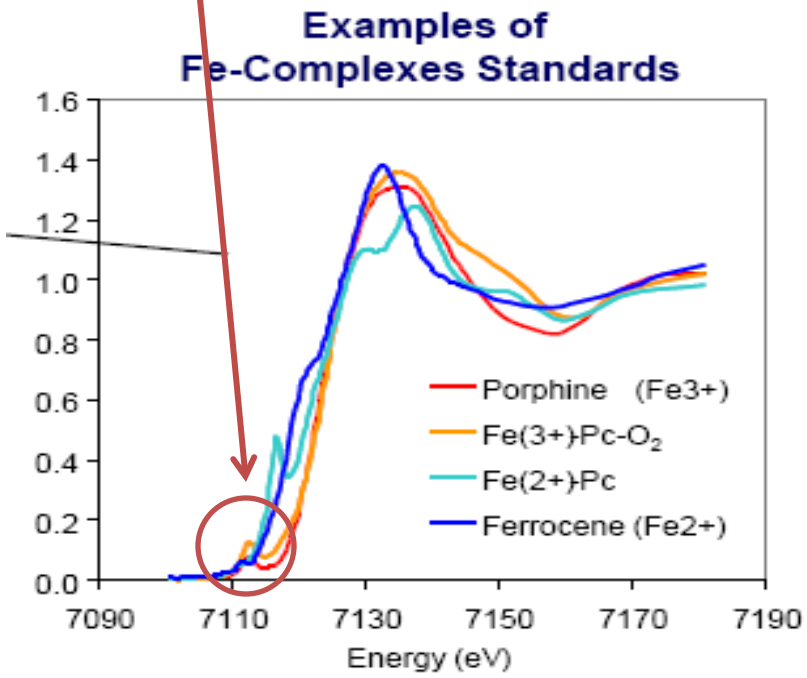


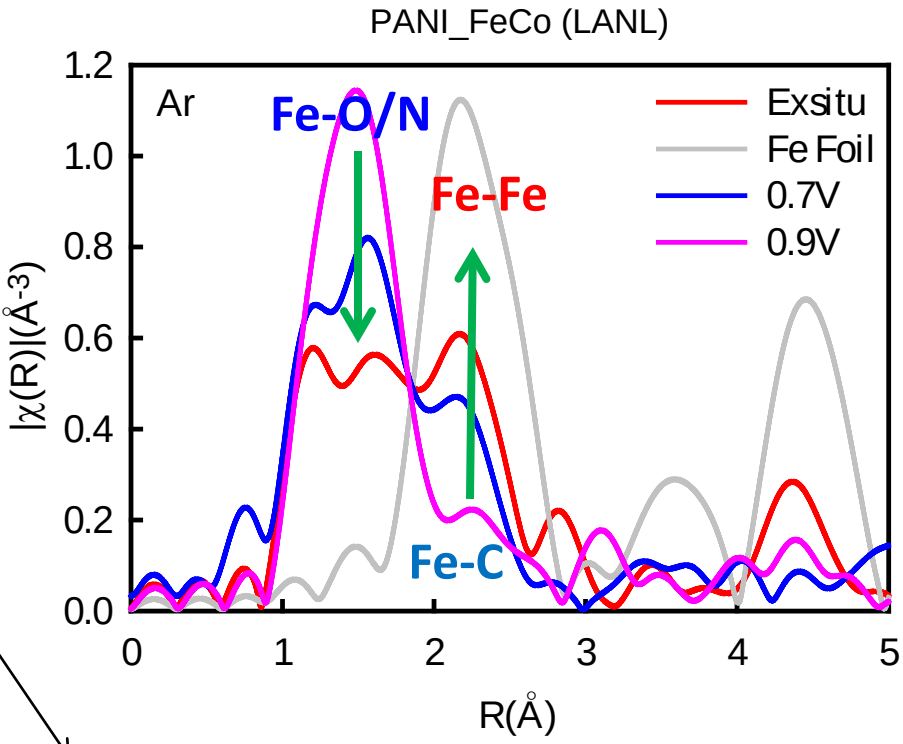
Non-significant shift observed, spectra show the domination of Fe^{3+}.

LCF	Fe	Fe_2O_3
exsitu	0%	16%
0.3 V	7%	25%
0.9 V	11%	22%

No Fe NPs initially.







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

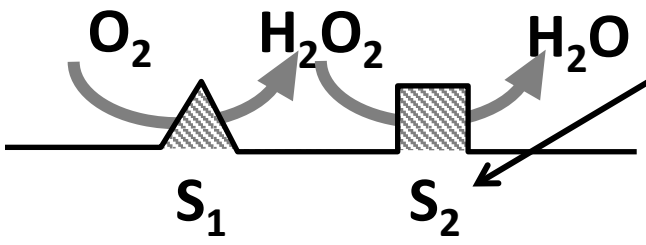
DFT (UNM): In acidic medium, H_2O_2 does not bind on Fe/Co-N_4.

The significant shift at 0.9 V is caused by oxidation of Fe NPs (and/or FeO) but not FeN_4.

Proposed mechanism

for LANL PANI/FeCo and others

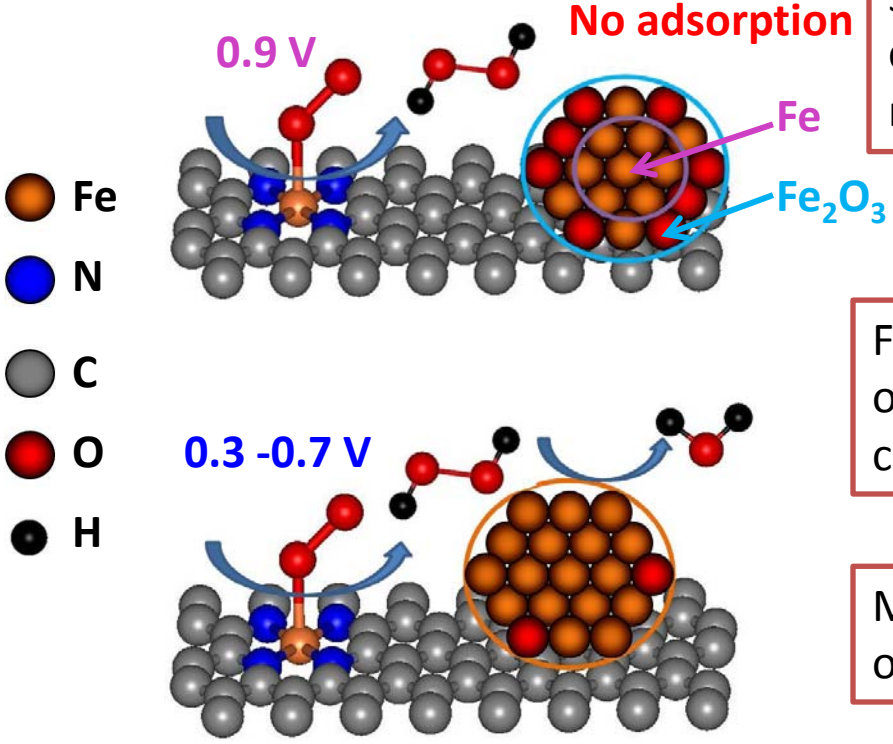
Dual site consequential:
2 x 2e- bifunctional mechanism



$Fe + H_2O_2 \rightarrow Fe_2O_3\ (Fe(OH)_3) + H_2O$

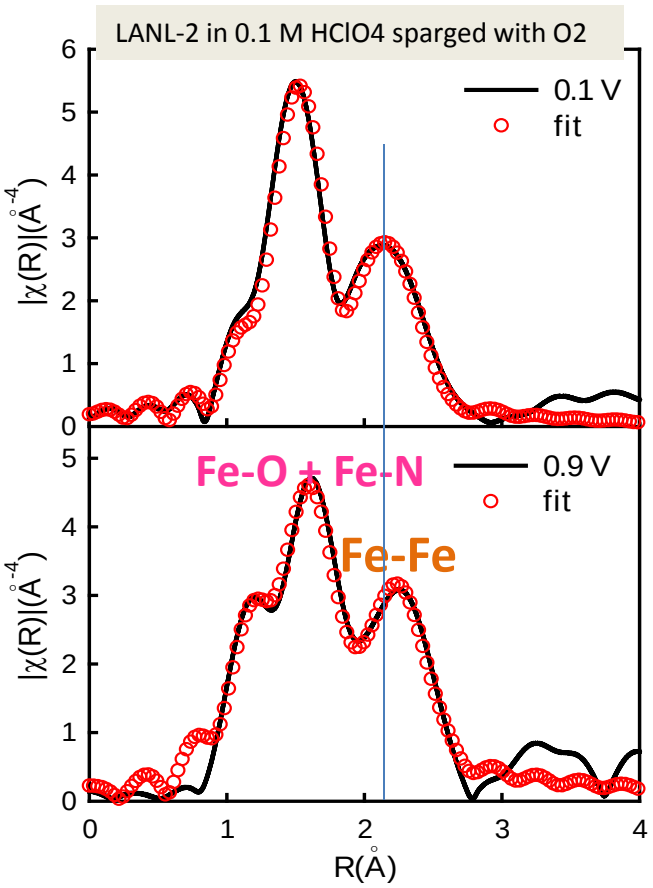
0.9 V: stabilized Fe_2O_3 inhibits the second step*

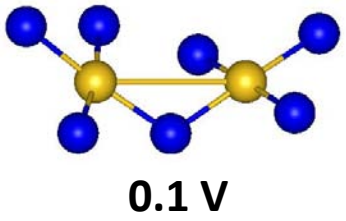
* Fe_2O_3 is very stable and cannot be dissolved sufficiently in acid to form Fe^{2+} or Fe^{3+}. On the contrary, FeO or Fe_3O_4 can be dissolved in the reduced state.



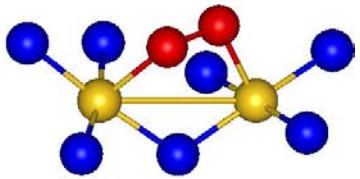
Further experiments (XPS) to clarify the content of the material before and after the cycling to confirm the transition between Fe and Fe_2O_3.

Multi-component nature make EXAFS analysis of Fe K-edge spectra virtually impossible





0.1 V



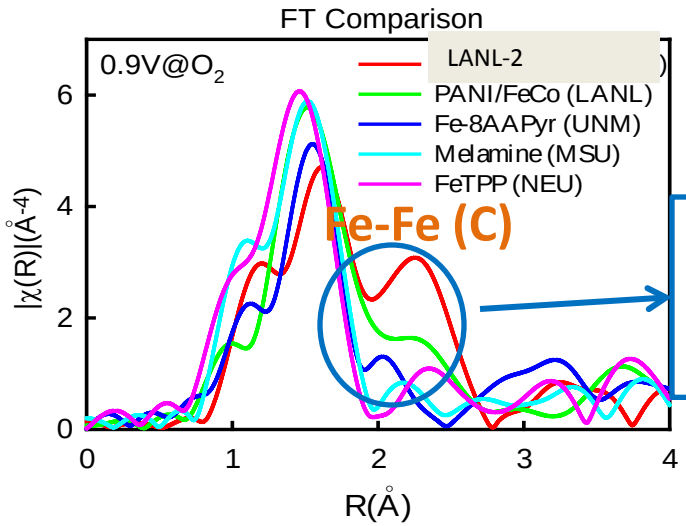
0.9 V

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

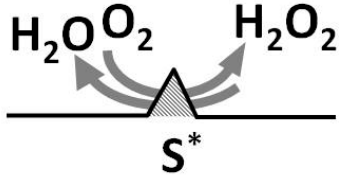
This distance is not from Fe NPs because:

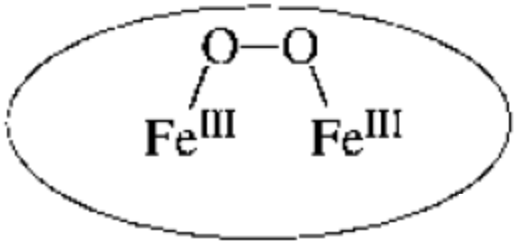
1. Non-significant edge shift.
2. No Fe NPs initially.
3. No increase in the first peak, but slight increase of Fe-Fe BD at 0.9 V.
4. Sustained Fe-Fe peak at 0.9 V.
5. The better performance.

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



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

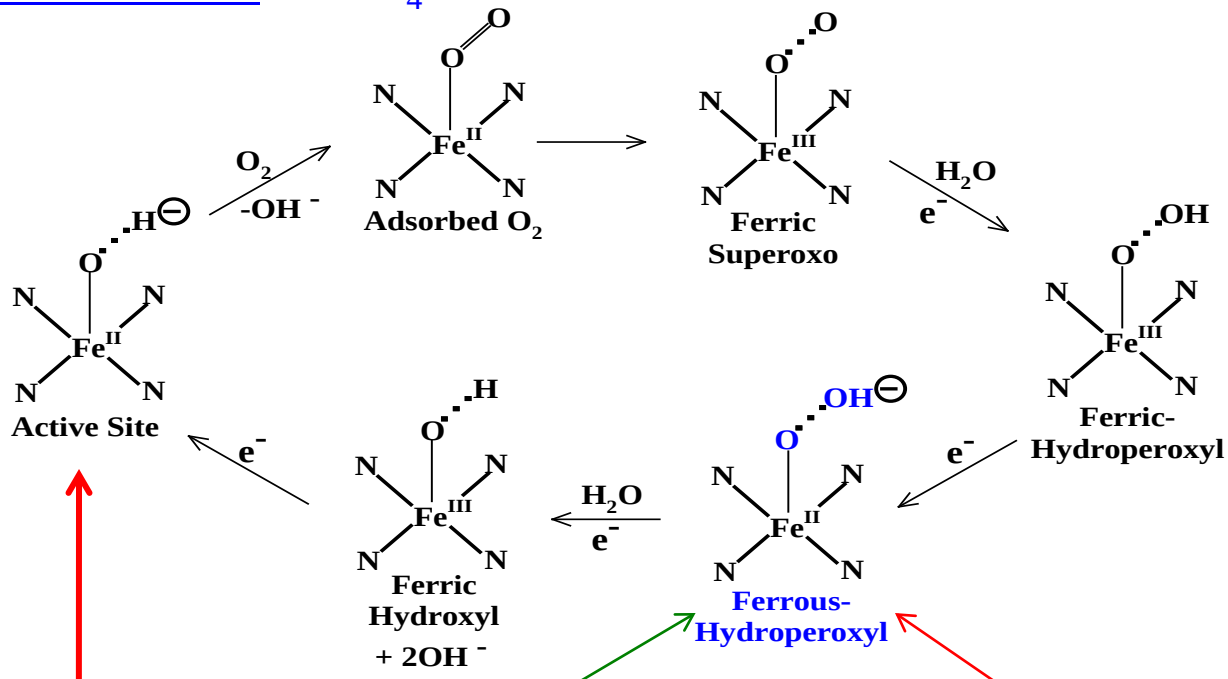


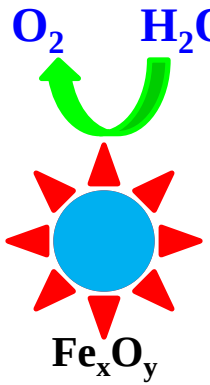


*Jungwon Hwang, et al., Science 287, 122 (2000)

Oxygen Reduction Mechanism on Fe-N_4 Sites

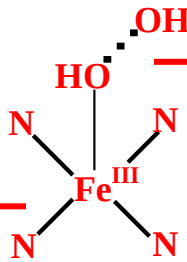
In Alkaline Media – Fe-N_4 sites are true $4e^-$ sites





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

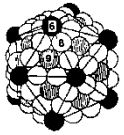
In Acidic Media



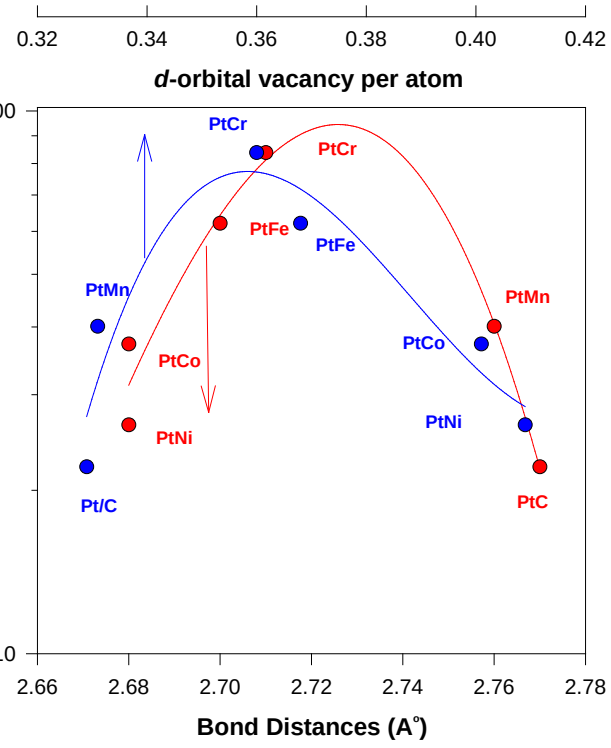
???

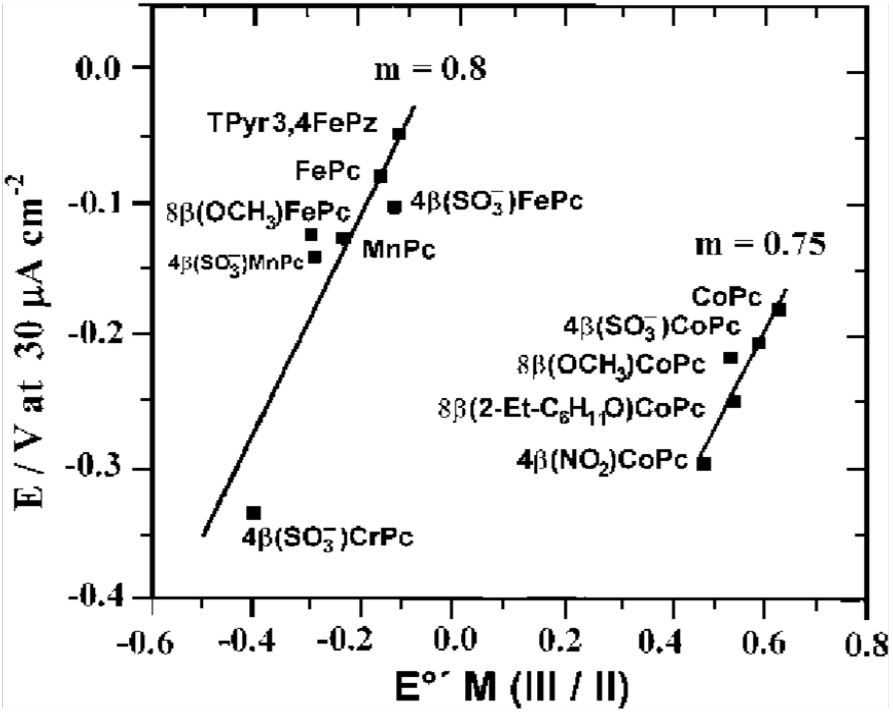
Fe-N_4 sites predominantly yield peroxide in acidic media

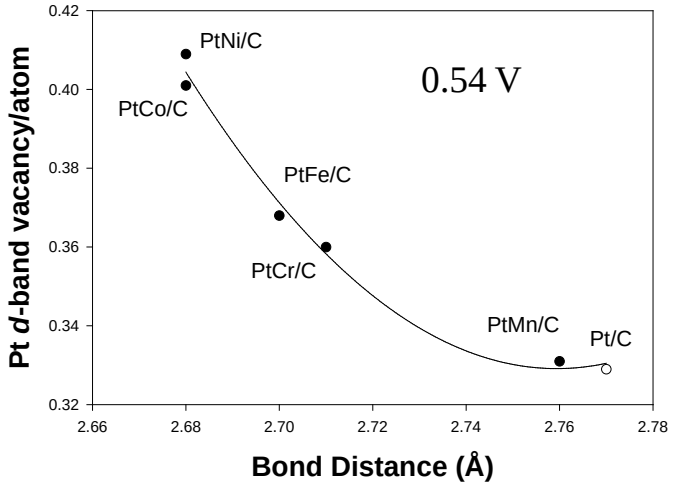
Do Volcano Curves Apply?



Pt and Pt Alloys







Summary Slide

Evolution studies of ORR active sites as function of pyrolysis temperature in FeTPP structures suggest:

- Direct correlation of Fe2+/Fe3+ redox potential shift (of FeN4 center) with temperature, and ORR onset
- In-situ XAS suggest incorporation of Fe-N4 moieties into graphene layer (upon high temperature treatment) are the active sites
- Presence of other Fe-moieties (Fe-metallic/FexOy) – unstable in acid/no impact on catalytic activity

LANL PANIFeCo catalyst – at least two stable Fe-moieties present – FeN_4/FeN_{2+2} and Fe-metallic/FexOy –both seem to play a role in ORR activity (dual 2x2e mechanism??) – changes of the FT peaks (Fe-Fe, Fe-N/O) together with Δμ signals supports the oxidation of metallic form of Fe and the redox behaviors.

Possibility: *passivation/oxidation of the secondary active site (Fe/Fe_xO_y) at high potentials.*

(Fe-structures similar to most analyzed MNC catalysts with similar ORR performance)

LANL PANI+CN-Fe – same as above, presence of FeNx and Fe-metallic species observed, with much higher input of the last versus other catalysts at high potentials

– no energy shift and no FT peak changes in-situ XAS suggests:

- Possibility1: no passivation of the metallic Fe form through oxidation
- Possibility2: FeN_{2+2} structure when Fe center in mainly in 3^+ form from the start
- Possibility3: 'bridge' Fe-Fe structure – direct 4e mechanism possible