# DFT Modeling of PGM-free Catalyst Activity and Durability

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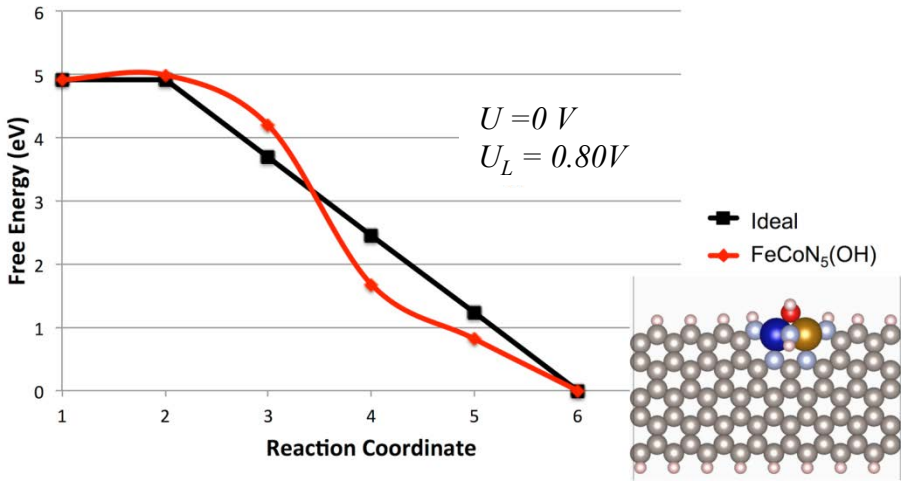


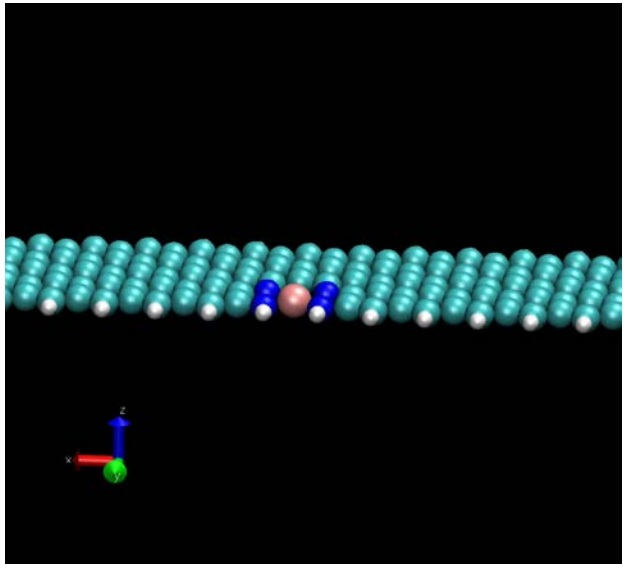

*LA-UR-16-25411*

# Summary

- Modeling Goals
- Overview of LANL Modeling Capabilities
- Which Structures?
- Activity Approach
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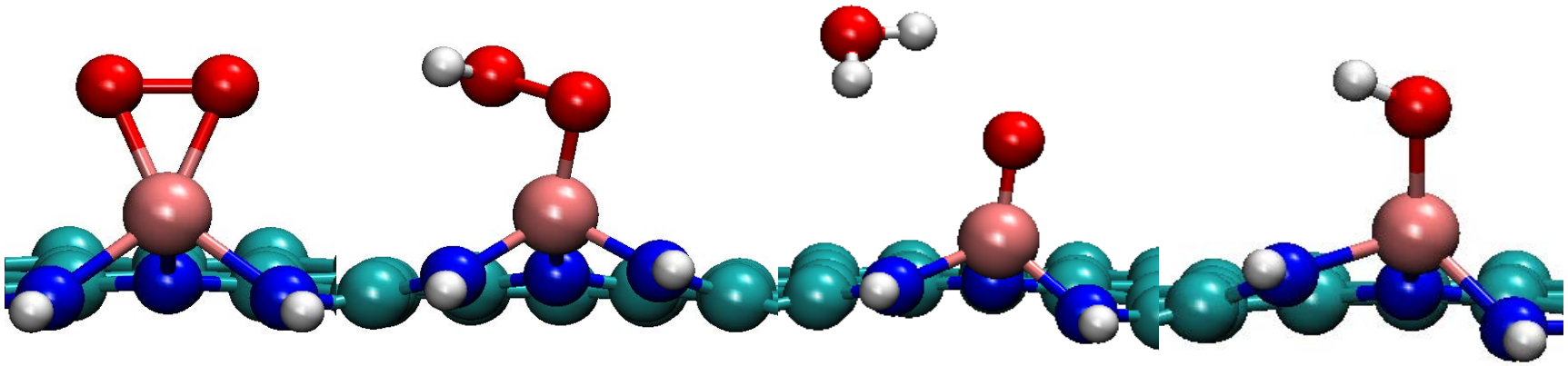
- Durability Approach
  - First-principles Molecular Dynamics
- Vibrational Signatures
  - Linking Structure to Signature

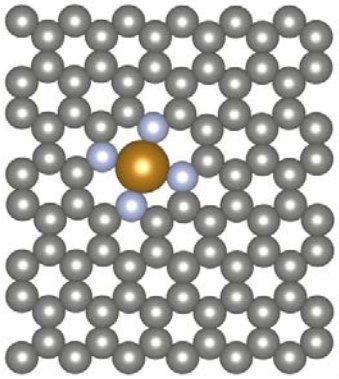
- Paths Forward
  - Replacing Fe
  - Ligand Modification
  - Strain Engineering



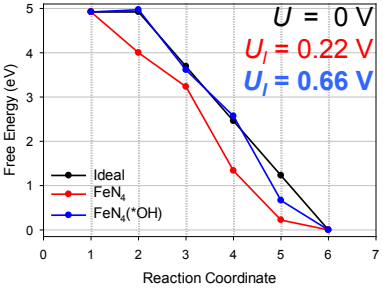
# Modeling Goals

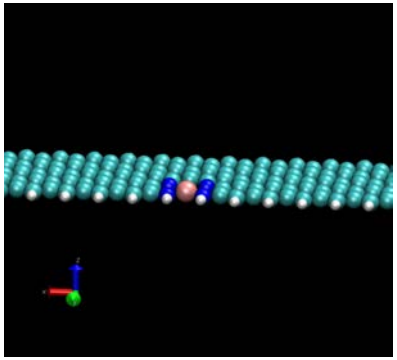
- Use modeling approaches to:
  - Guide synthesis of improved PGM-free electrocatalysts
  - Aid characterization of synthesized materials by linking atomic scale structure to experimental spectroscopic signatures and observed properties

- Utilize automation to speed throughput of calculations
- Leverage software developed as part of the Materials Genome Initiative (MGI) Generate structure:property library accessible via web portal



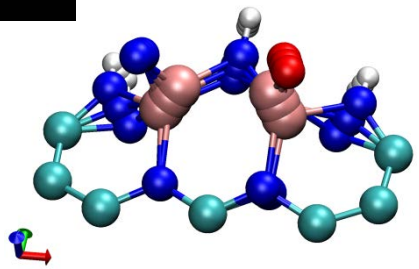
Activity Descriptor



*Knock on displacement threshold energy (?)*

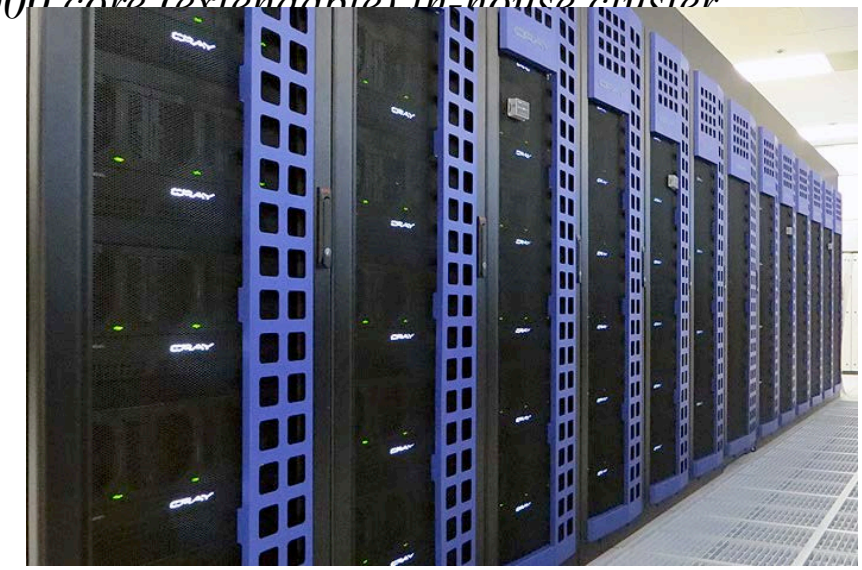
Durability Descriptor



Vibrational Signatures

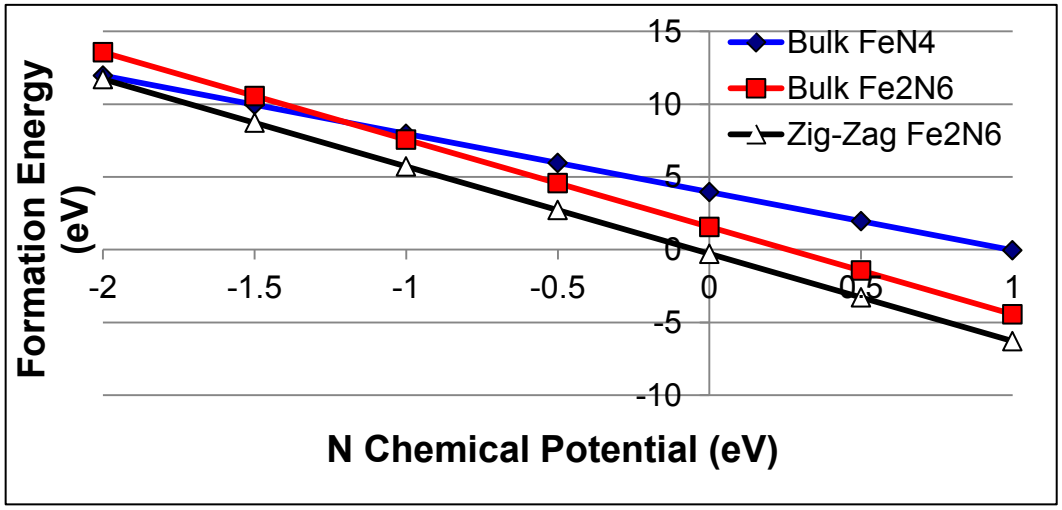
# LANL Modeling Capabilities

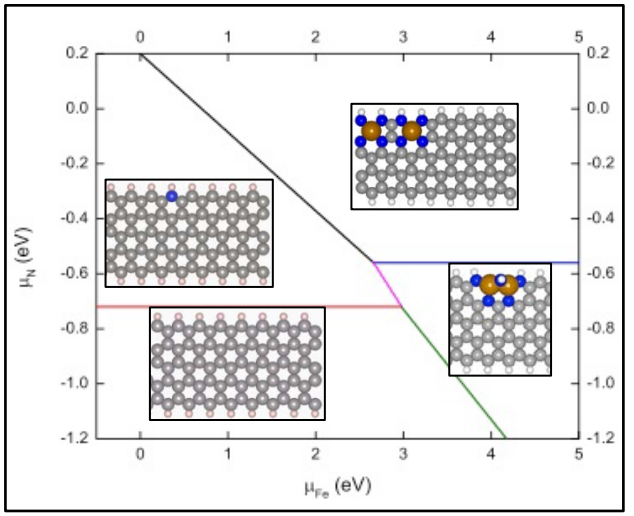
- Combination of computing facilities and theory expertise for materials modeling
- Utilized codes:
  - *Vienna ab initio Simulation Package (*VASP)
  - Amsterdam Density Function Suite (ADF)
  - Gaussian09
  - Large-scale Atomic/Molecular Massively Parallel Simulator (LAMMPS)
- Computing Resources:
  - *LANL IC Wolf Cluster* – 9856 Intel Xeon cores, 205 Tflops/s (peak)
  - *LANL IC Moonlight Cluster* – 4928 Intel Xeon cores + 616 GPUs, 488 Tflops/s (peak)
  - *LANL IC Pinto Cluster* – 2464 Intel Xeon cores, 51 Tflops/s (peak)
  - *Dedicated 1000 core (extendable) in-house cluster*



# Active Site Structures

- Which structures to consider?
  - Guided by relative thermodynamic stability determined via Metropolis Monte Carlo search and DFT studies
    - N-coordinates metal
    - N-metal complexes have lower formation energies at edges
    - Edge-N-metal complexes thermodynamics driven to form small clusters
  - Previously proposed structures
  - Bio-mimetic guidance
  - Combinations and permutations of above based on modeling insight
    - Spontaneous ligands

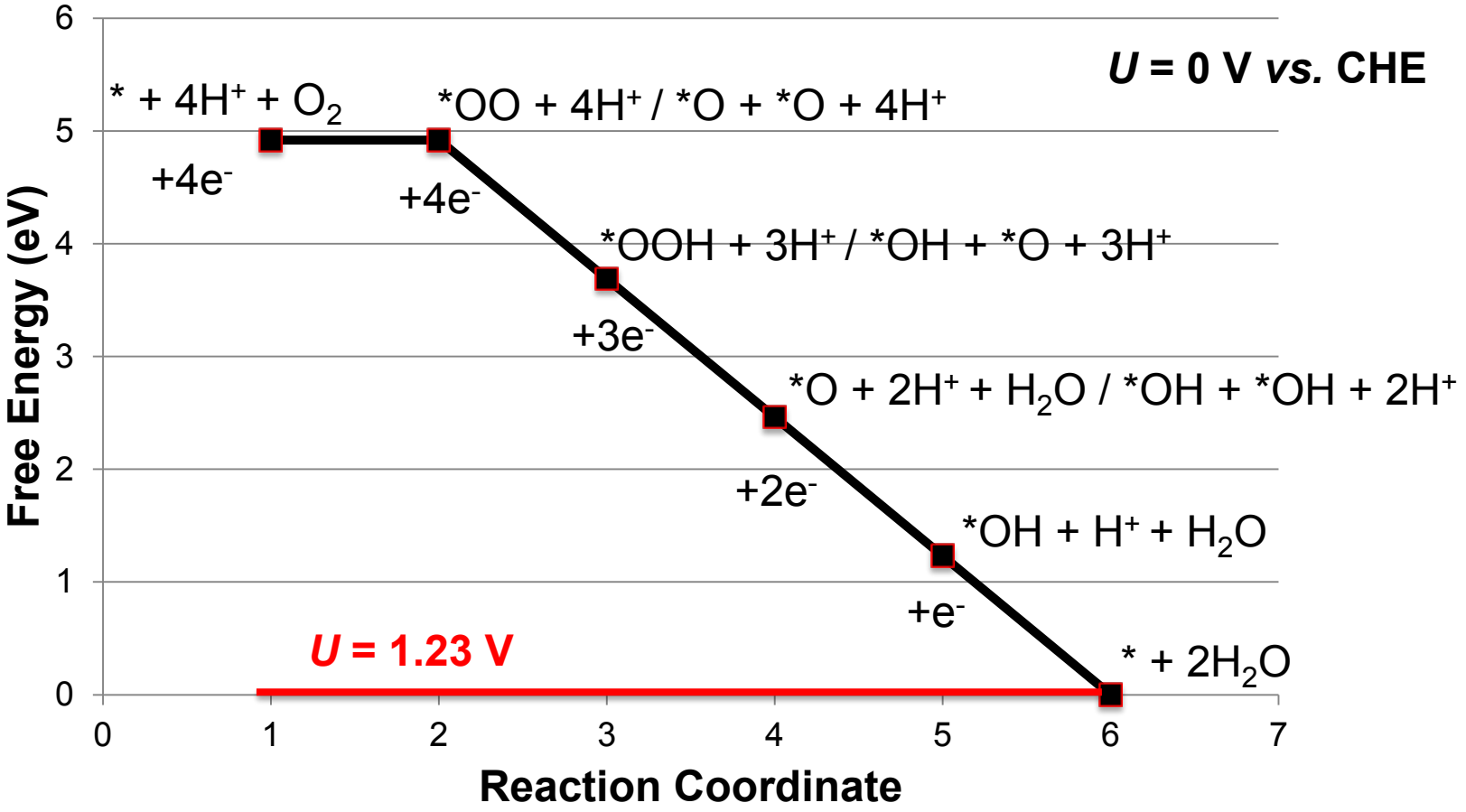



Holby and Taylor, *App. Phys.* Lett., **101**, 0641012, 2012; Holby, Wu, Zelenay, and Taylor, *ECS Trans.* **50**, 1839, 2013; Holby, Wu, Zelenay, and Taylor, *J. Phys. Chem. C*, **118**, 14388, 2014; Holby and Taylor, *Sci. Rep.* **5**, 9286, 2015; Holby and Zelenay, *Nano Energy*, in Press (2016).

# Activity Approach: Calculation of PGM-free ORR Activity via DFT

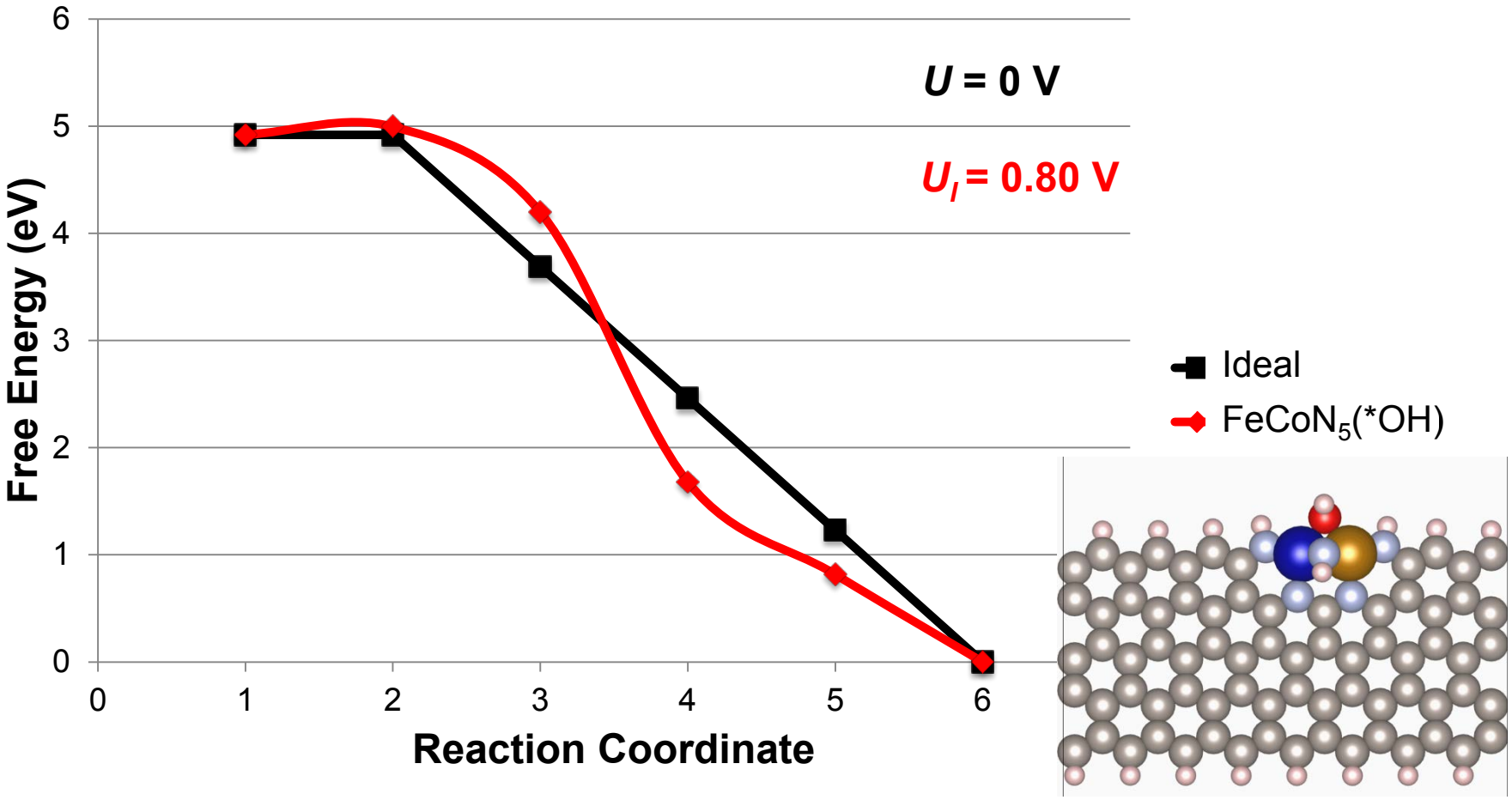
$$O_2 + 4H^+ + 4e^- \rightarrow 2H_2O \qquad U_{rev} = \text{reversible potential} = 1.23\ V$$




Nørskov *et al., J. Phys. Chem. B,* **108**, 17886, 2004; Anderson, *Phys. Chem. Chem. Phys,* **14**, 1330, 2012; Studt, *Catal. Lett.*, **143**, 58, 2013.

Calculation of **maximum exergonic potential**, $U_l$, as ORR activity descriptor; computational hydrogen electrode (CHE); DFT of ORR intermediate binding energies

# Activity of Predicted Stable Structures – $FeCoN_5$(*OH)



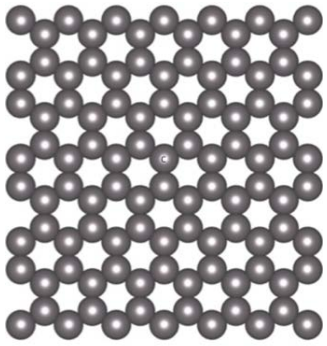

- 2 $FeCoN_5$(*OH) defects more thermodynamically stable than $Fe_2N_5$(*OH) + $Co_2N_5$(*OH)
- $FeCoN_5$(*OH) + *OO → *OOH is potential determining step

Holby and Taylor, *Sci. Rep.*, **5**, 9286, 2015.

# Durability Approach: First-Principles Molecular Dynamics

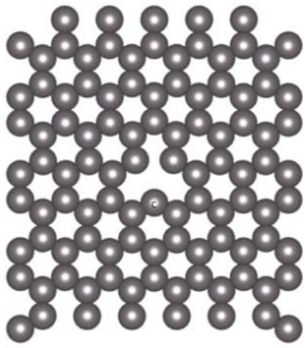
- Need computational descriptor of durability for application of high-throughput modeling
- Complex corrosion or poisoning phenomenon: includes kinetic barriers, defects, adsorbates, *etc*.
  - How to best simplify? Can simplified model capture complex behavior?

Graphene



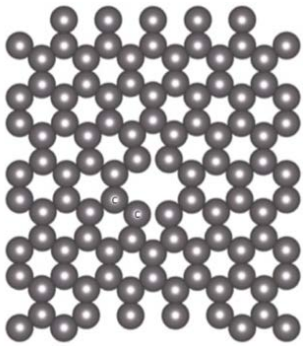
$E_{KODTE}$ = 185 kV

Monovacancy



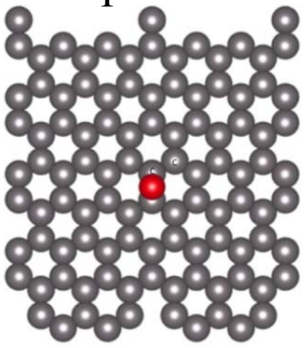
$E_{KODTE}$ = 135 kV

Divacancy



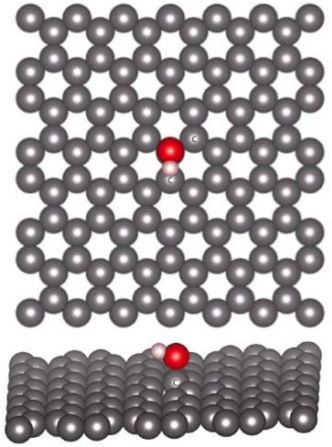
$E_{KODTE}$ = 155 kV

Epoxide



$E_{KODTE}$ = 170 kV

Hydroxide



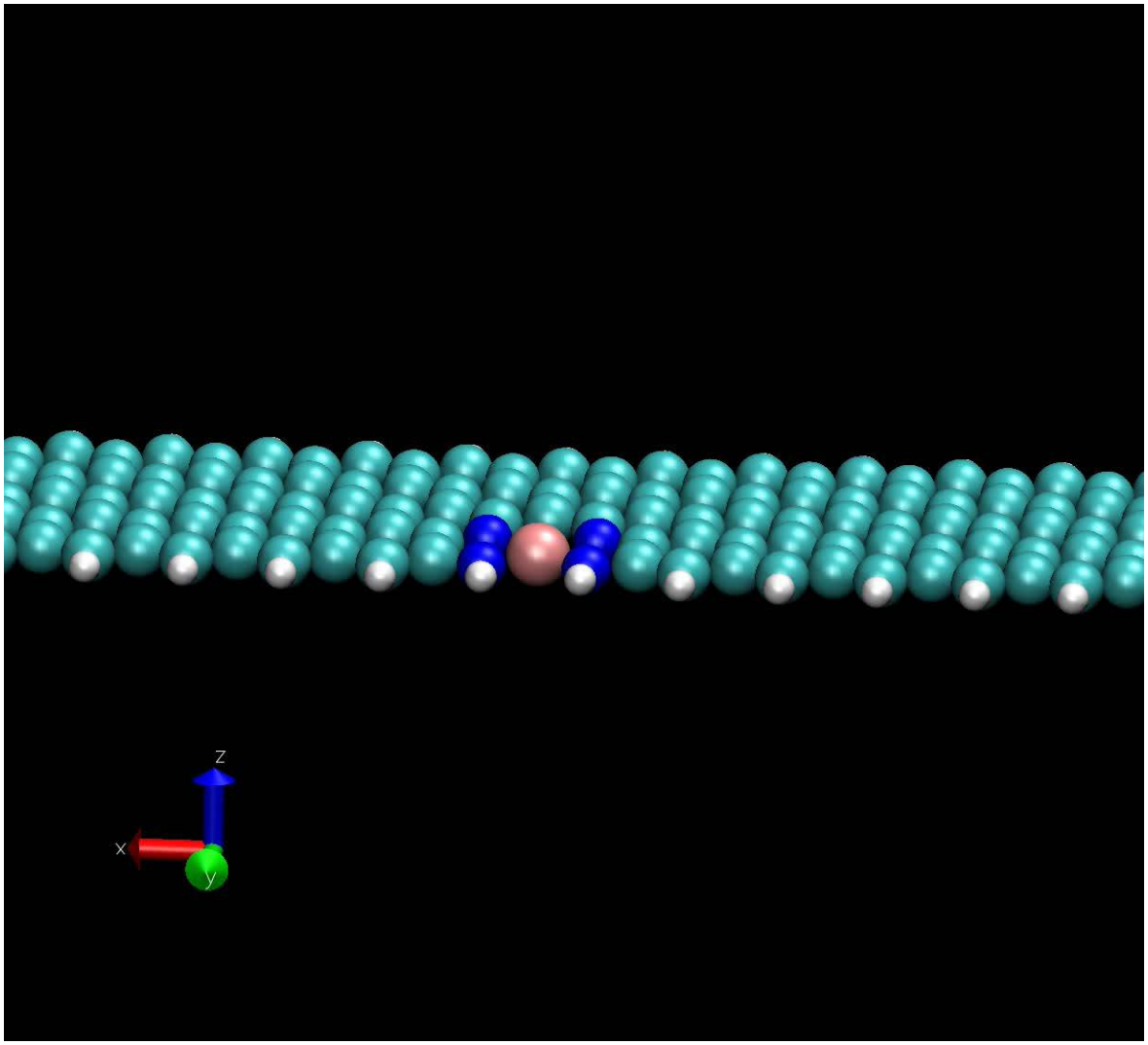
$E_{KODTE}$ = 160 kV

- Tested beam damage model (knock on displacement threshold energy, $E_{KODTE}$) for C neighboring defects and adsorbates as initial test of durability descriptor
- Further testing / validation required (ENABLE synthesis / modeling comparisons and Mn/Fe/Co test)
- *Plausible durability descriptor hypothesized and initial simulations prove computational accessibility in high-throughput environment*

Holby, *Fuel Cells,* in press.

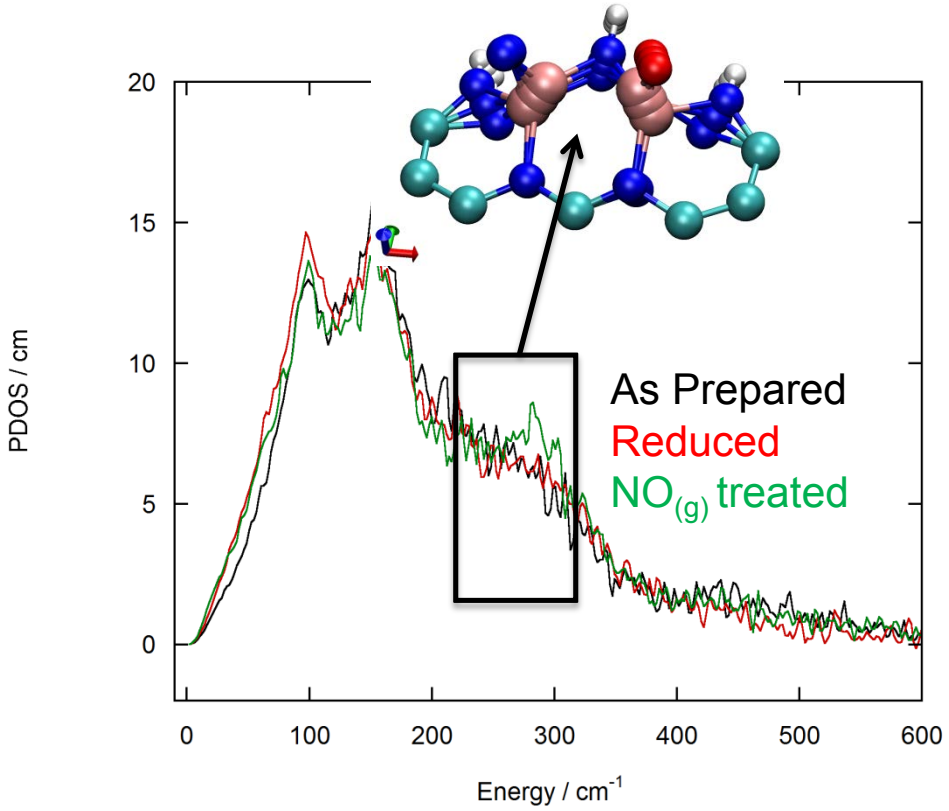
# Durability Approach: First-Principles Molecular Dynamics

- Simulation of $e^-$ hitting edge N of an $FeN_4$ edge structure, displacing edge NH structure
- N atom most susceptible to removal for both $FeN_4$ edge (124 kV) and bulk (150 kV)



# Vibrational Signatures

- Finite-difference method after relaxation with stricter convergence criteria (6N single point DFT calculations required)
- Gives zero point energy (ZPE), vibrational entropy, and vibrational normal modes
- Normal modes with and without probe molecule can be used for comparison to experimental techniques (*e.g.,* Nuclear Resonance Vibrational Spectroscopy, NRVS)




$Fe_2N_5$ active site model (presumably reduced from $Fe_2N_5$(*OH) ) predicts both NO dissociation as well as relevant NRVS peaks… do other structures?

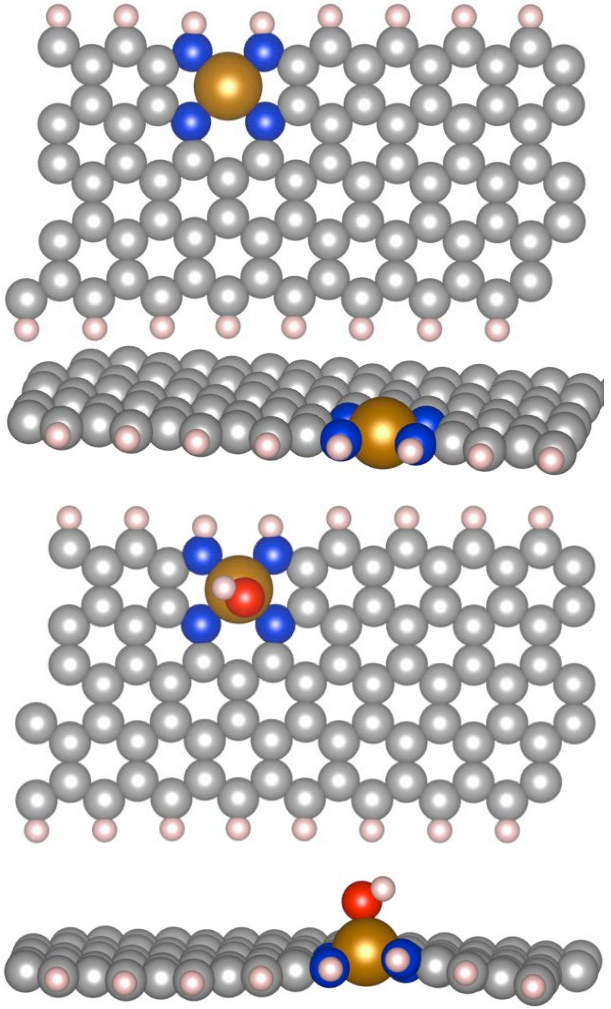
# Paths Forward: Replacing Fe

- Do otherstructures spontaneously form an *OH ligand and does it affect ORR activity? – Use Me-$N_4$ edge structure from stability study
- What role does *Me* species (*Me* = Mn, Fe, Co, Ni) play in activity and reaction pathway?

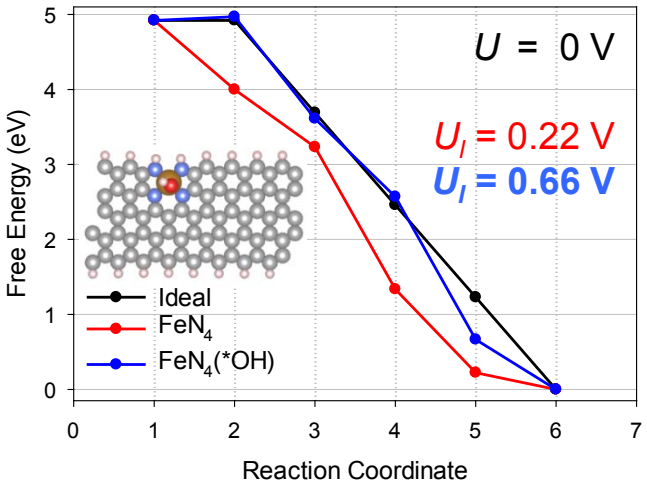
Calculated *via* Vienna *ab initio* Simulation Package (*VASP*) on 5×8 C pair ZZ edge graphene nanoribbons, PBE-GGA with Grimme dispersion correction and 15 Å vacuum with 5×1×1 K-pt mesh and 400 eV plane-wave energy cutoff

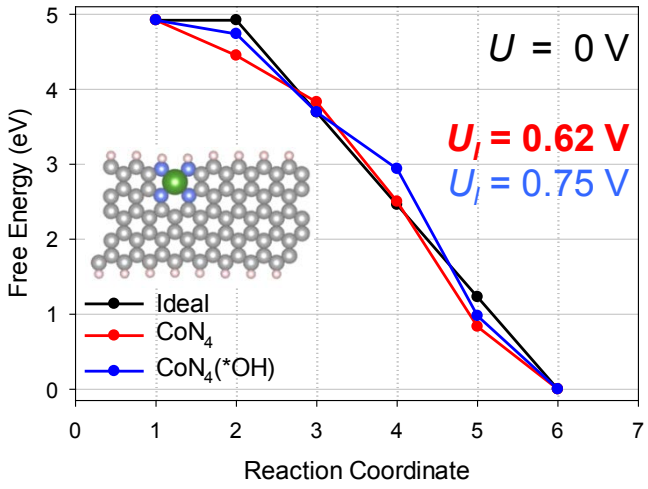
## Considered Active-Site Structures

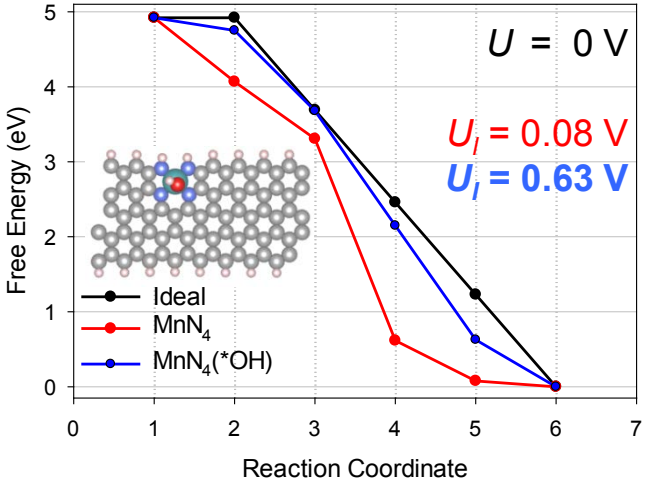
| | |
|---|---|
| $MnN_4$ – ZZ | $MnN_4$(*OH) – ZZ |
| $Mn_2N_5$ – ZZ | $Mn_2N_5$(*OH) – ZZ |
| $FeN_4$ – ZZ | $FeN_4$(*OH) – ZZ |
| $Fe_2N_5$ – ZZ | $Fe_2N_5$(*OH) – ZZ |
| $CoN_4$ – ZZ | $CoN_4$(*OH) – ZZ |
| $Co_2N_5$ – ZZ | $Co_2N_5$(*OH) – ZZ |
| $NiN_4$ – ZZ | $NiN_4$(*OH) – ZZ |

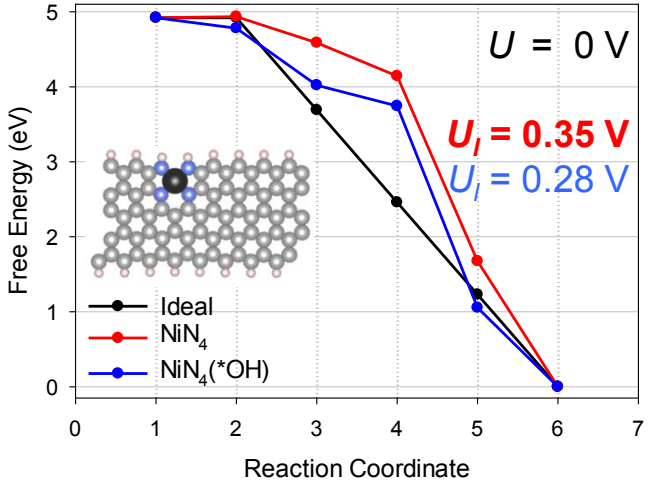


# Theoretical Modeling of Fe-free ORR Potential Energy Surfaces



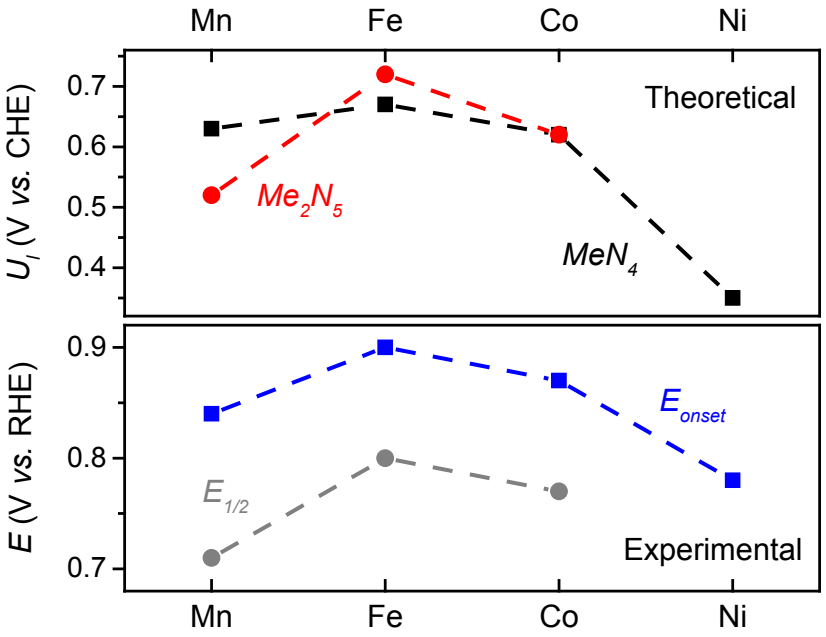



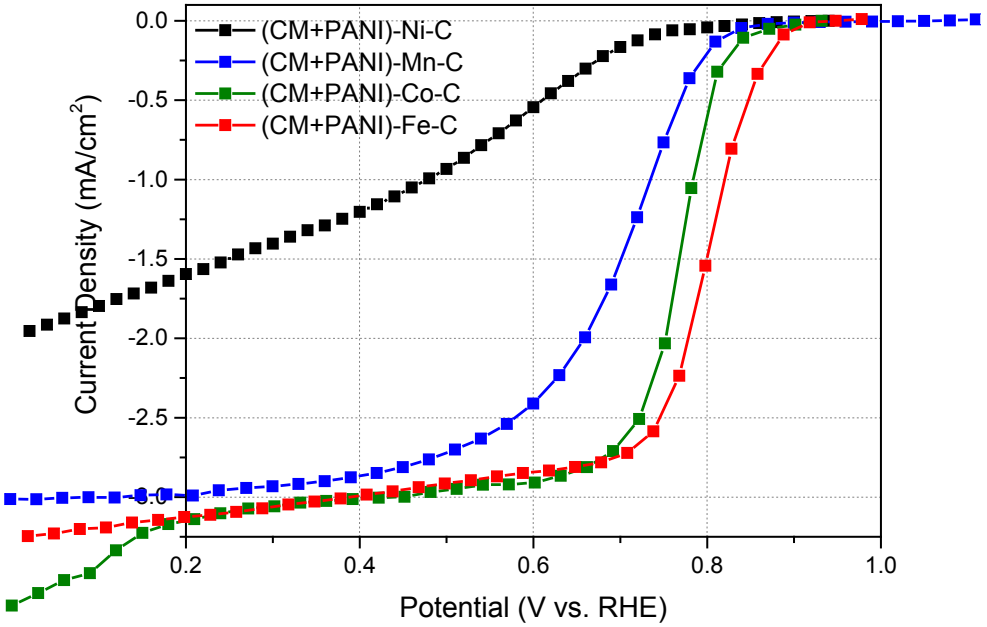

- Calculation of **ORR pathway** → persistent *OH for edge $MnN_4$ and $FeN_4$ (but not $CoN_4$ or $NiN_4$)
- Activity descriptor, $U_l$, prediction without *OH modification: $U_{l,Co} > U_{l,Fe} > U_{l,Mn} > U_{l,Ni}$
- With *OH modification of Mn and Fe: $U_{l,Fe} > U_{l,Mn} \approx U_{l,Co} > U_{l,Ni}$

# Fe-free ORR Catalysts—Experiment and Theory

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




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




*OH modification determined to occur for $MnN_4$, $FeN_4$ and $Me_2N_5$

No *OH modification determined to occur for $CoN_4$ and $NiN_4$

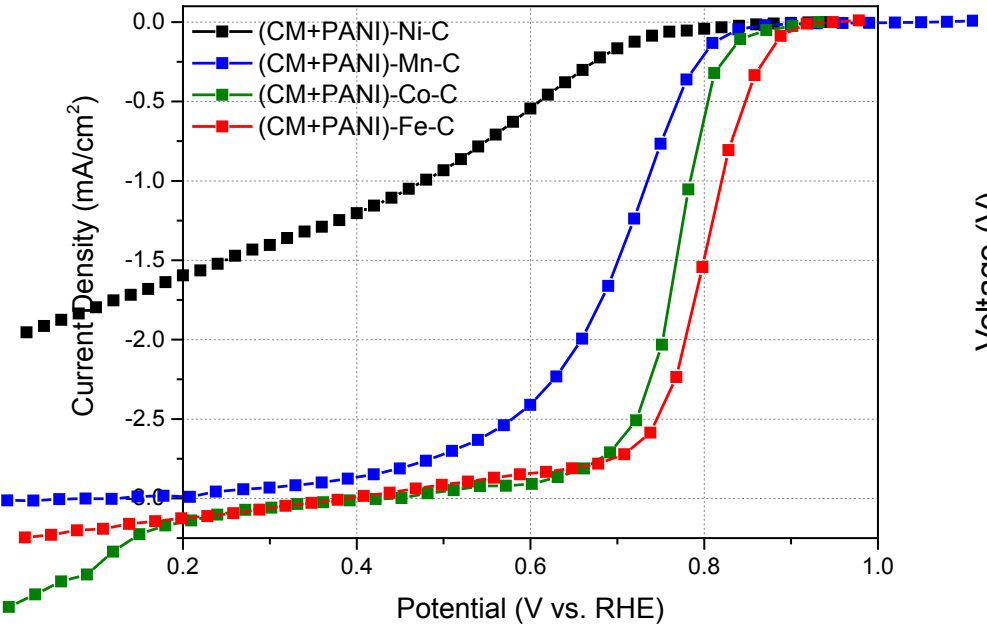
Theoretical prediction of spontaneous *OH ligand modification of active site structures explains shift in activity trend with *Me*-N-C catalysts

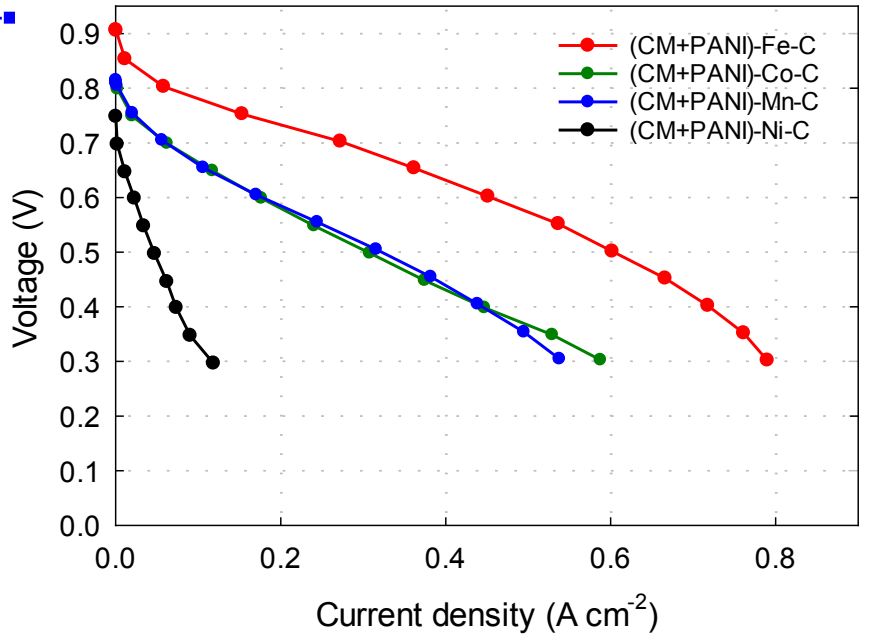
$$U_{l,Fe} > U_{l,Co} \geq U_{l,Mn} > U_{l,Ni}$$

# ORR Activity of (CM+PANI)-*Me*-C Catalysts: RDE and Fuel Cell

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

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

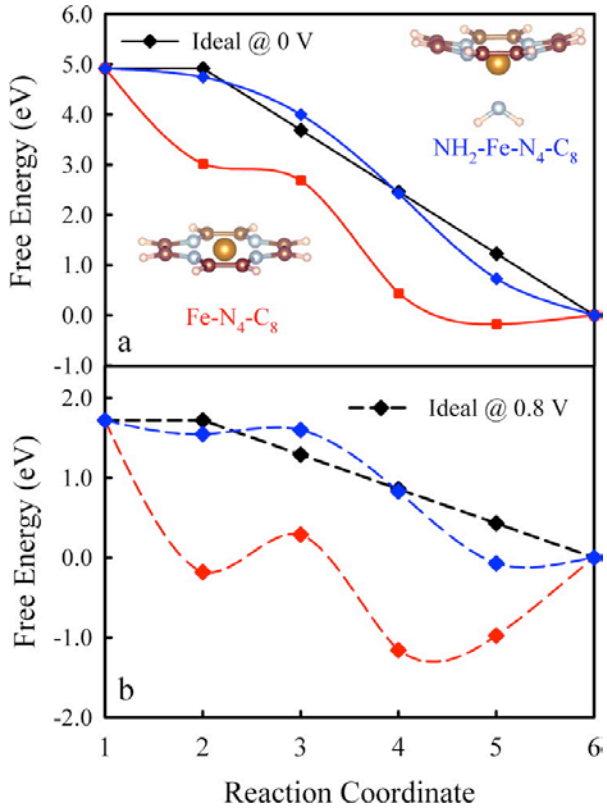


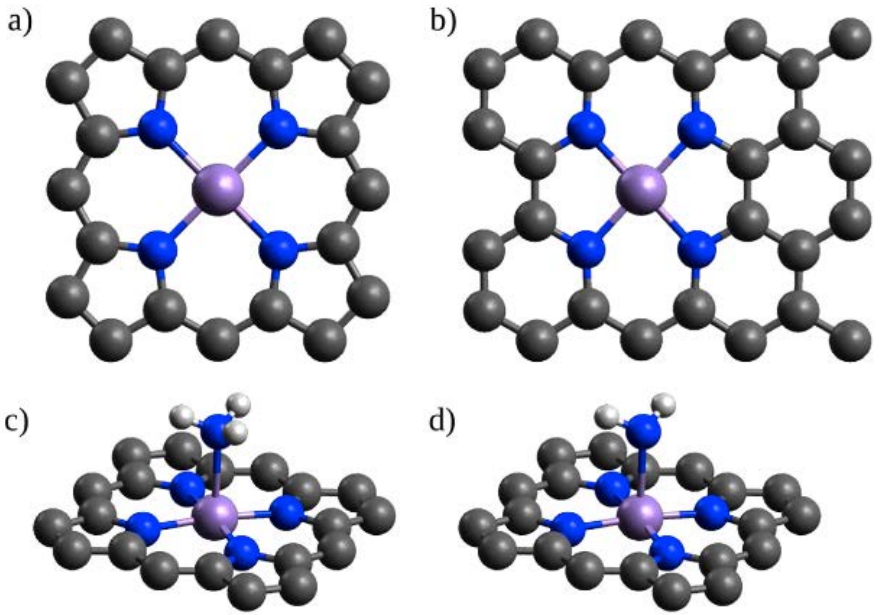

Promising activity observed from Mn- and Co-based catalysts as alternative to Fe-free ORR catalysts, but further development in MEA fabrication and catalyst design necessary to approach activity of Fe-based catalysts

# Paths Forward: Ligand Modification

- Ligands (spontaneously formed or otherwise) have been shown to be one path forward to improve electrocatalytic activity
- What *persistent* ligand might be added via synthesis to improve material performance?
  – OH and $NH_x$ suggested in literature




Jia, *et al., ACS Nano* **9**, 12496, 2015.



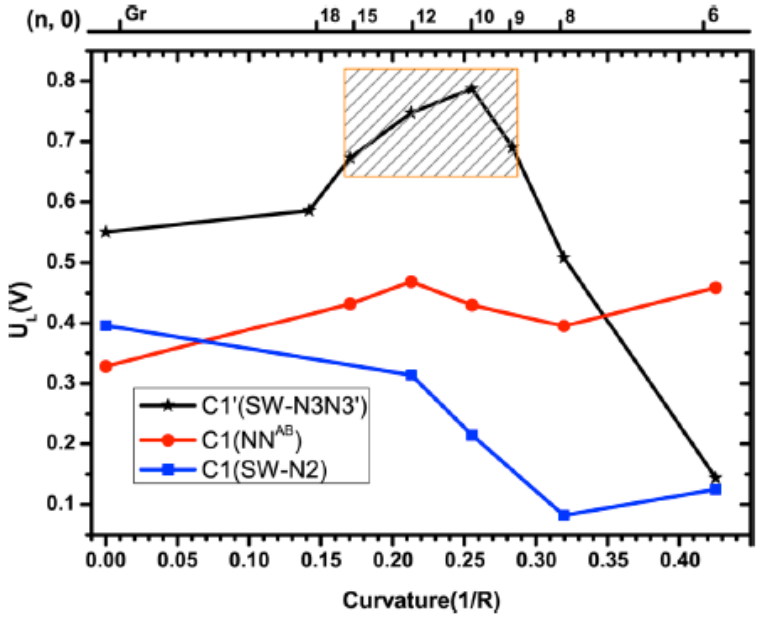

Busch, *et al., Nano Energy,* in Press. 2016.

# Paths Forward: Strain Engineering

- Strain modification of electrocatalyst sites proposed for a variety of other systems, including metal-free ORR catalysts and PGM

## CNT Curvature Effect

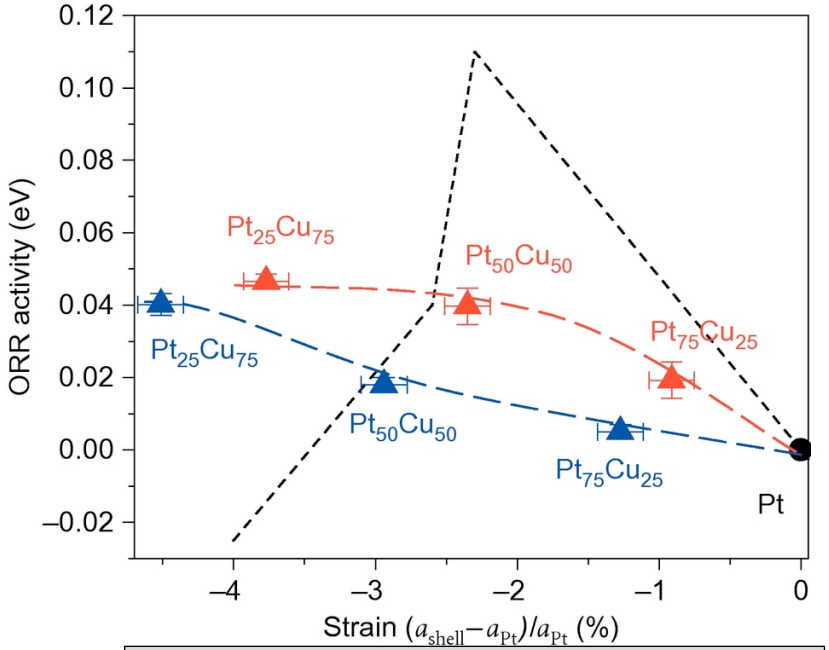
*"The ORR activity of this structure can be tuned by the curvature around the active site."*




Chai, *et al., JACS* **136,** 13629, 2014.

## Cu Induced Lattice Strain of Pt Core Shell Nanoparticles

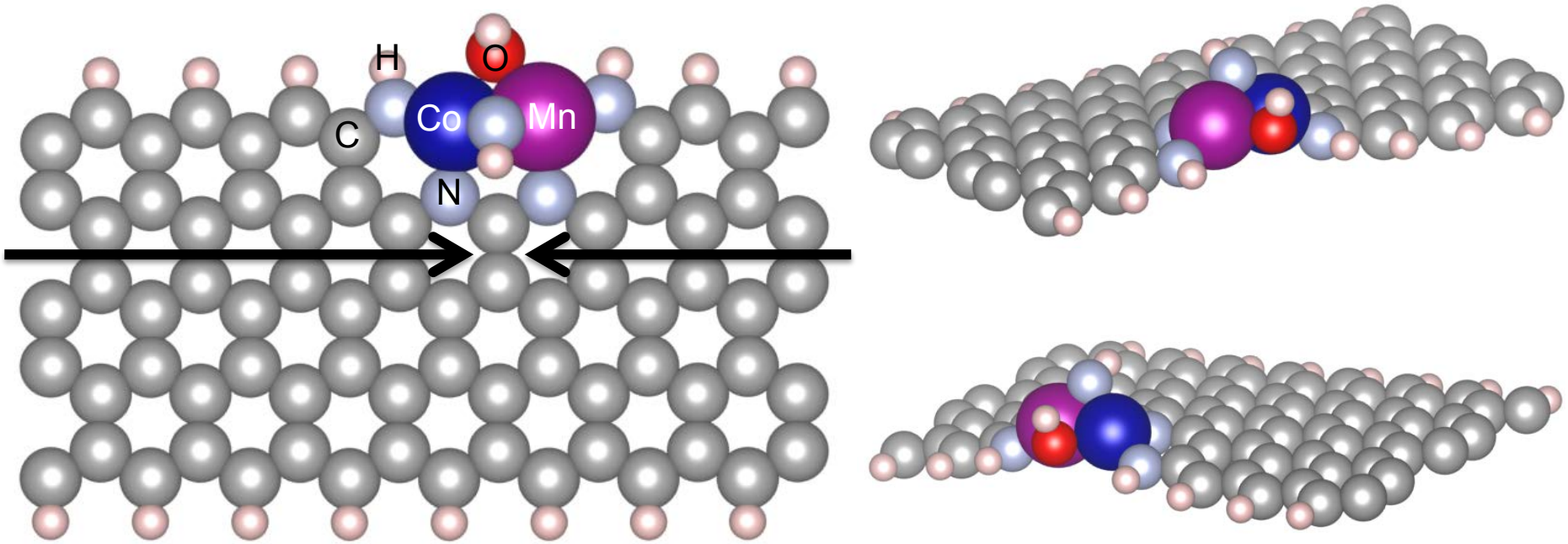
*"Moderate compressive lattice strain is predicted to enhance the rate of ORR catalysis."*




Strasser *et al., Nature Chemistry*, **2**, 454, 2010.

# Paths Forward: Strain Engineering

Strain Engineering of $MnCoN_5$(*OH)




- $MnCoN_5$(*OH) has the highest Fe-free $U_l$ value calculated so far ($U_l$ = 0.67 V)
- Compressive uniaxial strain of zig-zag nanoribbon leads to less strongly bound *O and *OH
- Variability of activity due to strain – suggests possible long-range structural effects on activity

*1% compressive uniaxial strain of $MnCoN_5$(*OH) structure increases calculated $U_l$ to 0.70 V and 2% compressive uniaxial strain increases calculated $U_l$ to 0.71 V*

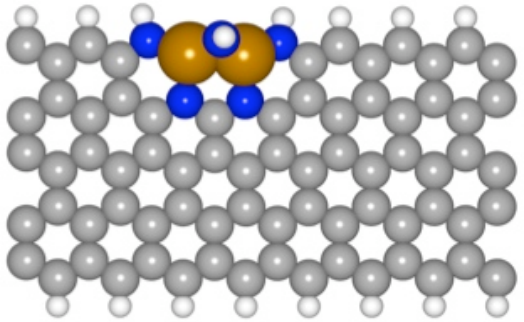
# Acknowledgements


**U.S. Department of Energy** for funding of “Advanced Cathode Catalysts” project through **Office of Fuel Cell Technologies (EERE)**

**Los Alamos National Laboratory Institutional Computing Program** for computational support.

# Backup Slides

# Activity of Predicted Stable Structures

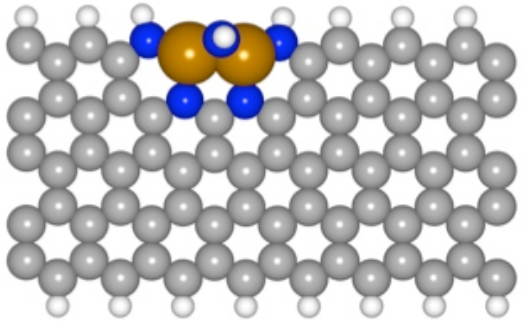





- $Fe_2N_5(*OH) + *OH \rightarrow H_2O$ is potential determining step

Holby and Taylor, *Sci. Rep.*, **5**, 9286, 2015.

# Activity of Predicted Stable Structures

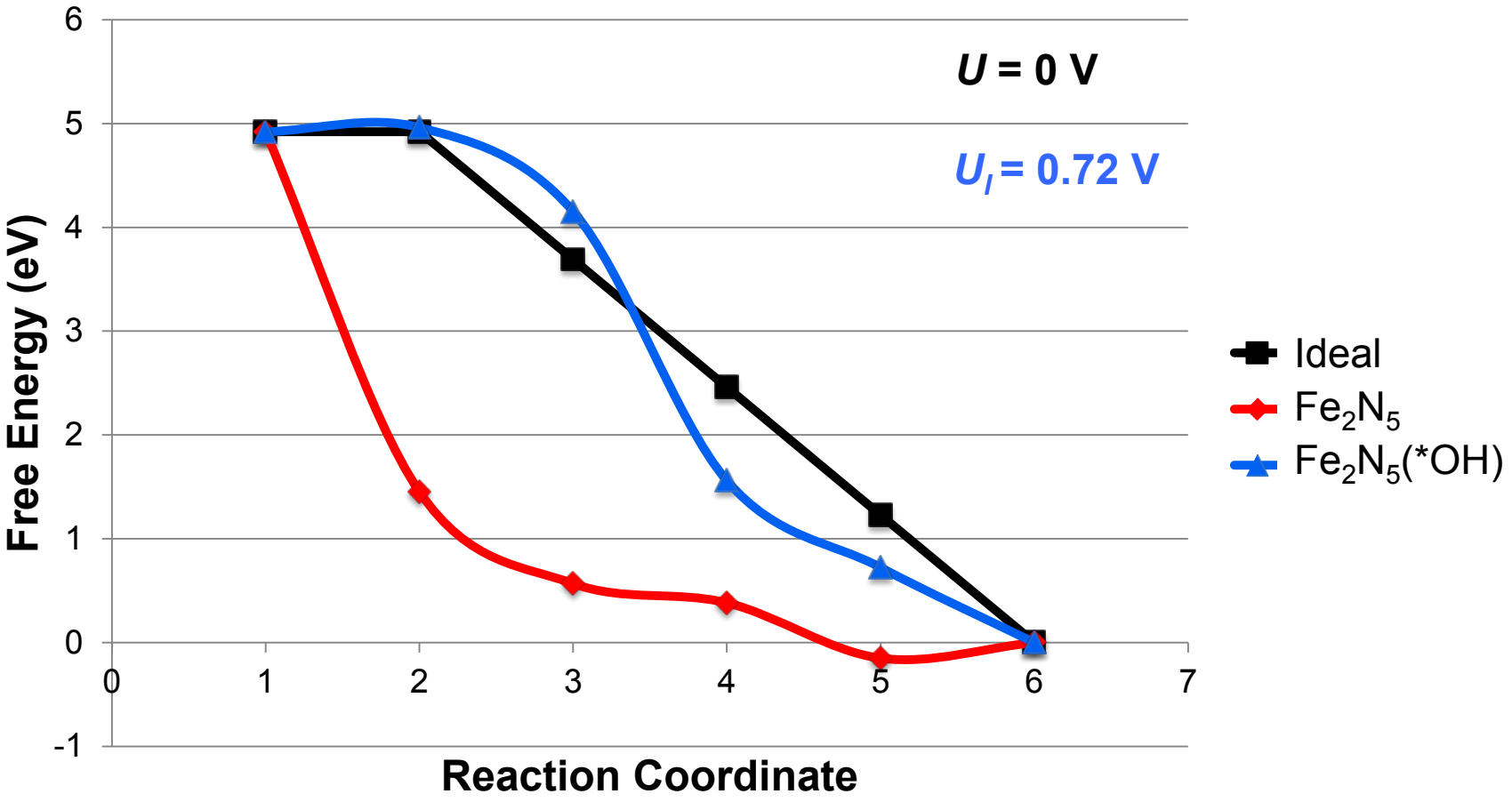





- Poor activity from $Fe_2N_5$ structure due to OH "overbinding"

Holby and Taylor, *Sci. Rep.*, **5**, 9286, 2015.

# Activity of Predicted Stable Structures – $Fe_2N_5$(*OH)

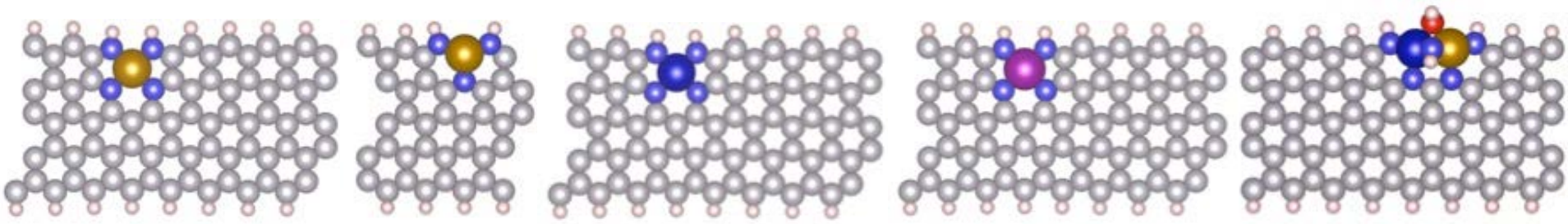



- $Fe_2N_5$(*OH) + *OH → $H_2O$ is potential determining step

Holby and Taylor, *Sci. Rep.*, **5**, 9286, 2015.

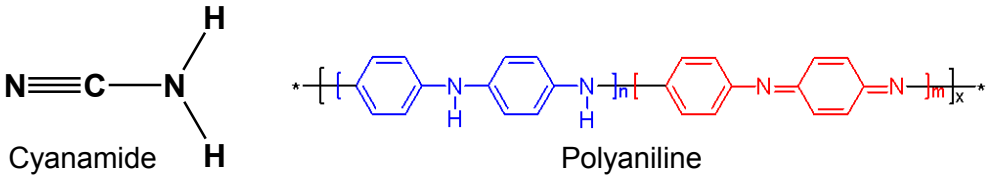
# Active Site Structures

- $M\text{-}N_3$, $M\text{-}N_4$, $M_2\text{-}N_5$, $M_2\text{-}N_6$ (M = Mn, Fe, Co, Ni) in bulk, zig-zag edge, and arm-chair edge with and without ligands are main focus



Holby and Taylor, *App. Phys.* Lett., **101**, 0641012, 2012; Holby, Wu, Zelenay, and Taylor, *ECS Trans.* **50**, 1839, 2013; Holby, Wu, Zelenay, and Taylor, *J. Phys. Chem. C*, **118**, 14388, 2014; Holby and Taylor, *Sci. Rep.* **5**, 9286, 2015; Holby and Zelenay, *Nano Energy*, in Press (2016).

# Synthesis of CM+PANI Systems




Carbon support

(Co, Mn, Ni) chlorides

First heat treatment at 900°C in inert atmosphere

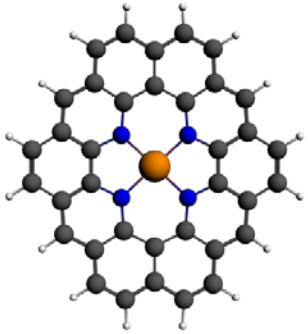
0.5 M $H_2SO_4$ leach at 80-90°C

Second heat treatment at 900°C in inert atmosphere

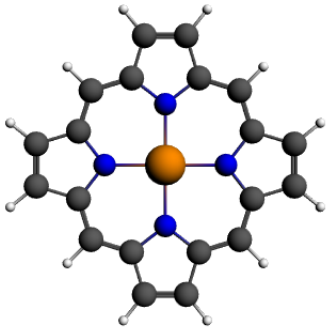
ORR performance evaluation; characterization

# Molecular Comparison – "$FeN_4C_{10}$" vs. "$FeN_4C_{12}$" Sites

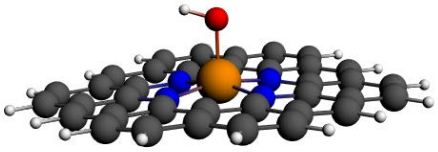
**Calculated via Amsterdam Density Functional (ADF) Suite, Dispersion Corrected PBE-GGA, TZP basis set with no frozen core**



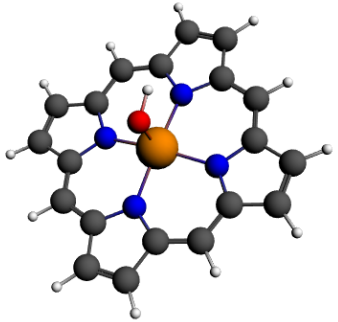
"$FeN_4C_{10}$"



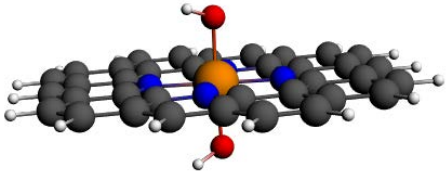
"$FeN_4C_{12}$"



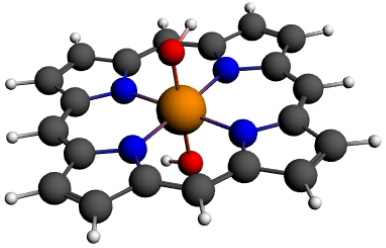
$U_{*OH}$ = -0.031 V



$U_{*OH}$ = 0.266 V



$U_{*OH}$ = 0.536 V

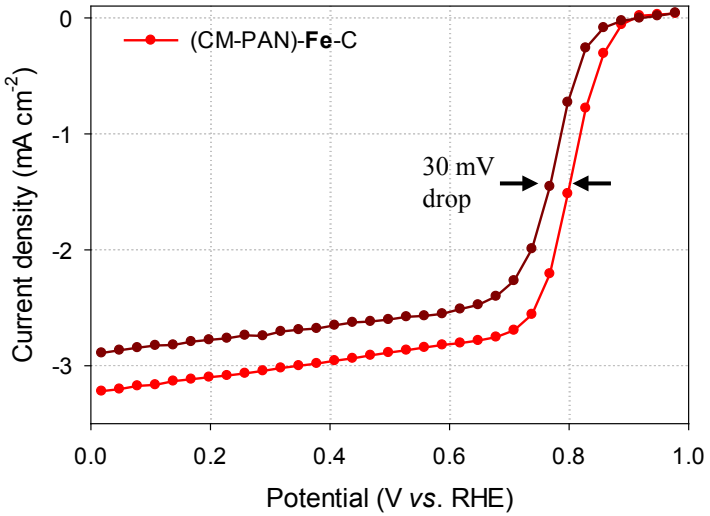


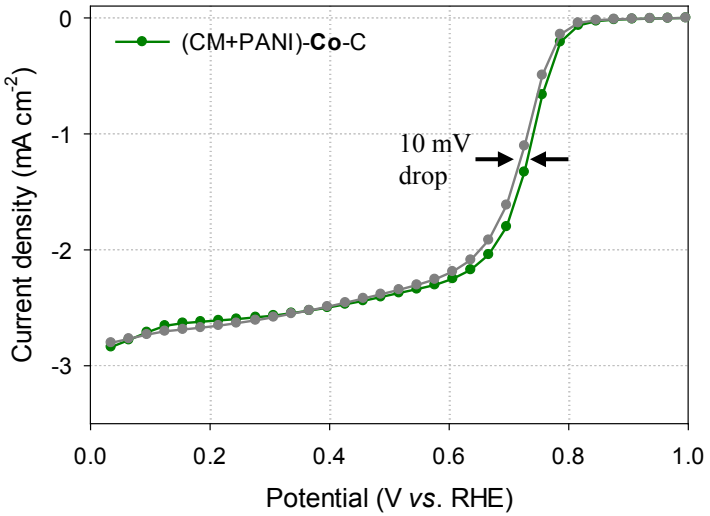
$U_{*OH}$ = 0.424 V

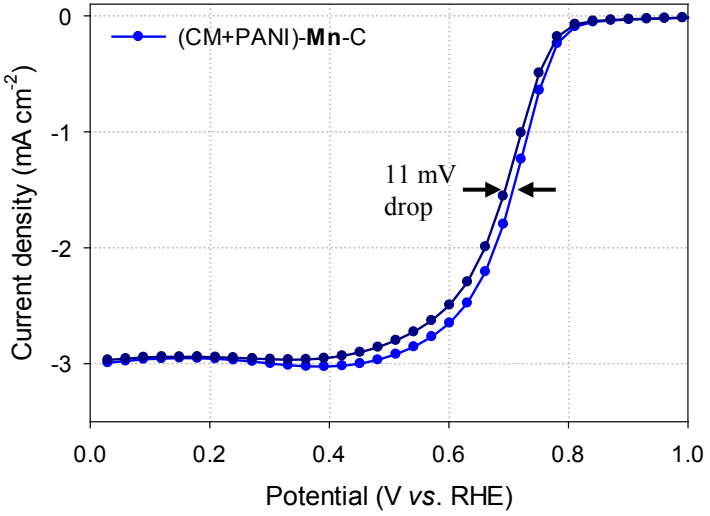
Zitolo *et al., Nat. Mat.*, **14**, 937942-, 2015.

# Stability of (CM+PANI)-*Me*-C Catalysts after 10,000 Cycles

**ORR:** 0.60 mg/cm$^2$; 0.5 M $H_2SO_4$; 900 rpm; 25ºC; Ag/AgCl (3 M KCl) reference electrode; graphite counter electrode; steady-state potential program: 30 mV steps, 30 s/step; Durability cycling: 0.6 - 1.0 V; $N_2$ saturation; 100 mV/s.




Highlight: Although slightly lower activity, better stability observed with Co and Mn catalysts