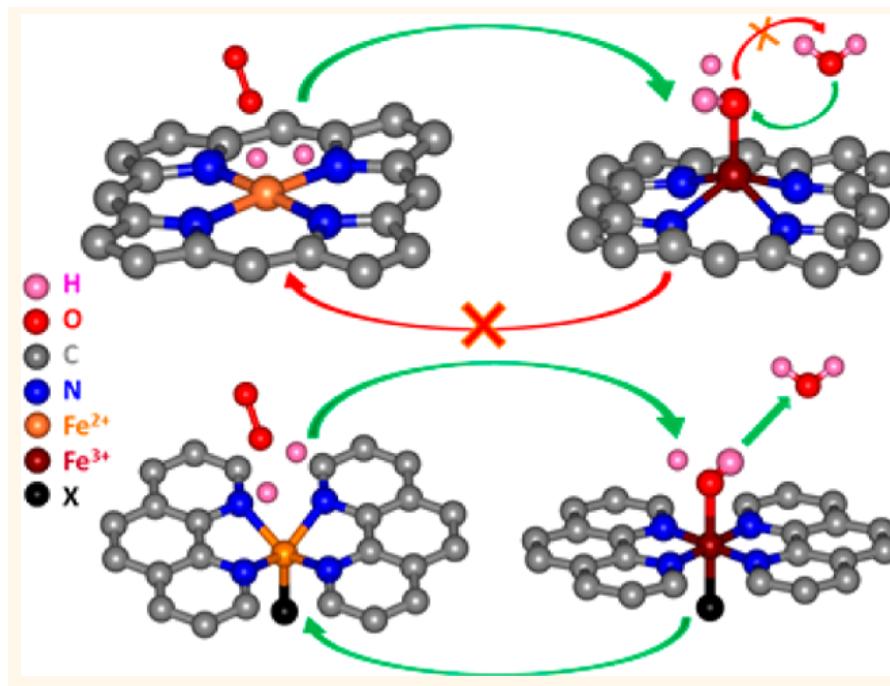


# *Understanding Iron-based catalysts with efficient oxygen reduction activity from XANES at the Fe K-edge*

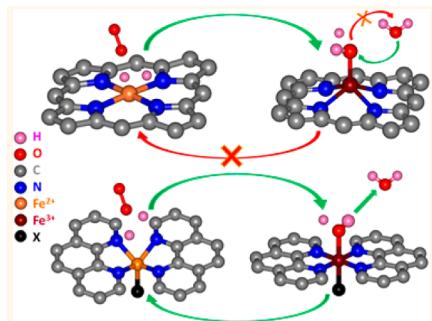
Bernardo Barbiellini



# *Design of materials for clean energy demand*

## Material Design

Fuel Cell and batteries



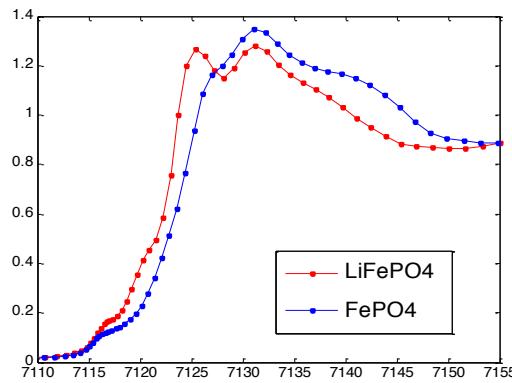
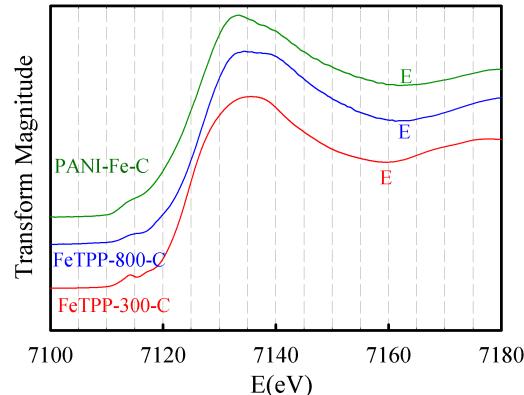
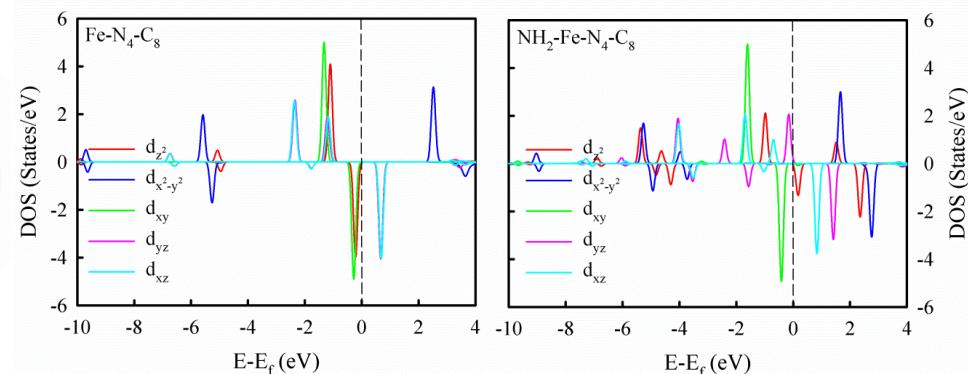
## Spectroscopy

XAS Iron K edge

Find good *descriptors*  
for optimal active sites

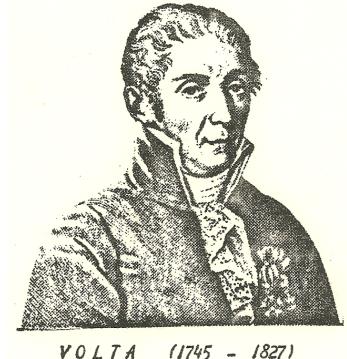
## Theory & Simulation

DFT VASP with PBE functional

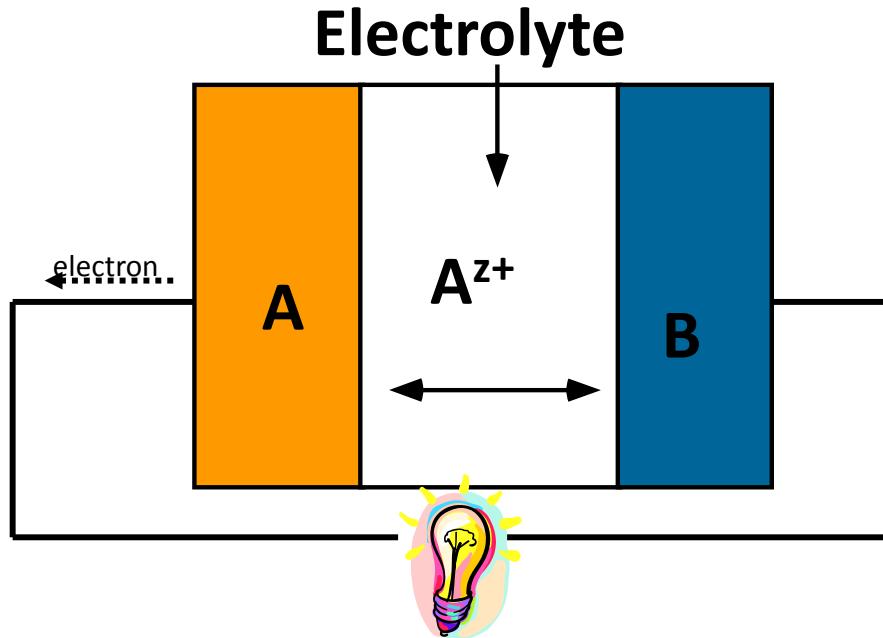


**Ultimate Goal : Close up the feedback loop for rational/speedy development**

# Electrochemical energy

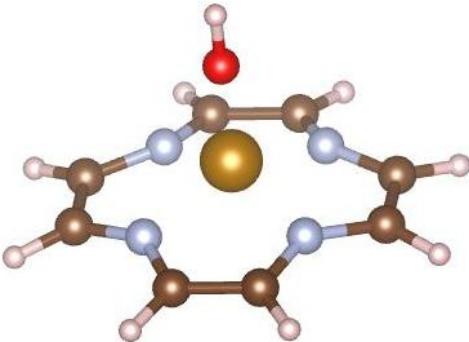


Convert chemical energy from a reaction directly into electrical energy



- ❑ A and B want to react
- ❑ Reactants are separated by electrolyte which only allows ionic species  $A^{z+}$ .
- ❑ Electrons are forced through outside circuit
- ❑ Complete (exact) conversion of chemical reaction energy ( $\Delta G$ ) into electrical energy

Battery or Fuel Cell

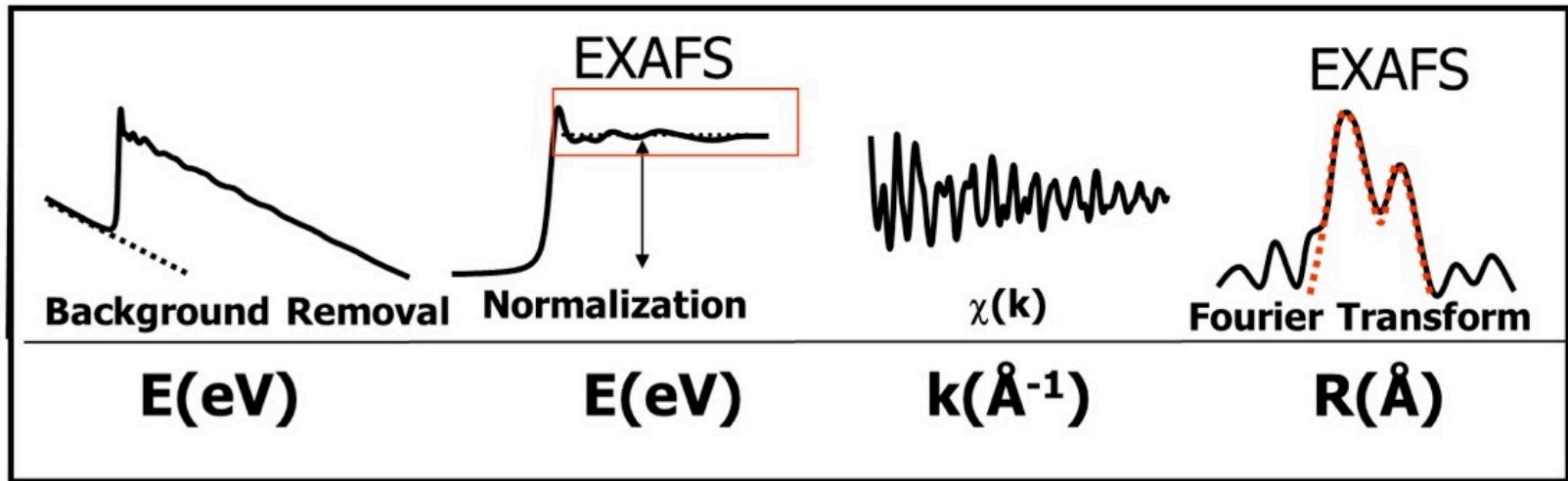


# Motivations

- Oxygen reduction reaction (ORR) is a key processes to produce energy.
- Currently ORR relies on platinum, which is a precious metal.
- Materials problems & the prohibitive cost of precious metals.
- The development of a nonprecious metal catalysts for the ORR is needed.

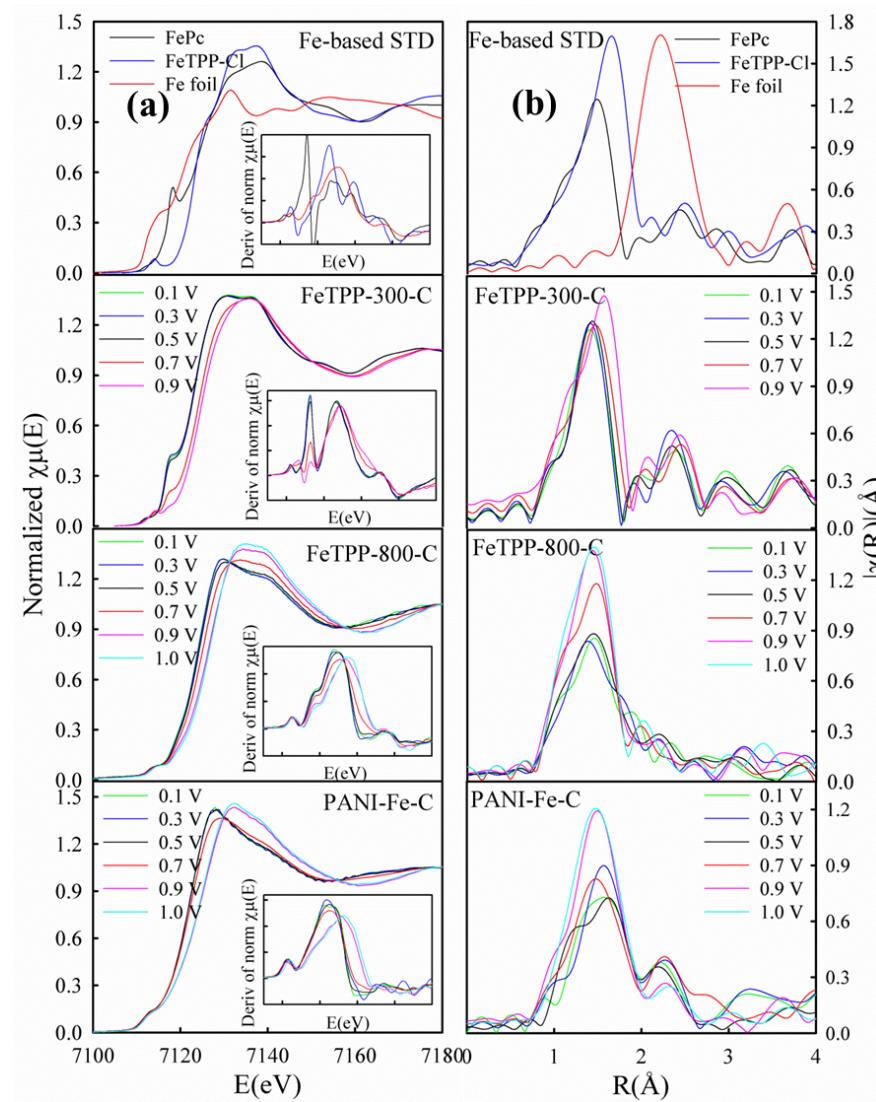
Qingying Jia, Nagappan Ramaswamy, Hasnain Hafiz, Urszula Tylus, Kara Strickland, Gang Wu, Bernardo Barbiellini, Arun Bansil, Edward F. Holby, Piotr Zelenay, and Sanjeev Mukerjee,

# XAS analysis of Fe K edge

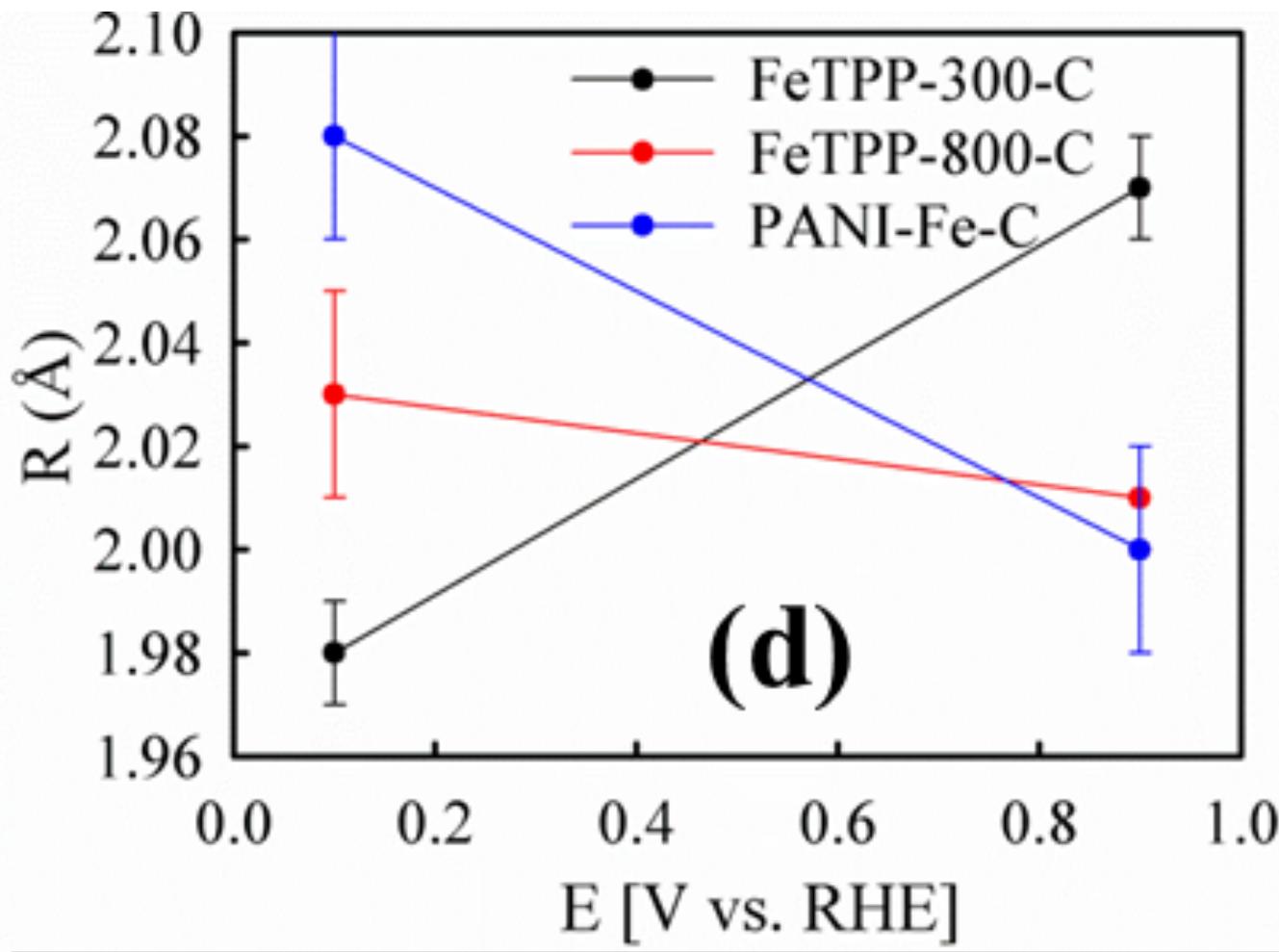


XAS offers insights into electrode processes by providing simultaneous electronic and structural information on the electrode materials under actual *in situ* cell operating conditions

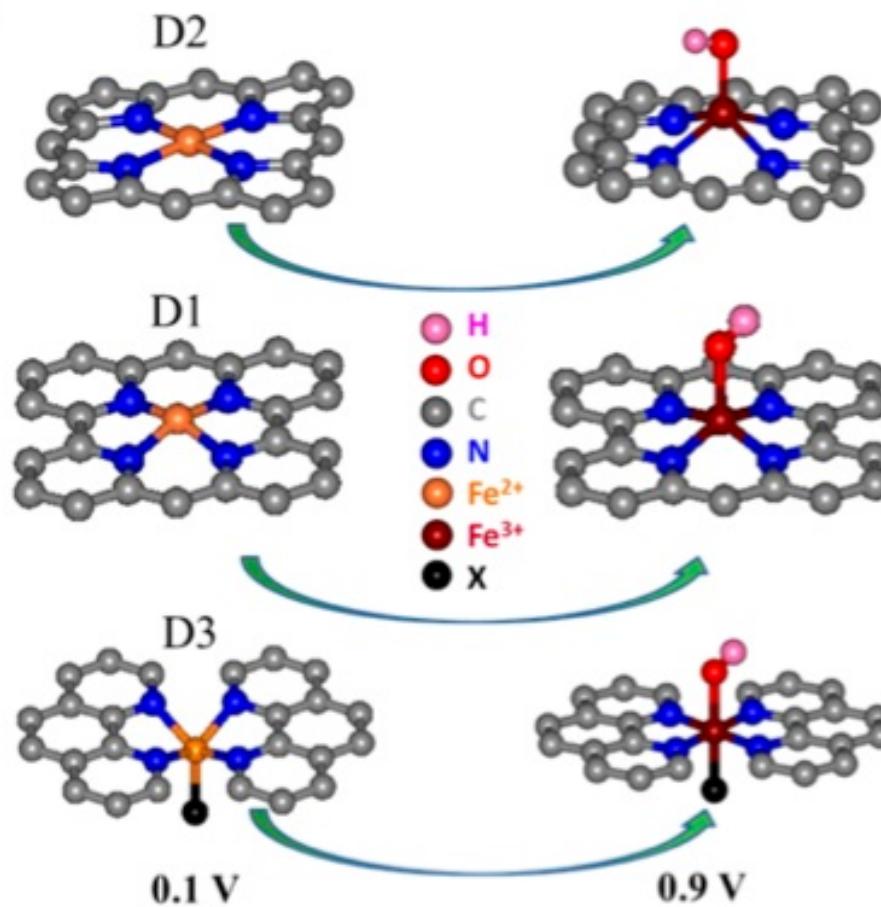
# XAS curves



# XAS derived Fe–N switching behavior

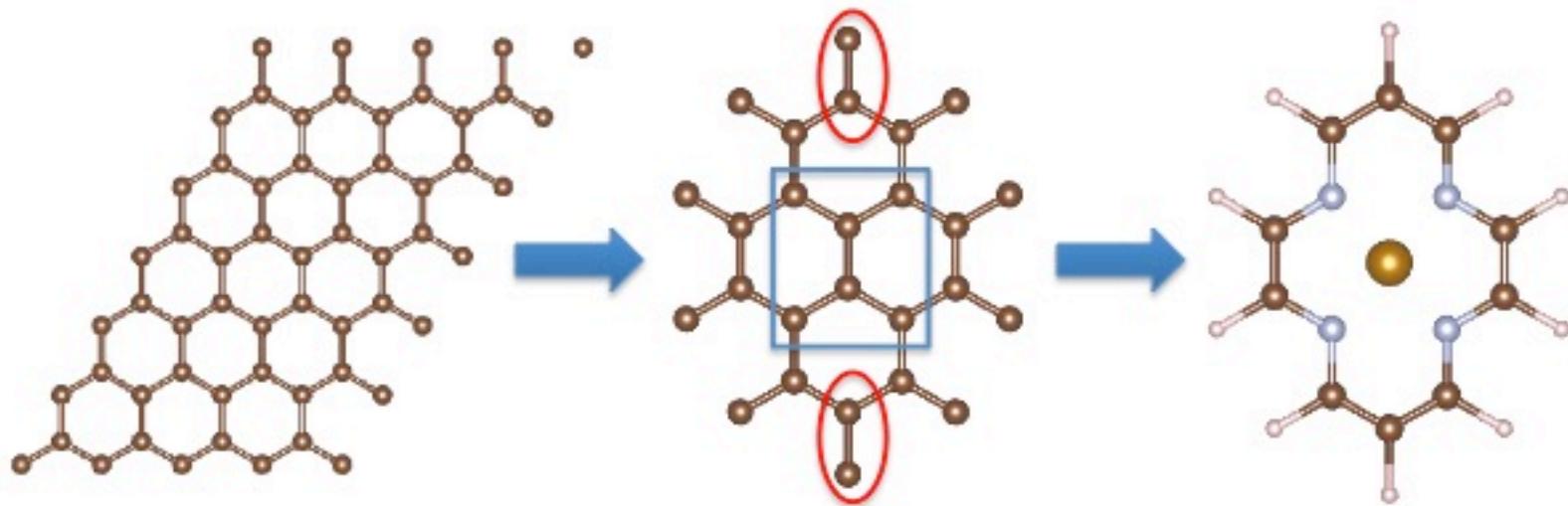


# XAS derived Fe–N switching behavior: possible descriptor for genomic search

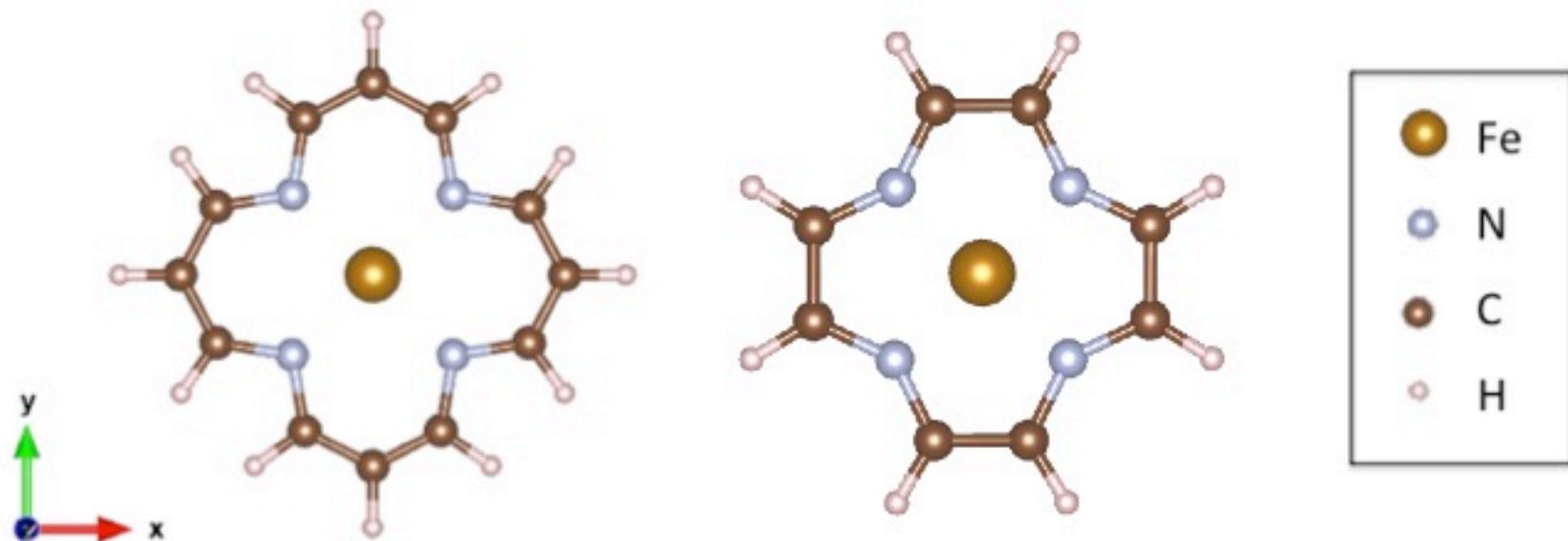


D3 is the most active site and exhibits distinctly different Fe displacement with respect to N

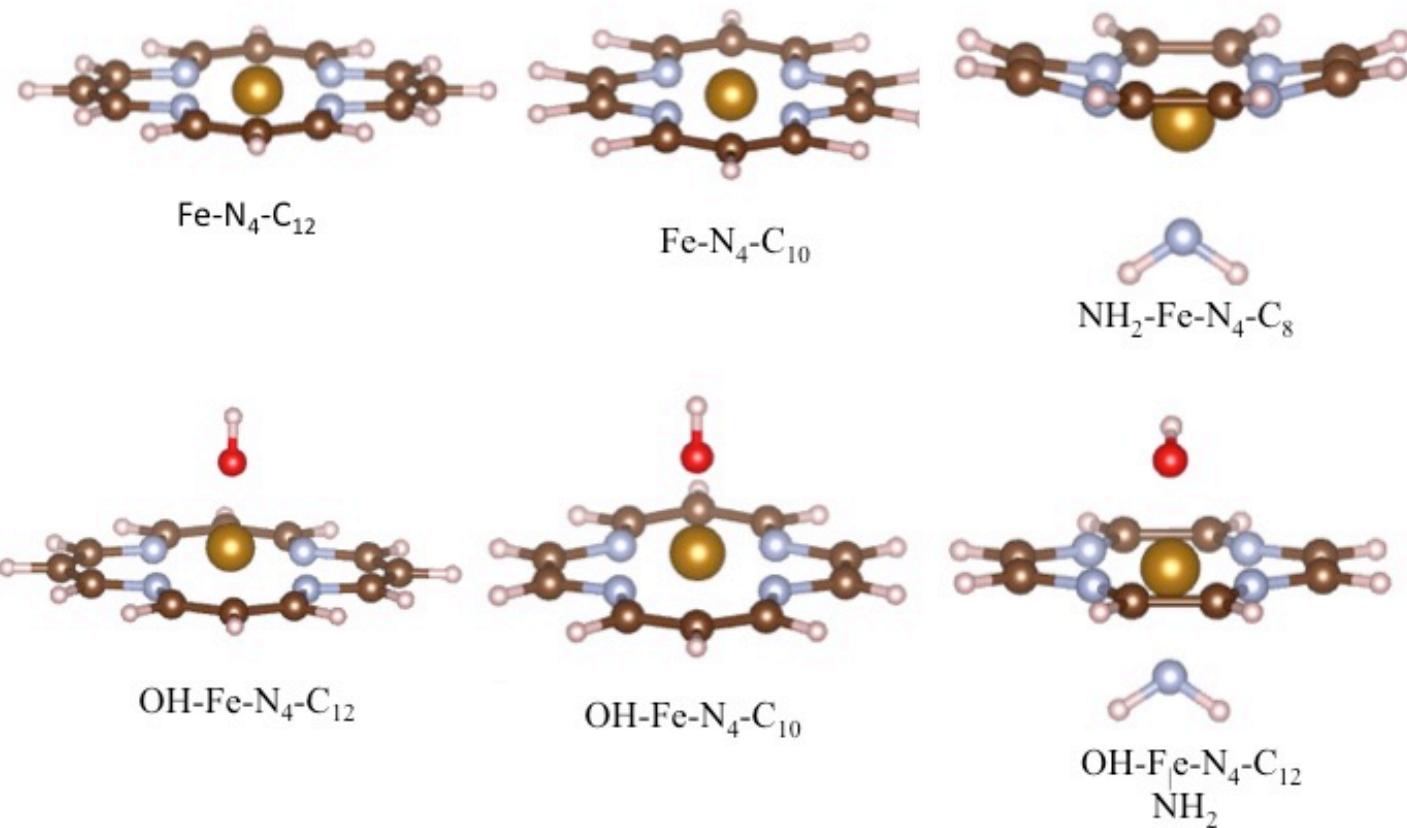
# Fe-N<sub>4</sub>-C<sub>10</sub> fragment



# Fe-N<sub>4</sub>-C<sub>x</sub> cluster models (x=8, 12)



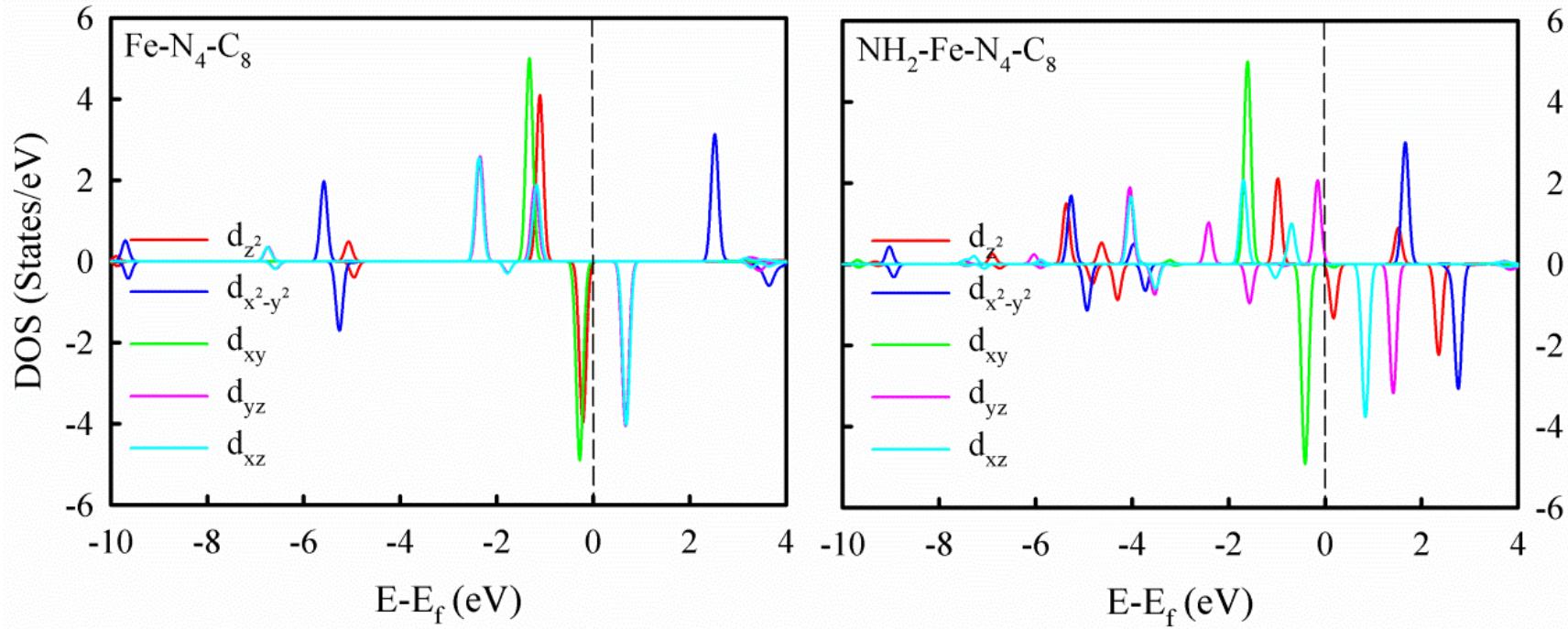
# Side views of three models of the active sites



# Bond lengths in Angstrom

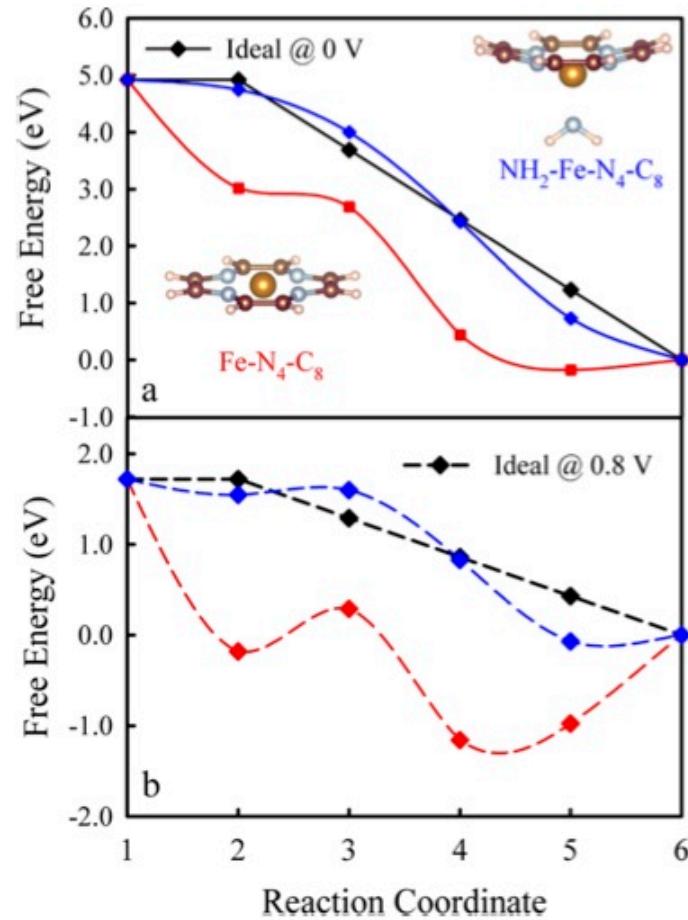
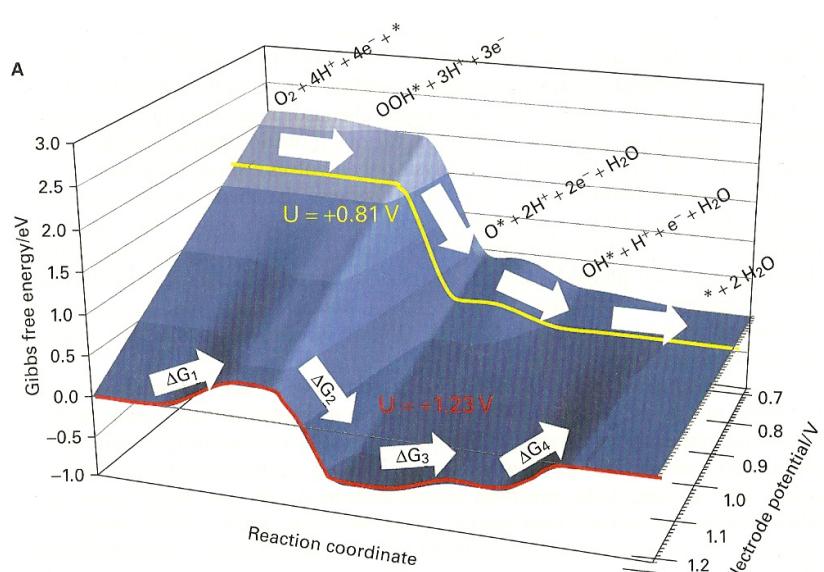
	Fe-N <sub>1</sub>	Fe-N <sub>2</sub>	Fe-N <sub>3</sub>	Fe-N <sub>4</sub>	Fe-N <sub>axi</sub>	Fe-OH
FeN <sub>4</sub> C <sub>12</sub>	2.03	2.03	2.03	2.03		
FeN <sub>4</sub> C <sub>12</sub> -OH	2.21	2.22	2.21	2.21		1.79
FeN <sub>4</sub> C <sub>10</sub>	1.89	1.89	1.89	1.89		
FeN <sub>4</sub> C <sub>10</sub> -OH	1.90	1.90	1.90	1.90		1.81
FeN <sub>4</sub> C <sub>8</sub>	1.83	1.85	1.83	1.85		
FeN <sub>4</sub> C <sub>8</sub> -OH	1.87	1.87	1.87	1.87		1.77
NH <sub>2</sub> -FeN <sub>4</sub> C <sub>8</sub>	1.89	1.89	1.89	1.89	1.86	
NH <sub>2</sub> -FeN <sub>4</sub> C <sub>8</sub> -OH	1.87	1.87	1.87	1.87	1.88	1.86

# Electronic Structure

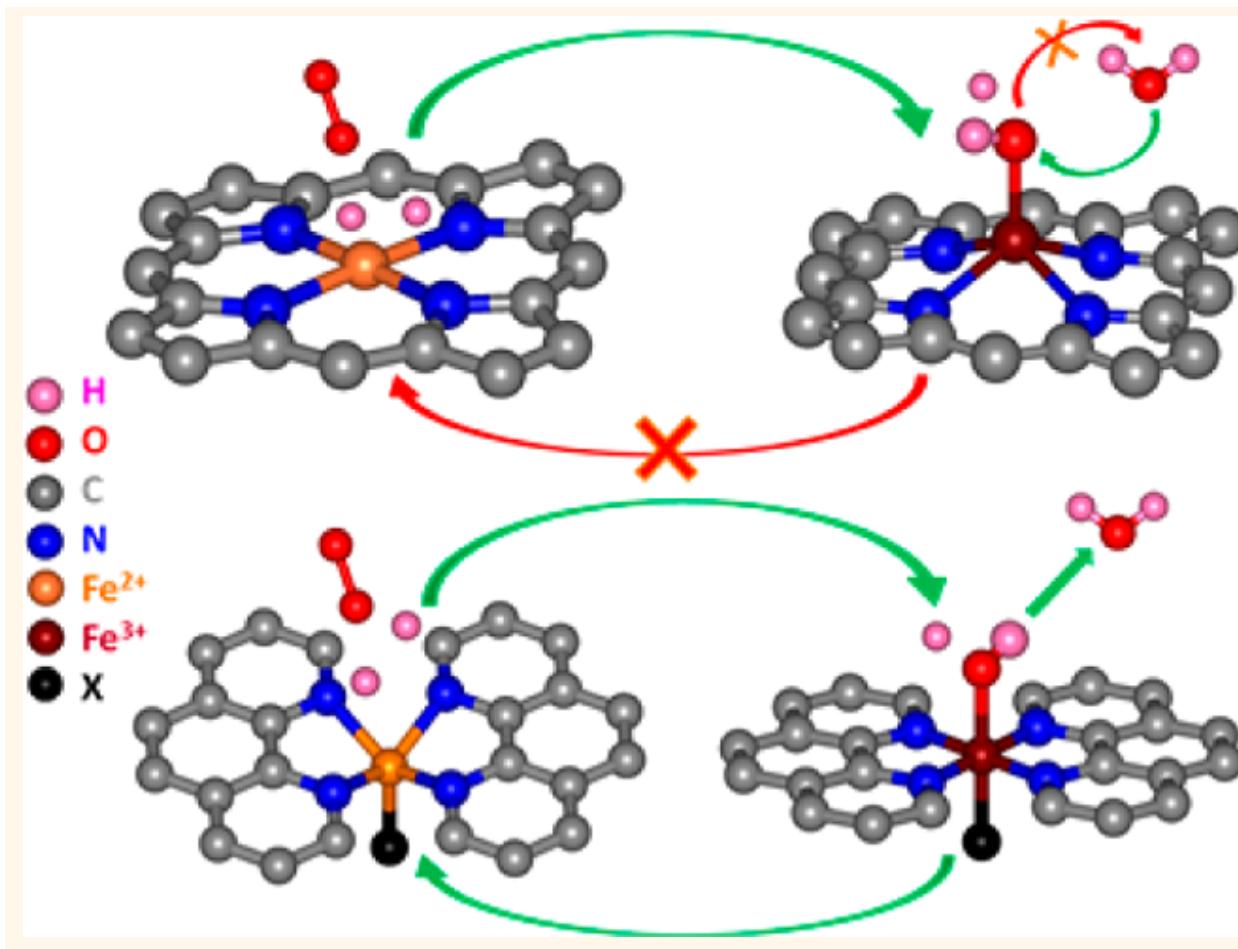


	BE(eV)	OH	$e_g (d_z^2)$ -electrons
Fe-N <sub>4</sub> -C <sub>12</sub>	-3.16		0.94
Fe-N <sub>4</sub> -C <sub>10</sub>	-2.26		1.04
Fe-N <sub>4</sub> -C <sub>8</sub>	-3.51		1.67
NH <sub>2</sub> -Fe-N <sub>4</sub> -C <sub>8</sub>	-2.61		1.11

# Reaction Path & optimal catalysts



# Non precious metal FeN<sub>4</sub> site for ORR



Qingying Jia, Nagappan Ramaswamy, Hasnain Hafiz, Urszula Tylus, Kara Strickland, Gang Wu, Bernardo Barbiellini, Arun Bansil, Edward F. Holby, Piotr Zelenay, and Sanjeev Mukerjee, ACS Nano 9 (2015) 12496 DOI: 10.1021/acsnano.5b05984