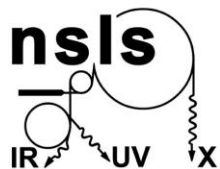




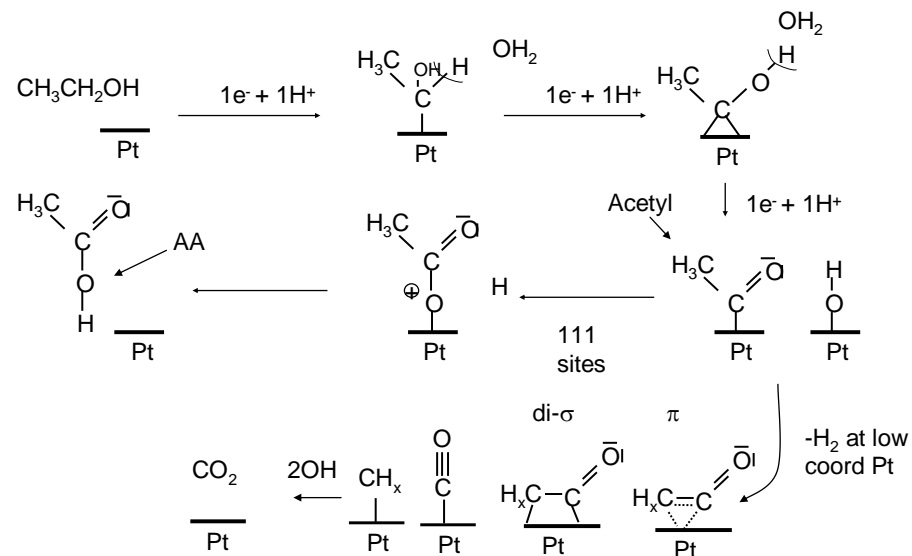
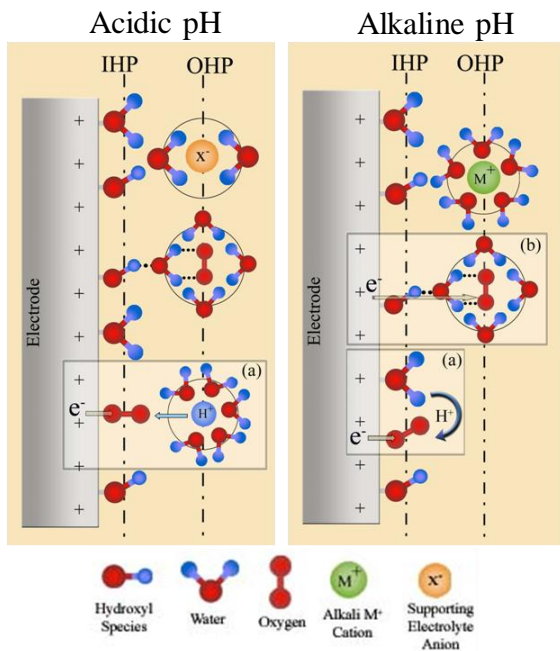
# Electrocatalysis in Alkaline Electrolytes - Research Overview

Sanjeev Mukerjee

Nagappan Ramaswamy, Qinggang He, Daniel Abbott,  
and Michael Bates



Department of Chemistry and Chemical Biology  
Northeastern University, Boston, MA 02115

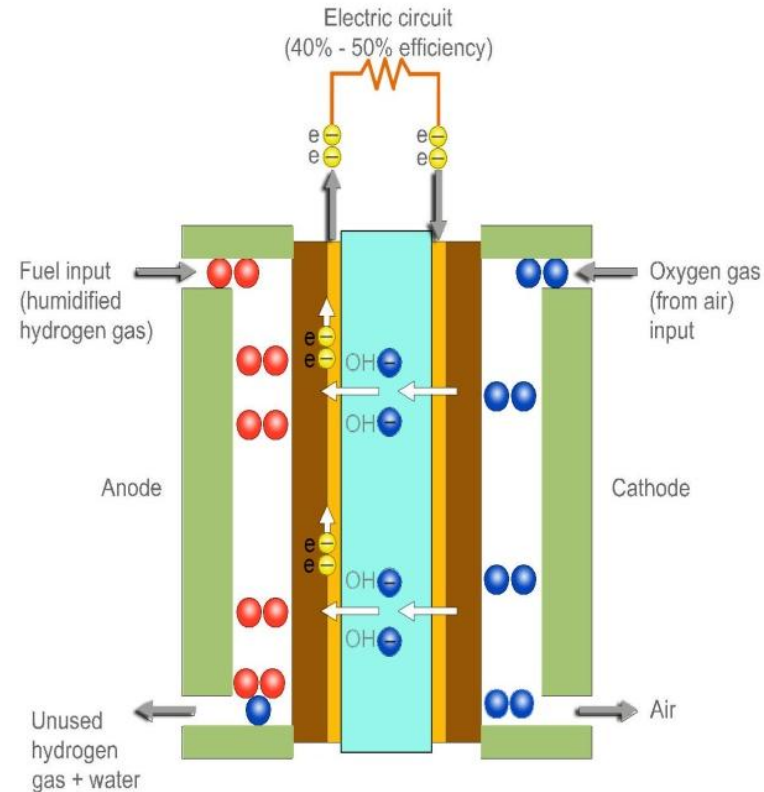




# OVERVIEW



- General Overview – Advantages of High pH
- ORR Mechanistic Understanding
  - Question of Kinetic Facility in Alkaline Medium?
  - Inner- vs. Outer-sphere Electron Transfer
- Non-noble Metal Macrocycle Electrocatalyst
  - Origin of ORR Activity
  - Redox Potential Tuning
  - Influence of Graphitic Defects
- Smart Catalysts for Anodic Oxidation
  - Homogeneous Mediation using Metal-organic Complexes
- Alkaline Membrane Fuel Cell Studies
  - Interfacial Challenges and Future Prospects





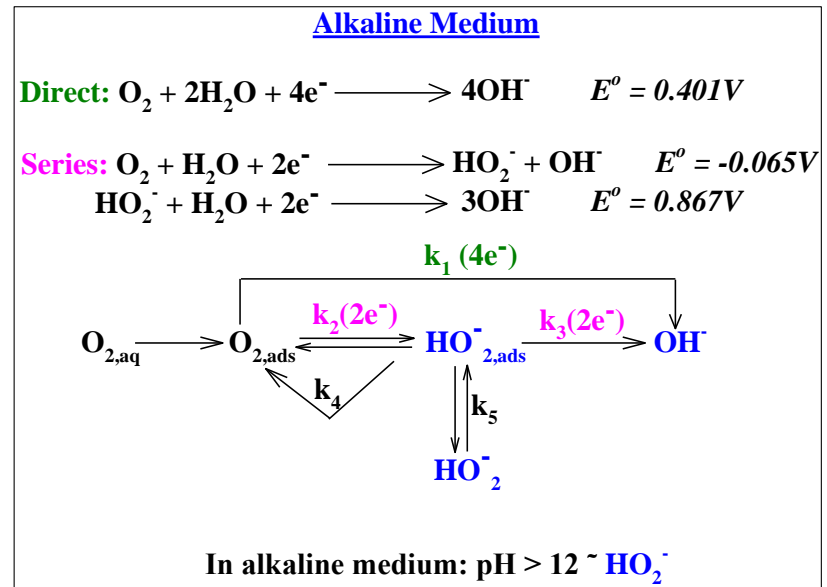
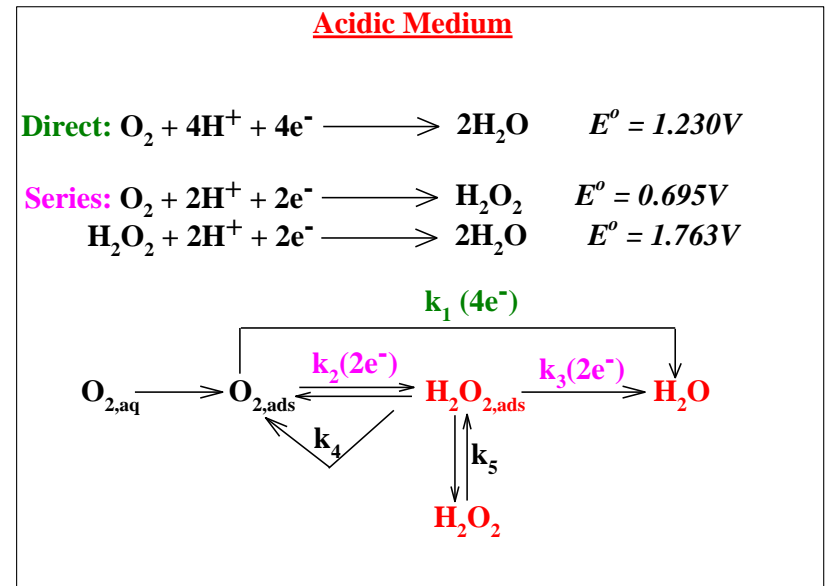
# ORR - Acid vs. Alkaline Medium: Thermodynamic Advantages



SHE Scale	O/R
1.230V	O <sub>2</sub> /H <sub>2</sub> O
0.401V	O <sub>2</sub> /OH <sup>-</sup>
0.000V	H <sup>+</sup> /H <sub>2</sub>
-0.301V	O <sub>2</sub> /O <sub>2</sub> <sup>-</sup>
-0.828V	H <sub>2</sub> O/H <sub>2</sub>

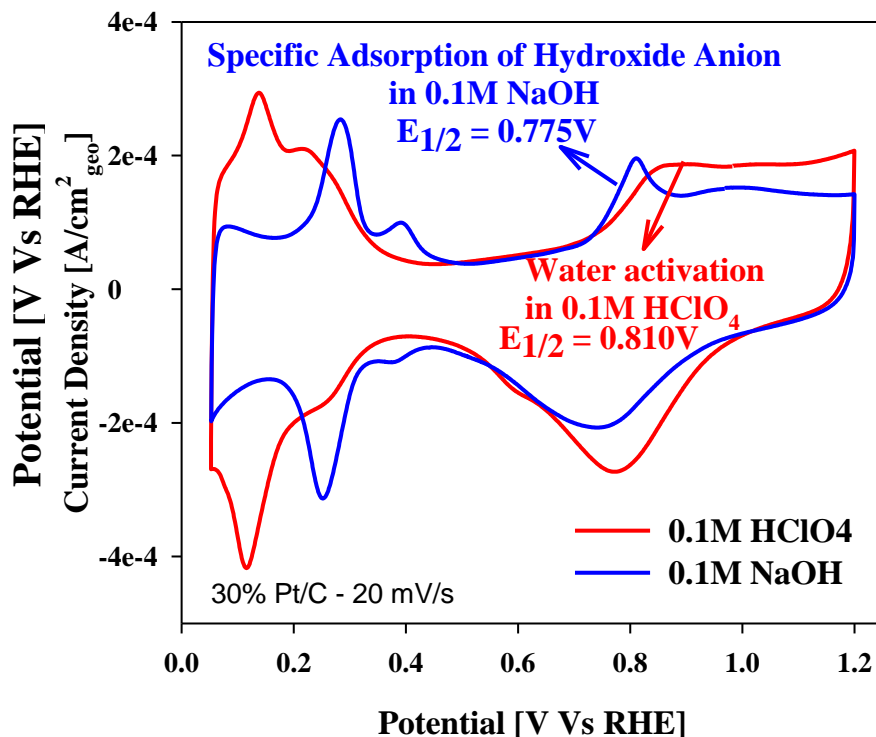
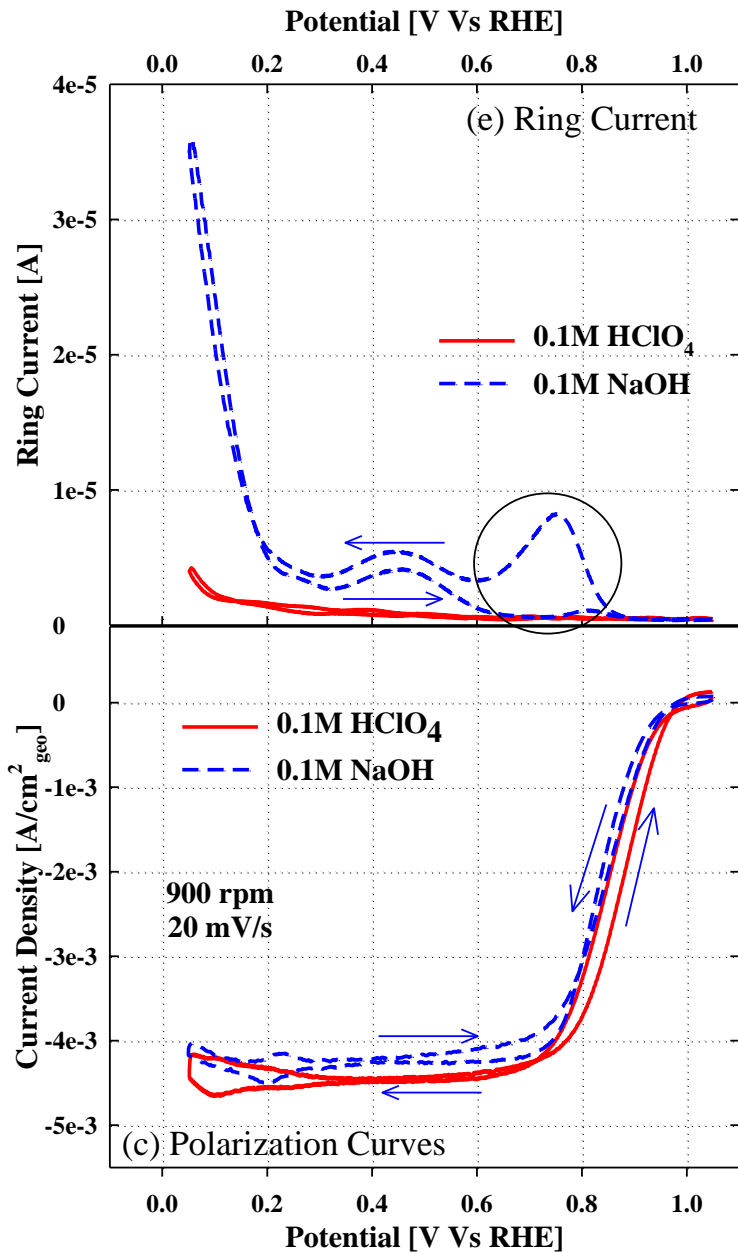
$\eta = 1.53V$  (spanning from 1.230V to -0.301V)  
 $\eta = 0.70V$  (spanning from 0.401V to -0.301V)

- 1) Nernstian Potential Shift
- 2) Affects Adsorption Strengths of spectators, and intermediate species





# How Facile is ORR in Alkaline Medium?

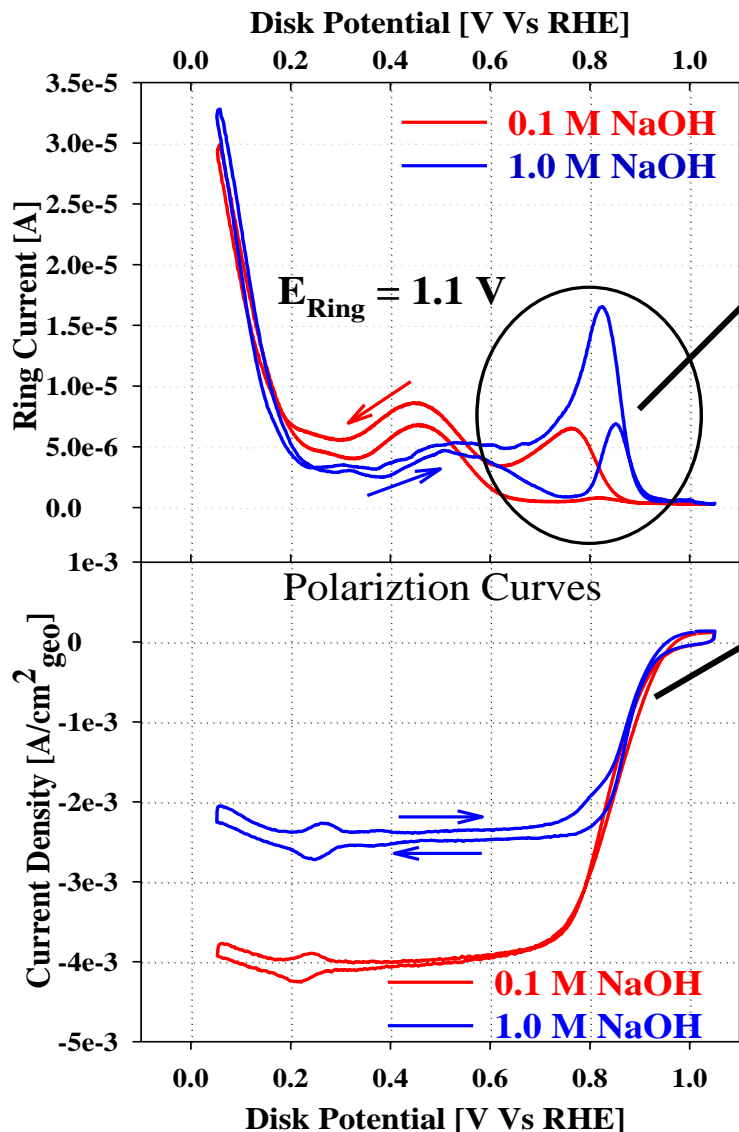


➤ ORR on Pt better in non-adsorbing acidic electrolyte like 0.1M HClO<sub>4</sub>

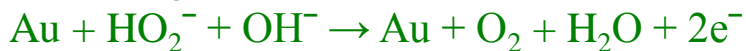
Outer sphere electron transfer process  
 ➤ Most claims of increased kinetic facility in alkaline fuel cell are based on comparisons with phosphoric acid fuel cell in alkaline medium responsible for peroxide anion formation



# Effect of Specific Adsorption of Hydroxide Anions in Alkaline Medium



Gold Ring Electrode:



$\text{HO}_2^-$  related to specifically adsorbed oxides on Pt



Outer sphere electron transfer process responsible for peroxide anion formation in alkaline medium

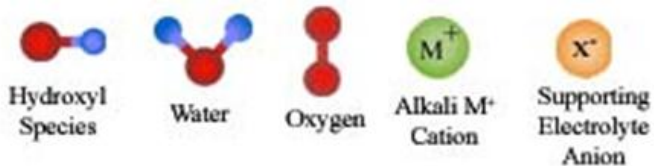
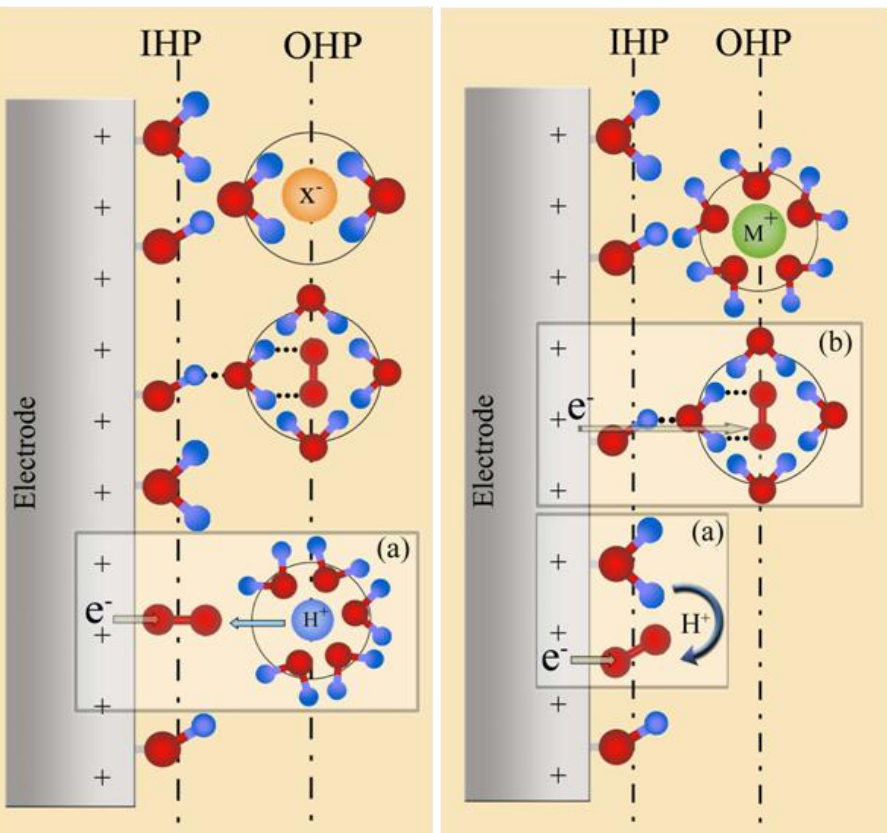


# Inner-sphere and Outer-sphere Electron Transfer Mechanisms



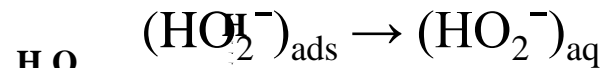
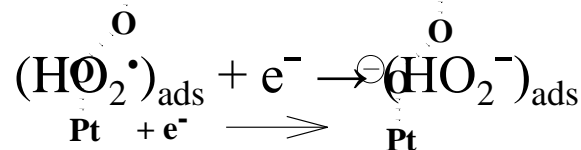
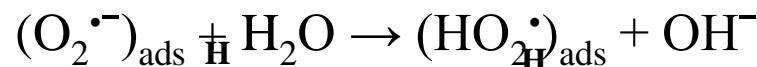
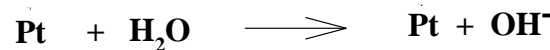
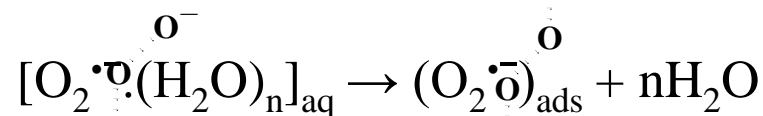
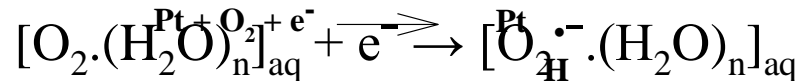
Acidic pH

Alkaline pH

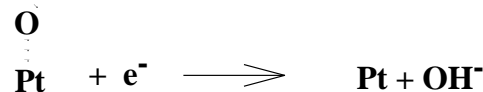


Desired  $4e^-$  transfer on oxide free Pt site

## Outer-Sphere Electron Transfer



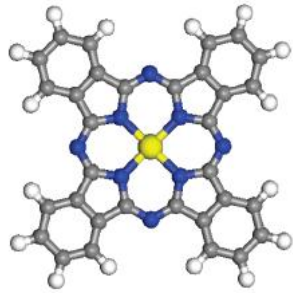
Specific adsorption of hydroxide anions promote outer-sphere electron transfer in alkaline medium



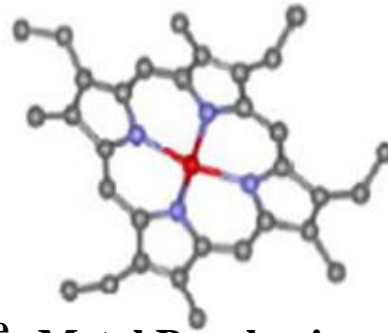
Inner-sphere and outer-sphere electron transfer compete in alkaline medium



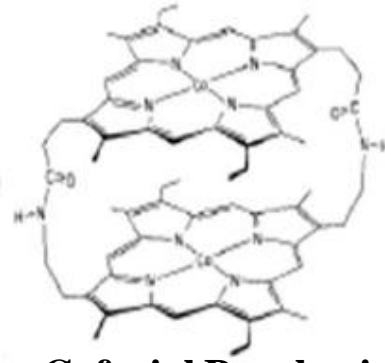
# Literature Survey on non-PGM Cathode Catalysts



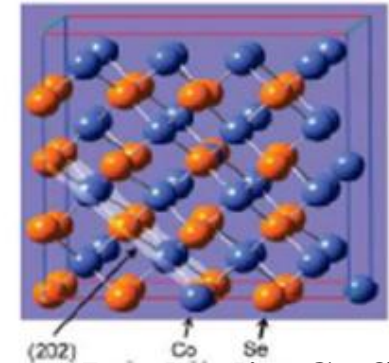
**Metal Phthalocyanine**  
D. Chu et al - ARL



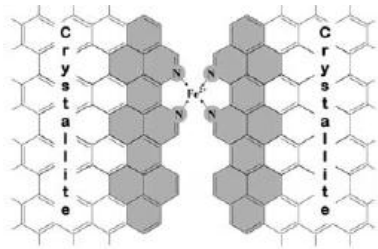
**Metal Porphyrin**  
Mukerjee et al



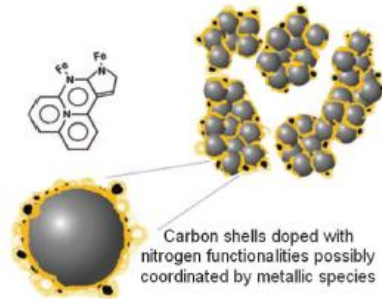
**Cofacial Porphyrin**  
Anson et al



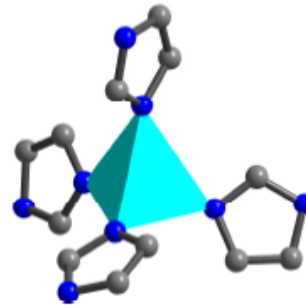
**Pentlandite  $Co_9Se_8$**   
Anderson et al



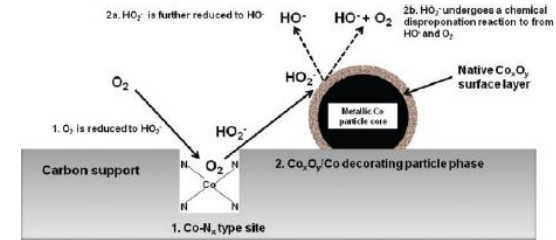
**Fe/N/C**  
Dodelet et al



**M-Polymer Composite**  
Zelenay et al



**M-Organic Framework**  
D. Liu - ANL



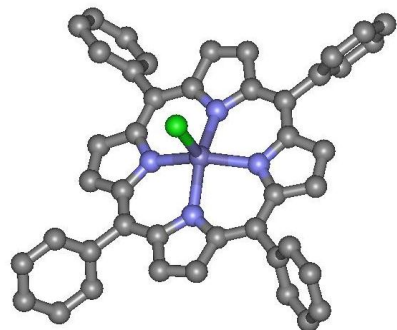
**Open Framework**  
Atanassov et al

**The starting complex is immaterial. Its important to know how the self-assembly and distribution of the active site takes place!!!**

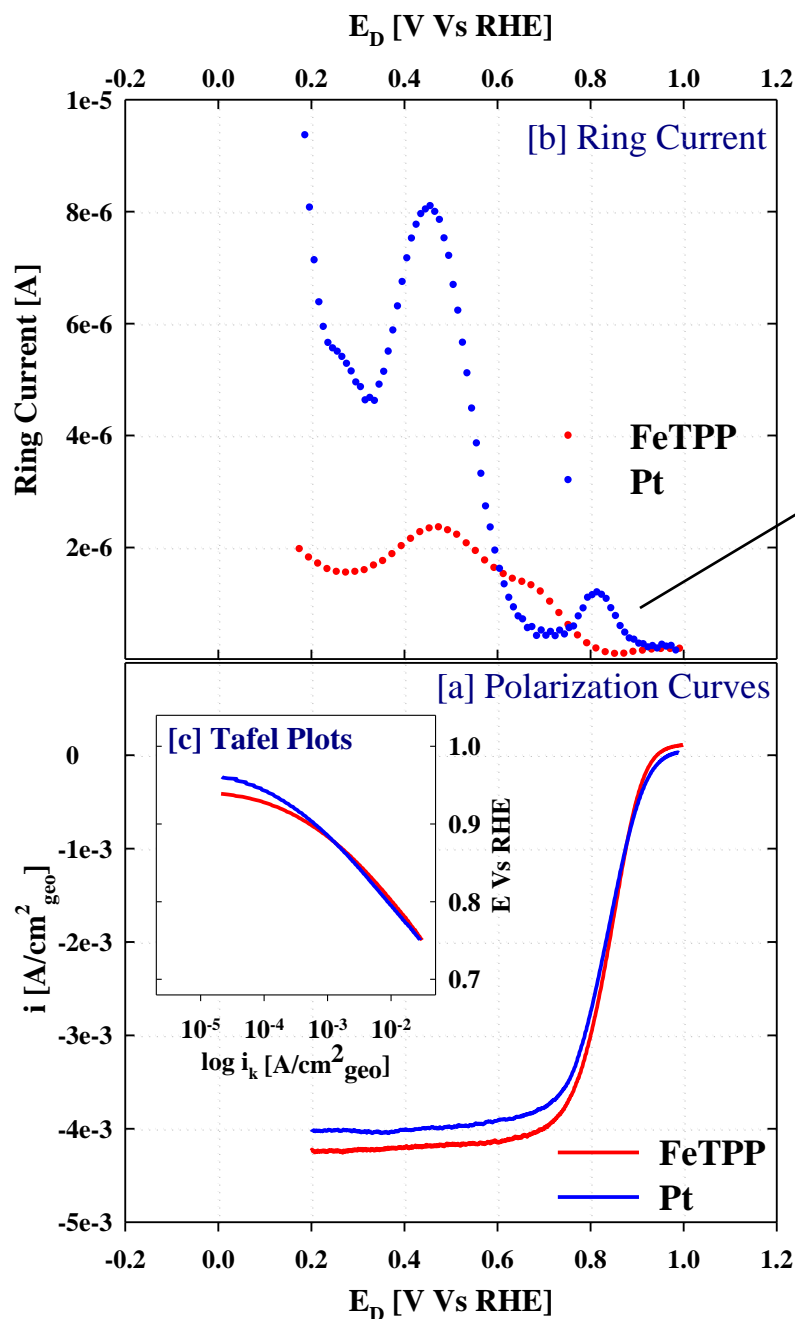
**Bottom-up approach needed in catalyst synthesis rather than a random mixing of precursor materials and heat treatment.**



# ORR Activity of FeTPP/BPC Pyrolyzed at 800°C



**FeTPP on Black Pearl Carbon pyrolyzed at 800°C**

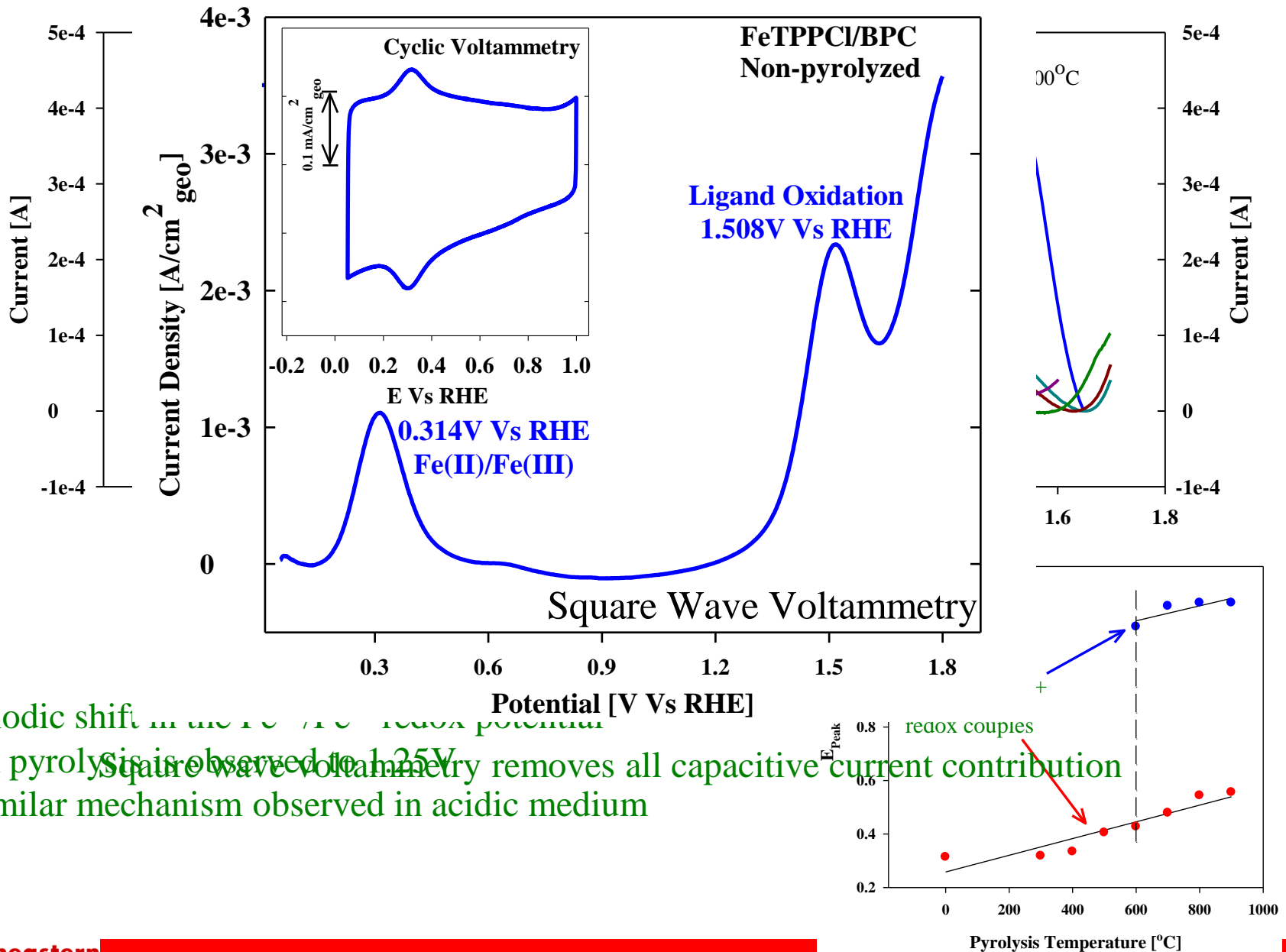


Pyrolyzed FeTPP exhibits remarkably low H<sub>2</sub>O<sub>2</sub> yield due to its exotic structure as explained in the next slides



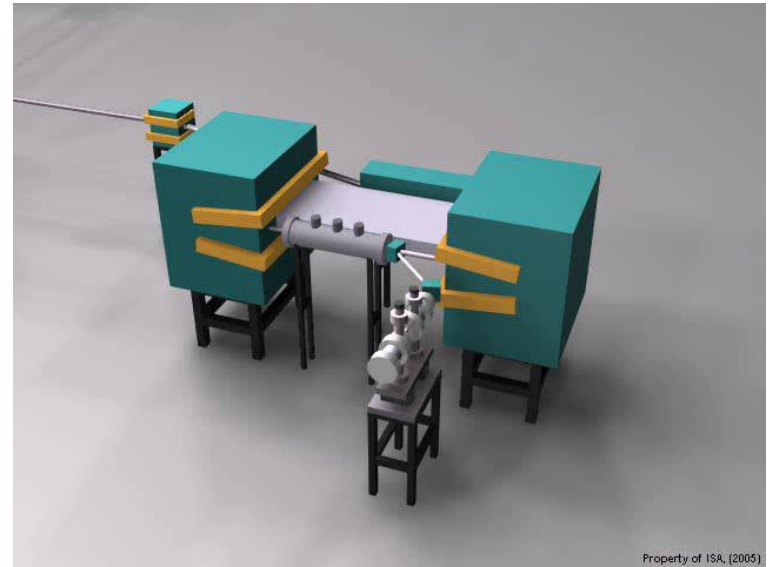


# Square Wave Voltammetry - Evolution of Fe<sup>2+</sup>/Fe<sup>3+</sup> Redox Potential

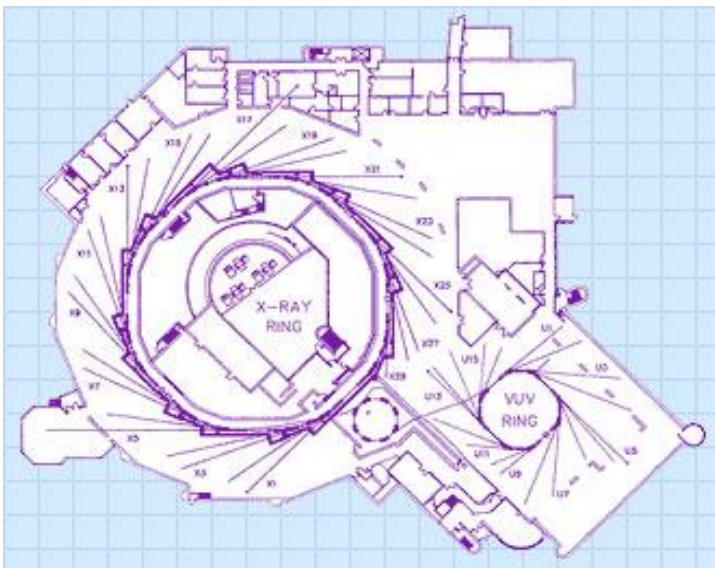




# Synchrotron Principles



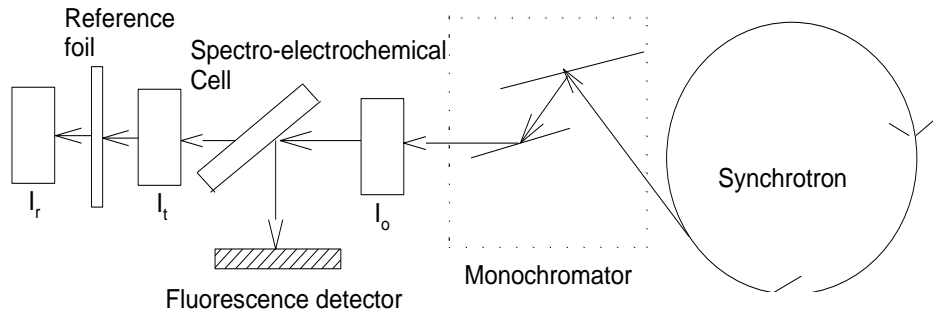
Property of ISA, (2005)



Property of ISA, (2005)



# Principles of X-ray Absorption Spectroscopy

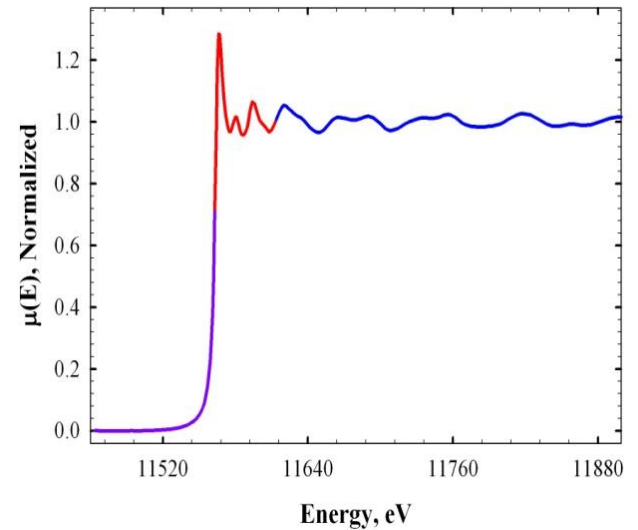
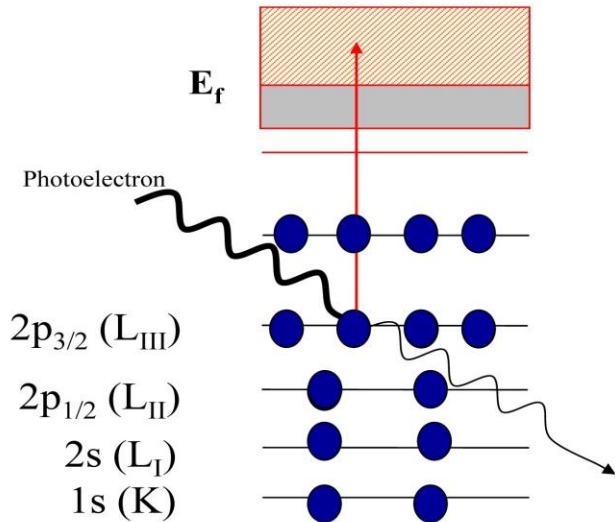
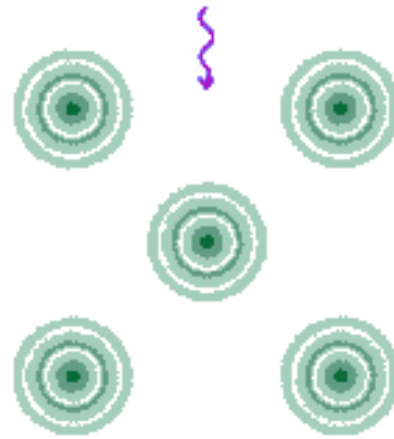


## XANES (< 50 eV)

- Absorber site symmetry (e.g.  $T_d$ ,  $O_h$ , etc)
- Electronic configuration
- Geometric Binding Site

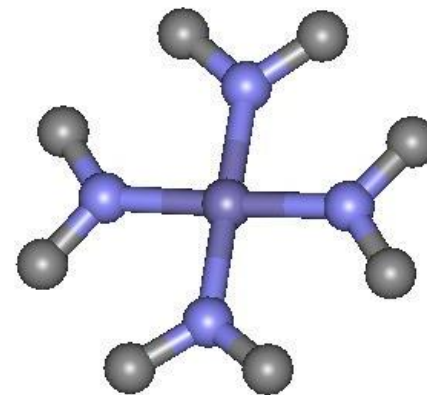
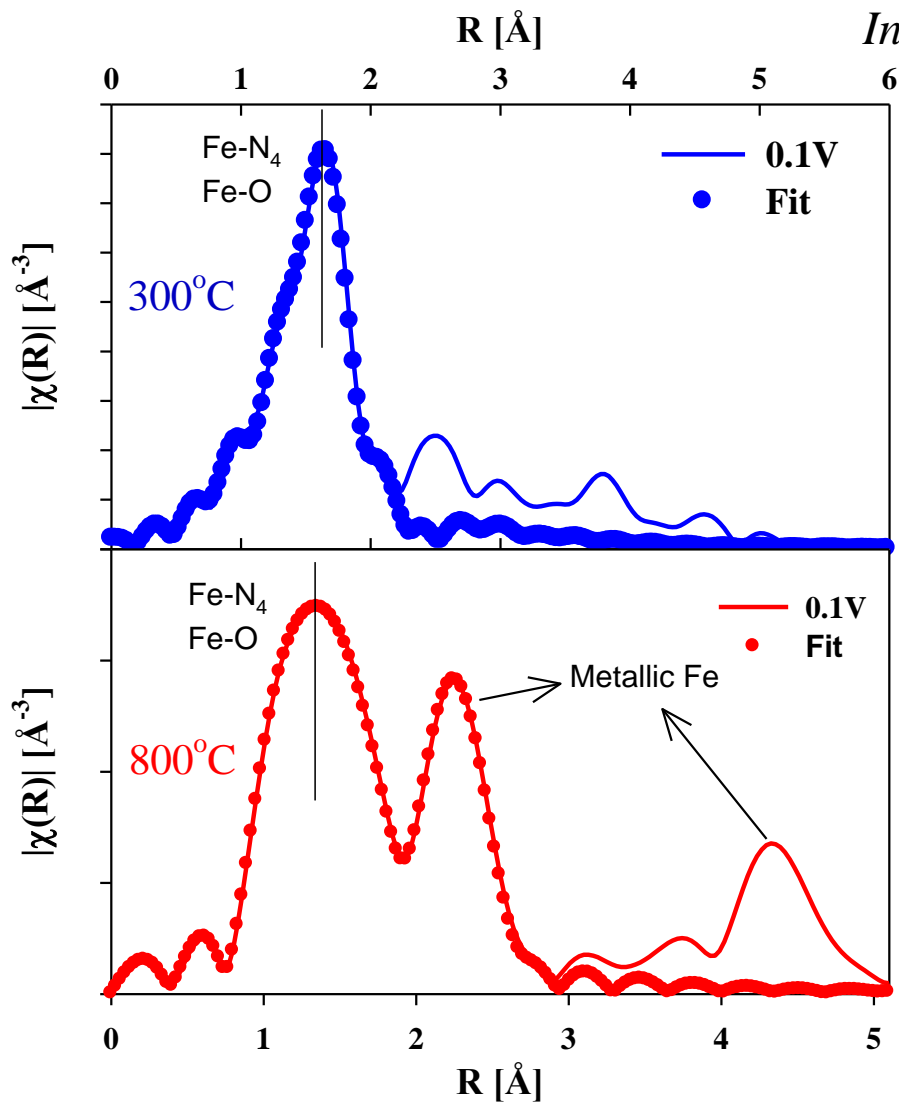
## EXAFS (> 50 eV)

- Geometric information
- Bond length
- Coordination number
- *BULK* short range order





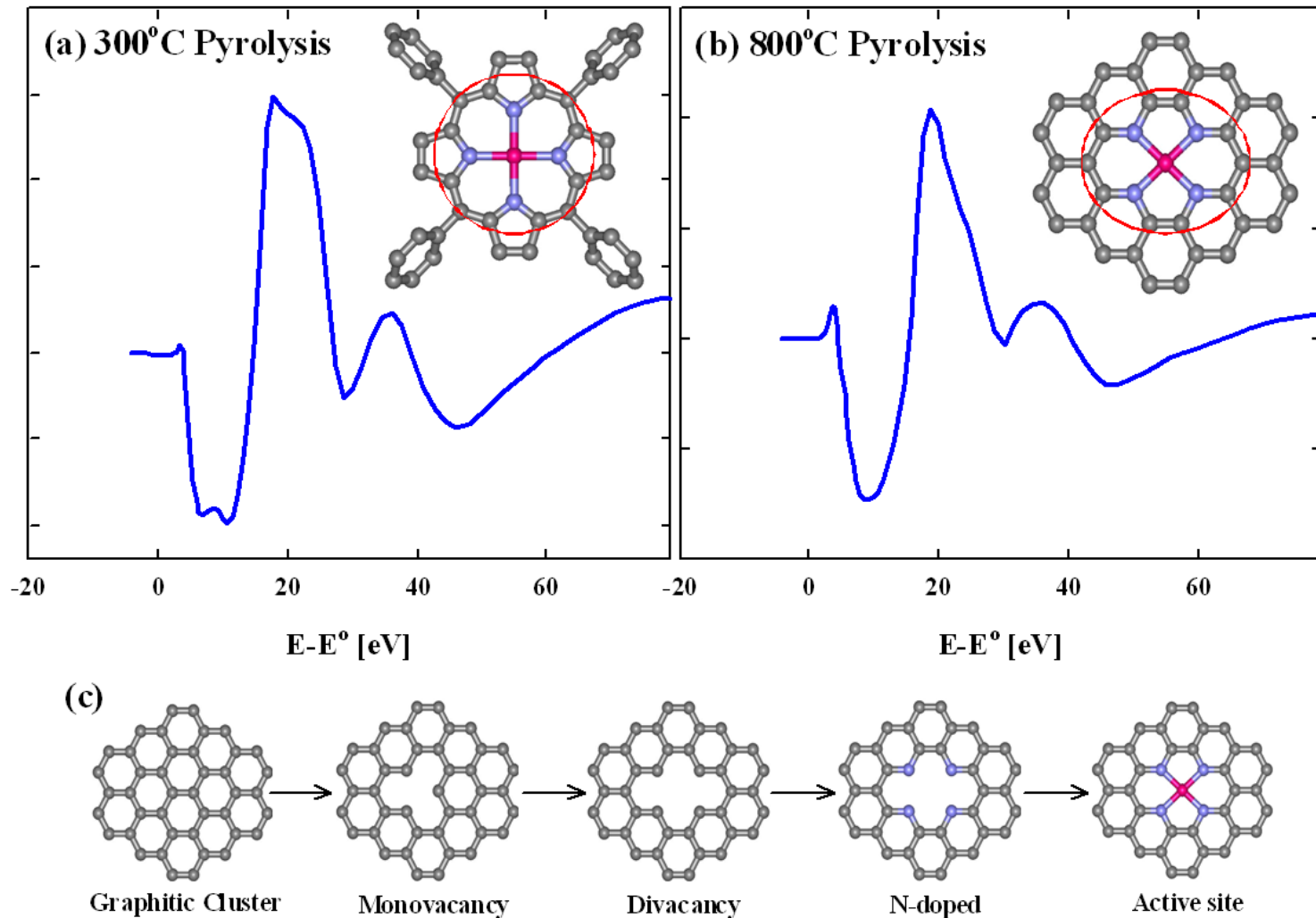
In situ 0.1M NaOH electrolyte @ 0.1 V vs. RHE



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



# Delta Mu – Identification of Active Site and Oxygen Adsorption Mode

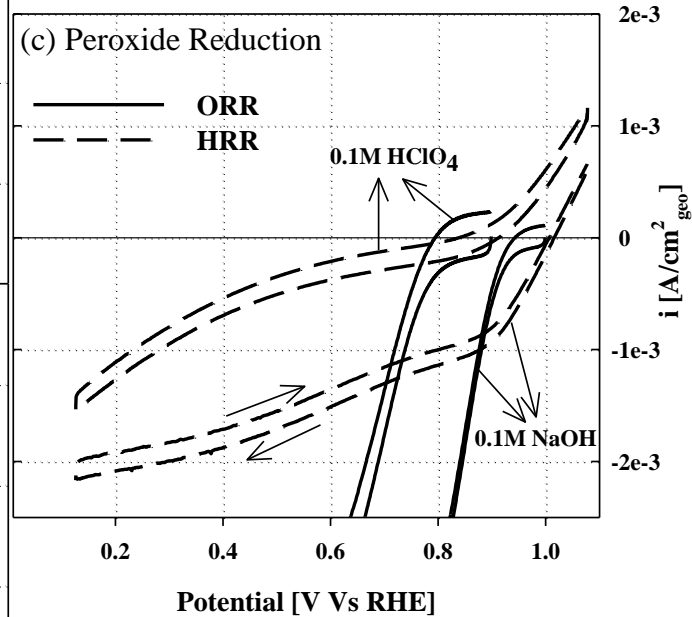
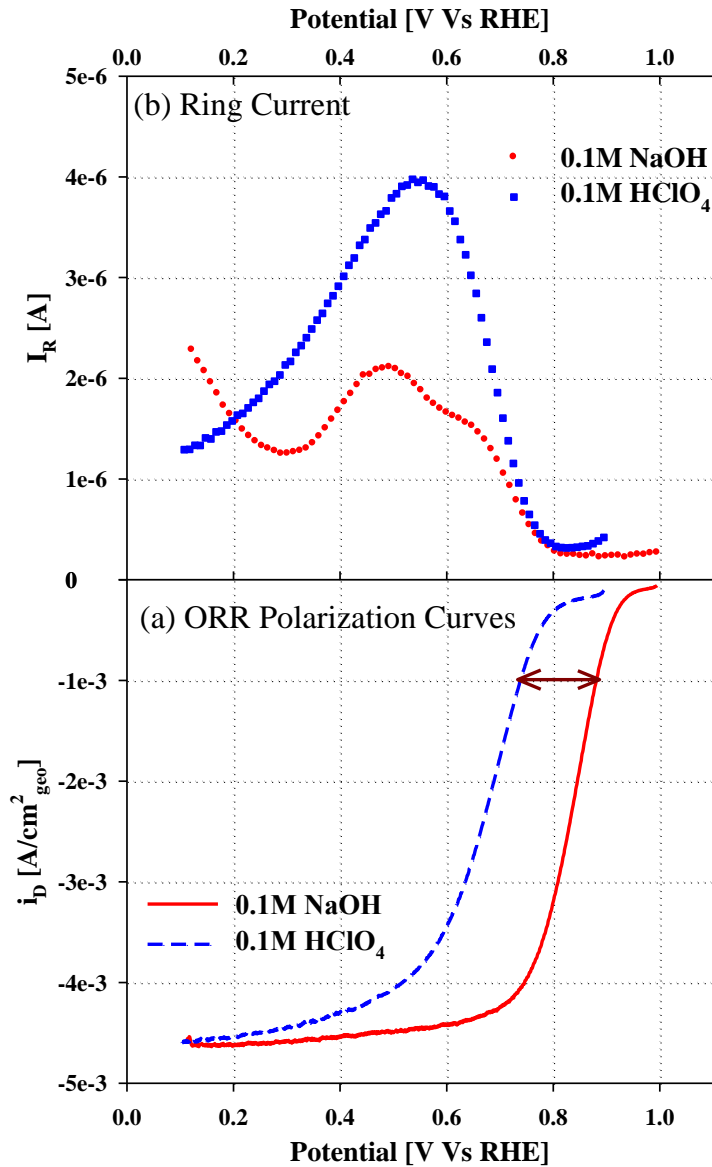


Defective sites are regions of higher chemical potential and hence anodic shift in redox potential

➤ Increasing defect sites is key to increasing active site density



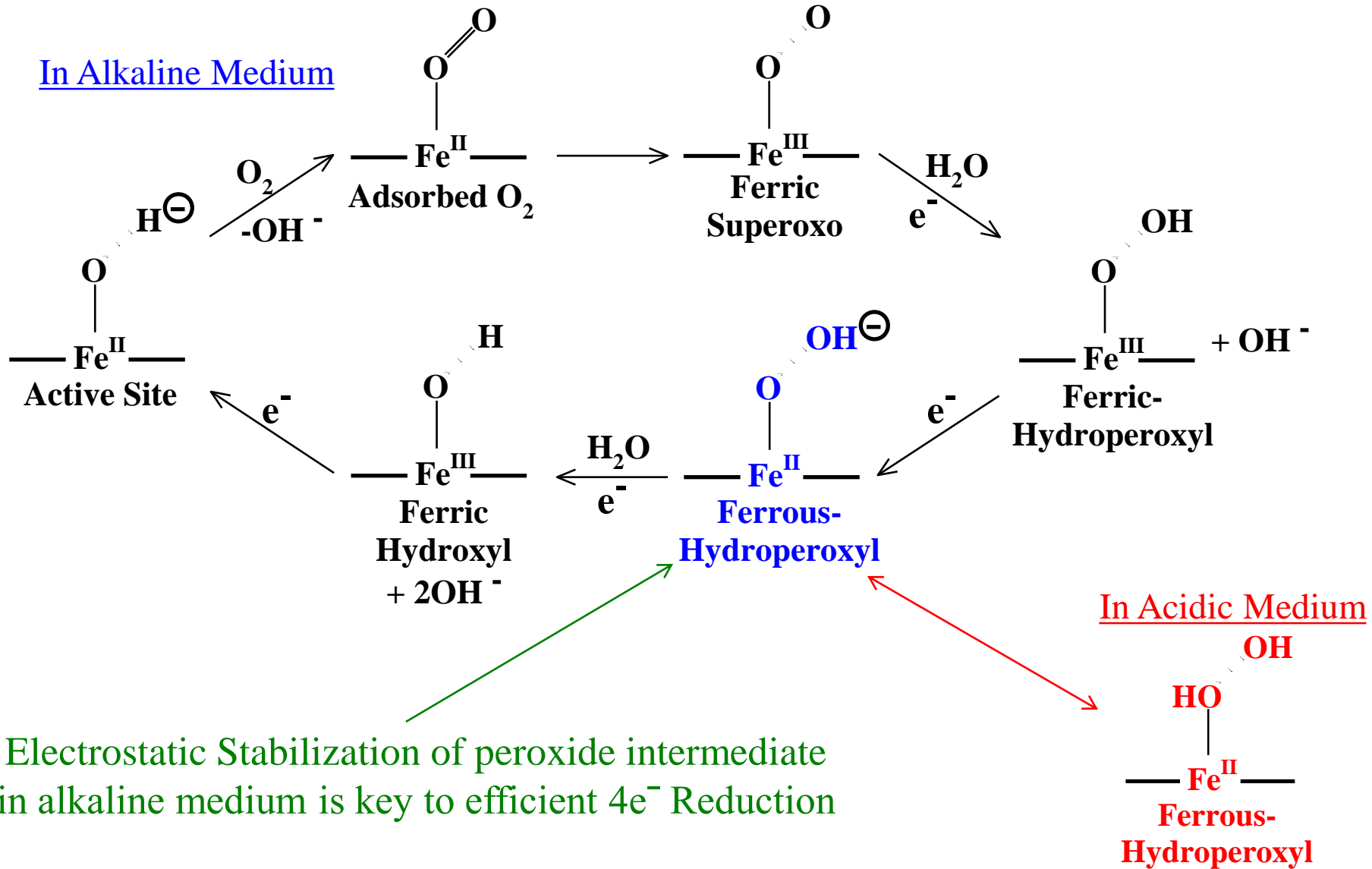
# ORR on FeTPP/C: Acid vs. Alkaline



**Peroxide Intermediate is more stable on FeTPP in alkaline medium**

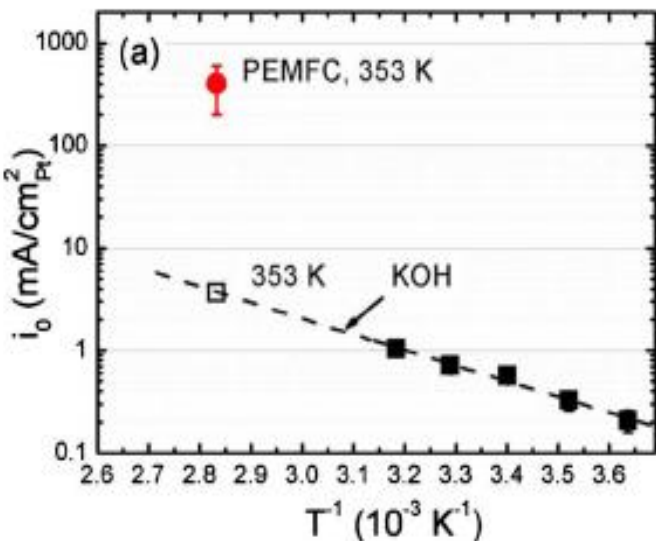


# Oxygen Reduction Mechanism on Fe-N<sub>4</sub> Sites



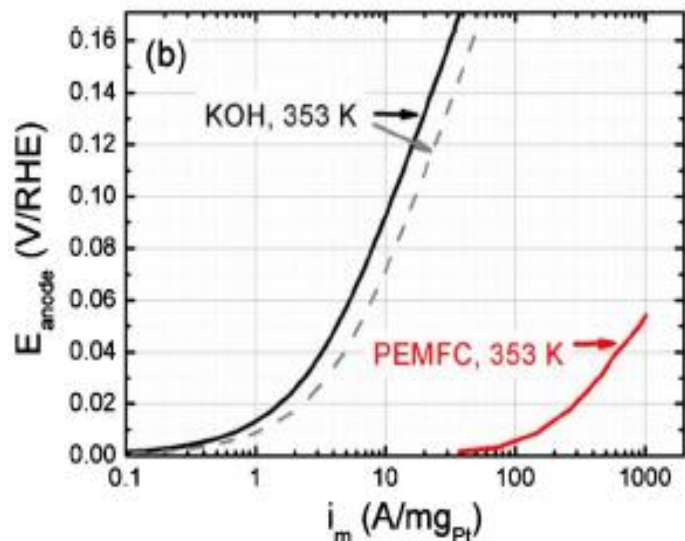
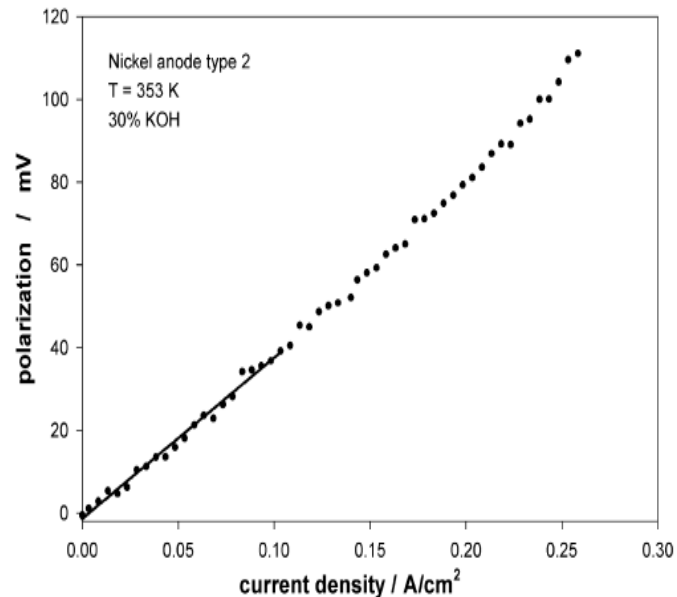


# Alkaline hydrogen oxidation – AEMFC Anodes

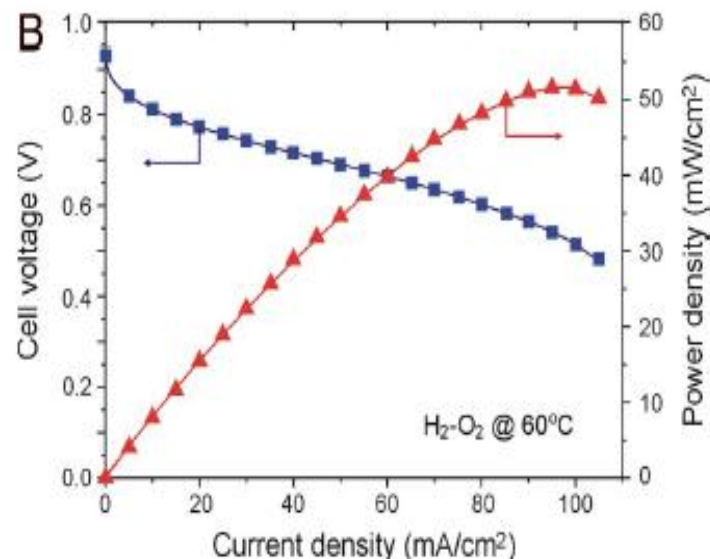


HOR/HER  $i_0$  much lower in alkaline vs. acid media

Need high loading non-PGM catalyst on AEMFC anode



$P_{\text{max}}$  of 50mW/cm<sup>2</sup> obtained with: Cr-decorated Ni nanoparticles on anode & Ag nanoparticles on cathode



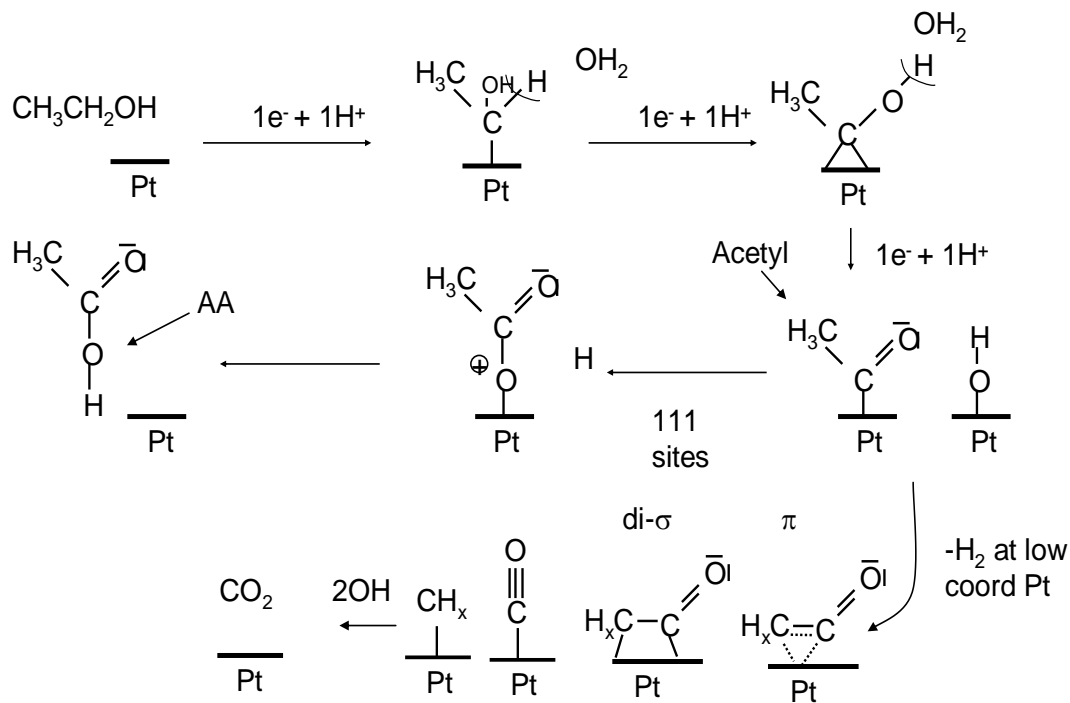
Gasteiger et al. *JACS* 2010

Lu et al. *PNAS* 2008

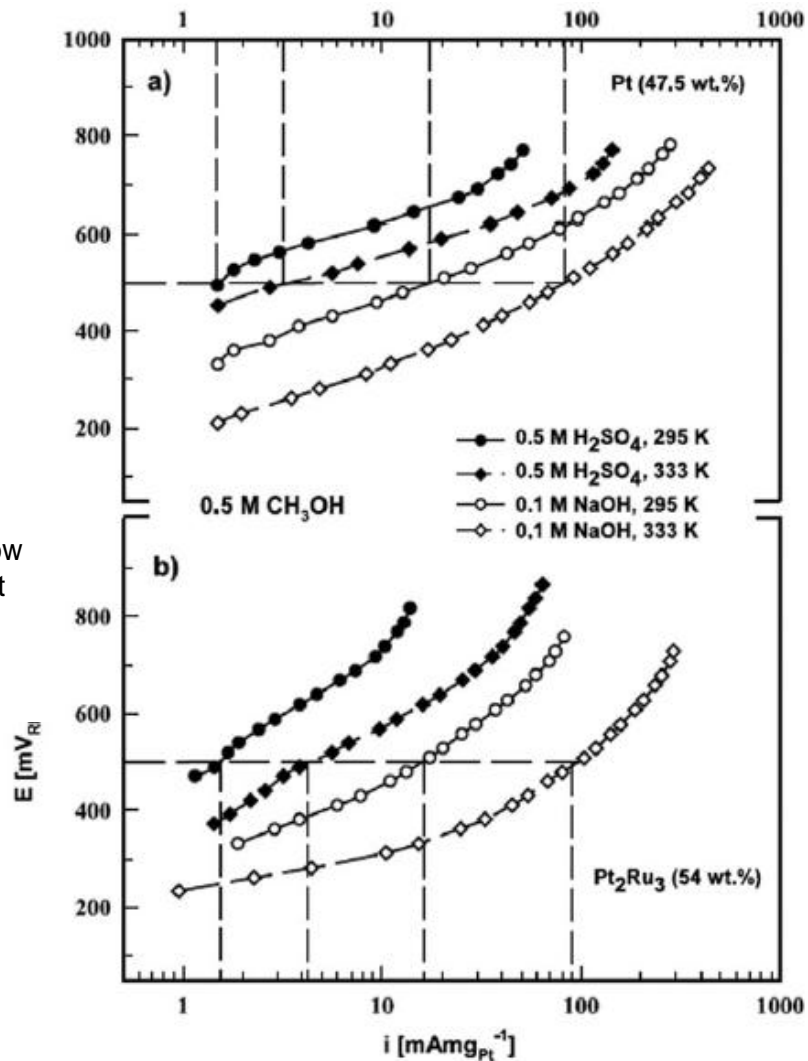




# Literature Survey on Methanol/Ethanol Oxidation Anode Catalysts



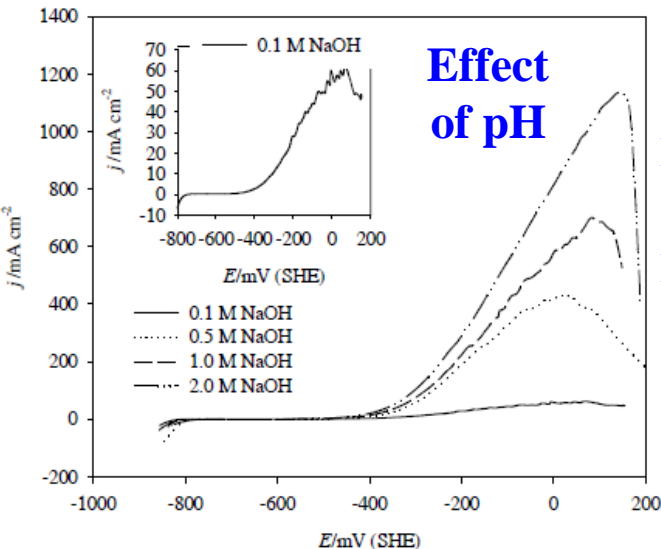
Adzic, R. R., *Electrochim. Acta* **2010**, 55, 4331-4338



Markovic, N.M., *Electrochim. Acta* **2002**, 47, 3707

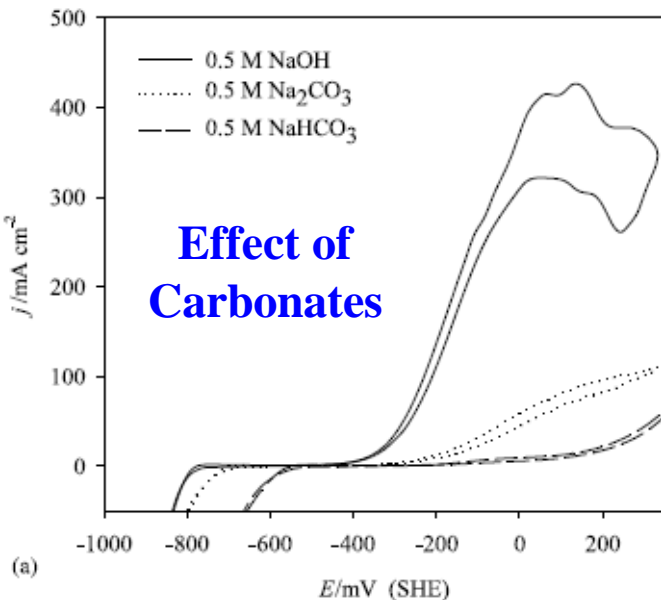


# Methanol Oxidation: Effect of pH, and Carbonates



- Increasing pH or NaOH concentration increases MOR activity
- Effect of carbonate is two-fold
  - Decreasing conductivity and increasing viscosity
  - Decreasing MOR activity by competitively adsorbing with hydroxide anions

K. Scott et al, **2004**, *Electrochem. Acta*, 49, 2443



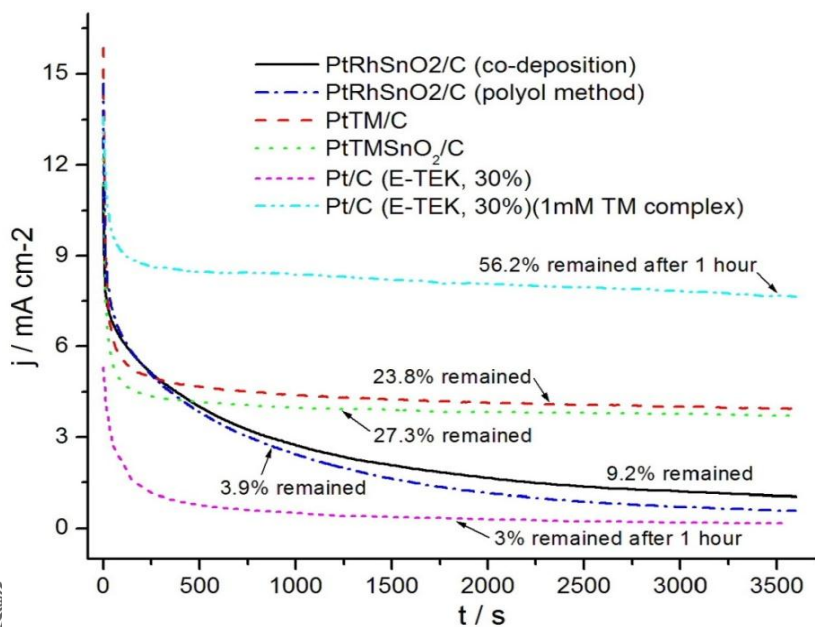
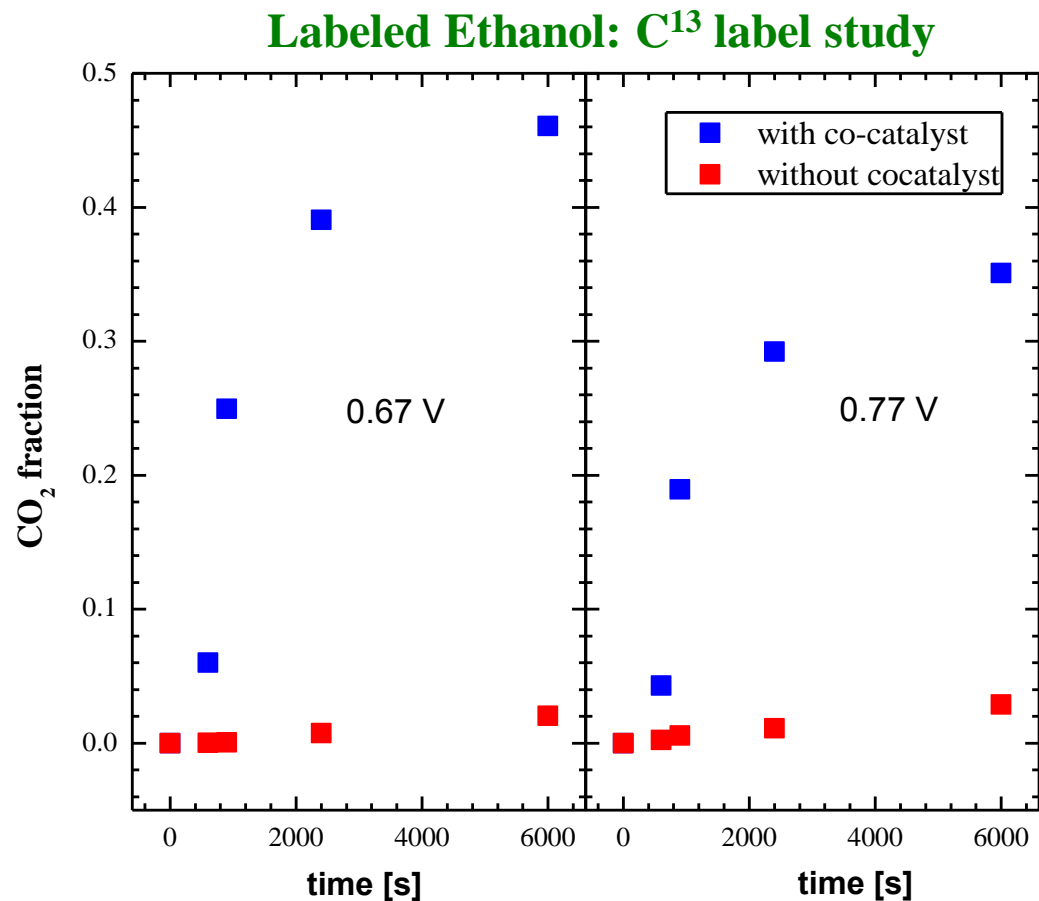
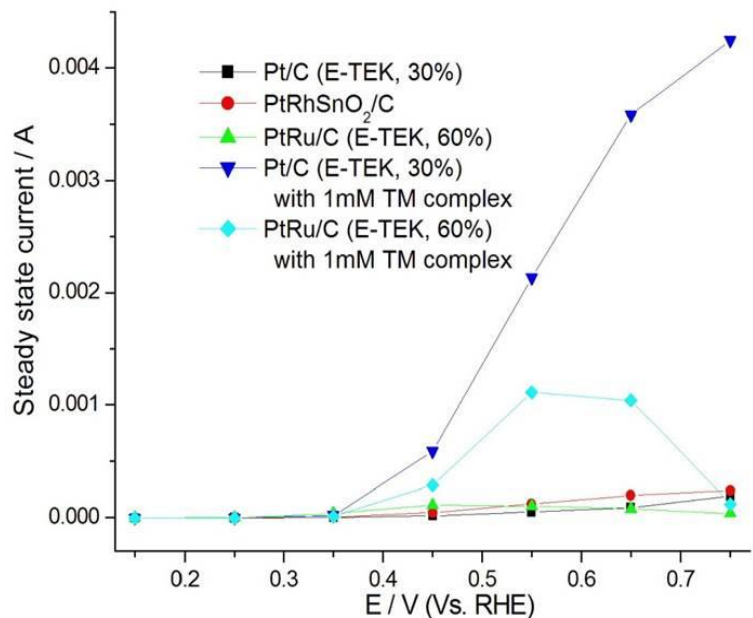
(a)

K. Scott et al, **2003**, *J. Electroanal. Chem*, 547, 17

	H <sup>+</sup>	OH <sup>-</sup>	CO <sub>3</sub> <sup>2-</sup>
Mobility (cm <sup>2</sup> V <sup>-1</sup> s <sup>-1</sup> )	36.25	20.5	3.5
Infinite Diffusion Coefficient (10 <sup>-5</sup> cm <sup>2</sup> /s)	9.3	5.3	0.9



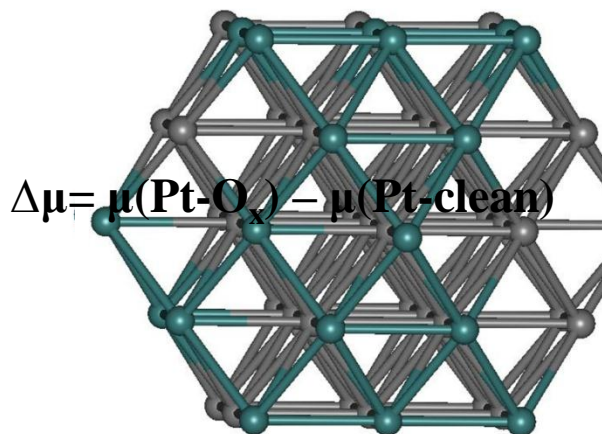
# Enhanced Electrocatalytic Processes: Polyvalent smart catalyst (TM) effect on C-C cleavage



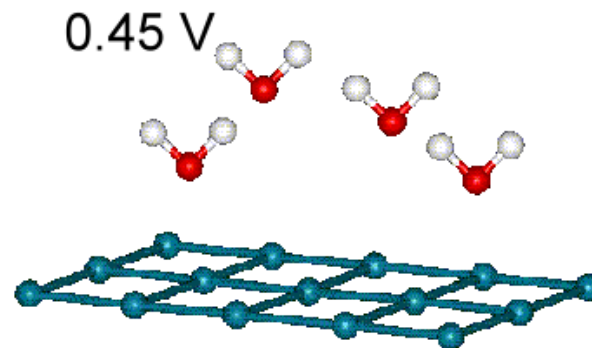
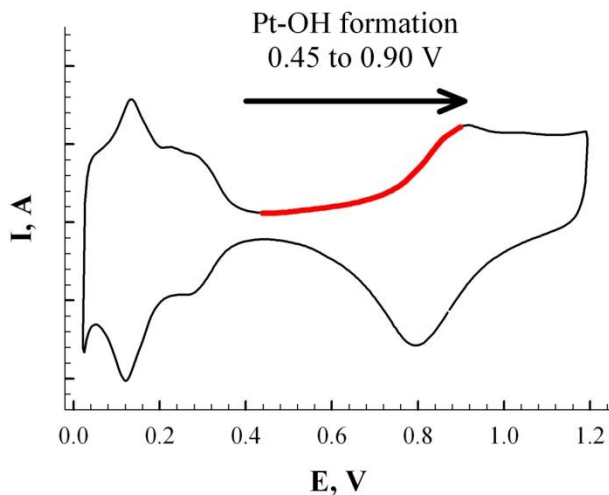
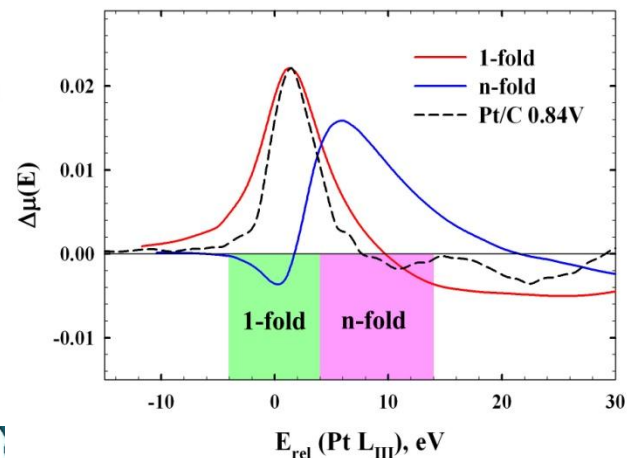
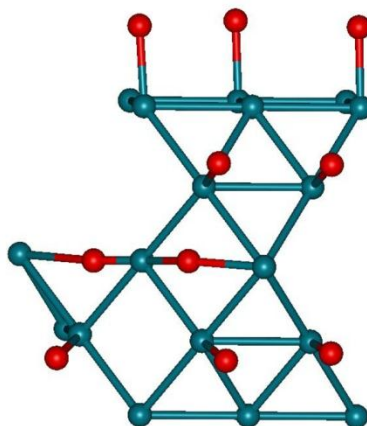


# Atomic Level Picture of Electrocatalytic Pathways via Determination of Specific Adsorption Sites

Grey = bulk

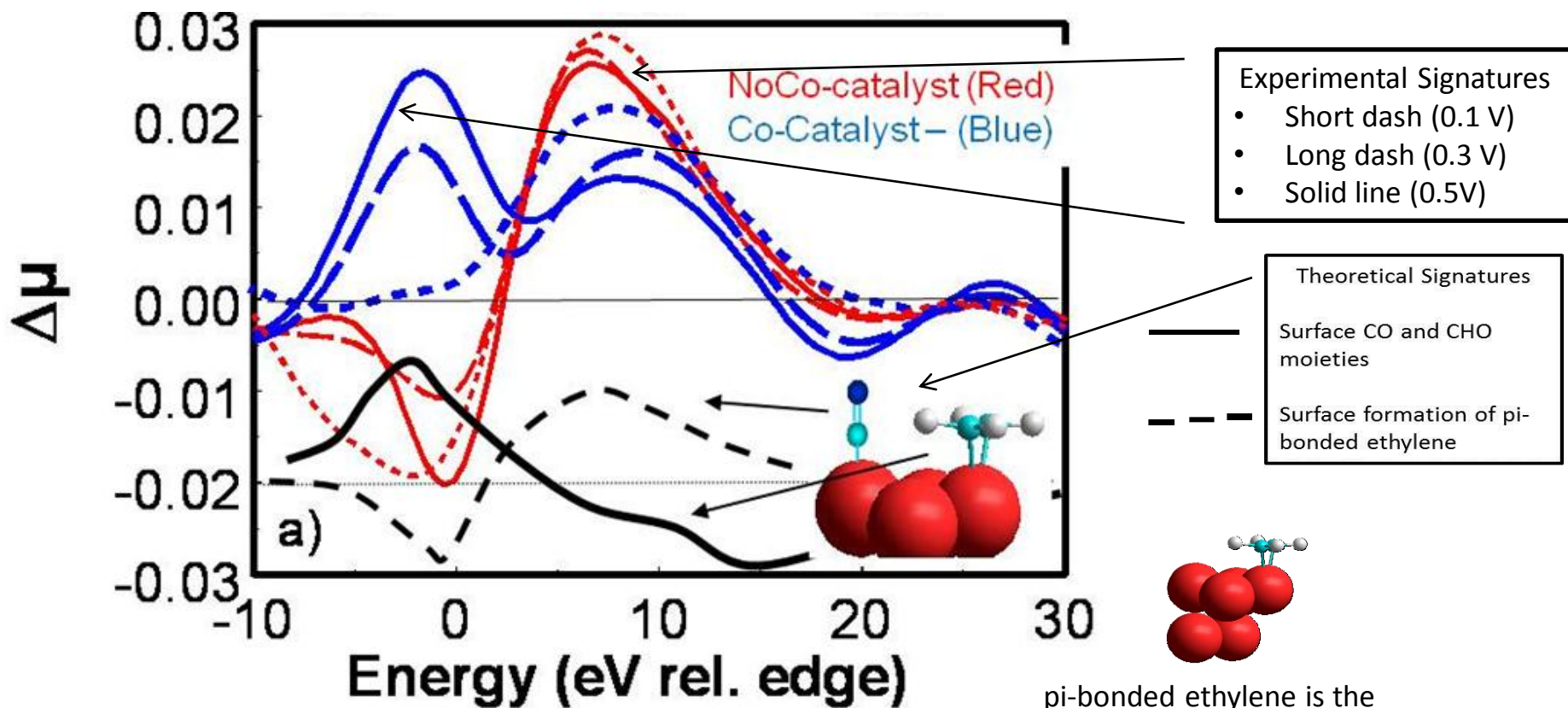


Pt-O<sub>x</sub>





# Proof of Pi-bonded ethylene pathway using synchrotron based in situ XANES on Pt for EtOH oxidation in KOH solution with and without co-catalyst in solution



Comparison of theoretical and experimental signatures for oxidation of ethanol with and without co-catalyst for identifying species on the surface as a function of potential

pi-bonded ethylene is the mechanistically favored route to CO<sub>2</sub>

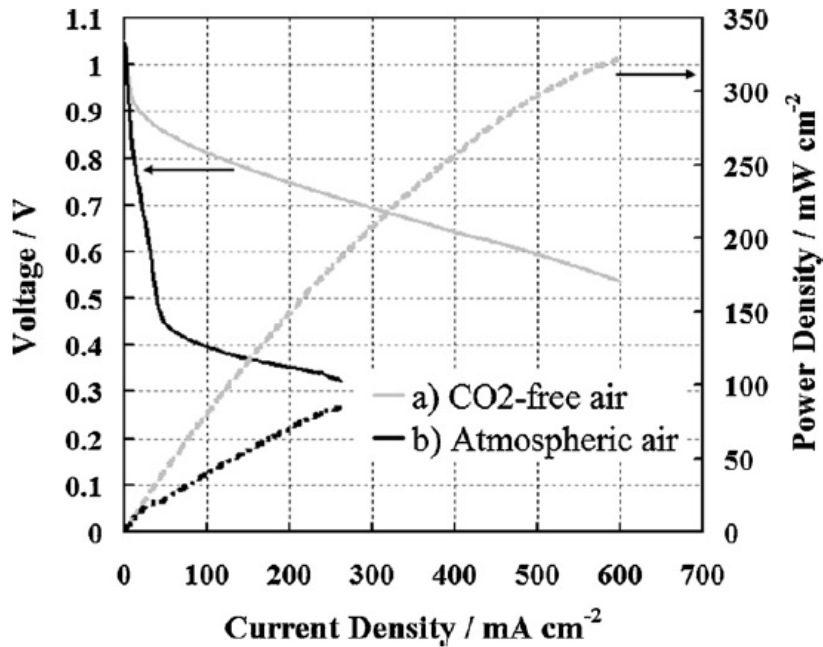


Acetyl species is mechanistically favored toward acetic acid route

Presence of co-catalyst favors formation of pi-bonded Ethylene type intermediate and hence enhances C-C Bond Cleavage



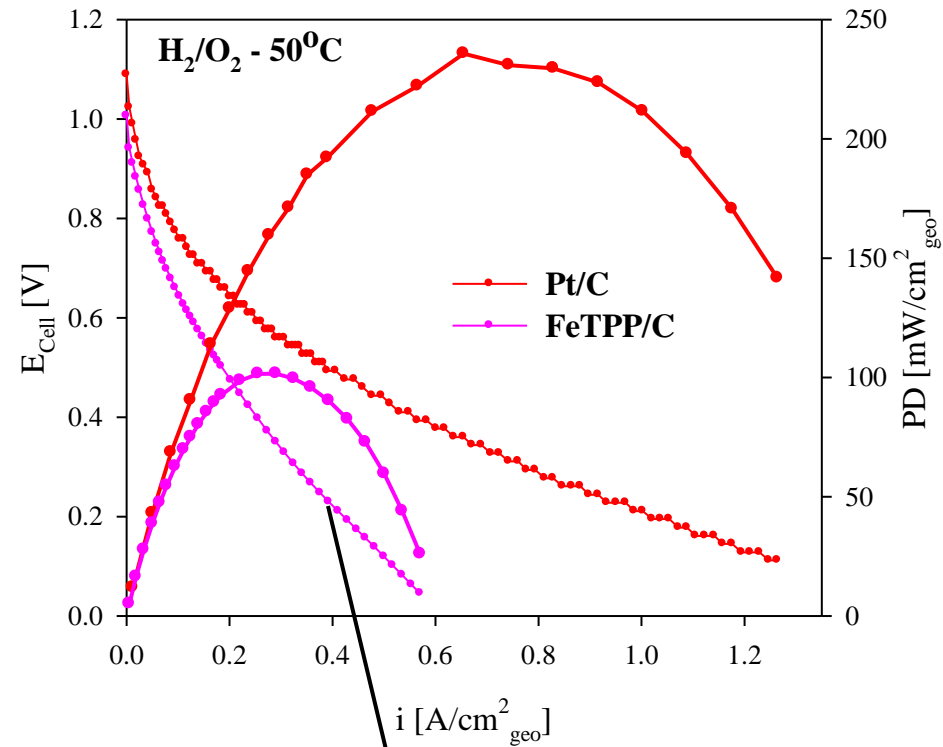
# Literature Survey on Alkaline Membrane Fuel Cell Performance



Pt-catalysts, H<sub>2</sub>/Atmospheric Air  
Acta, 2010

**Use of alcohol feed in the absence of KOH on the anode leads to power densities of only ~10 mW/cm<sup>2</sup>.**

**Challenge lies at anode interface (vide infra)  
Specific Adsorption of Quaternary Ammonium  
Cations is the killer**

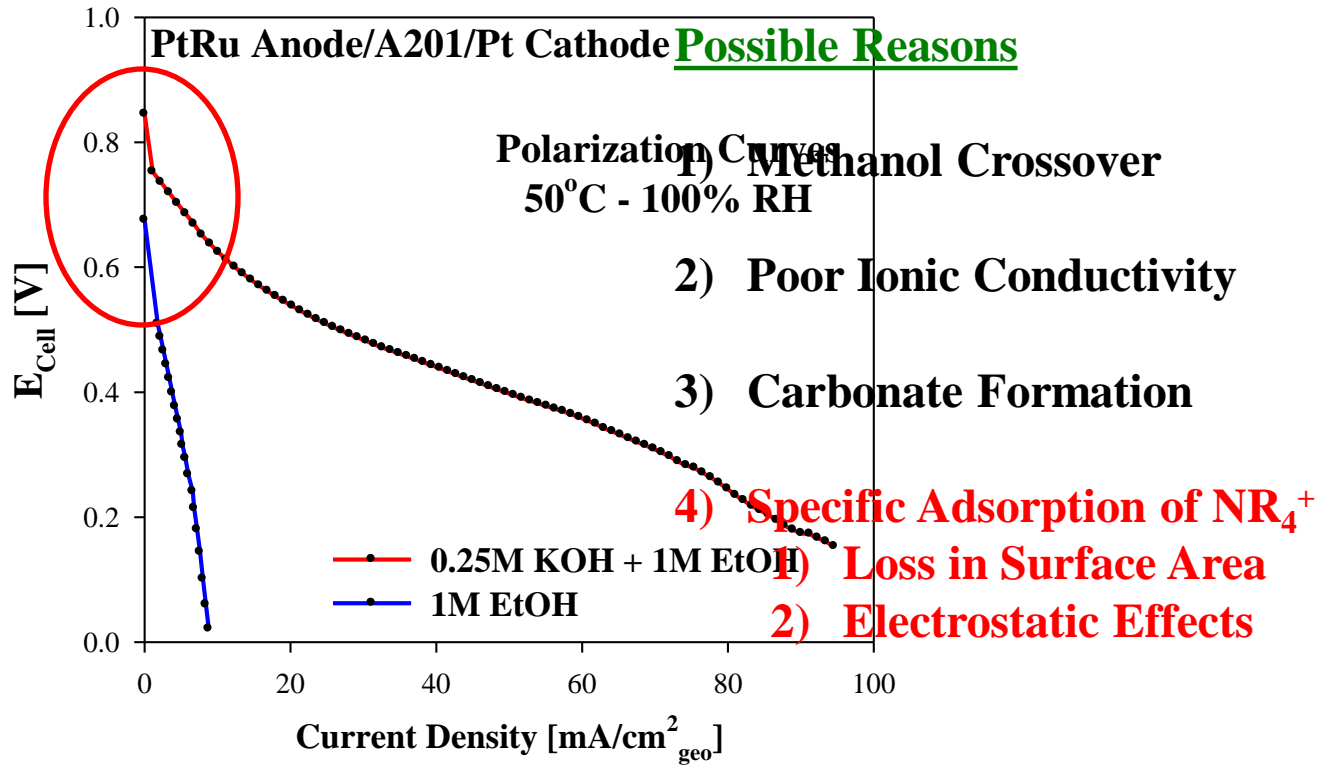


**Thicker Electrodes with  
Non-PGM Cathodes**

**Better Ionomer Solutions  
Needed**



# Direct Ethanol AMFC – PtRu Anode



Anode: PtRu on Toray Paper ( $4\text{mg}_{\text{PtRu}}/\text{cm}^2 + 1\text{mg}_{\text{AS4}}/\text{cm}^2$ )

Cathode: BASF 30% Pt/C on GDL ( $1\text{mg}_{\text{Pt}}/\text{cm}^2, 28.5\% \text{AS4} + 1\text{mg}_{\text{AS4}}/\text{cm}^2$ )

Membrane: Tokuyama A201

**Steep cell voltage loss right in the activation overpotential region**

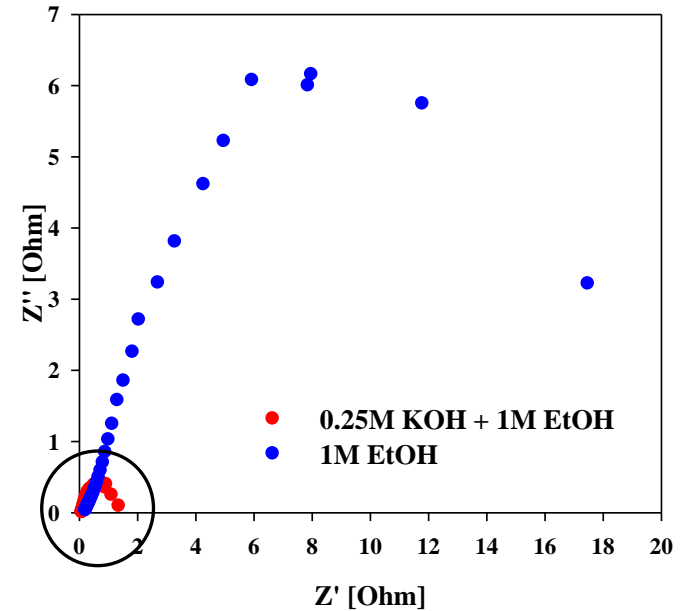
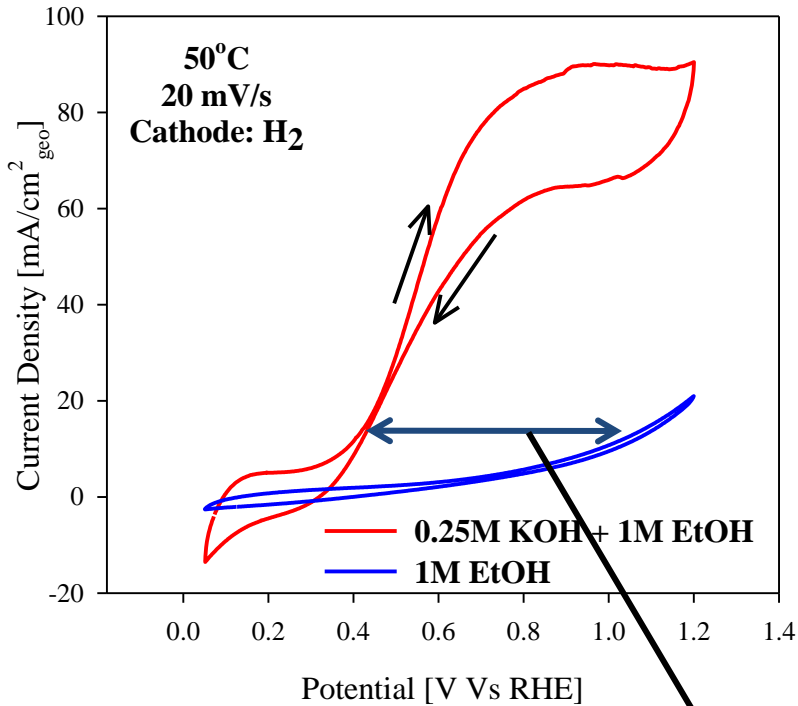


# Ethanol Oxidation on Pt and PtRu Anodes



Cell Temp: 50°C, H<sub>2</sub> Feed on Cathode used as reference electrode, Anode Feed: 8ml/min

Ethanol Oxidation on Pt Anode at 50°C



**Presence of KOH**  
 Significant overpotential for EtOH oxidation in 1M EtOH  
 ➤ Decreases the charge transfer resistance  
 ➤ Increasing the ionic conductivity potential is the key to

	Ionic Resistance [Ohm]	Charge Transfer Resistance [Ohm]
0.25M KOH + 1M EtOH/O <sub>2</sub>	0.109	1.31
1M EtOH/O <sub>2</sub>	0.591	16.85

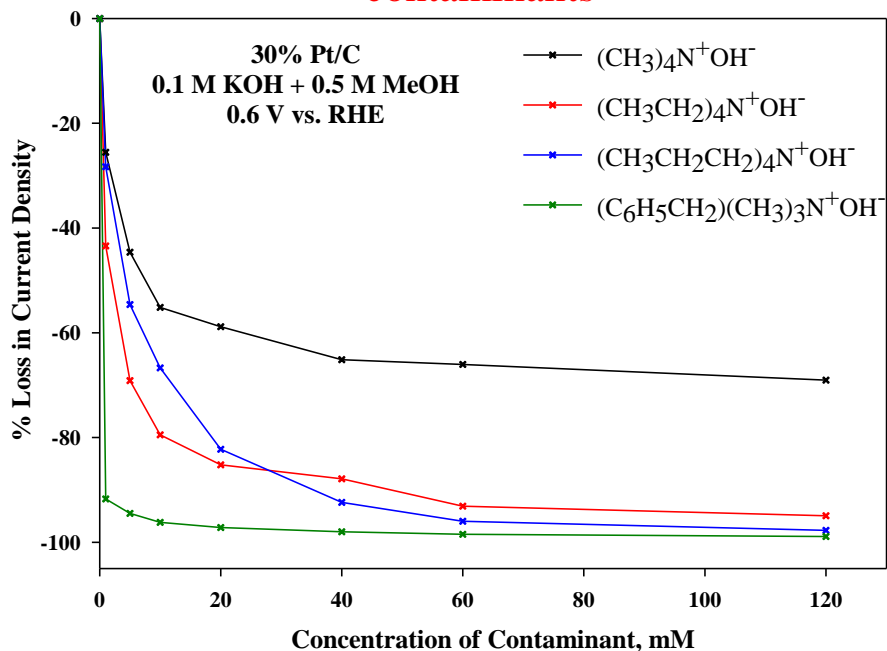




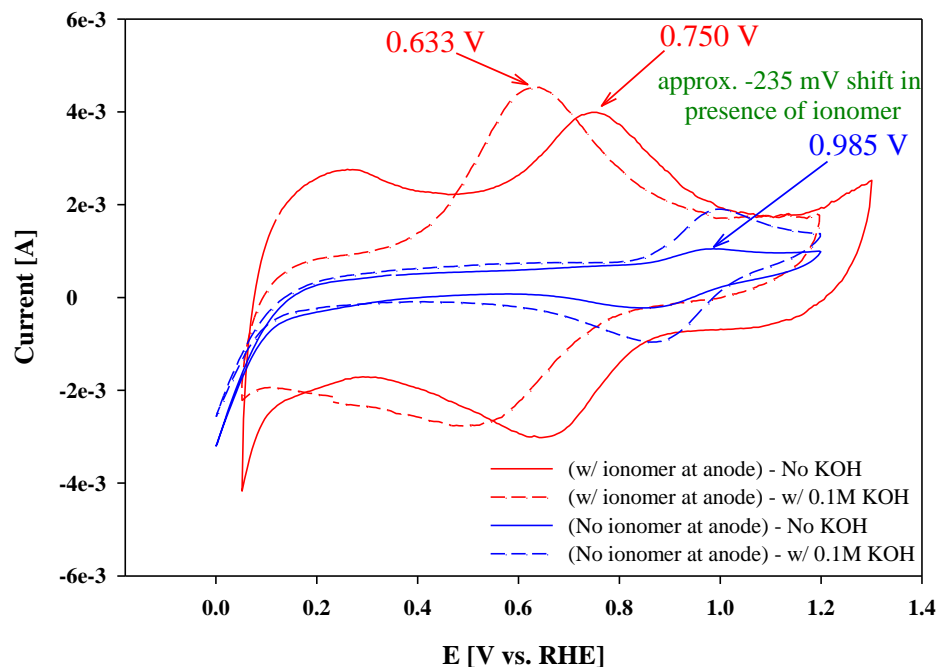
# Specific Adsorption of Quaternary Ammonium Ions



Percent loss in MeOH oxidation current in 0.1M KOH electrolyte in the presence of various ammonium group based contaminants



Experiments with charged redox couples

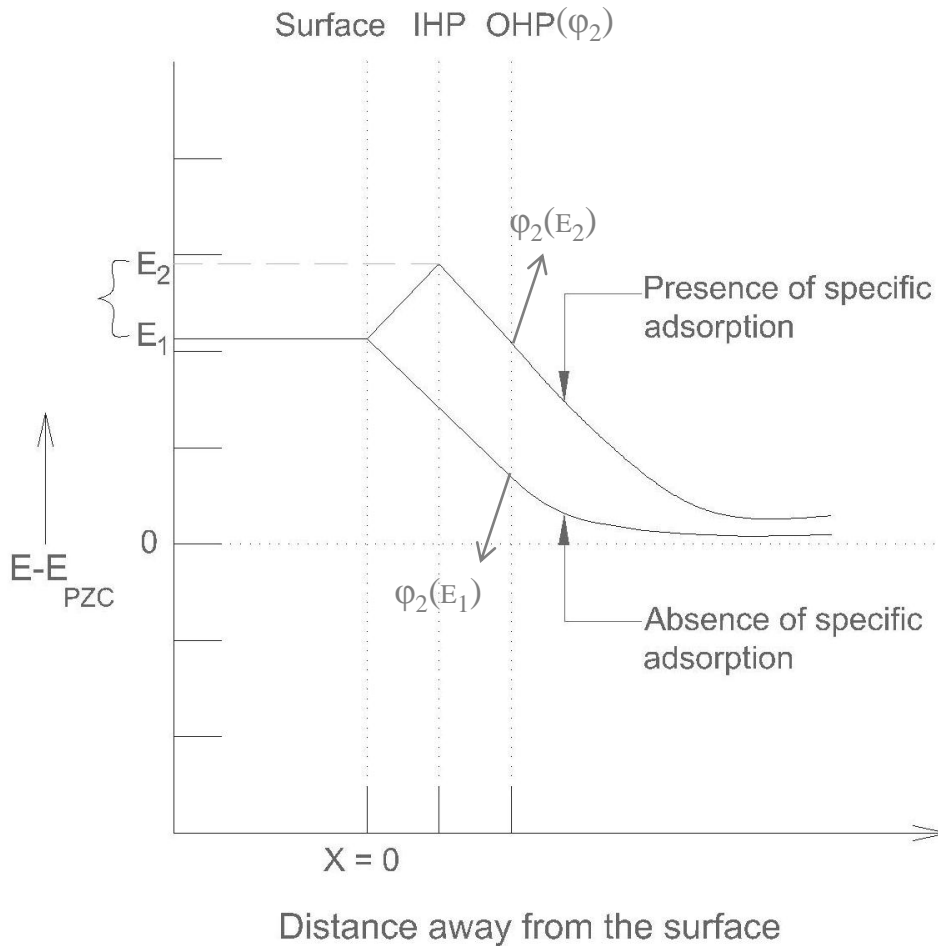


Indicates strong specific adsorption of  $\text{NR}_4^+$  and its effect on interfacial electron transfer

1. Loss of surface area (blocking effect)
2. Electrostatic effects (may hinder  $\text{OH}^-$  transport across IHP)



# Specific Adsorption of Quaternary Ammonium Ions



## Current Hypothesis

- Potential drop across the electrochemical double layer
- Unfavorable Electrostatics in the Inner-Helmholtz Plane
- Future work needed in this direction



# CONCLUSIONS



## ORR - General Mechanistic Considerations

- Inner- and Outer-sphere electron transfer steps compete in alkaline medium
- Higher stability of peroxide intermediate is the primary kinetic advantage in alkaline media

## ORR - Pyrolyzed Non-noble Catalysts

- Redox potential shift of  $\text{Fe}^{2+}/\text{Fe}^{3+}$  metal center upon pyrolysis
- Defect sites on graphitic plane hosts active sites

## Ethanol Oxidation - Smart catalyst (TM) redox couple

- Exhibits the highest reported enhancement of ethanol oxidation.
- Selectivity to produce  $\text{CO}_2$
- Delta-Mu indicates *pi-bonded ethylene intermediate*

## Future Prospects - Interfacial Challenges

- **Results with  $\text{H}_2/\text{O}_2$  are promising**
- **Understanding specific adsorption of quaternary ammonium ions at the anode interface is key**



## Important Considerations for Future Electrocatalysis Research

- Need to unravel Anode Electrode Issues: Electrostatics, Reaction Centers for Hydride formation and Oxidation
- Need for Increase in site density for Non PGM reaction centers
- Role of liquid electrolytes from an interfacial perspective
- Interaction of ionomer with active site: Specific adsorption etc.
- Durability issues need to be determined in conjunction with the operating conditions and the choice of ionomer.



# Acknowledgements

## Funding Agencies

