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

2010 DOE Hydrogen Program Fuel Cell Project Kick-Off

P. I. Name: Sanjeev Mukerjee
Department of Chemistry and Chemical Biology,
Northeastern University, 360 Huntington Av., Boston, MA
02115

September 28, 2010

This presentation does not contain any proprietary, confidential, or otherwise restricted information

Overview Slide

- Timeline: 8/01/2010 t0 01/31/2013 (Budget period 1)
  2/1/2013 to 7/31/2014 (Budget period 2)
- Budget: $ 4,942301.00 (Federal), $ 1,437714.00 (cost share); Total $ 6,38015.00
- Barriers
  - Activity Targets for Non PGM catalysts: exceed 130 A/cm^3 (2010) and 300 A/cm^3 (2015).
  - Durability at temperatures ≤ 80°C, 2000 hrs (2010); 5000 hrs (2015)
- Partners
  - Northeastern Univ., (Prime) Boston: S. Mukerjee (P.I) and S. Smotkin
  - Univ. of Tennessee, Knoxville: Prof. T. Zawodzinski
  - Univ. of New Mexico, Albuquerque: Prof. P. Atanassov
  - Michigan State University: Prof. S. Barton
  - BASF Fuel Cells, Somerset, NJ: Dr. E. DeCastro
  - Nissan Motors: Dr. K. Adjemian
  - Los Alamos National Lab: Dr. P. Zelenay

Overview

Timeline

- Project start date: 8/1/2010
- Project end date: 7/31/2014
- Percent complete: Just Started

Barriers

- Barriers addressed
  - Current status: 130 A/cm^3 @ 0.8 $V_{iR\ free}$ ~ 80°C
  - Target (2015): 300 A/cm^3 @ 0.8 $V_{iR\ free}$
  - Durability: 2000 hrs (current), 5000 hrs (2015)

Budget

- Total project funding
  - DOE share: $ 4,942301.00
  - Contractor share: $ 1,437,714.00
- Funding received in FY10: $ 750,000
- Funding for FY11

Partners

- Univ. of Tennessee, Knoxville: Prof. T. Zawodzinski
- Univ. of New Mexico, Albuquerque: Prof. P. Atanassov
- Michigan State University: Prof. S. Barton
- BASF Fuel Cells, Somerset, NJ: Dr. E. DeCastro
- Nissan Motors: Dr. K. Adjemian
- Los Alamos National Lab: Dr. P. Zelenay

Project lead: Northeastern Univ., (Prime)
Boston: S. Mukerjee (P.I) and S. Smotkin

Relevance

- Information to include:
  - Objectives: To develop new classes of non pgm electrocatalysts which would meet or exceed DOE 2015 targets for activity and durability. This will enable decoupling PEM technology from Pt resource availability and lower MEA costs to less than or equal to $ 3/KW
  - Impact
    - Lower MEA cost to less than or equal to $ 3/KW
    - Independence from Pt and other precious metal global availability
    - Greater independence to poisons which typically effect of Pt & Pt alloys (i.e., sulfur, CO etc.), Hence ability to tolerate H_2 with greater impurity.

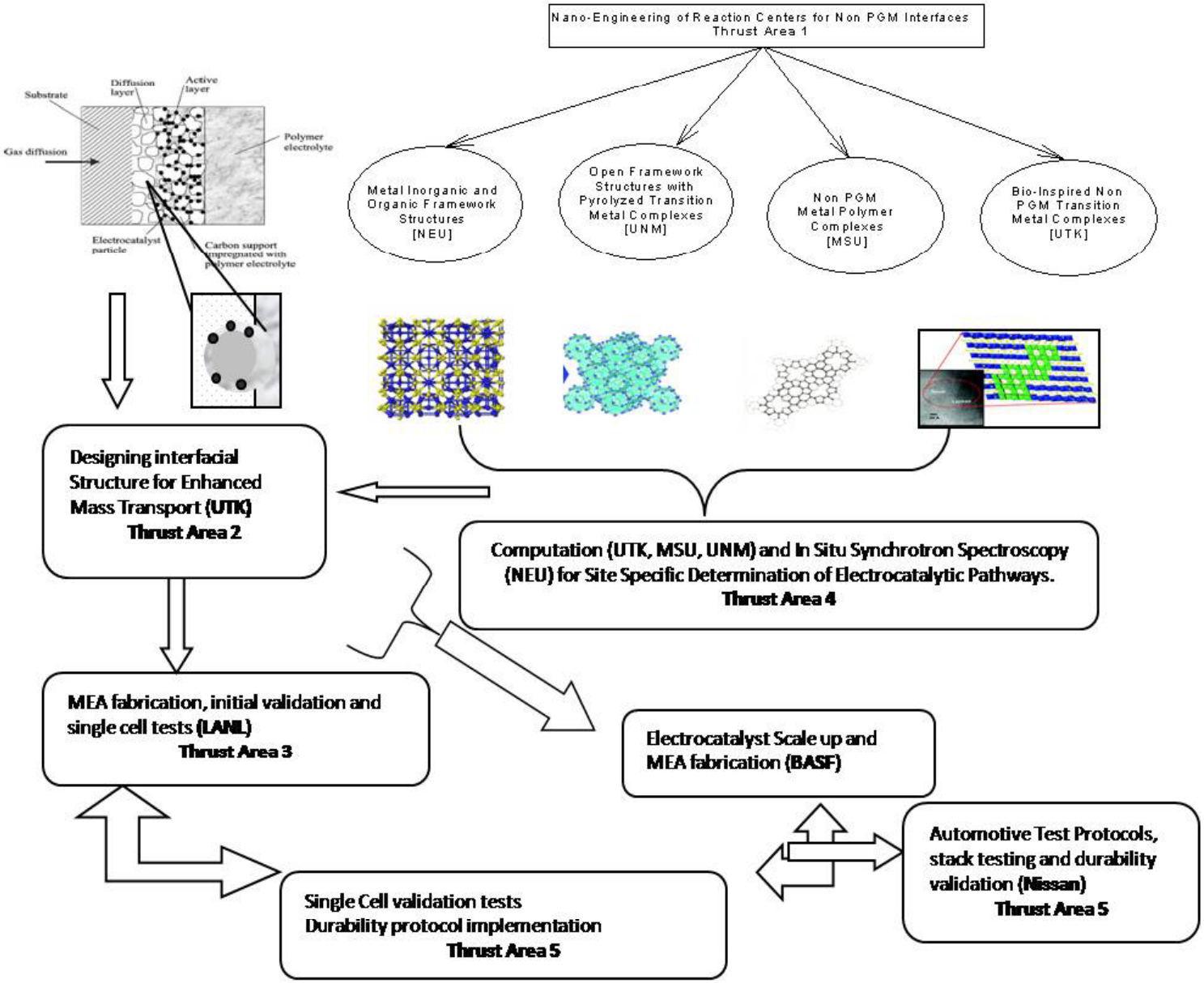
Overall Approach

- **Overall technical approach:**
  - **Comprehensive materials development strategy encompassing**
    - **Novel new reaction centers under the broad categories of**
      - Metal oxides
      - Metal polymer composites
      - Metals in controlled ligand environments
    - **Controlling Metal support interactions**
      - For ensuring reaction center dynamics
      - Efficient mass transport of charged and solute species
    - **Ensuring Stability via careful control of reaction center's electronic structure**
  - **Computing transport and reaction dynamics**
    - Reaction dynamics at complex reaction layer for oxygen and oxide bonding
    - Transport modeling in multi-layer structures
  - **In situ Synchrotron Spectroscopy**
    - For elucidating electrocatalytic pathways in complex reaction centers
    - Quantifying degradation with element specificity under in situ operating conditions
  - **Membrane Electrode Assembly and Cell Testing**
    - Fabrication of reaction layers with superior ionic and reactant transport
    - MEA fabrication , Single Cell Tests
    - Stack fabrication and validation
    - Durability tests using DOE protocols
- **Program Technical Barriers and Approach to Overcome them**
  - Current volumetric Power density is ~ 130 A/cm^3 which is close to 2010 DOE target. 2015 target is 300 A/cm^3 which requires (a) development of new classes of materials, (b) redesign of the catalyst support and (c) understanding at a fundamental level (i) transport of charged and solutes species and (ii) electrocatalytic and degradation pathways under actual operando conditions. Our approach addresses all these issues for meeting 2015 DOE target.
- **Milestones and Go/No go decisions:**

  Milestones (2011)
  - Materials Development: RDE measurement of volumetric power density
    - Meet and exceed ~ 130 A/cm^3 (iR free) at 0.8 V RHE (80°C or below) 2011- Q4
    - Durability measurements based on DOE protocols to project stability within DOE specifications (2011) Q3
    - Initiation of in situ measurements for degradation and electrocatalytic studies (2011) Q3
    - Initiation of Membrane Electrode Fabrication for Single Cell Studies (2011) Q3
  - Computational efforts for electrocatalysis and transport measurements
    - Set up protocols for computational efforts and generate first set of data for comparison with experiments Q2

  Go/No Go Decisions (2011)
  - Materials Screening based on above mentioned benchmark (Q2, 2011)
  - Computation approach assessment based on its predictive capabilities and short listing of approaches (2011, Q3)

Project Scope, Objectives and Management



Project Tasks, Milestones and Go/No-Go Decisions

Task. 1: Materials Preparation

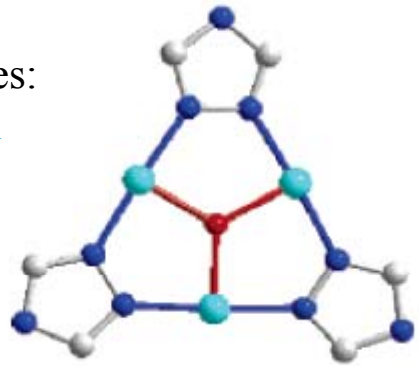
Participating Institutions: NEU, MSU, UNM, UTK and BASF

- **NEU: Development of Polynuclear Reaction Centers**
  - Synthesis of Trinuclear Co-Triazoles
  - Bi and Tetra-Nucleating Ligands for Coordinated Polymers
  - Biomimetic Coordination Polymer Systems
- **MSU: Development of MNC Catalysts**
  - Varying N-Precursor Materials
  - Varying Metal Precursors
  - Incorporation into Open Framework Templated Structures
- **UNM: Open Framework Templated Structures**
  - Metal Organic Systems
  - Si based Templated Open framework structures
- **UTK: Development of Enzyme Mimics**
  - Organometallic Complexes of known ORR active enzyme systems
  - Using N based Ligands to control E-density of active metal centers
  - Tandem multi-element enzyme mimics
- **BASF: Materials Scale Up**

Go/No go decision based on 130 A/cm^3 at 0.8 $V_{iR\ free}$ or 100 mA/cm^2 (iR free) single cell

Northeastern University –Materials Development (Task 1.1)
Polynuclear Reaction Centers
Synthesis of Trinuclear Co-Triazole Metal Organic Framework

Color codes:
Co-cyan
O-red
N-blue
C-white



Trinuclear Cobalt system with a μ_3-oxo center using triazole ligands.

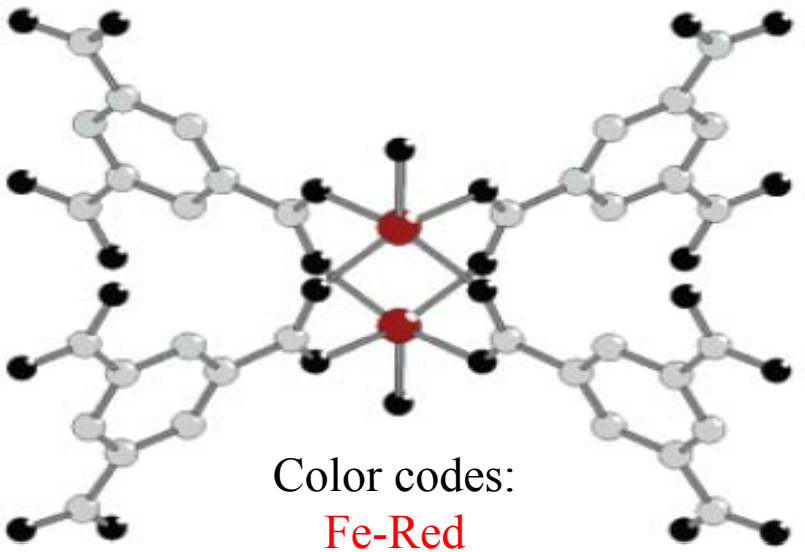
- 1,2,4-Triazole used as ligands to coordination transition metal ions at its N_2 and N4 position sites
- Transition metal ions bound together by a μ_3-oxo center
- Synthesis accomplished under hydrothermal conditions and/or by using microwave irradiation

Advantages of Metal-Organic Framework Materials:

- High density of catalytic sites at a regular periodic array
- Onus of reactant binding and electron transfer shared amon g several active sites place in close proximity

Q. Zhai, Z. Lu, S. Chen, et.al., *Crystal Growth and Design*, **2006**, 6(6), 1393-1398

Northeastern University –Materials Development (Task 1.1)
Biomimetic Coordination Polymer Systems

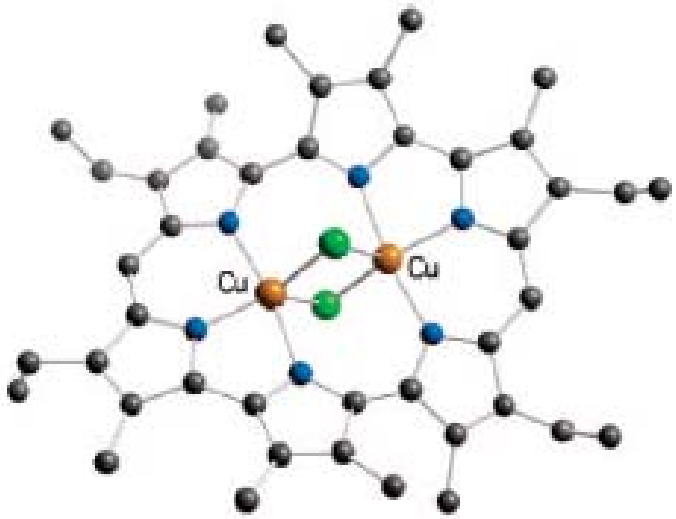


Color codes:
Fe-Red
O-Black
C-Gray

- Di-iron non-heme active site
- Biomimetic metal-organic framework involving mixed valent Fe sites
- Framework structure (as opposed to individual metal-organic compounds) imparts higher thermodynamic stability to the metal centers.

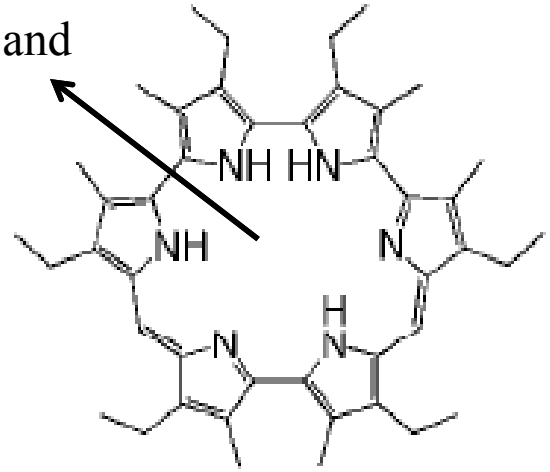
L. Xie, S. Liu, C. Gao, R. Cao, et.al., *Inorg. Chem.*, **2007**, 46, 7782-7788

Northeastern University –Materials Development (Task 1.1)
Expanded Porphyrins – Increased cavity for accommodation of more than one metal center



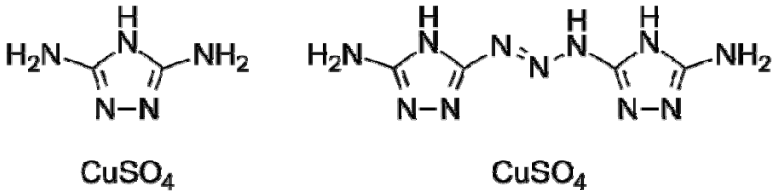
- Tetrapyrrolic macrocylces synthesized with large cavities to accommodate more than one metal center
- This property is defined as the "polynuclearity" of the metal centers
- These class of materials involve a novel extension from the already known porphyrin macrocycle electrochemistry

Expanded porphyrin cavity involving both pyrrollic and pyridinic N-coordination groups



J. Sessler, and E. Tomat, *Acc. Chem. Res.*, **2007**, 40, 371-379

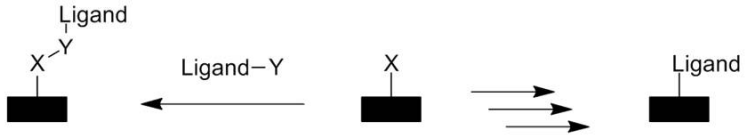
UTK Materials Initiative: Ligands for Oxygen Reduction Currently Under Investigation (Task 1.1.3)



- 1,2,4-Triazine-based ligands for oxygen reduction identified ***previously***.
- Immobilization on carbon black facilitated by ***adsorption***.

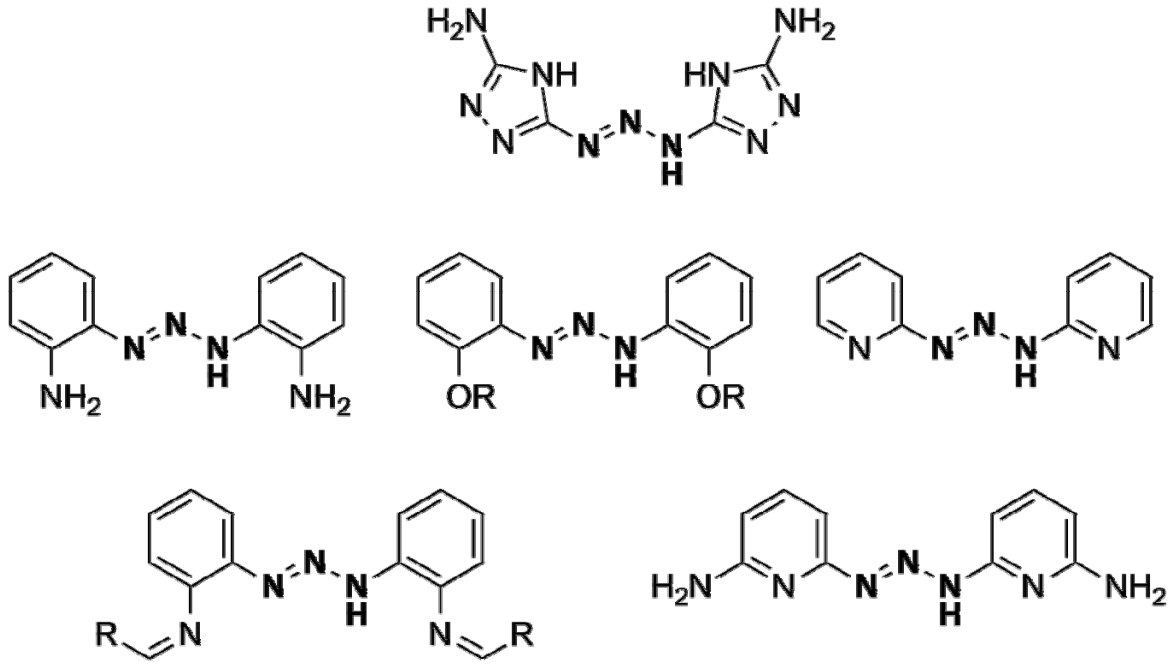
- Next generation ligands dissect the activity of more complex ***triazene***-bridged triazole ligand. Which is more important, triazole or triazene?
- Immobilization on carbon black facilitated by ***adsorption*** of $CuSO_4$ complexes.

Two distinct approaches for immobilization of ligands
- ***Stepwise synthesis*** of ligands on carbon black.
- Attachment of ***intact ligands*** onto functionalized carbon black.



Covalent attachment of ligands allows:
- Complexation of metals in a separate step using a ***broader range of conditions***.
- Use ***of different metal salts***.
- Preparation of complexes ***without dependence of solubility*** for deposition.

Next Generation Ligands for Oxygen Reduction Triazoles or Triazene?



Next generation ligands dissect the activity of more complex ***triazene***-bridged triazole ligand. Which is more important, triazole or triazene?

Immobilization on carbon black facilitated by ***adsorption*** of $CuSO_4$ complexes.

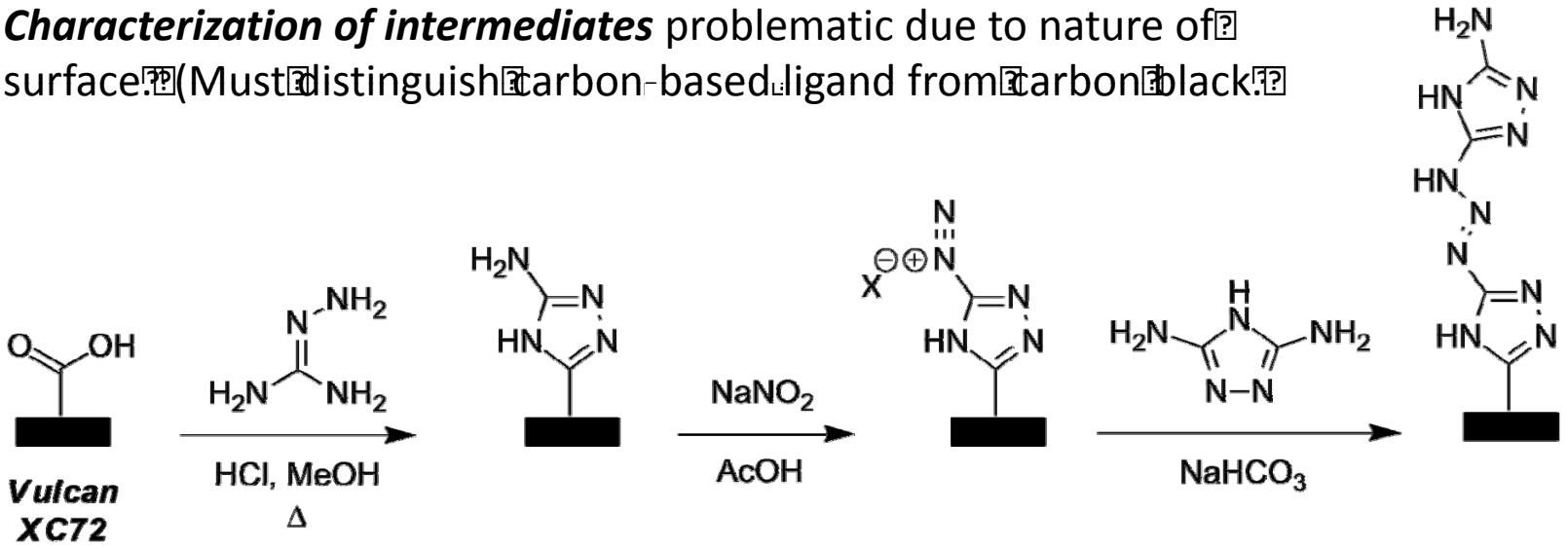
Ligands for Oxygen Reduction
Stepwise Synthesis on Carbon Black

Can be applied to ***several different families of ligands***.

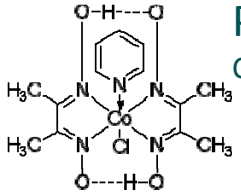
Greater efficiency (labor, chemicals).

Lack of purification steps could lead to immobilized ligands as well as impurities (***heterogenous surfaces***).

Characterization of intermediates problematic due to nature of surface. (Must distinguish carbon-based ligand from carbon black.)

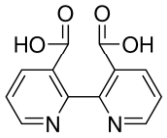


UNM-Task 1.1.2
Microemulsion-Templated Non-PGMColloidal Colloidal Approach to Transition Metal /N-C Catalysts



PBDM-Co

Chloro(pyridine)bis(dimethylglyoximato)cobalt(III)

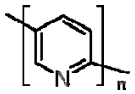


Dicar

2-2'-Bipyridine-3-3'dicarboxylic acid

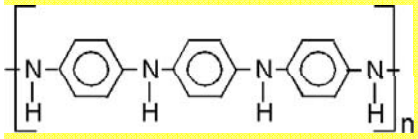
DMO

4-4'Dimethoxy-2-2'-bipyridine

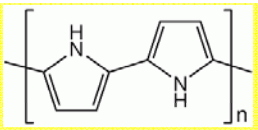


Poly - Pyridine

Poly(2,5pyridine)

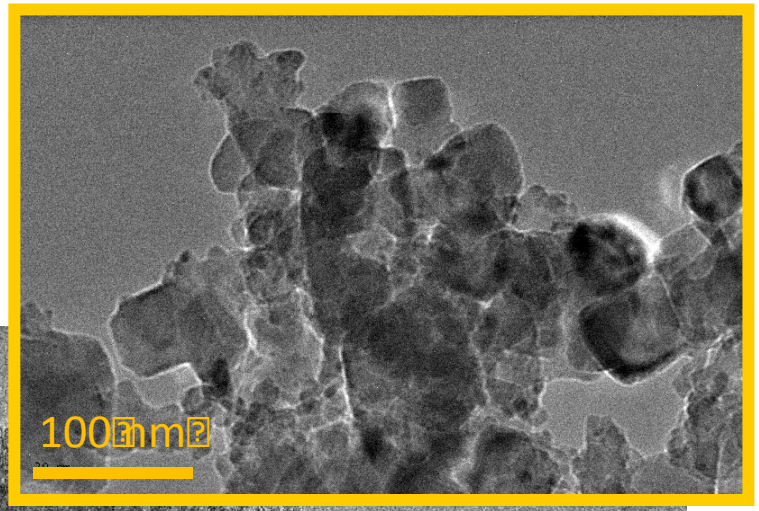


Polyaniline



Polypyrrole

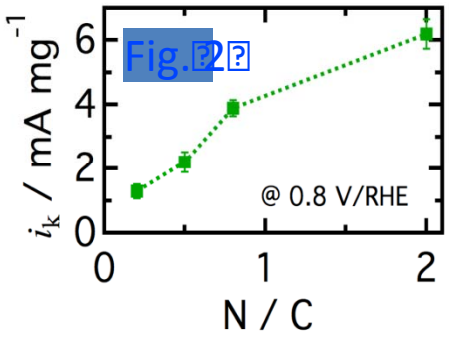
H_2NCN Cyanamide LANL

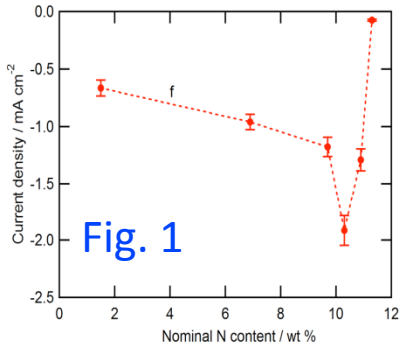


MNC Catalysts by High Pressure Pyrolysis (MSU) Task 1.1.4

Novel process to create metal-nitrogen-carbon (MNC) catalysts using autogenic pressure due to precursor gasification

- N content and catalyst activity increase with N precursor content (Fig. 1)
- Nitrogen-carbon ratio in precursor directly impacts catalyst activity (Fig. 2).

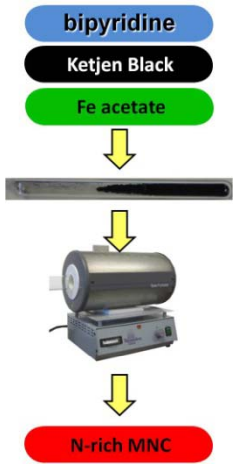


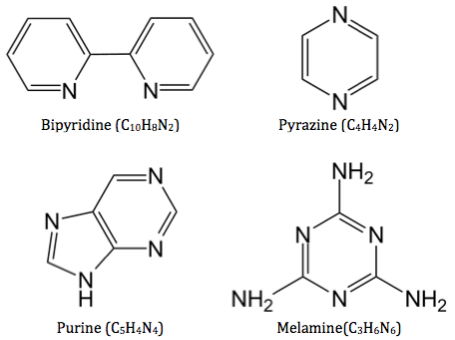


Open-framework templated structures (with UNM).

Allow detailed control of microporosity and mesoporosity within catalyst particles, leading to variation in active site density and activity, and accessibility of reactants and products to active sites through mesopores.

- Template morphology, composition, and structure will be correlated to catalyst performance.
- Observe active sites by XPS and XAS, and correlate to catalyst activity.
- Parametric studies will provide validation data with which to test simulations.





Scheme 1. Molecular structure of nitrogen precursors

BASF Fuel Cell
Task 1.5; Materials Scale-up strategies

- **BASF: Task 1.5, Scale up strategies based on in-house implementation of Synthesis Methods**
- ***Duration*** 12-30 mos
- ***Deliverables*** at 24 months*:* Catalysts incorportsted into MEAs for testing at LANL and Nissan to be used in validation at the 30 month period.

Milestone (@ 30 mos): 10-20 gm batch with ± 5 % variation.

- **Go/No Go @ 30 months,** Task 2: MEA performance benchmark reached at 100 mA/cm2 at 0.82 V vs. RHE (iR free) with H2/Air, 80C (ambient pressure), fully humidified conditions.

Task 2
Development of Novel Reaction Layer Formulations, Design of Gas Diffusion Layers and Fabrication of MEAs

Participating Institutions:

UTK- Design of Reaction Layer, Gas Diffusion Media and MEA fabrication

UNM- Design of Reaction Layers for Improved Mass Transport

MSU- porous Media for Novel Reaction Layers

BASF- Scale Up Strategies and MEA Fabrication in Large Scales

Milestones at 30 mo: MEA design translating 130 A/cm^3 to 100 mA/cm^2 at 0.8V (iR free)
Go/No go Decision based on achieving 1 A/cm^2 at 0.65 V (iR free)

MEA Preparation and Testing (UTK)

UTK will develop and offer as a service to the team both immobilization chemistry on carbon and MEA preparation capabilities

1. Inks for coating of membranes/decals will be developed using standard carbon samples
2. Dissemination of know-how and training amongst team members will be available
3. Testing at UTK on FC test stands
   - Standard polarization curve measurements with ac impedance
   - In situ voltammetry methods under development

Goal: Sort out mechanism of ORR on NPGMs

Catalyst and Electrode Scale up & Fuel Cell Testing

- **<u>BASF: Task 2.0, Scale up strategies based on in-house implementation of MEA and electrode structure developments at Case and LANL. This is expected to begin at the end of the first year.</u>**
- **Subtsk 2.1 (BASF): Incorporation into MEAs**
  - Using catalysts with best analytical performance, incorporate into gas diffusion electrodes by developing inks. Use either draw-down or small scale machine coating.
  - Laminate GDEs into a MEA using standard Celtec-P high temperature membranes (50cm^2).
- ***Duration*** 12-30 mos
- ***Deliverables*** at 24 months*:* MEAs for testing at LANL and Nissan to be used in validation at the 30 month period.

Small roll-to-roll coating machine

5Kg catalyst alloying oven

Catalyst Scale Up

- Assortment of reaction vessels from grams to 5Kg/batch
- Specialized hydrogen reduction / alloying ovens (5kg and 10Kg batch)

Coating Machines for Gas Diffusion Electrodes

From draw-down to roll-to-roll coaters

Fuel Cell Testing

- Expansion in 2011 to >30 single cell test stations

Go/No go decision based on achieving 130 mA/cm^2 at 0.8 V (iR free) and 1 A/cm^2 at 0.65 V (iR free).

Task 3
Testing and Durability Measurements

Participating Institutions:

NEU- Electrocatalyst Testing –RRDE Measurements
High Throughput Screening in Segmented Cells with MEAs
In situ Synchrotron Measurements of Durability

UNM- Materials Durability Screening
Electrode Durability Studies-Liquid Electrolytes, Half Cell Config
Ex-Situ Spectroscopic Measurements for Durability

UTK- MEA Testing in Single Cells

LANL- Validation by MEA Testing and Durability Measurements

BASF- Large Scale MEA Tests

Nissan- MEA Tests for Automotive Applications

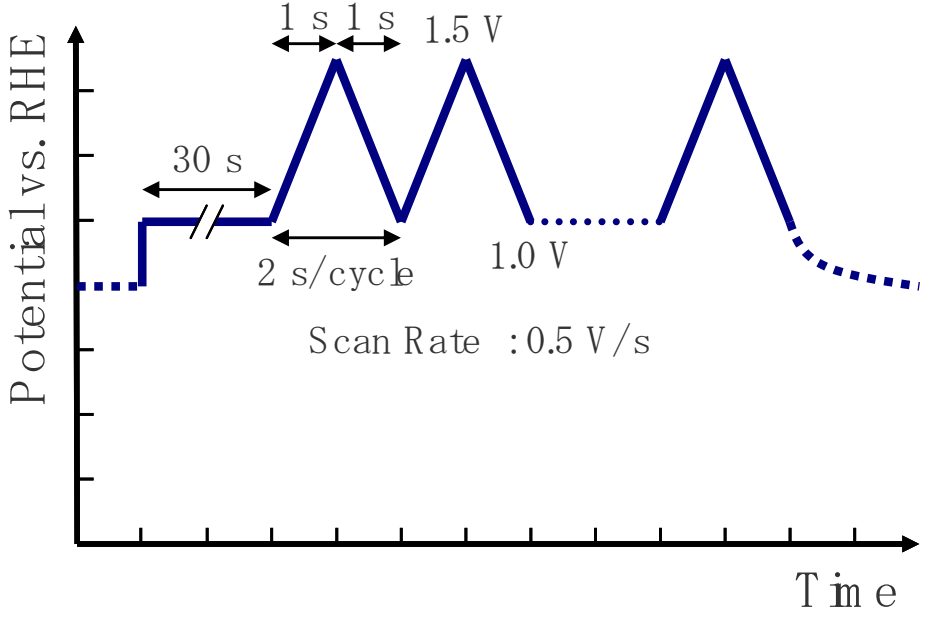
Milestone at 24 mo: Getting single cell test beds on a common protocol for testing and validation

Go/No go decision on materials choice: Less than 40 % loss after 5000 hrts at T ≤ 80°C

Durability Testing-Task 3-Nissan

- The goal of the accelerated degradation testing is to generate data for benchmarking and understanding of fundamental degradation mechanisms under start/stop and load-cycling using the novel non-platinum based catalysts and supports

Start-Stop Durability: *ex-situ & in-situ*



Focused on studying the carbon corrosion effects observed during cell start-up due to the formation of the hydrogen-air front

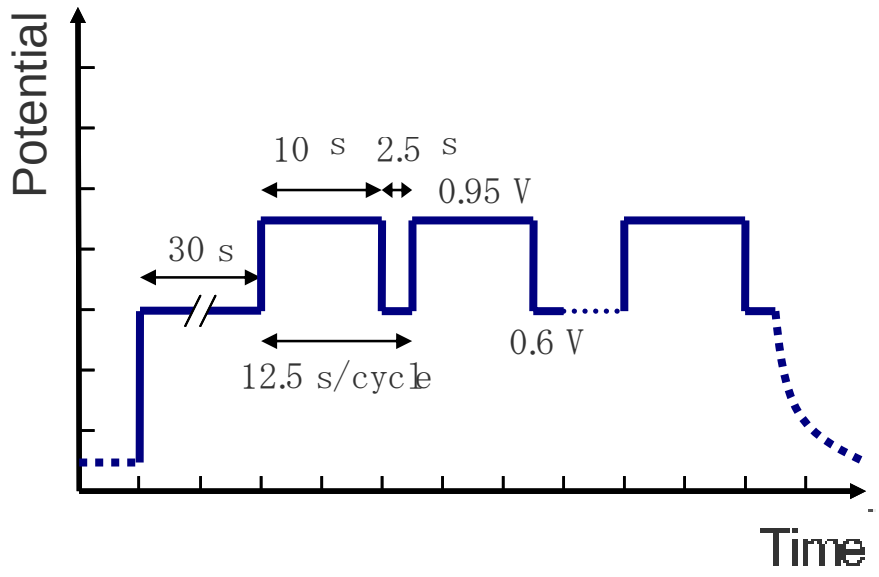
Peak Potential is increased from the standard DOE protocol value of 1.2V as this potential may be too mild for testing of new robust catalysts and supports

ECA is measured at 0, 20, 50, 100, 200, 500 and 1000 cycles

Durability Testing-Task 3 Nissan

- The goal of the performance and accelerated degradation testing is to generate data for benchmarking and understanding of fundamental degradation mechanisms on start/stop and load-cycling using the novel non-platinum based catalysts

Load Cycling: *ex-situ & in-situ*



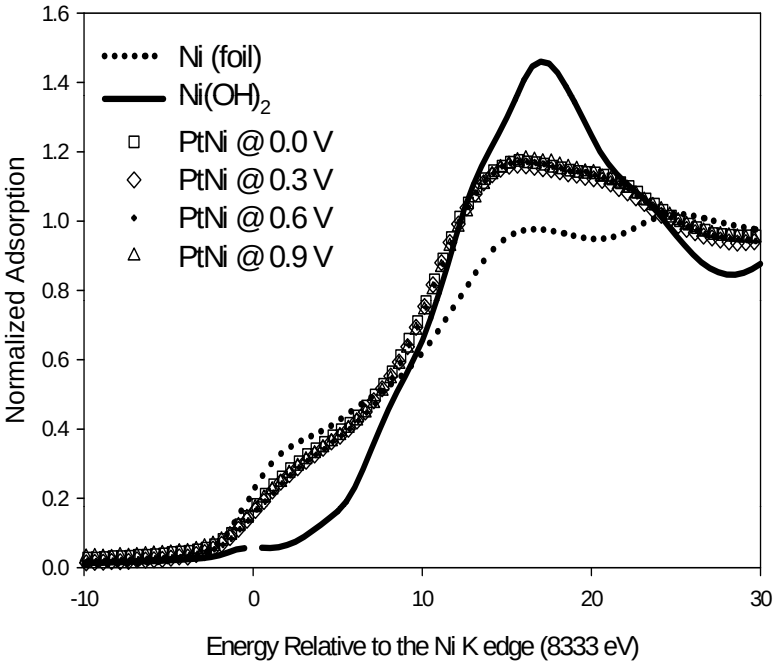
Under these conditions, carbon corrosion is not significant, therefore, the major losses observed is due to Pt dissolution and migration on the support and through the ionomer to the membrane and anode.

ECA is measured at 0, 20, 50, 100, 200, 500 and 1000, 2000, 5000 and 10000 cycles

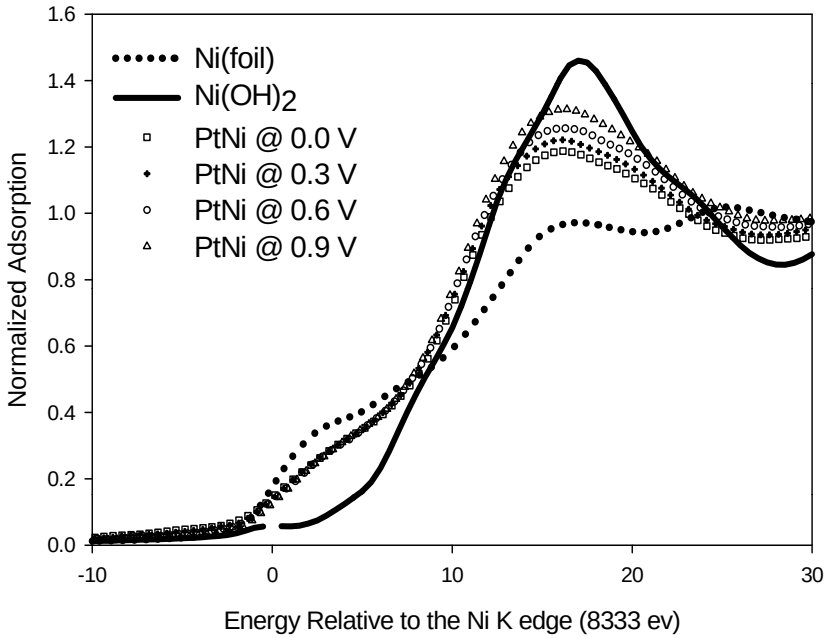
Northeastern University

Using XANES as a Tool for Quantitative Estimation of Corrosion under Cell Operating Conditions with Element Specificity

PtNi/C Pre-washed in 1M $HClO_4$



PtNi/C Not Pre-washed in 1M $HClO_4$



Normalized XANES at the Ni K edge for PtNi/C (a) for sample washed in 1M $HClO_4$ for 24 hours and (b) for as received sample, measured under inert conditions in a spectro-electrochemical cell at room temperature. Linear combination of spectra can provide quantitative corrosion information as a function of potential with element specificity

BASF The Chemical Company · The University of Tennessee Knoxville · The University of New Mexico · Michigan State University · Nissan · Los Alamos National Laboratory Est. 1943

Task 4: Mechanistic Studies and Spectroscopy

Participating Institutions:

UNM- Ex situ Studies with XPS and PCA analysis

NEU- In situ Spectroscopy with Synchrotron and FTIR Measurements

SMU- Macroscopic Modeling

UTK- Molecular Level Computation (Ab-Initio and MD Simulations)

UNM- DFT Calculations

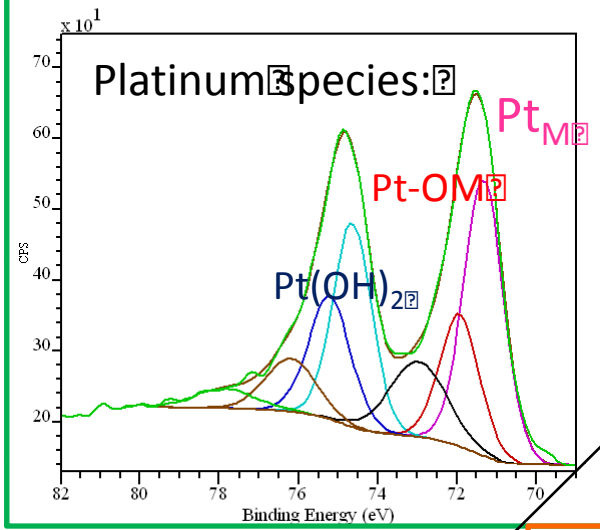
Milestones (12 mo): Development of a unified In situ synchrotron spectroscopy beam line access and analysis protocol

(12 mo): Establishing student and postdoc collaboration using cyber-tools

Task 4: Multi-Analytical Approach (Ex-Situ)

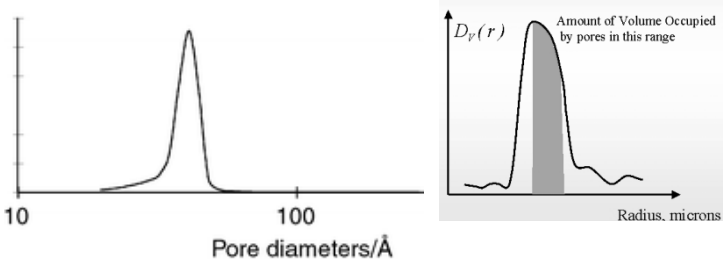
Northeastern University

XPS analysis:
- Elemental composition:
- Chemical speciation

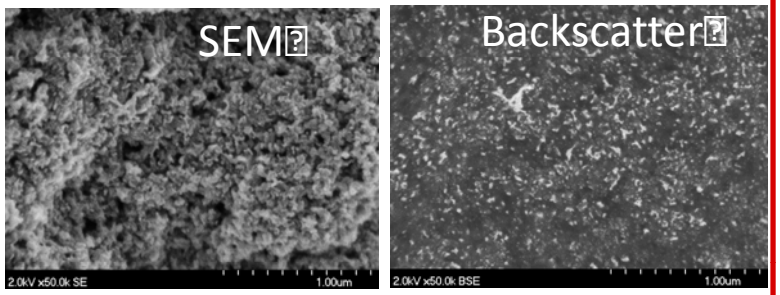


Model based on statistical correlation among all variables /parameters

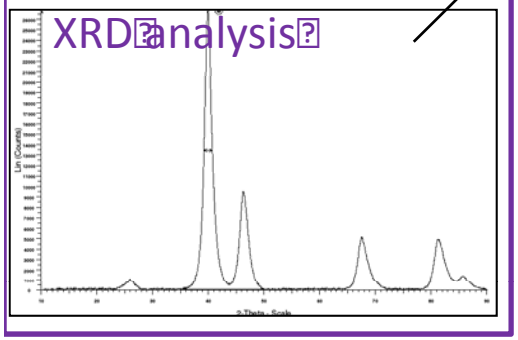
Adsorption analysis:
BET surface area
Pore size of the support
Pore Volume of the support



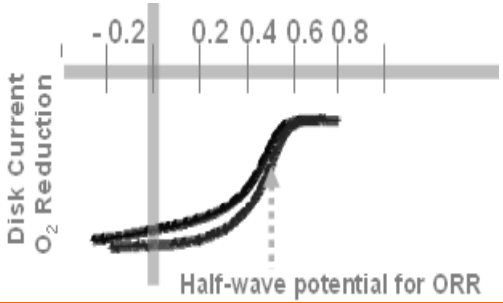
SEM analysis:
Roughness:
Ra, Rsk;
Pt particle distribution



XRD analysis

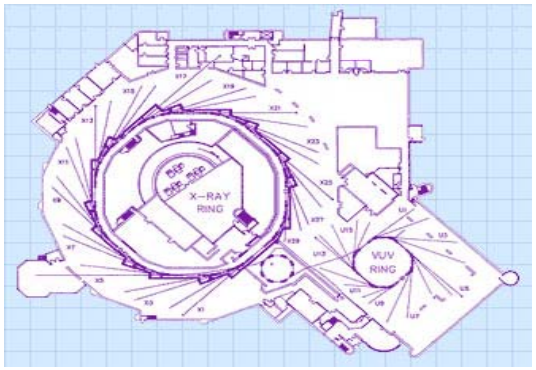


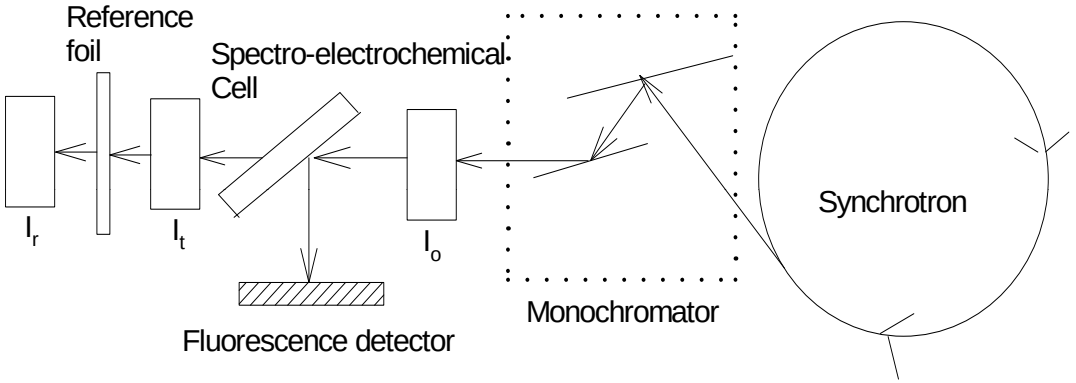
Electrochemical characterization

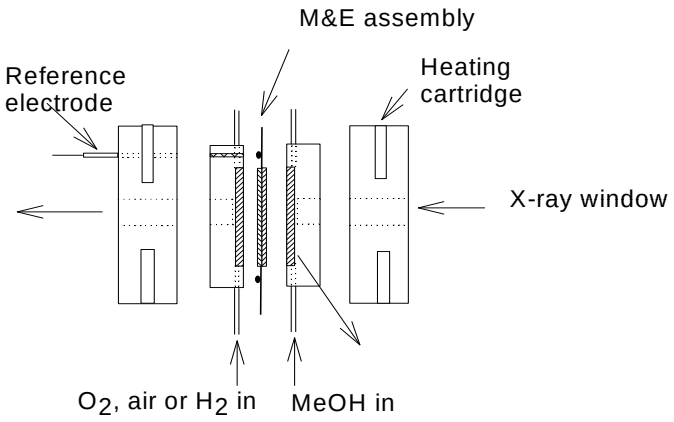


BASF The Chemical Company · The University of Tennessee Knoxville · The University of New Mexico · Michigan State University · Nissan · Los Alamos National Laboratory Est. 1943

Synchrotron Principles



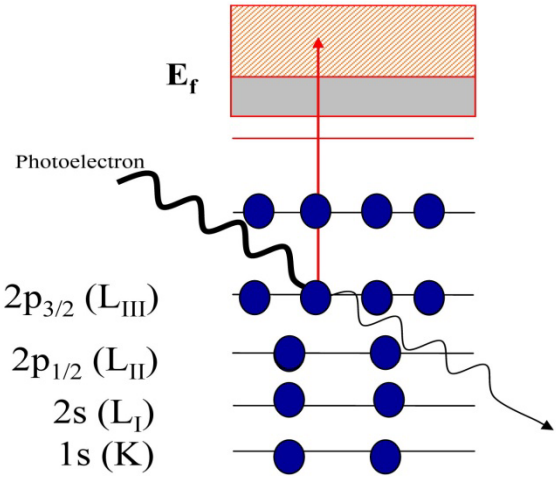




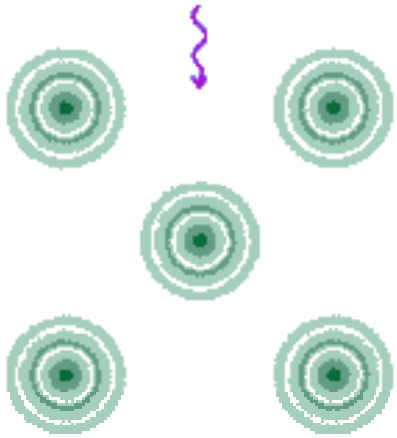
Joe Ziegelbauer

Tom Arruda

Principles of X-Ray Absorption Spectroscopy



Scattering

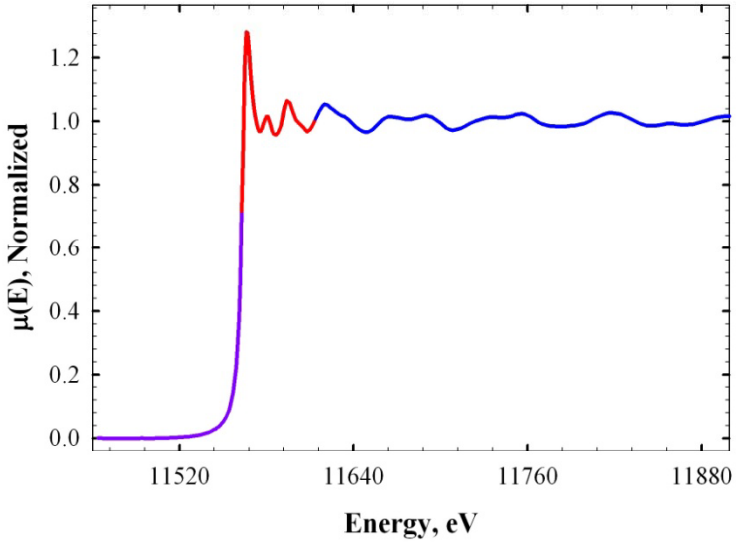


XANES (< 50 eV)

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

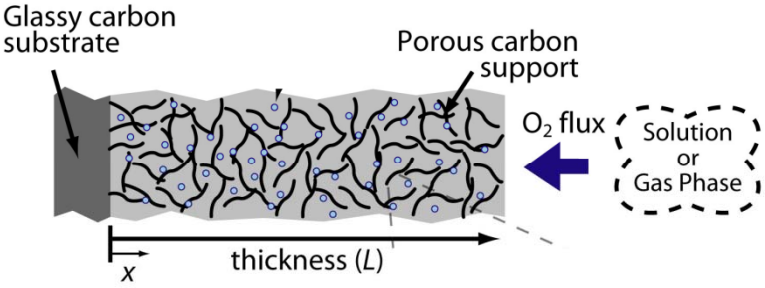
EXAFS (> 50 eV)

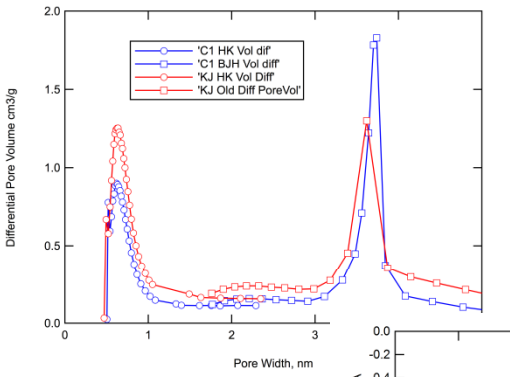
- Geometric information
- Bond length
- Coordination number
- *BULK* short range order



Microscale Transport Simulations (MSU)-Task 4

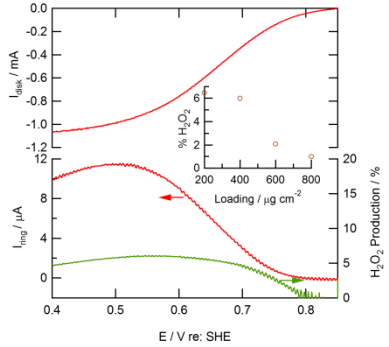
- Open-framework structures provide monodisperse structures amenable to numerical simulation
- Stochastic model of **intraparticle** transport/reaction using inputs including
  - catalyst structure and composition (XPS, CHN, XAS)
  - micro and mesoporosity (BET, pore size distribution)
- Model will be applied to predict catalyst performance.
  - Controlled RDE and RRDE measurements
  - Parametric composition and fabrication studies





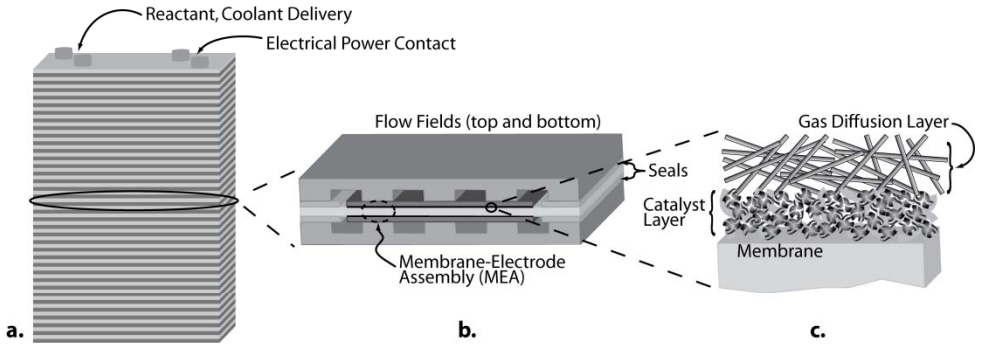
Microporosity measurements

RDE/RRDE studies



Macroscale Transport Simulations (MSU)-Task 4

- Building on microscale simulations, quantitative modeling of complete electrode catalyst layers
- Reaction kinetics and transport on the scale of the catalyst particle will be described by microscale simulation results.
- Multiphase model to account for water transport in thick electrodes.
- Structural information from ESEM-FIB measurements will be incorporated into the model
- Model results will be validated against polarization and transient impedance experiments.

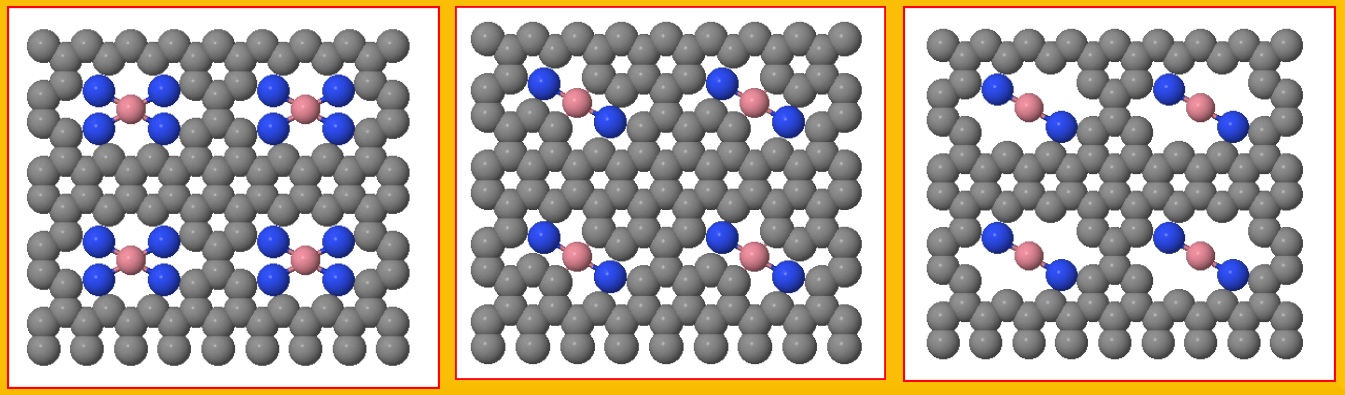


DFT of Non-Pt Catalysts (Task 4) UNM

- Nx defects are not thermodynamically stable.
- Co-Nx defects can be themodynamically stable.
- Chemical route to increase number of reaction sites.
- Passivation of Co due to CoO formation unlikely.

Pyrolic defects

- Edges of sheets.
- Binding energies.
- Electronic structure.
- Charge transfer.
- Deactivation.



Modeling of Mass Transport (UTK)

Calculations will drive understanding of trade-offs between mass transport and active complex utilization in CL

1. Develop generic model of transport/reaction coupling in cathode
   a) Based on previous work
2. Introduce specific aspects of electron transfer kinetics of ORR with NPM catalysts
3. Develop multi-step kinetic simulation of ORR pathway

Modeling to Probe Mechanism (UTK)

Several types of calculations will be used to aid in understand controlling features and electron transfer mechanism in catalytic complexes

1. Electronic Structure calculations to probe electronic states of complexes and O_2 binding
   a) Correlated with experimental studies of complexes
2. Electronic Structure calculations to probe reaction pathway
3. Inclusion of electrode potential and environmental effects using AIMD simulations

Collaborations

Partners (this project)

- Northeastern Univ., (Prime) Boston: S. Mukerjee (P.I) and S. Smotkin
- Univ. of Tennessee, Knoxville: Prof. T. Zawodzinski
- Univ. of New Mexico, Albuquerque: Prof. P. Atanassov
- Michigan State University: Prof. S. Barton
- BASF Fuel Cells, Somerset, NJ: Dr. E. DeCastro
- Nissan Motors: Dr. K. Adjemian
- Los Alamos National Lab: Dr. P. Zelenay

Other collaborators:

(1) Jean Paul Dodelet: CNRS, Canada

(2) Zifeng Ma, Shanghai Jiao Tong University

Proposed Future Work (FY 2011)

- Screening of initial tranche of materials using RRDE & array fuel cells and single cell polarization measurements for down-selected electrocatalysts.
- Initial attempts to improve mass transport in gas diffusion medium. Novel approaches to electrode preparation, additives for improved oxygen solubility and fabrication of MEAs
- Modeling of mass transport in electrode layers to be in sync with design of electrode structures (layer by layer approach)
- First set of in situ synchrotron measurements along with PCA analysis of the ex situ and in situ data
- First set of DFT calculations on metal oxides and development of approaches to simulate triazoles.

Summary Slide

- Current efforts focus on liganding non PGM metals onto carbon supports for effecting improved ORR performance and stability. Such as those shown by LANL group.
- Our effort encompasses development of novel bi-dentate and tetra-dentate complexes where tandem electron transfer to oxygen can be fecilitated using two or three transition metals with different oxidation states.
- Current status of the non PGM field puts the volumetric power

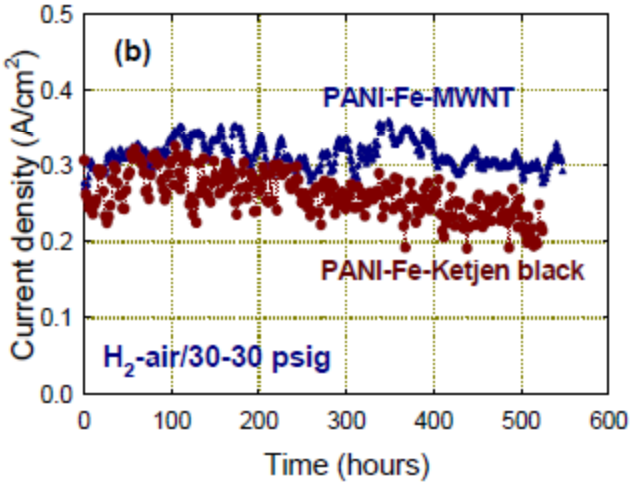
- In situ determination of charge transfer at the reaction center is expected to yield important leads for improved design of reaction centers.

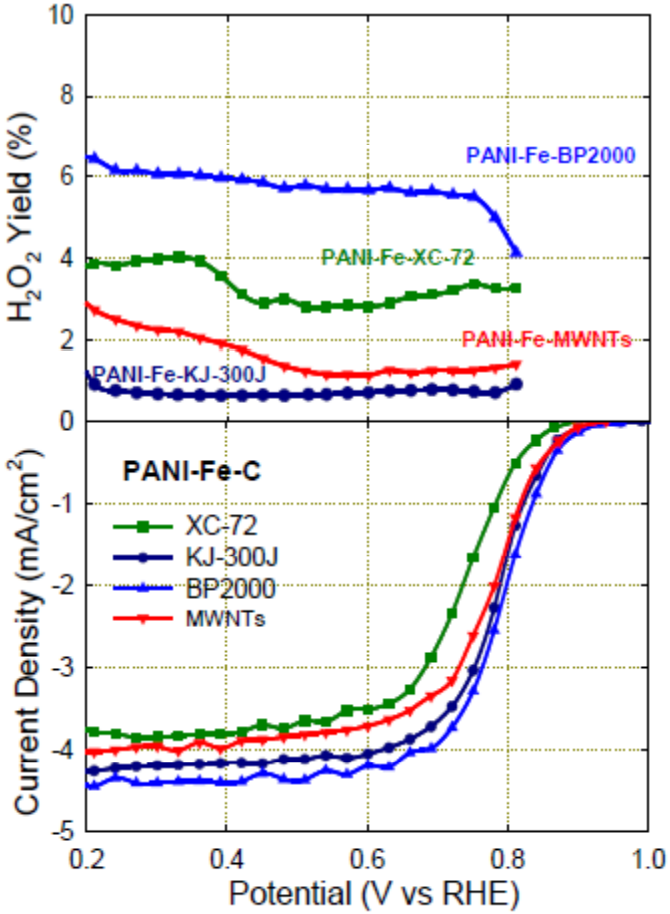
Supplemental Slides

Non PGM Catalysts
Current state of the Art

- Chalcogenides (limited success)
- Metal Oxides (possible candidates for anode electrode)
- Metal – N complexes
- Inorganic Framework structures
- Metal Organic Framework systems
- Metal Polymer Composites

Metal Polymer Composites

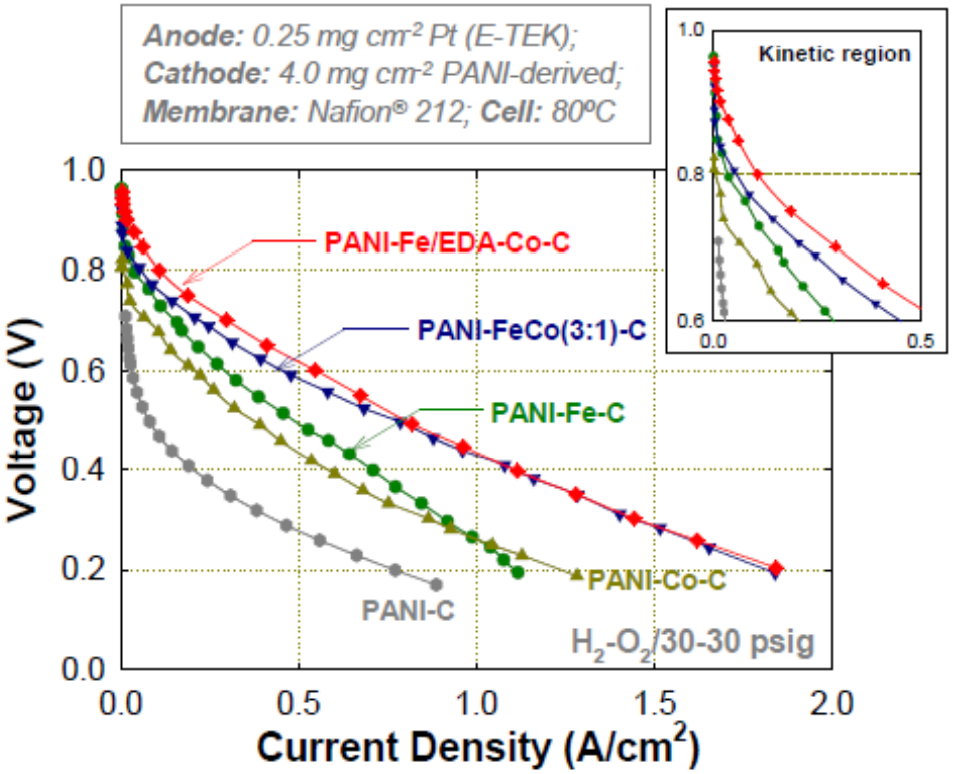


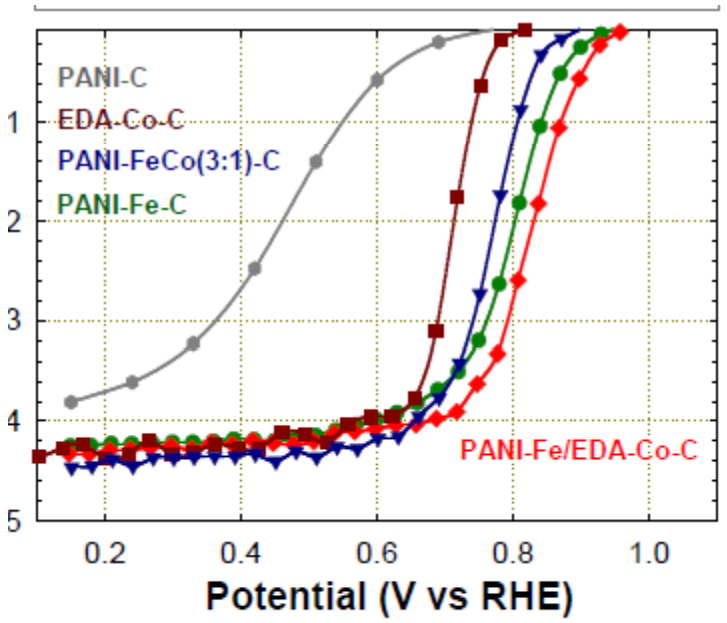


- PANI-Fe-MWNT-most stable
  - Open support structure enhances mass transfer
  - 1.8% H_2O_2 at 0.4V
  - Stable performance for ~500 hours

Wu and Zelenay. ECS Transactions 25 (1) (2009)

Metal Polymer Composite

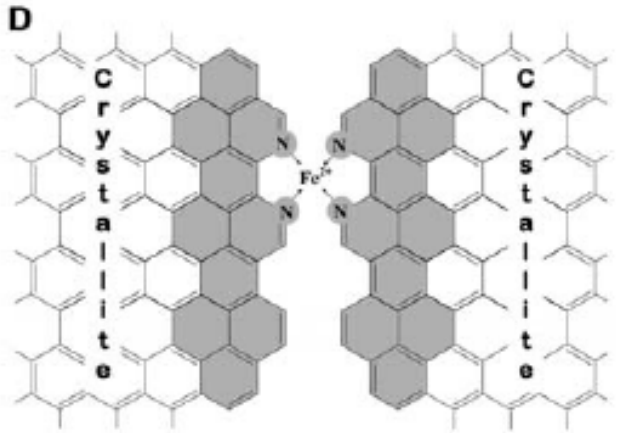


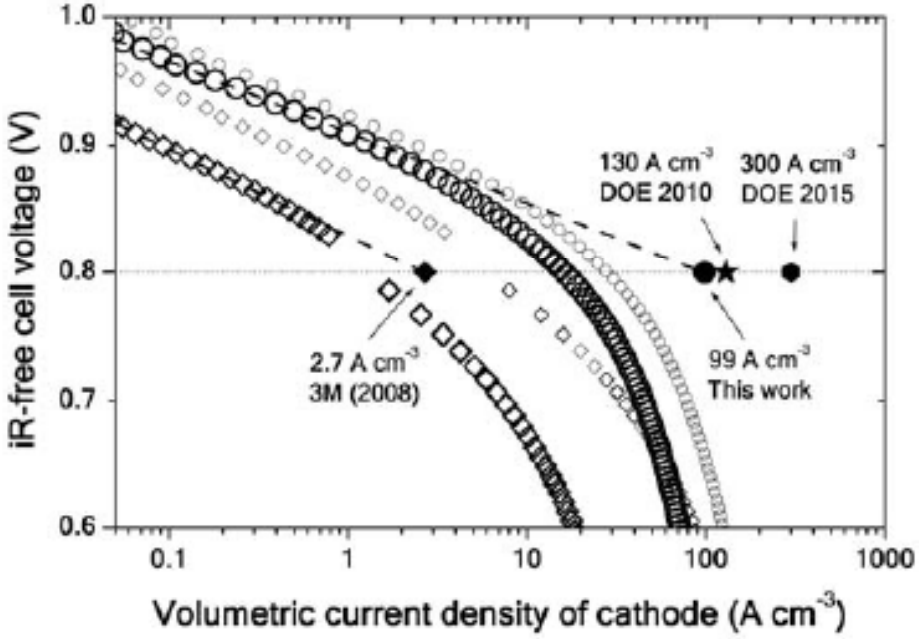


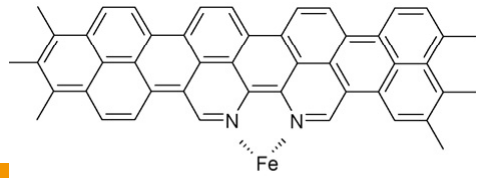
- PANI-Fe/EDA-Co-C
  - Improved activity at lower loading
  - 100 A/cm^3 at 0.80 V
  - Performance degradation at 0.60 V

Pyrolyzed Metal Organic System

- Pore filler method
  - disordered N-bearing C source planetary ball-milling
  - Pyrolyzed first with Ar at 1050°C and then NH3 at 950°C
  - 99 A/cm^3 at 0.8V
  - 50% performance loss after 40 hours
- Micropore-hosted Fe-N2+2/C site
  - high turn-over frequency and selectivity for ORR
  - believed to be obtained by heat treatment in NH3.

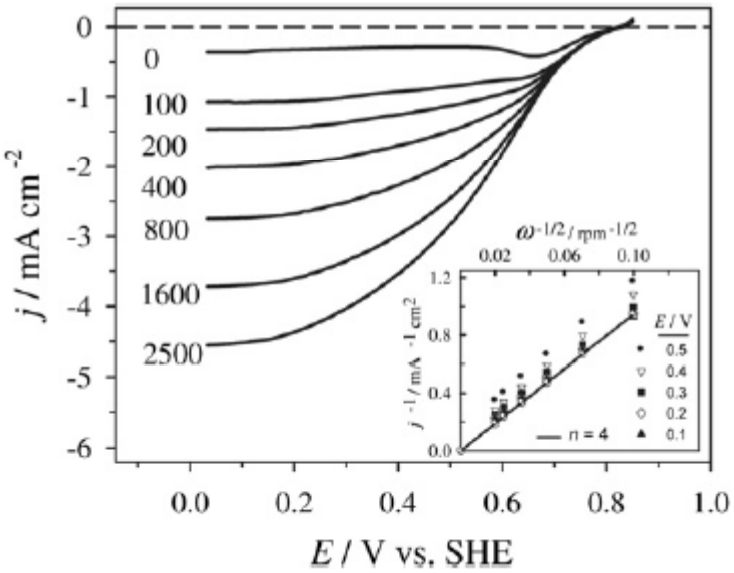






Transition Metal Chalcogenide

- CoSe/C
  - Prepared by microwave-assisted polyol method
  - 20% loading
  - Poor stability in acidic media
  - Tolerant to alcohol and formic acid

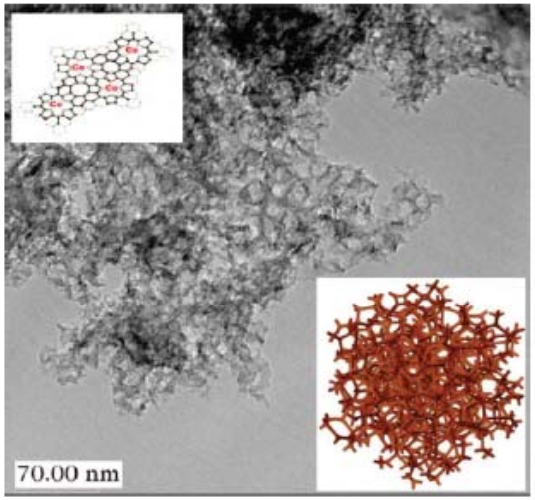


Most work in this area is with Pt group metals so I did not include it

Parisa Nekooi, Int J of Hydrogen Energy, 2010, 35, 6392-6398

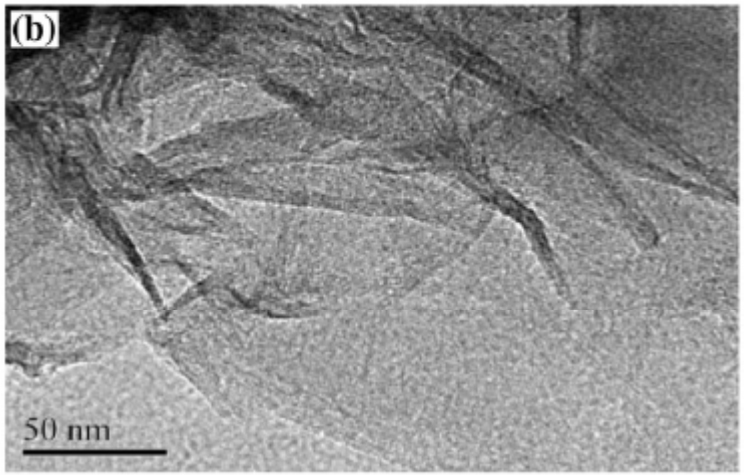
Support Materials

- Self-Templating
  - Precursor is deposited on a non-carbon carrier
  - Compound is pyrolyzed and then carrier is removed
  - Material is porous with graphite like domains
  - Pore size is optimized and transport is enhanced



Joseph M. Ziegelbauer. , J. Phys Chem C **2008**, *112, 8839-8849.*

- Graphene Sheets
  - High surface area
  - Many edge sites an pyridinic N sites
  - 35 times more massactivity than Vulcan carbon
  - 50% lower ORR activity than Pt
  - More active in acidic media
  - 7% H_2O_2 produced at 0.70 V
  - Highly selective for four-electron pathway

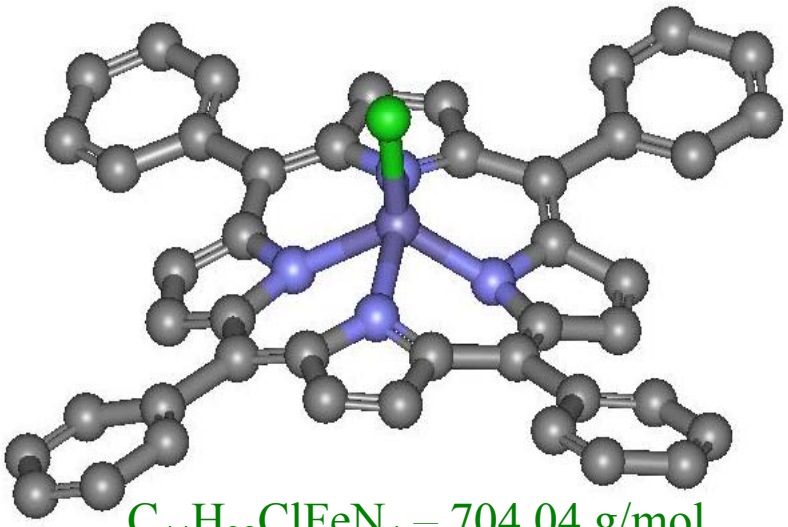


Ki Rak Lee. Electrochemistry Communications, **2010**, *12, 1052-1055.*

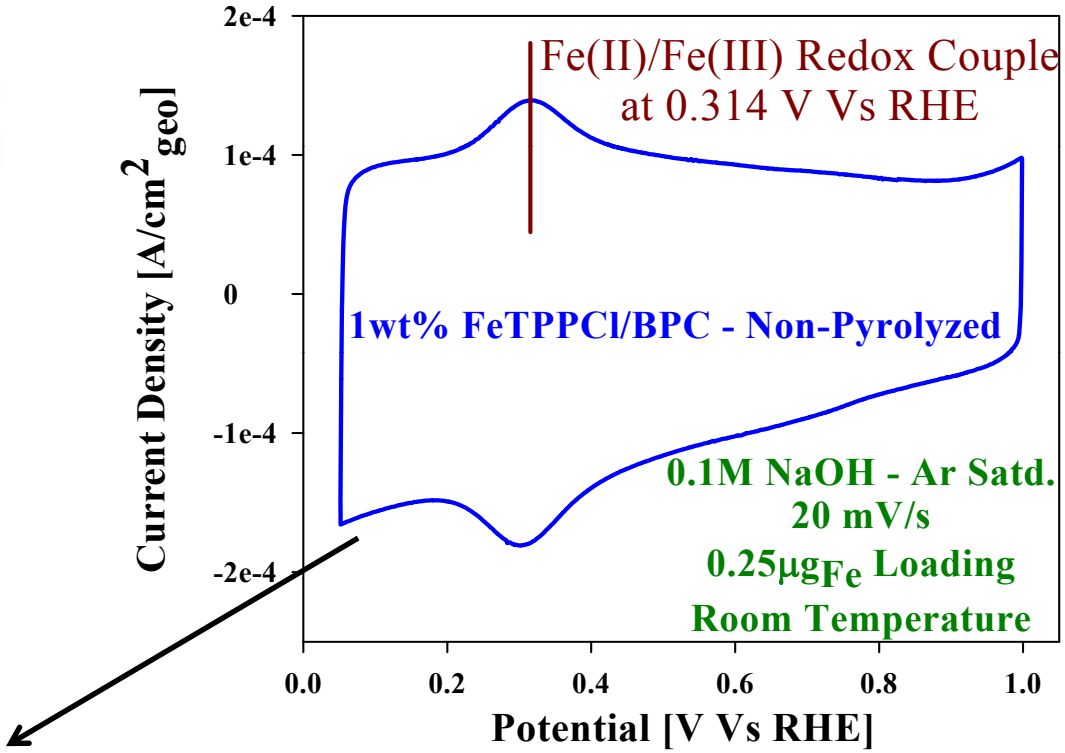
Iron (III) meso-tetraphenylporphyrin – Cyclic Voltammogram

- Catalyst – FeTPP (1wt% Fe)
- Support - Black Pearl Carbon – (1379m^2/g)
- Pyrolyzed at temperature 0000°C-1100°C

- GC Disk Area – 0.247 cm^2_{geo}
- $Loading_{on\ GC}$ – 0.25 μg_{Fe}



$C_{44}H_{28}ClFeN_4$ – 704.04 g/mol
Fe Content – 7.95 wt%



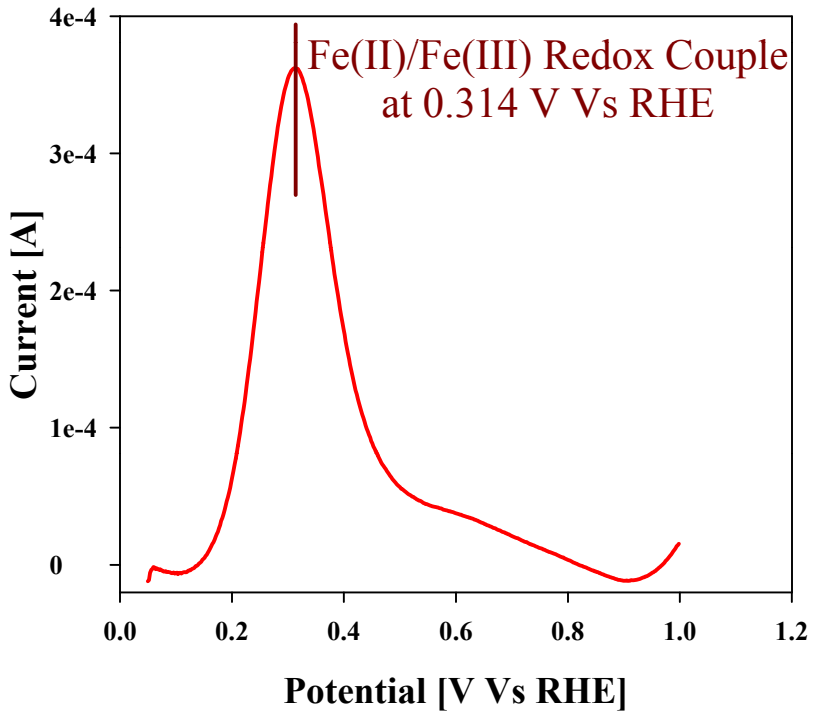
High Surface Area Carbon support causes huge double layer

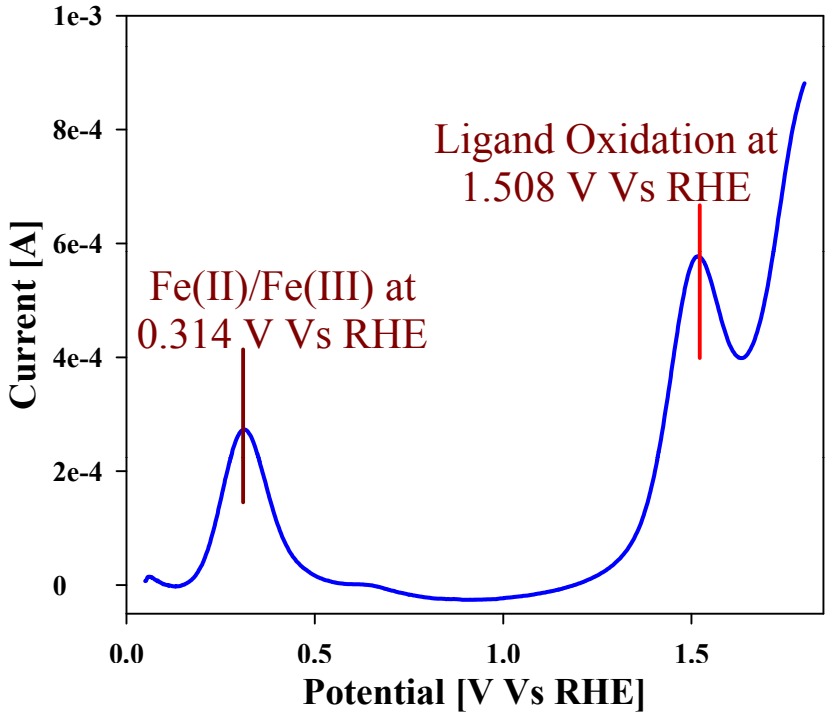
Iron (III) meso-tetraphenylporphyrin – Square wave Voltammetry

Frequency – 10Hz Step Size – 20 mV

Amplitude – 50 mV Scan Direction - Anodic

FeTPP/BPC – Nonpyrolyzed samples



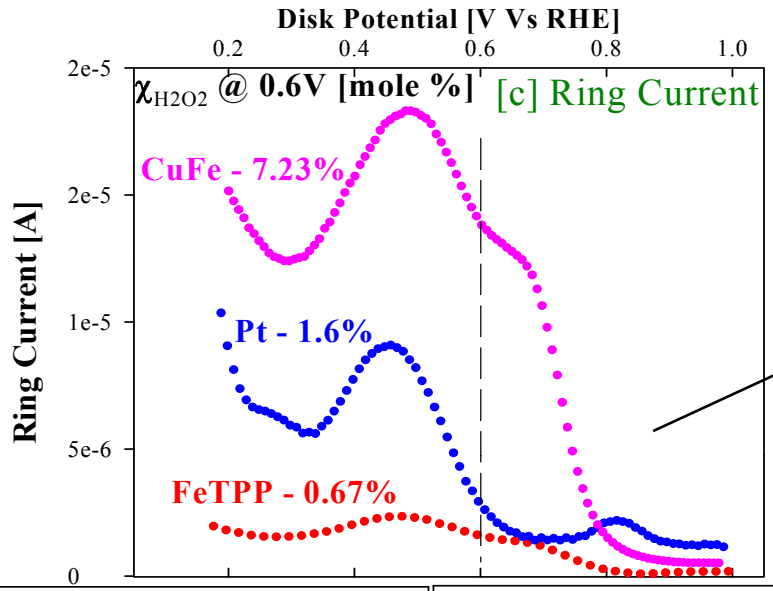


SWV allows accurate quantification of charge

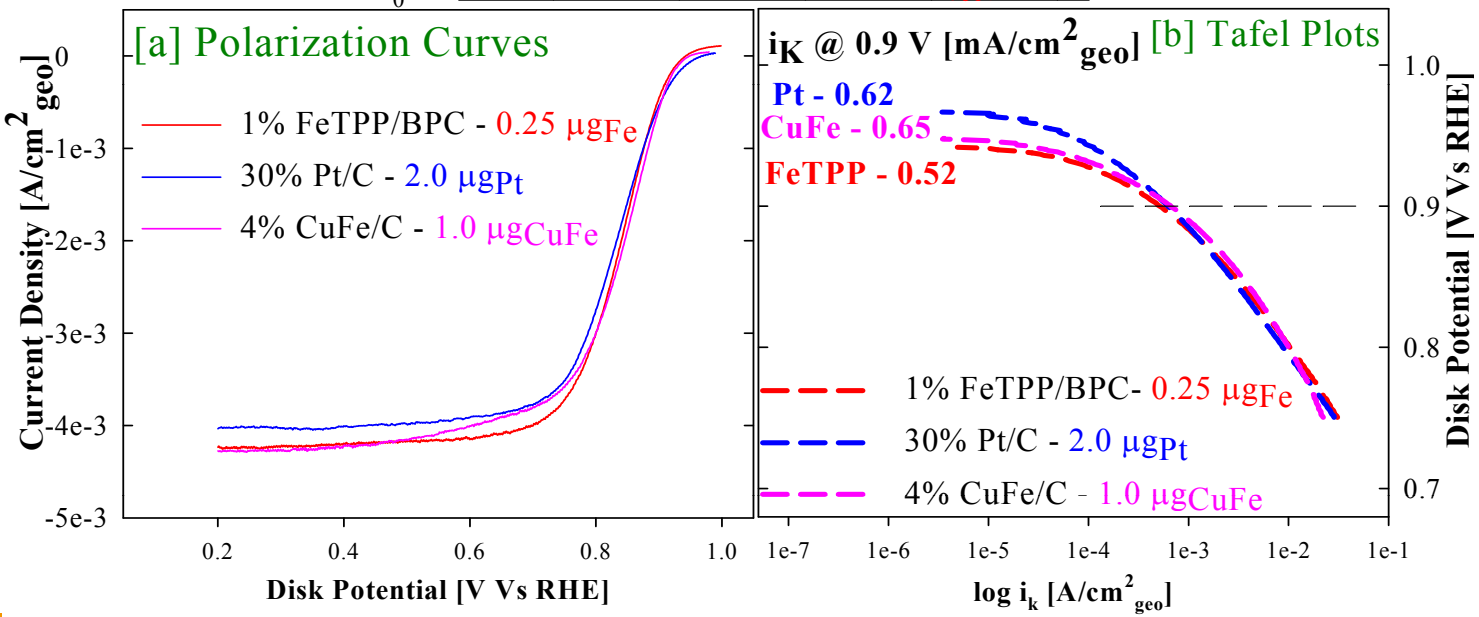
ORR Activity of FeTPP/BPC Pyrolyzed at 800°C

RRDE Experimental Conditions

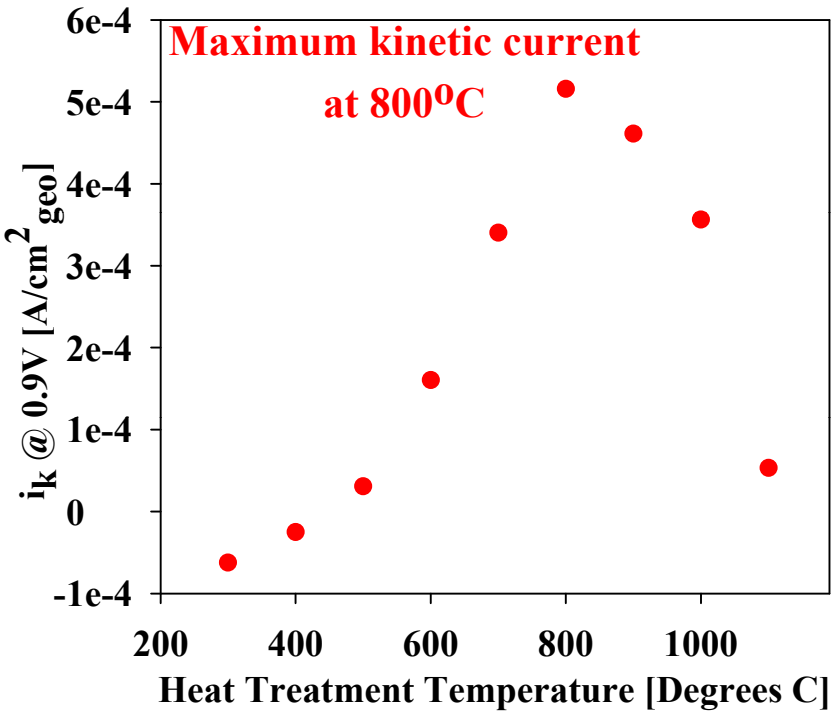
O_2 Satd. 0.1M NaOH
20 mV/s
900 rpm
E_{Ring} = 1.1V Vs RHE
Room Temperature

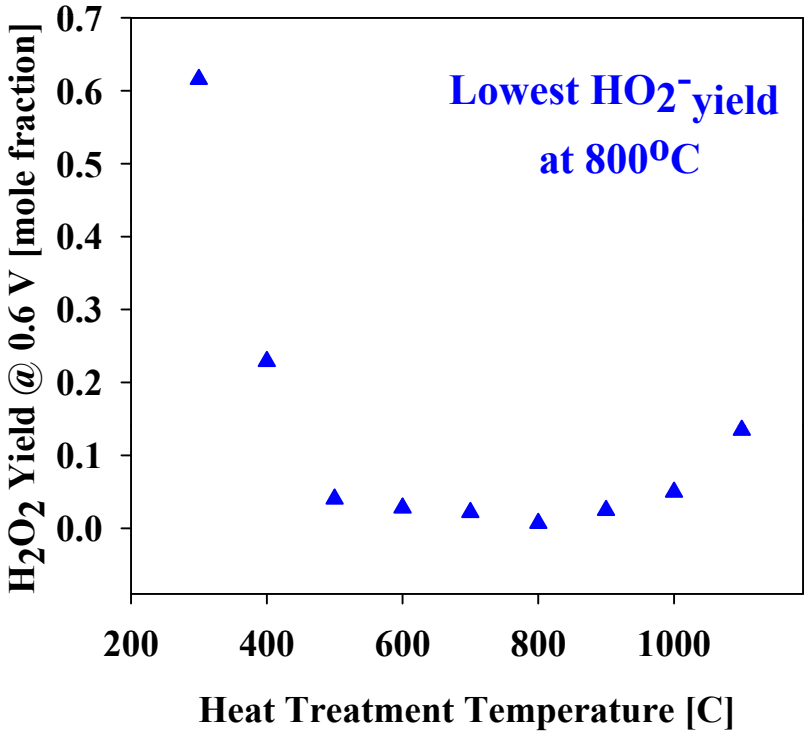


Pyrolyzed FeTPP exhibits remarkably low H_2O_2 yield due to its exotic structure as explained in the next slides



FeTPP/BPC – Effect of Pyrolysis Temperature

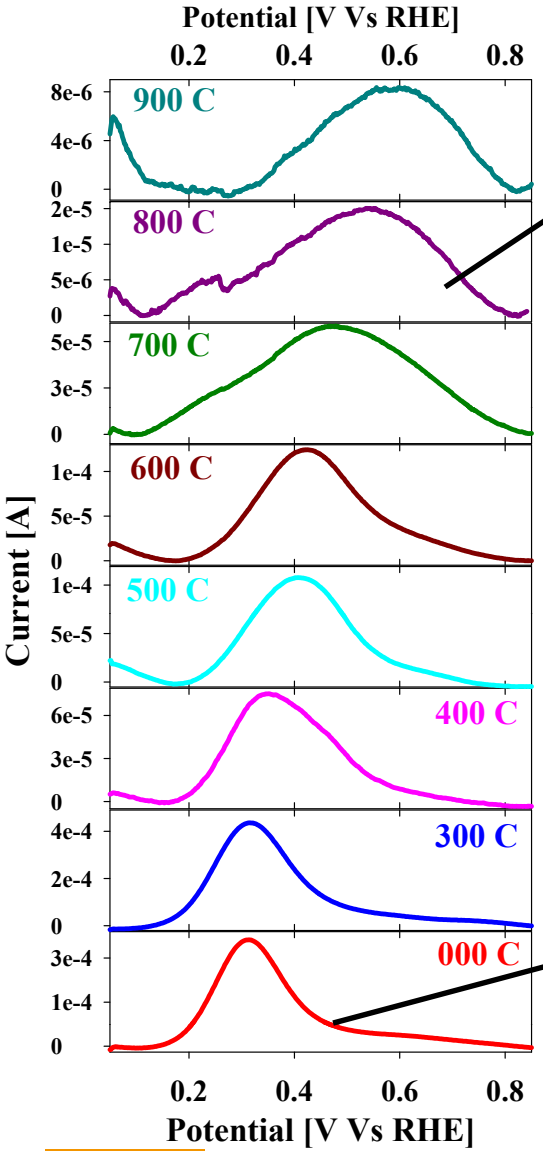




Tremendous increase in kinetic current and decrease in peroxide yield observed as the pyrolysis temperature of FeTPP supported on Black Pearl Carbon is increased. This is attributed to the possible dimeric character of the pyrolyzed iron porphyrin sample as elucidated by the X-ray absorption spectroscopy in the next slide.

Highest Kinetic Current and Lowest Peroxide Yield achieved at 800° C

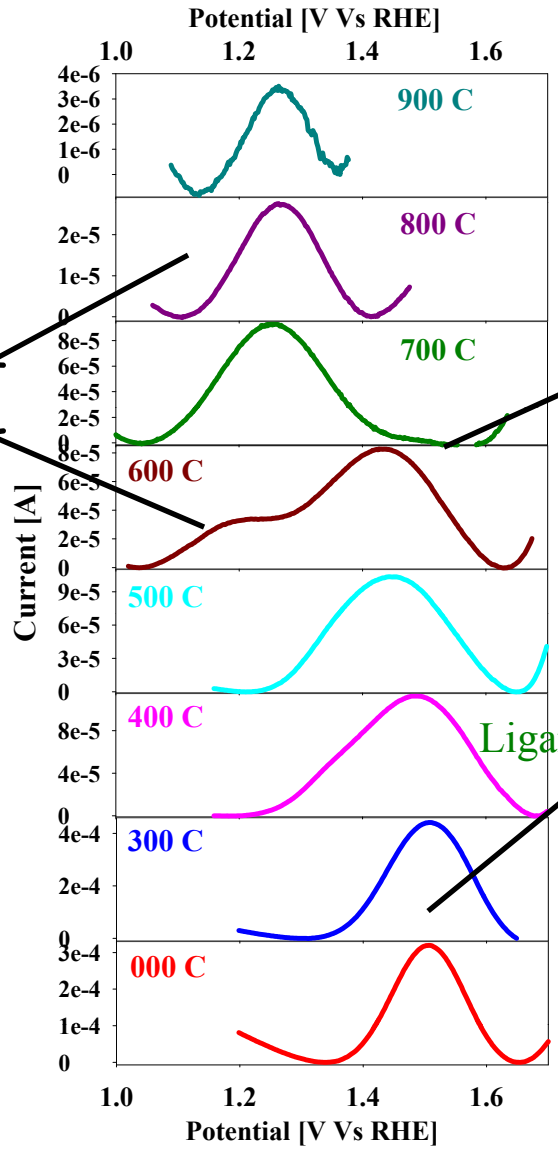
ORR Mechanism Analysis - Evolution of Redox Potential



Fe(II)/Fe(III) transition broadens and shifts more anodic

New redox transition observed above 600°C Assigned to Fe(III)/Fe(IV)

Sharp Fe(II)/Fe(III) transition



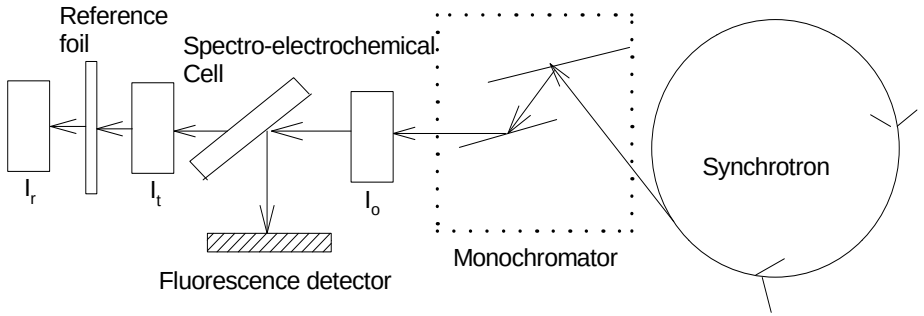
Ligand oxidation not observed anymore above 700°C pyrolysis

Ligand Oxidation

In Situ X-ray Absorption Spectroscopy

Advantages

- ***High Intensity***
- ***Energy Tunable***
- ***Element Specific***
- ***Insitu Operating Conditions***



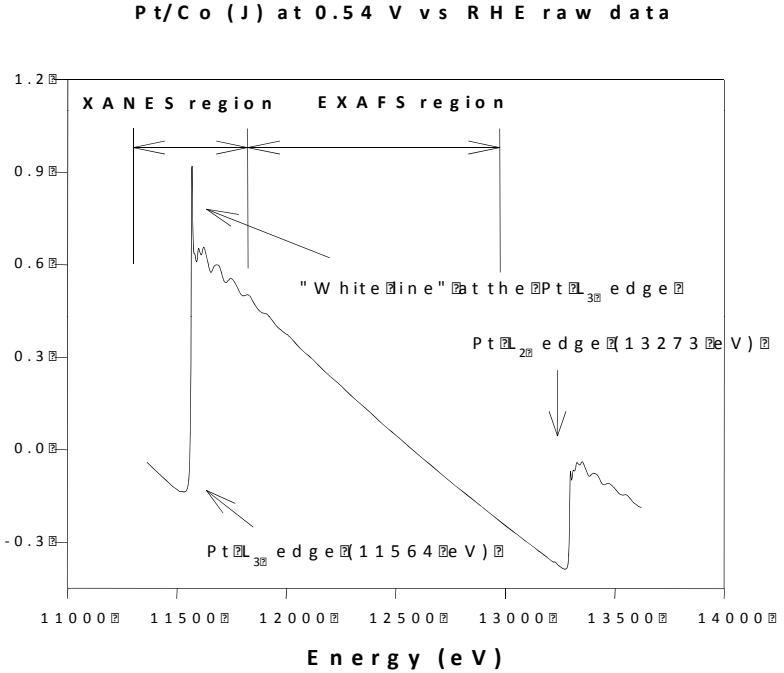
XANES Spectra

Physical Basis

Multiple scattering by low energy photo-electrons

Information

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



EXAFS Spectra

Physical Basis

Modulation of X-ray absorption by back scattered photo-electrons

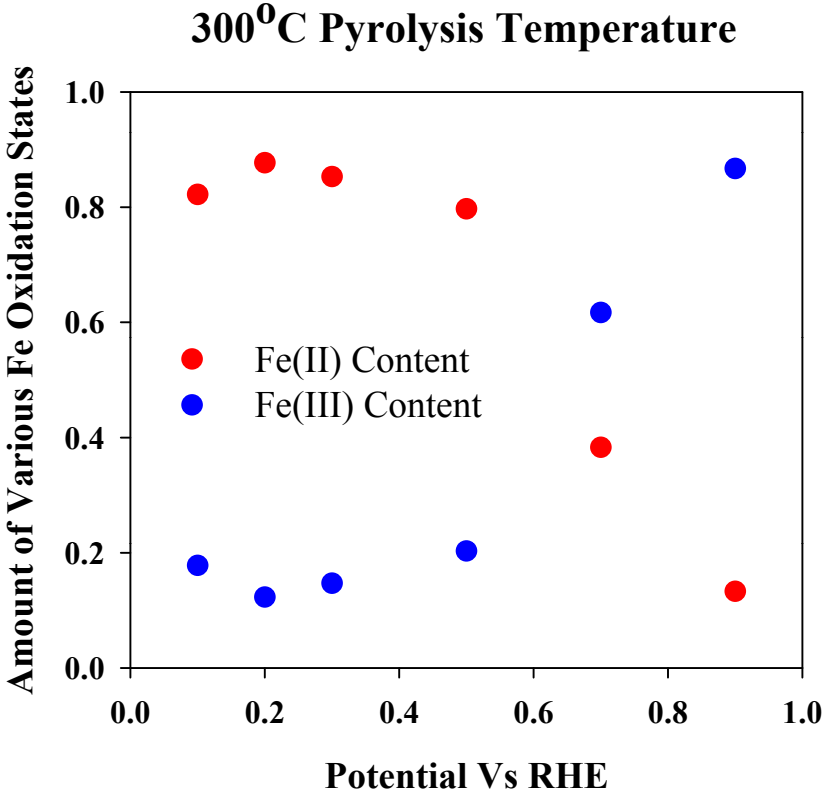
Information

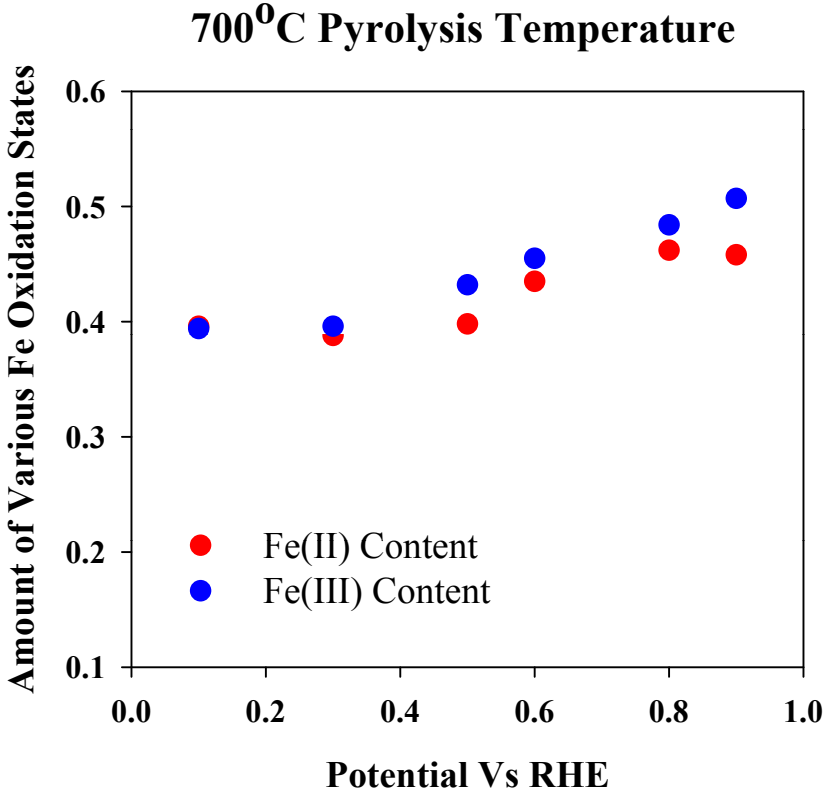
- **Determination of short range atomic order (bond distance, coordination number, Debye Waller factor *etc.*,)**

Synchrotron Experiments → *Insitu* Measurements

FeTPP/BPC – Efforts to Understand ORR Mechanism

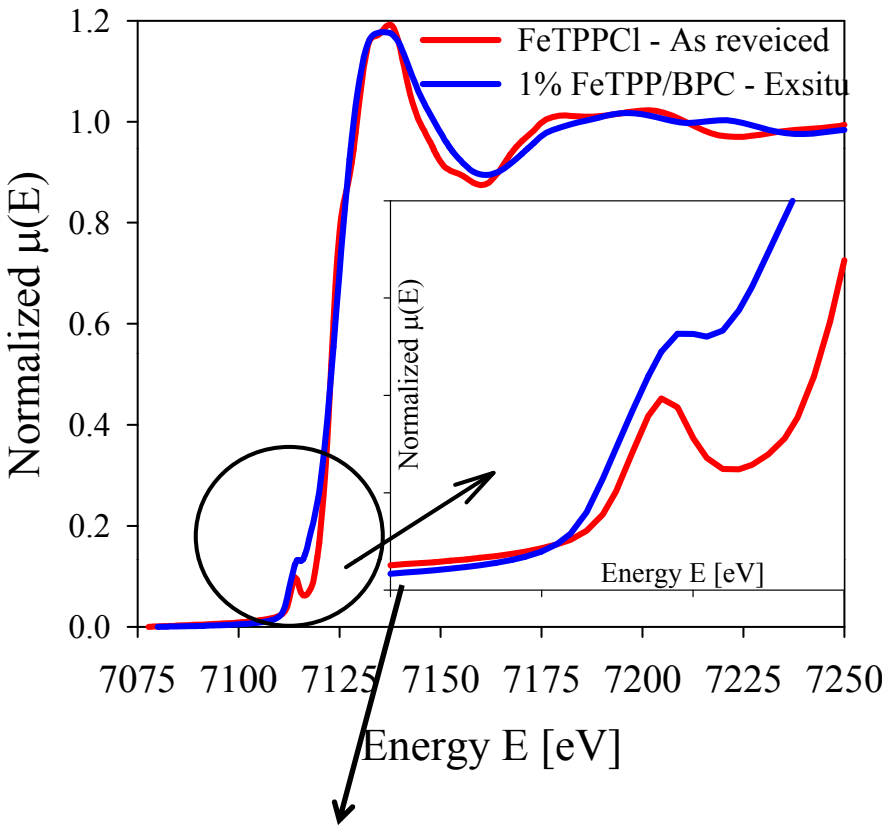
Linear Combination Fitting Analysis of various oxidation states of Fe under insitu conditions



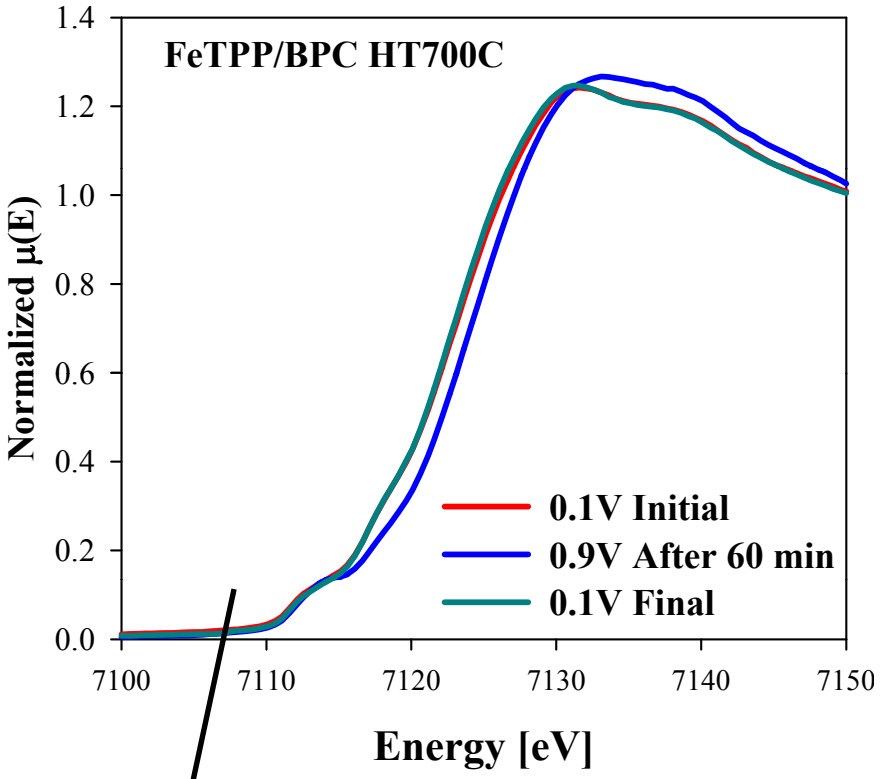


- Existence of equal fraction of Fe(II) and Fe(III) valence states at 700°C indicates a possible dimer formation during pyrolysis
- Fe(II) and Fe(III) fractions situated in close proximity perform ORR in tandem

FeTPP/BPC – Nature of Active Site and Stability

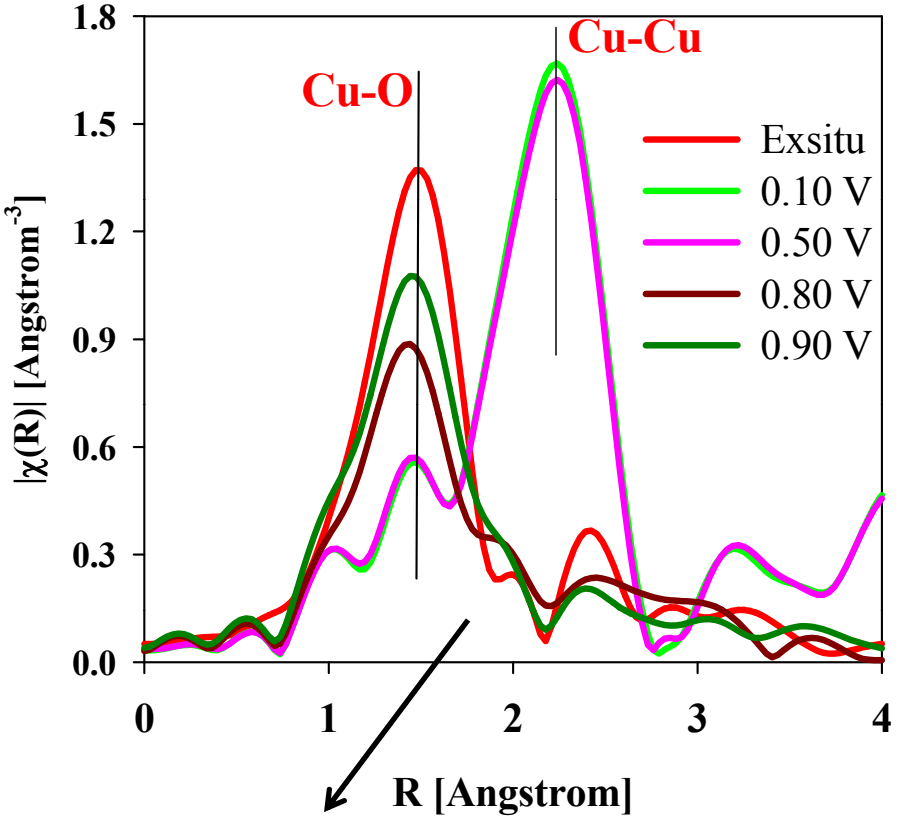


XANES Region indicates the preservation of Fe-N_x active site

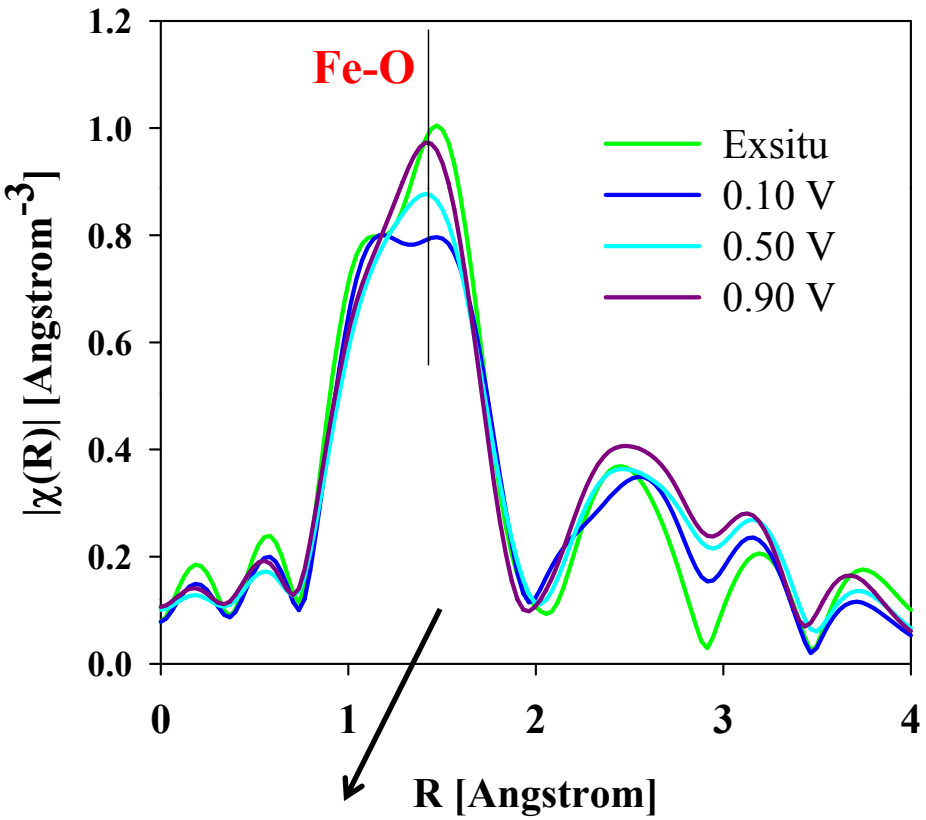


No loss of active site after holding at an oxidizing potential of 0.9V Vs RHE

Nature of Catalyst site in CuFe/C



Cu shows reversible oxide formation and likely the active site for ORR



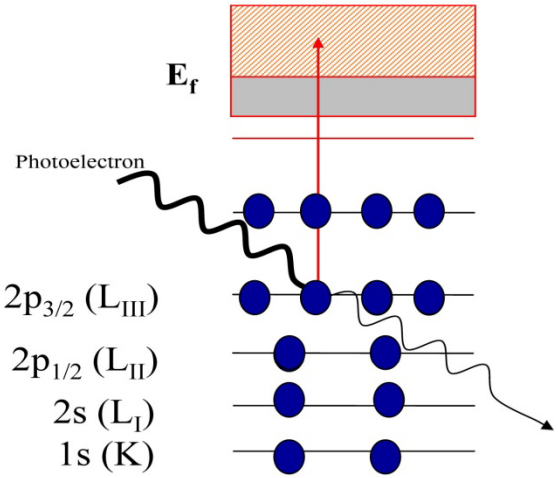
Fe is completely exists in oxide form at all potentials

CONCLUSIONS

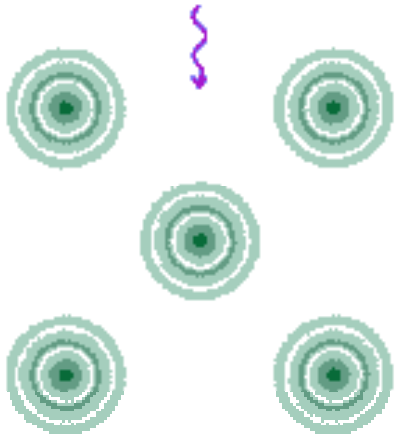
ORR on pyrolyzed Iron macrocycle

- Square wave voltammetry and XANES analysis indicate the existence of equal fraction of Fe(II) and Fe(III) states under *insitu* conditions
- Presence of dimeric catalytic sites have been understood to be the key towards facile ORR on these class of materials

Principles of X-Ray Absorption Spectroscopy



Scattering

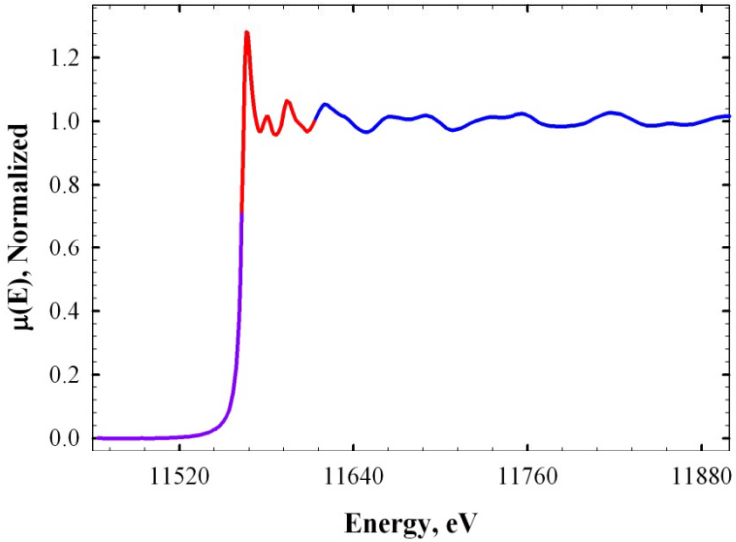


XANES (< 50 eV)

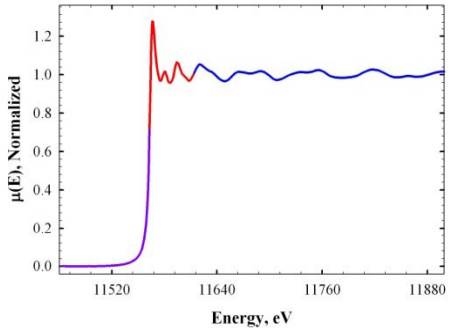
- Absorber site symmetry (e.g. T_d, O_h, etc)
- Electronic configuration
- Geometric Binding Site

EXAFS (> 50 eV)

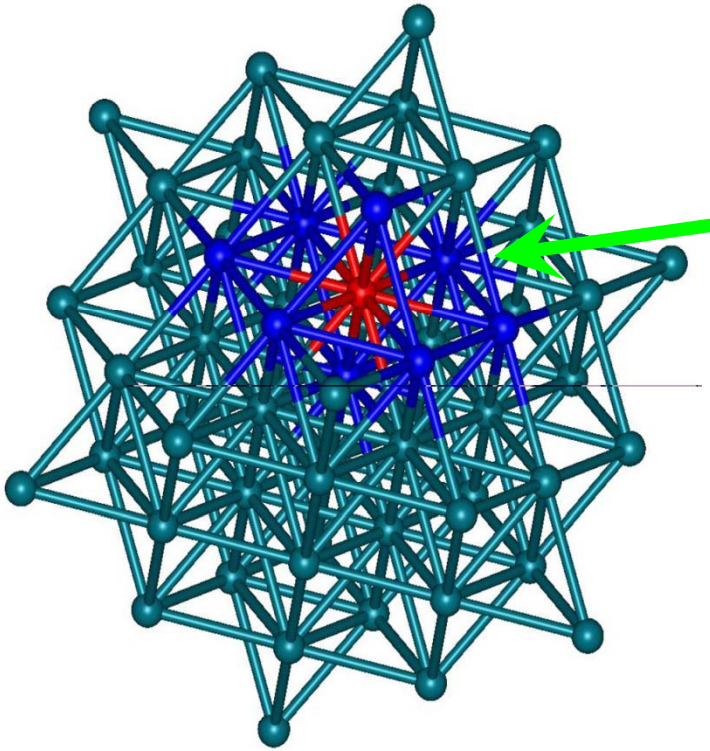
- Geometric information
- Bond length
- Coordination number
- *BULK* short range order

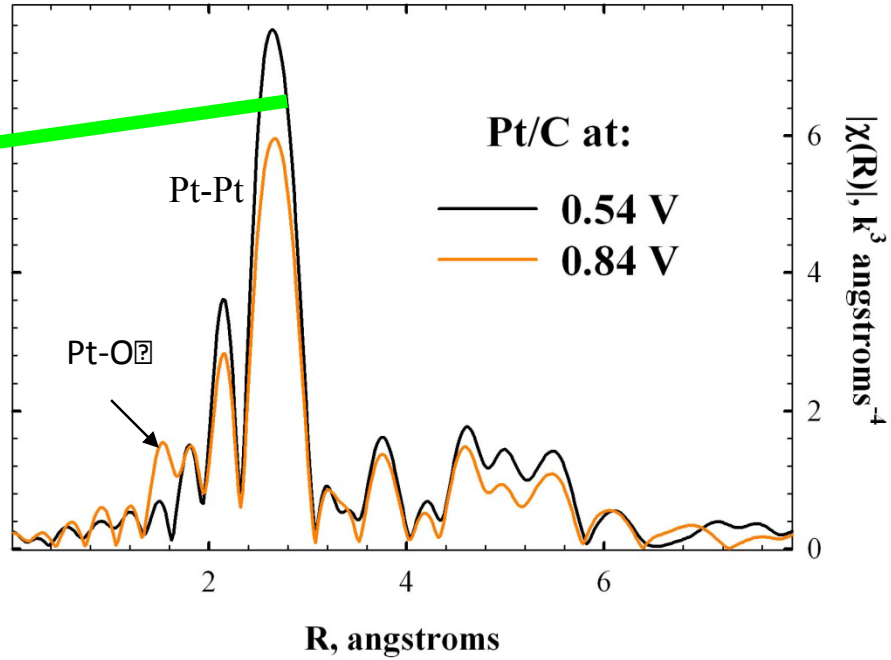


Principles of XAS



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

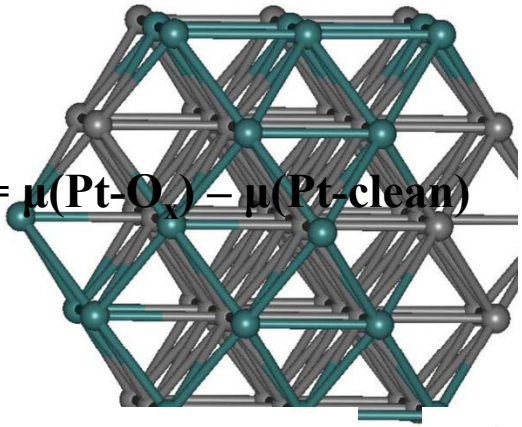




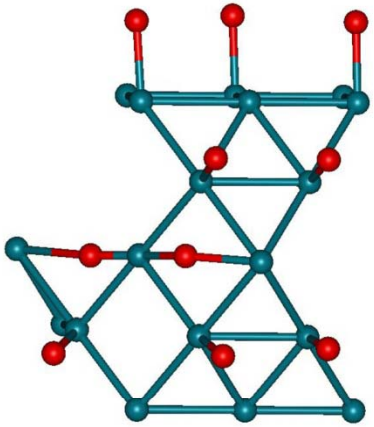
Atomic Level Picture of Electrocatalytic Pathways via Determination of Specific Adsorption Sites

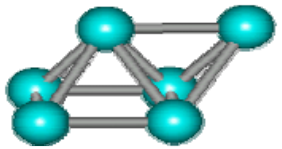
Grey = bulk

$\Delta\mu = \mu(\text{Pt-O}_x) - \mu(\text{Pt-clean})$

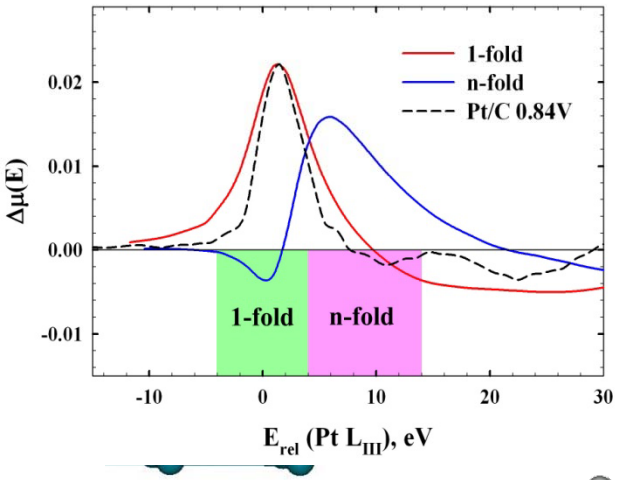


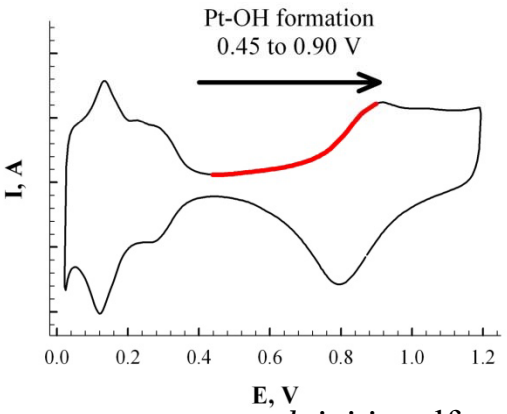
Pt-O



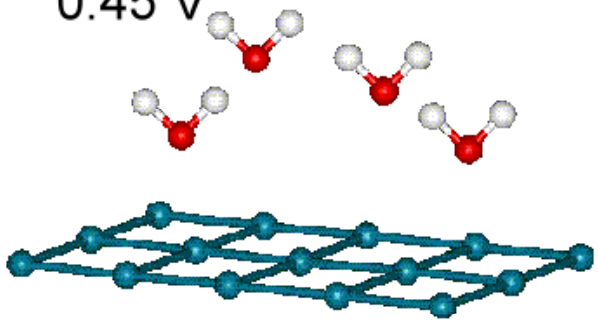


Pt_6 clean

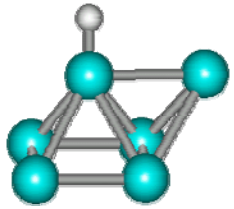




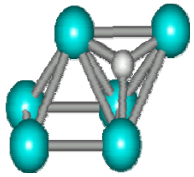
0.45 V



Pt_6 atop



Pt_6 hcp



-*ab initio* self-consistent real space multiple scattering Solves $H\Psi=E\Psi$, $\Psi=\Sigma$ atomic orbitals + plane waves

BASF The Chemical Company

The University of Tennessee Knoxville

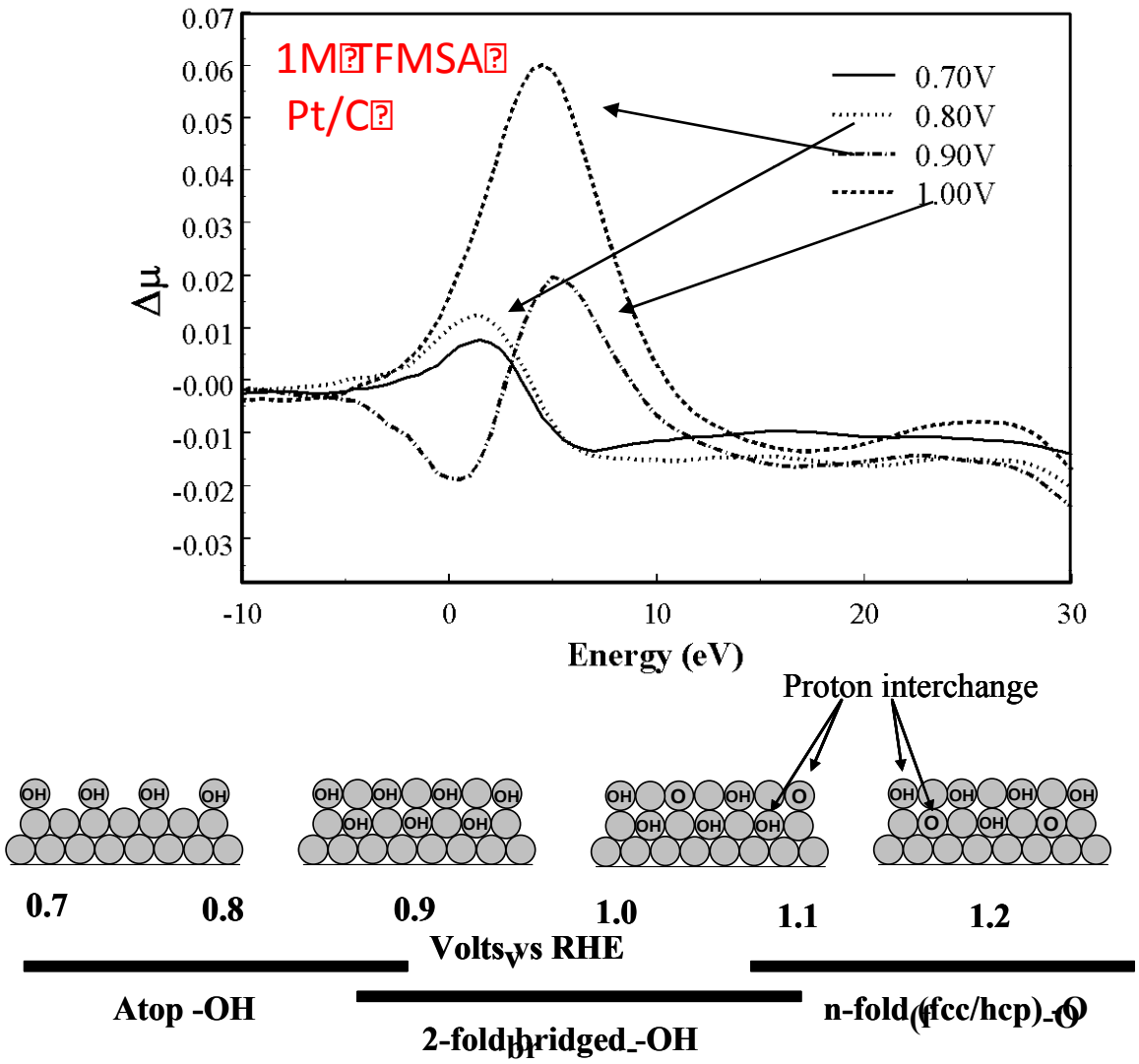
The University of New Mexico

Michigan State University

Nissan

Los Alamos National Laboratory Est. 1943

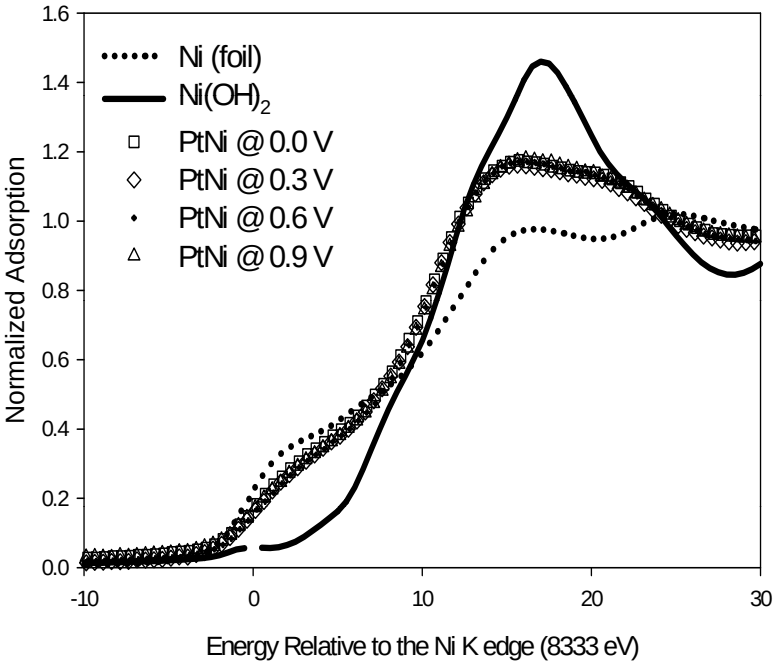
Direct View of Place Exchange on Pt Nano-particles



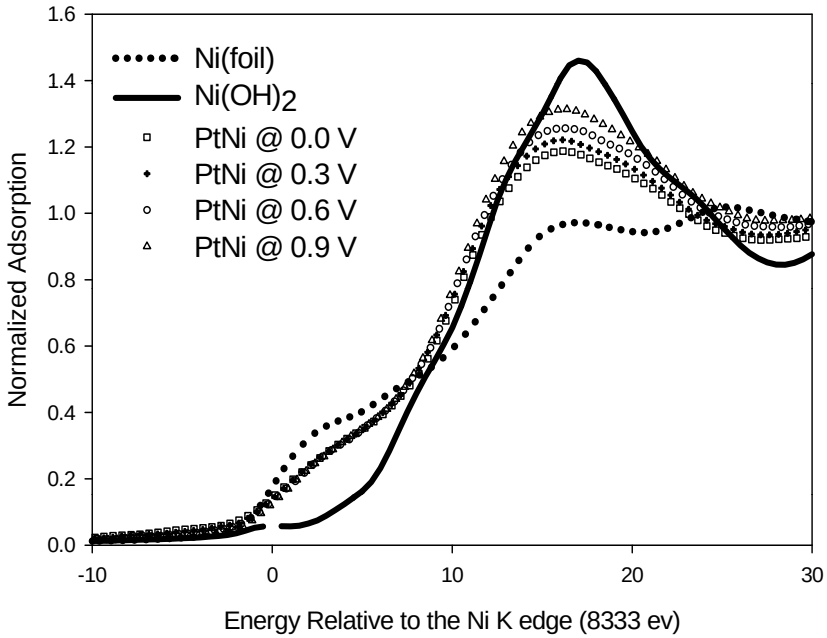
Northeastern University

Using XANES as a Tool for Quantitative Estimation of Corrosion under Cell Operating Conditions with Element Specificity

PtNi/C Pre-washed in 1M $HClO_4$



PtNi/C Not Pre-washed in 1M $HClO_4$



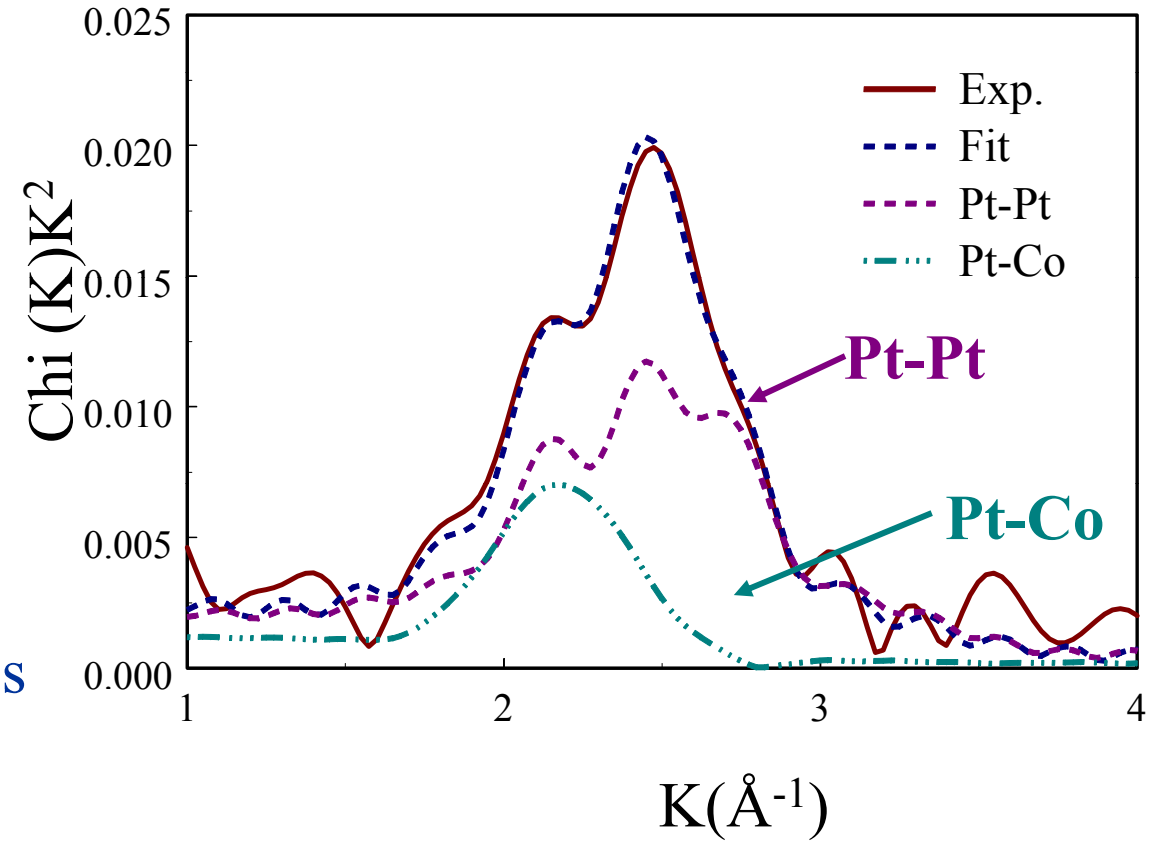
Normalized XANES at the Ni K edge for PtNi/C (a) for sample washed in 1M $HClO_4$ for 24 hours and (b) for as received sample, measured under inert conditions in a spectro-electrochemical cell at room temperature. Linear combination of spectra can provide quantitative corrosion information as a function of potential with element specificity

BASF The Chemical Company · The University of Tennessee Knoxville · The University of New Mexico · Michigan State University · Nissan · Los Alamos National Laboratory Est. 1943

Pt L_3 EXAFS
Determine M Distribution

–Multiple Shell Analysis
–K^2 weighting
–Fit data to determine coordination No.
  –Pt-Pt
  –Pt-M

–FEFF 8.0 References



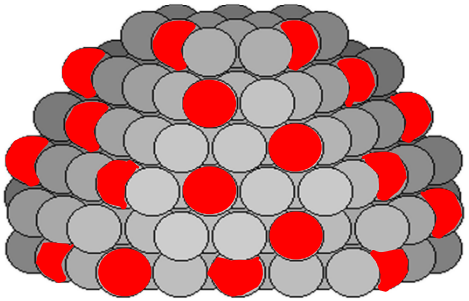
Theoretical Modeling

- ATOMS code (Bruce Ravel)
- 200 atom cluster
- Pt_3M 75:25 Ratio
- Determine average N

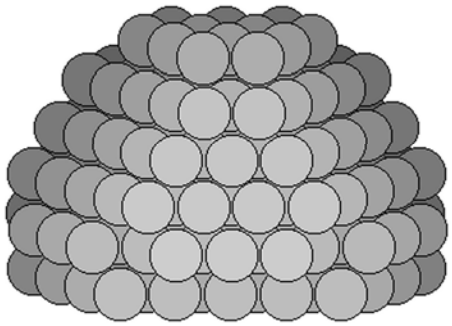
– Pt-Pt

– Pt-M

Homogenous

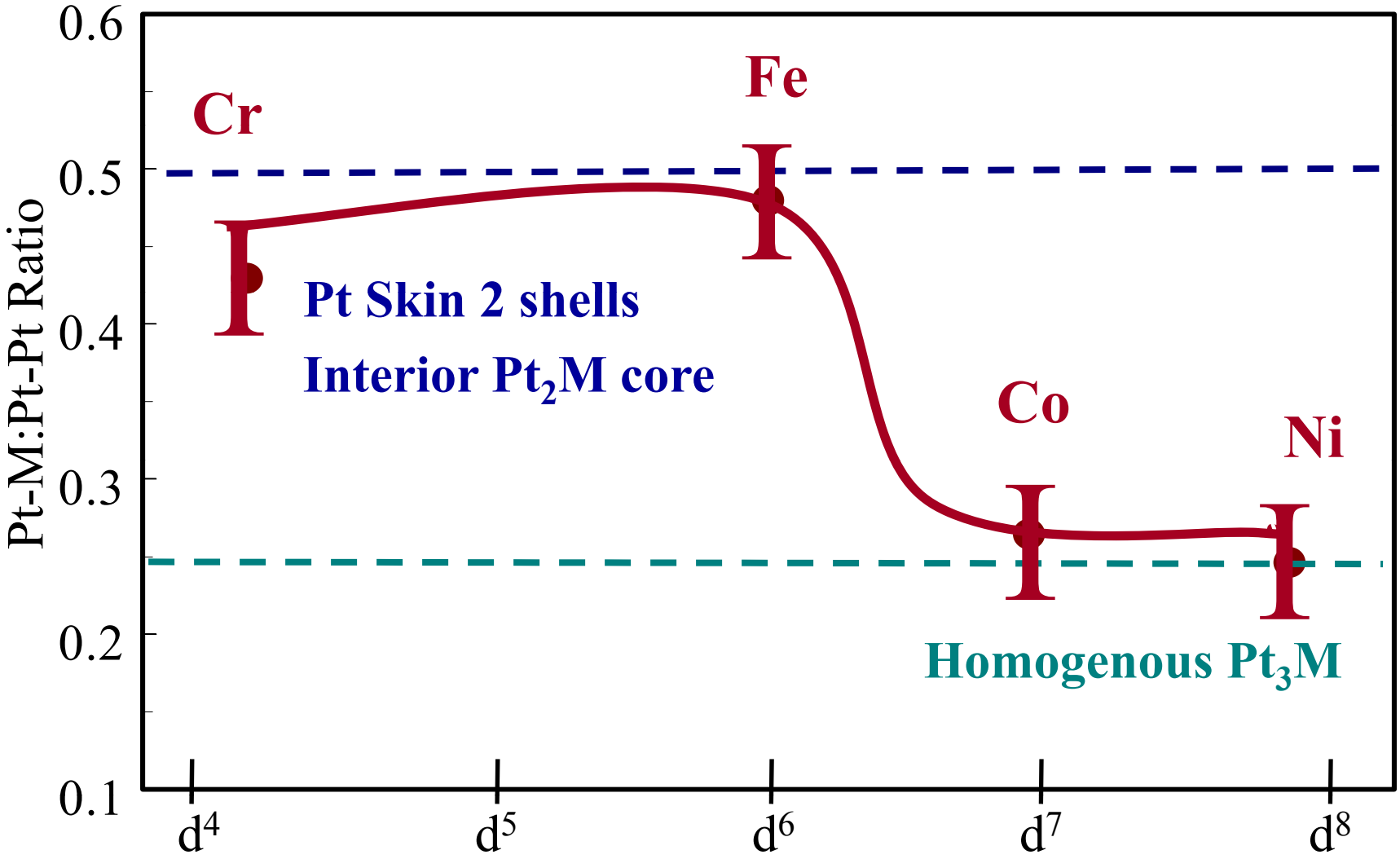


Outer Pt Shell



Pt **M**

Pt-M:Pt-Pt Ratio



Task 4: Mechanistic Studies and Spectroscopy

Participating Institutions:

UNM- Ex situ Studies with XPS and PCA analysis

NEU- In situ Spectroscopy with Synchrotron and FTIR Measurements

SMU- Macroscopic Modeling

UTK- Molecular Level Computation (Ab-Initio and MD Simulations)

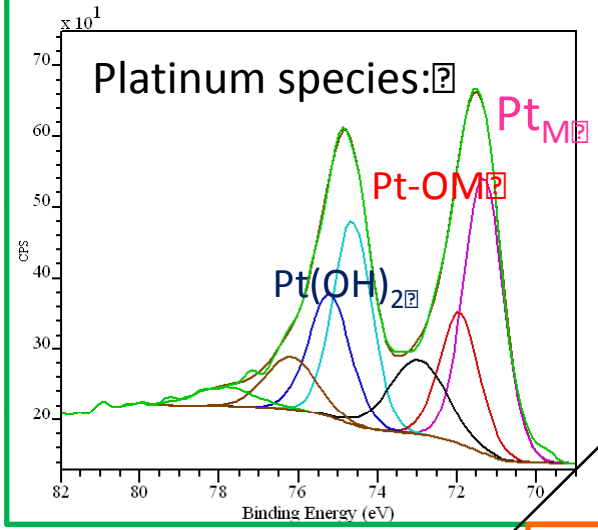
UNM- DFT Calculations

Task 4: Multi-Analytical Approach (Ex-Situ)

THE UNIVERSITY of NEW MEXICO

XPS analysis

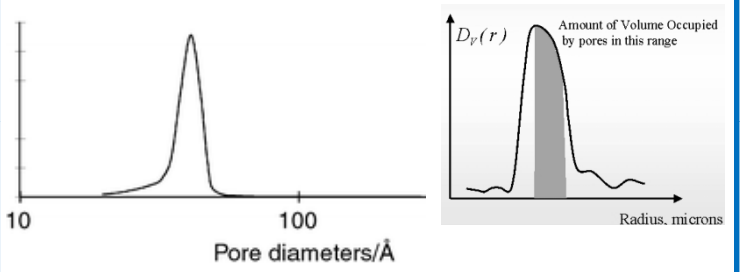
- Elemental composition:
- Chemical speciation



Model based on statistical correlation among all variables /parameters

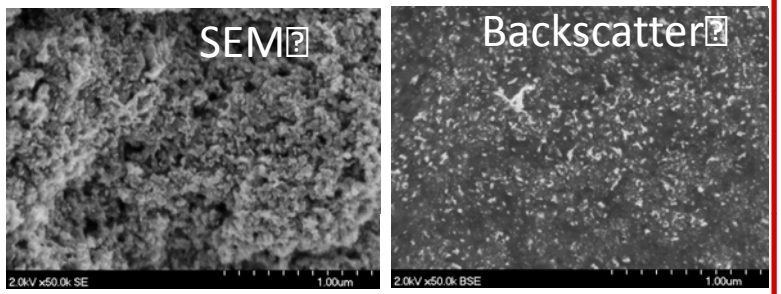
Adsorption analysis:

BET surface area
Pore size of the support
Pore Volume of the support

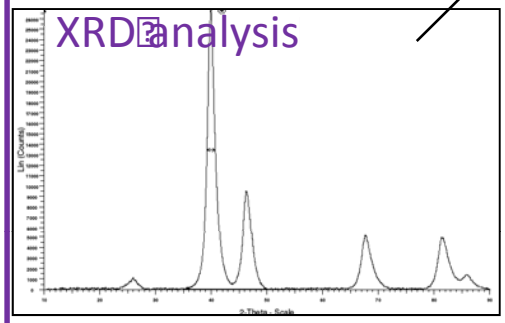


SEM analysis:

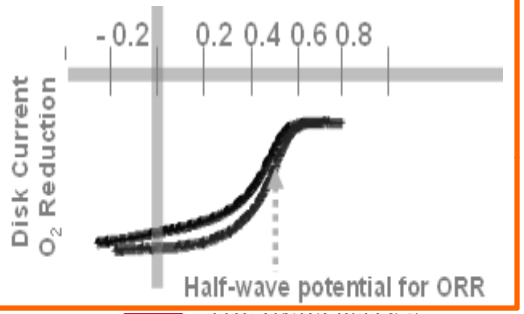
Roughness:
Ra, Rsk;
Pt particle distribution



XRD analysis



Electrochemical characterization



BASF The Chemical Company

THE UNIVERSITY of TENNESSEE KNOXVILLE

THE UNIVERSITY of NEW MEXICO

MICHIGAN STATE UNIVERSITY

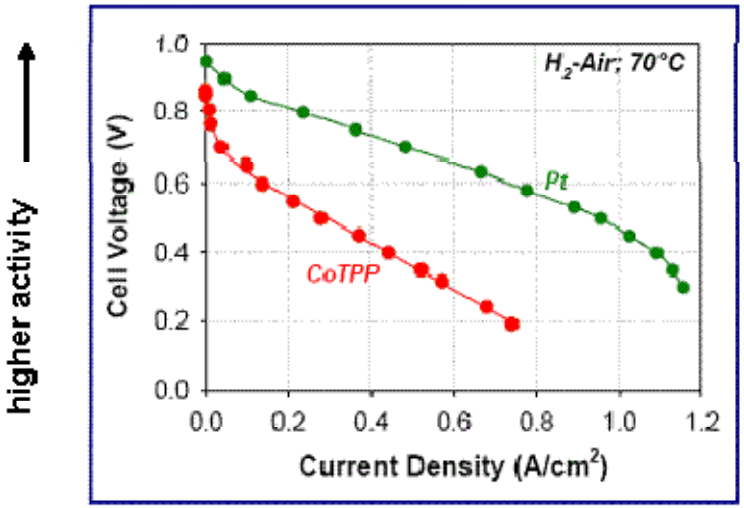
Kateryna Artyushkova

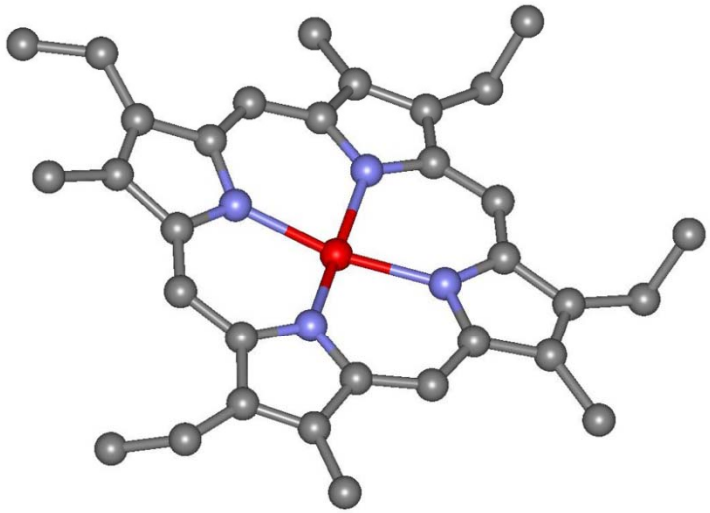
NISSAN

Los Alamos NATIONAL LABORATORY EST. 1943

In situ Studies using Synchrotron Spectroscopy-NEU

Liganded TM Site as Possible ORR
Active Material

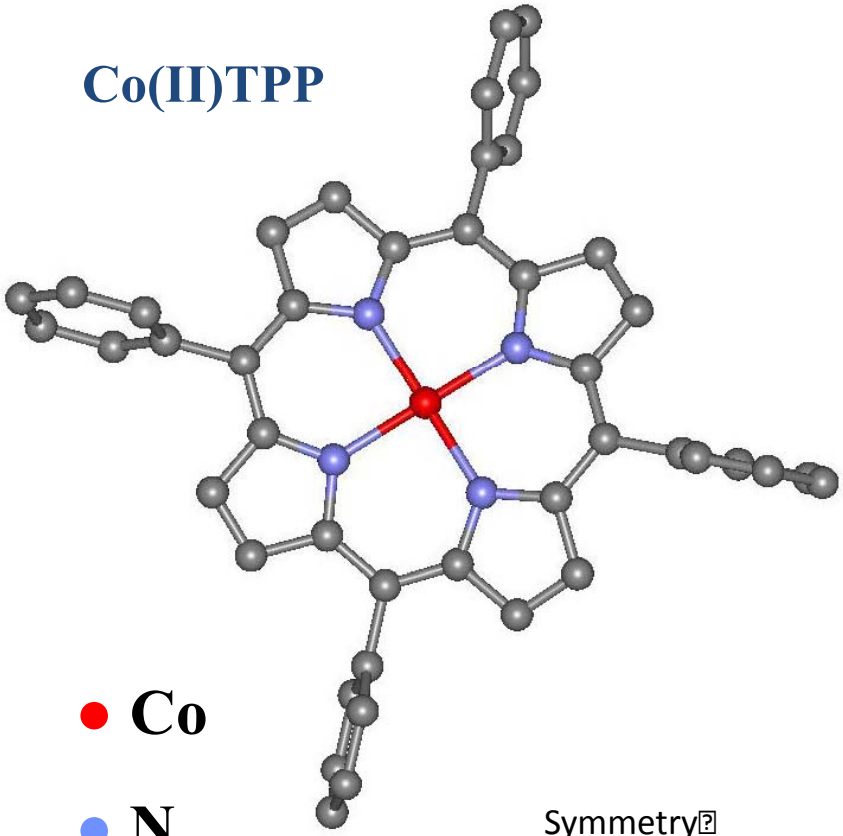




Steady-state polarization curves obtained in a hydrogen-oxygen single MEA fuel cell with a non-platinum cathode catalyst, prepared from pyrolyzed CoTMPP. The anode catalyst was an unsupported Pt black. Anode potential at all cell current densities can be assumed to within a few mV of the NHE potential.

CoN_4 Porphyrins: Gateway to Biocatalysis

Co(II)TPP



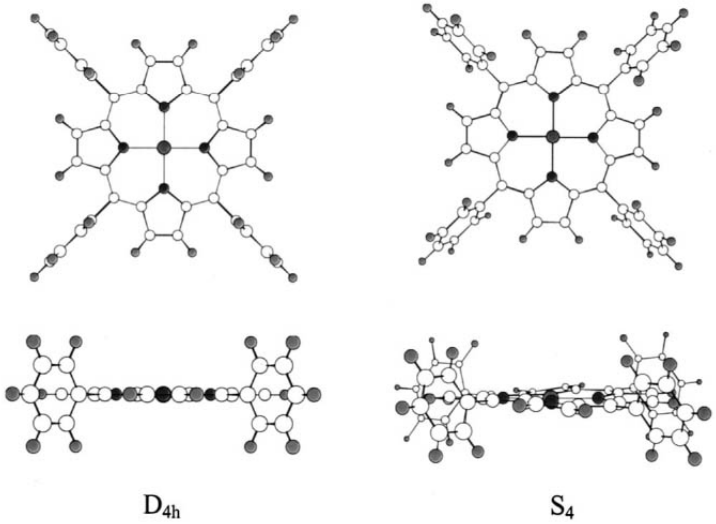
- Co
- N
- C

- Low spin Co(II)TPP (*I*42*d*)
- Predominant M-N_4 coordination
- Single active site per cluster
- "Ruffled" D_{4h} symmetry – actually S_4 (1,4)
- Co-N_{avg} = 1.968 Å (1- 3)

Symmetry

Low spin → high spin

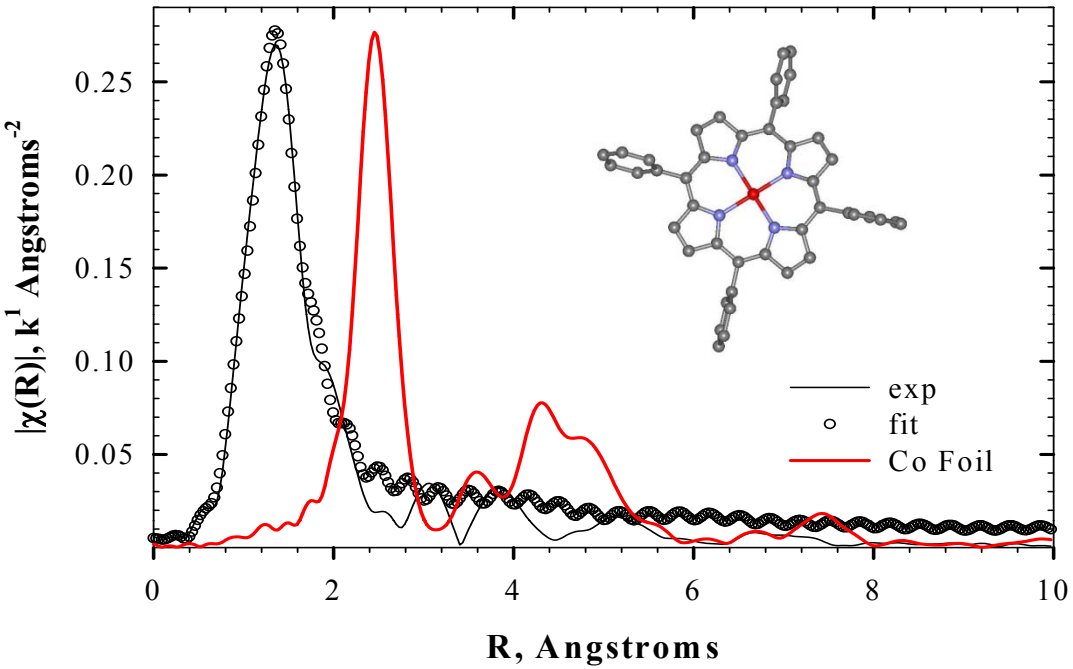
$E_g \rightarrow T_{2g}$



(1) Madura, P; Scheidt, W. R., *Inorg. Chem.*, 15(12), 3182 **(1976)**, **(2)** Van Doorsaler, S; Schweiger, A., *J. Phys. Chem. B*, 104, 2919 **(2000)**, **(3)** Liao, M; Scheiner, S, *J. Chem. Phys.*, 117(1), 205 **(2002)**. **(4)** Collman et al., *J. Amer. Chem. Soc.*, v97(10), 2676 **(1975)**

In Situ EXAFS

600˚C



0.40 V FT Fitting

S_0^2: 0.871 (FEFF)

$\Delta\sigma^2$: 0.005

All N: ±20%

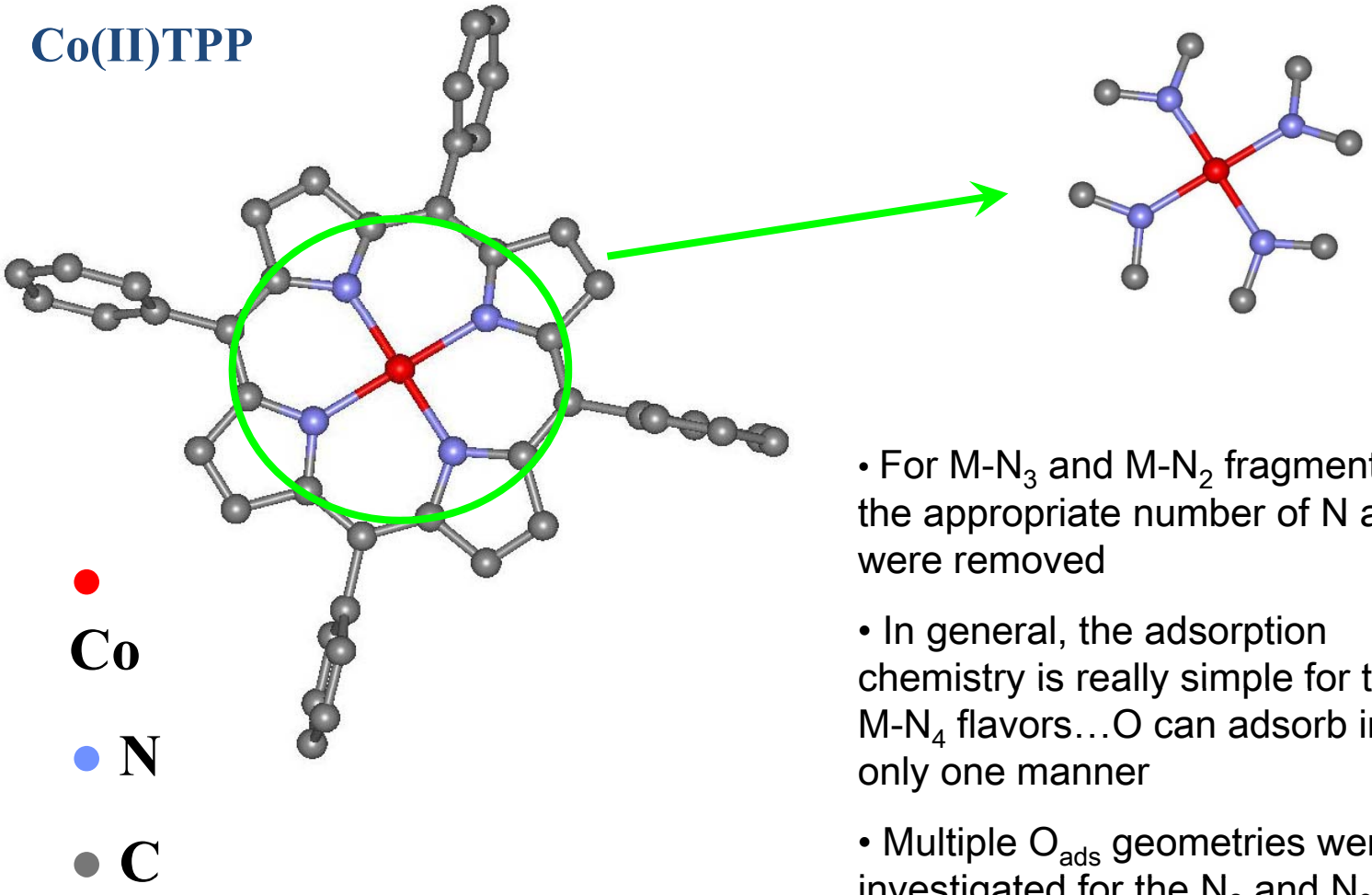
Material	N_{Co-N}	N_{Co-O}
600˚C	3.1	1.2
700˚C	3.8	1.8
800˚C	1.4	2.4

Co-N coordination correlates well with (*ex situ*, as-synthesized) XPS results

Beyond the first shell – FT XAS fitting is limited by inherent uncertainty

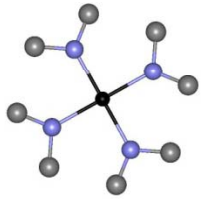
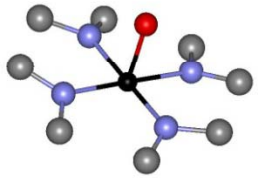
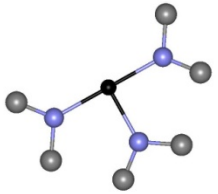
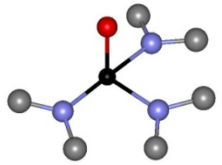
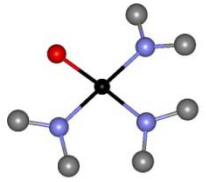
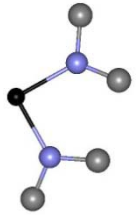
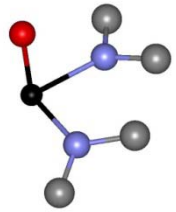
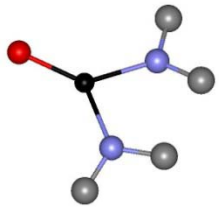
ALL fitting and analysis via the IFEFFIT suite: **http://cars9.uchicago.edu/ifeffit/**

FEFF Models



- For M-N_3 and M-N_2 fragments, the appropriate number of N atoms were removed
- In general, the adsorption chemistry is really simple for the M-N_4 flavors…O can adsorb in only one manner
- Multiple O_{ads} geometries were investigated for the N_2 and N_3-coordinated species

$$\Delta\mu = \mu(CoN_xC_yO) - \mu(CoN_xC_y)$$

N-coordination	Clean	"axial" O_{ads}	"equatorial" O_{ads}
N=4			N/A
N=3			
N=2			

● Co ● N ● O ● C

J. Ziegelbauer, T. Olson, S. Plylypenko, F. Alamgir, C. Jaye, P. Atanassov, and S. Mukerjee, *J. Phys. Chem.*, C **112**, 8839 (2008)

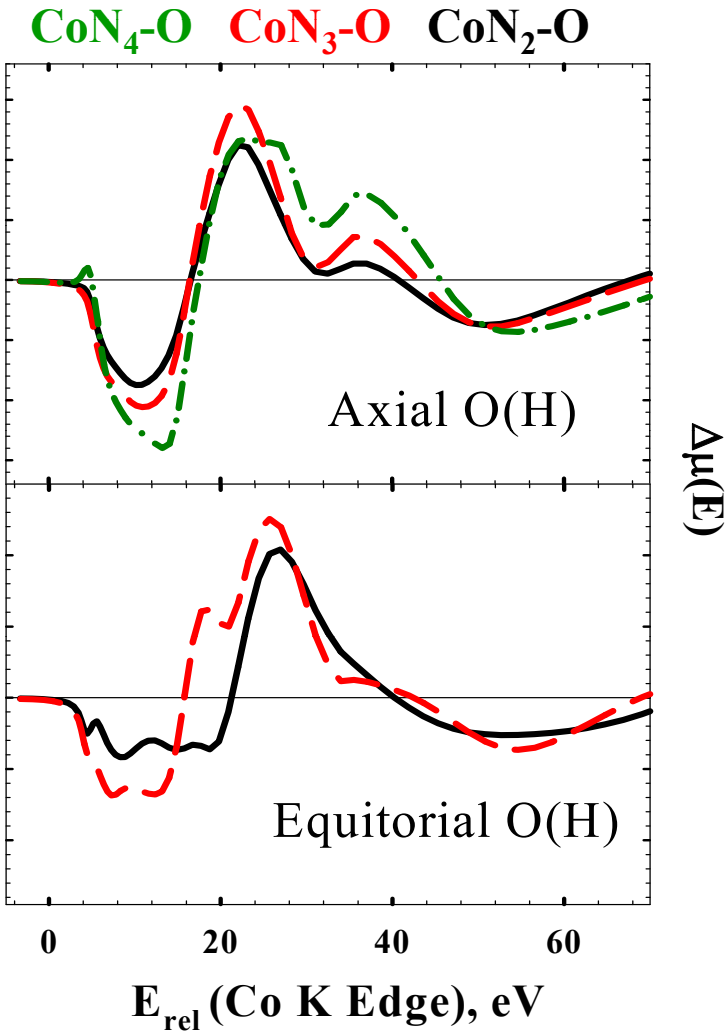
FEFF Results

Axial-O

- Double peak after minimum
- Difference increases with loss of N

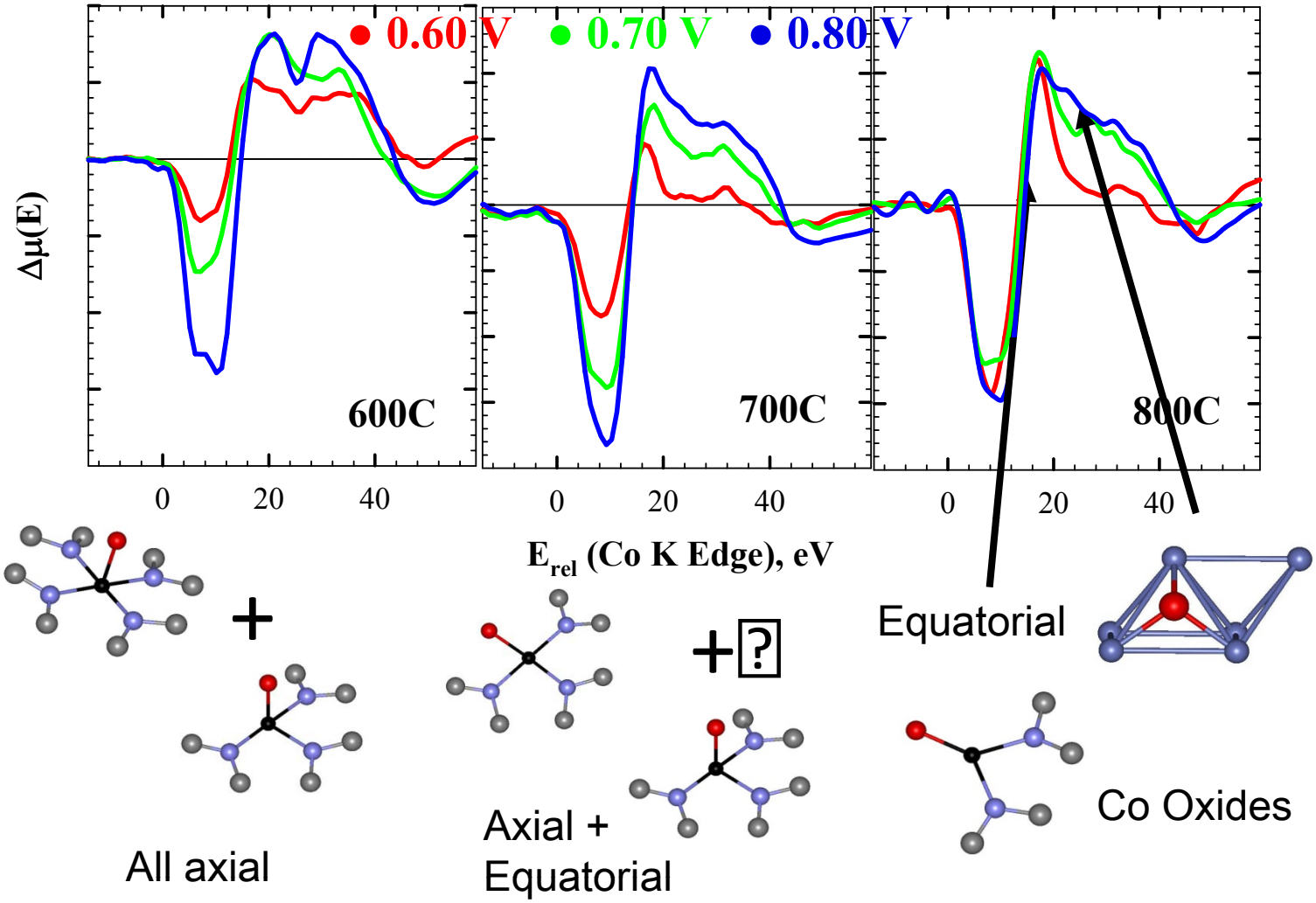
Equitorial-O

- N=2: Broad minimum, tailing maximum
- N=3: Reversed (from axial) double peaks
- Both: “Flattened” minimum



J. Ziegelbauer, T. Olson, S. Plylypenko, F. Alamgir, C. Jaye, P. Atanassov, and S. Mukerjee, *J. Phys. Chem.*, C **112**, 8839 (2008)

Pyrolyzed Co-based Porphyrins:



J. Ziegelbauer, T. Olson, S. Plylypenko, F. Alamgir, C. Jaye, P. Atanassov, and S. Mukerjee, *J. Phys. Chem.*, C **112**, 8839 (2008)

Pyrolyzed Co-based Porphyrins*:*
"Intimate EXAFS" - NEXAFS

1. **The porphyrins maintain a Co-N_4-type stoichiometry until 800°C**
2. **Co-N_4 = axial O_{ads}**
3. **Axial O_{ads} = efficient $4e^-$ ORR**
4. **In situ XAS + combined with the Δμ analysis unambiquously identified the morphology of the active clusters**
5. **Helped validate the method for future more complex structures**

Hydrodynamic methods of electrode kinetics

Sanjeev Mukerjee

- To find out what electrons, ions and molecules do during an electrode reaction
- To determine the rate of an electrochemical reaction occurring on an electrode surface
- To explore the mechanism of an electrode process

As an example, lets consider and (stick to) the oxygen reduction reaction (ORR) at electrode surfaces:

ORR involves a reaction intermediate:

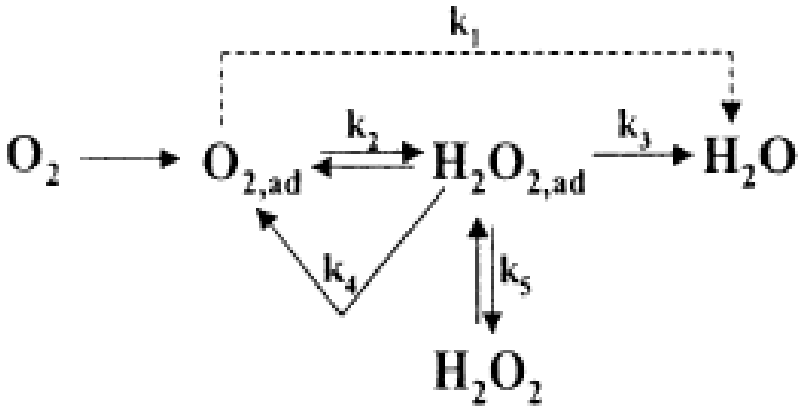
$$O_2 + 2H^+ + 2e^- \rightarrow H_2O_2$$

The hydrogen peroxide can react further:

$$H_2O_2 + 2H^+ + 2e^- \rightarrow 2H_2O$$

or leave by desorbing from the electrode surface:

Thus generating issues ($2e^-$ vs. $4e^-$, reactive radicals degrading the membranes) for PEM fuel cells that rely on ORR as cathode reaction



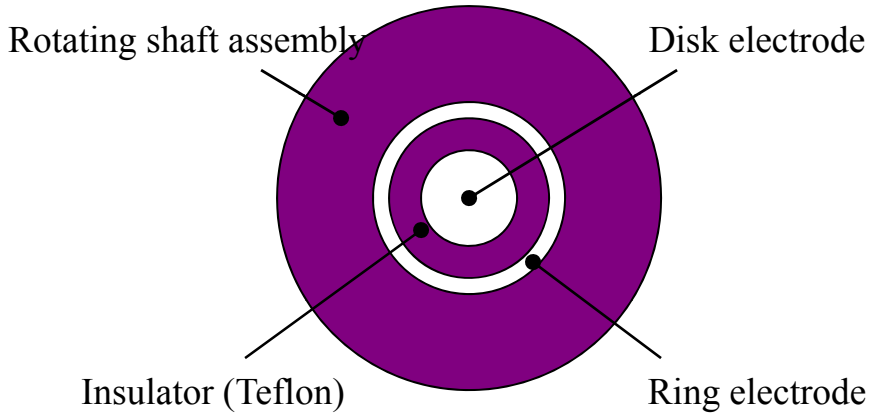
The above questions can thus be formulated as: What are the k values?, The H_2O ($4e^-$) or the H_2O_2 ($2e^-$) reaction pathway is the dominant?, In what extent (What is the peroxide yield)?

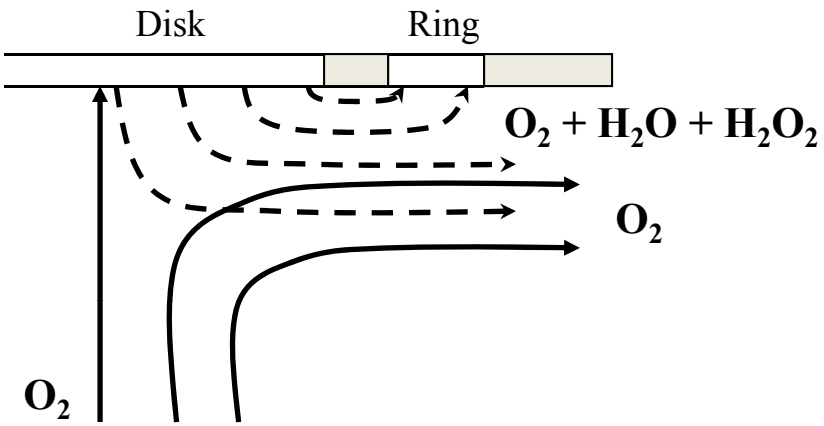
To answer all of these, one must be aware of the role of the reaction intermediate (H_2O_2)

Their motivation was to detect such intermediates that could come loose from the electrode and/or partially react further

Their idea was to use the help of **hydrodynamics** to do so

Rotating a disk electrode in the electrolyte (e.g. in an oxygen-saturated solution) – creating a solution pump

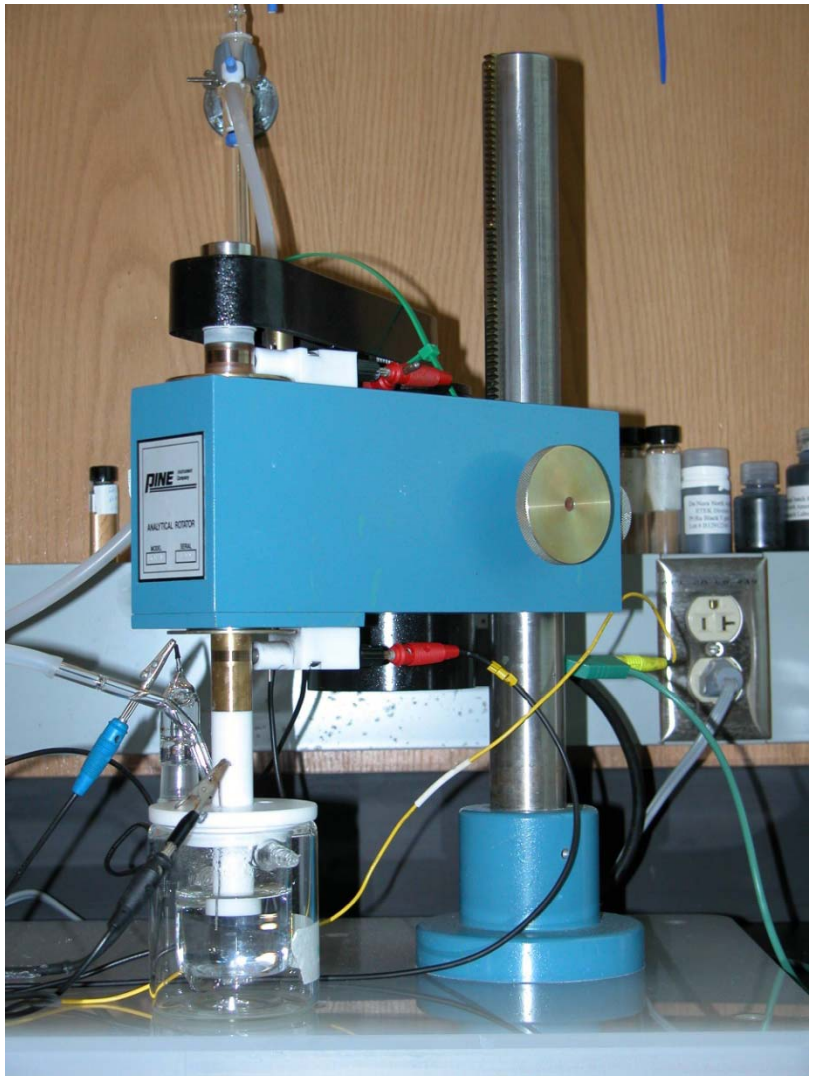




While the oxygen reduces on the electrode, the hydrogen peroxide intermediate does not remain adsorbed on the surface but is thrown sideways across the disk.

If an electrically isolated second "ring" electrode is also encircled around the central disk electrode, one can detect the radicals by setting the ring potential to a value where it is expected to react:

$$H_2O_2 + 2H^+ + 2e^- \rightarrow 2H_2O \qquad E^0 = 1.78V\ (>E_r)$$



(A picture for the entire setup can be seen in the first slide)

The disk and the ring electrode potentials are controlled separately: either by two potentiostats, or by one **bipotentiostat**

Rotator system (highly precise) with carbon brush current collectors

A usual **three electrode** (WE, RE, CE) **electrochemical** glass **cell** that accommodates pipes for gas bubbling as well as the WE shaft assembly

The **WE is** often an **interchangeable disk**, constituted by a slug **of glassy carbon, platinum, or gold disk**

The **ring electrode** (secondary WE) is either glassy carbon or gold

Albeit steady-state voltammetry can be conducted under well-stirred conditions, this is not amenable to rigorous mathematical treatment.

RDE (and RRDE) presents a well-defined hydrodynamic behavior

On the surface of the disk (somehow surprising)

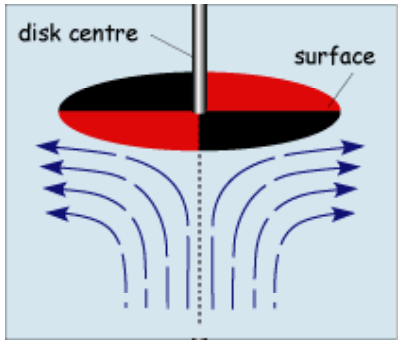
A thin layer of solution immediately adjacent to the electrode surface and manages to cling while appears to be motionless (from the perspective of the rotating electrode).

Faster electrode rotation makes the stagnant layer thinner – faster diffusion

Well defined mass transport of the analyte:

- vortex flow in the bulk solution continuously brings fresh analyte to the outer edge of the stagnant layer - convection
- analyte diffuses across stagnant layer. The thinner the stagnant layer, the faster the analyte can diffuse across it and reach the electrode surface - diffusion

Providing the rotation speed is kept within the limits that laminar flow is maintained then the mass transport equation is given by using Fick's second law:

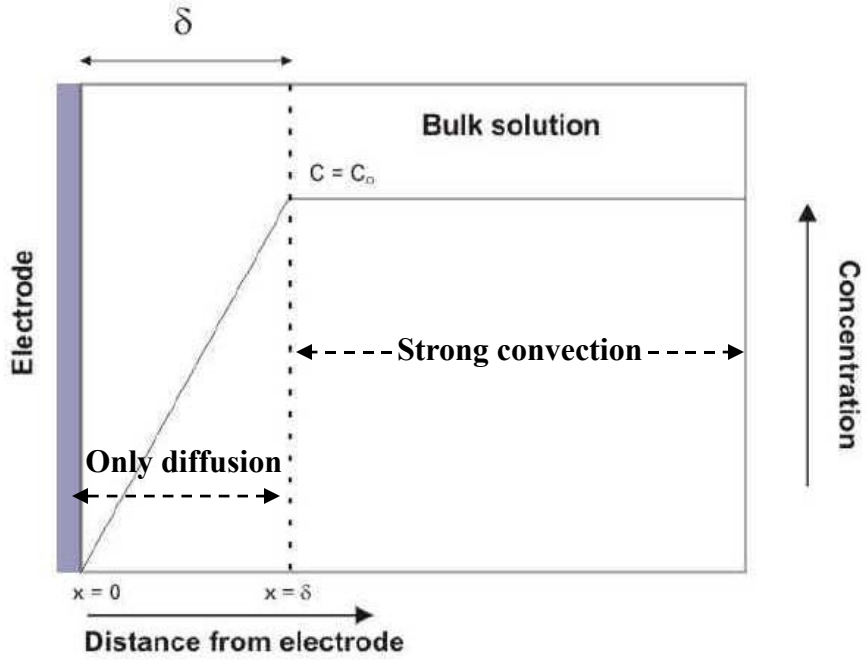


$$\frac{\partial[C]}{\partial t} = D_C \frac{\partial^2[C]}{\partial x^2} - v_x \frac{\partial[C]}{\partial x}$$

To predict the current one must solve this subject to the electrode reactions

Solving the mass transport equation at appropriate boundary conditions (x = 0 and x= ∞) is one approach

A more convenient approach is based on equating the mass transport and kinetic fluxes across the Nernst diffusion layer at the electrode surface



Levich derived an expression relating the thickness of the diffusion layer to experimental variables including the rotation rate:

$$\delta_\omega = [1.61\, D^{1/3}\, \nu^{1/6}]\, \omega^{-1/2}$$

where ***D*** is the diffusion coefficient,
ν is the kinematic viscosity,
and ω is the angular velocity.

(The rotation rates may have to be converted from rpm to radians per second using the relationship: $\omega = 2\pi f / 60$)

In order to hold the theory, one should not go beyond a minimum and a maximum rotation rate. While the former is necessary to keep the forced convection dominating over diffusion, the latter ensures the highly organized laminar flow pattern, otherwise no net solution movement occurs.

The Nernst diffusion layer concept permits a trivial derivation of the current density at a RDE at potentials where the electrode reaction is mass transport controlled.
Since the surface concentration of the electroactive species is zero, the **limiting (Levich) current** is given by:

$$i_L = n\,F\,A\,D\,(dc/dx)_{x=0} = n\,F\,A\,D\,c\,\delta$$

where ***n*** is the number of electrons involved in the electrode process,
F is the Faraday constant,
A is the surface area of the electrode

Substitution of the relationship what Levich deduced for δ leads to the **Levich equation**:

$$i_L = 0.62\,n\,F\,A\,D^{2/3}\,\omega^{1/2}\,\nu^{-1/6}\,c$$

Upon the Levich equation:

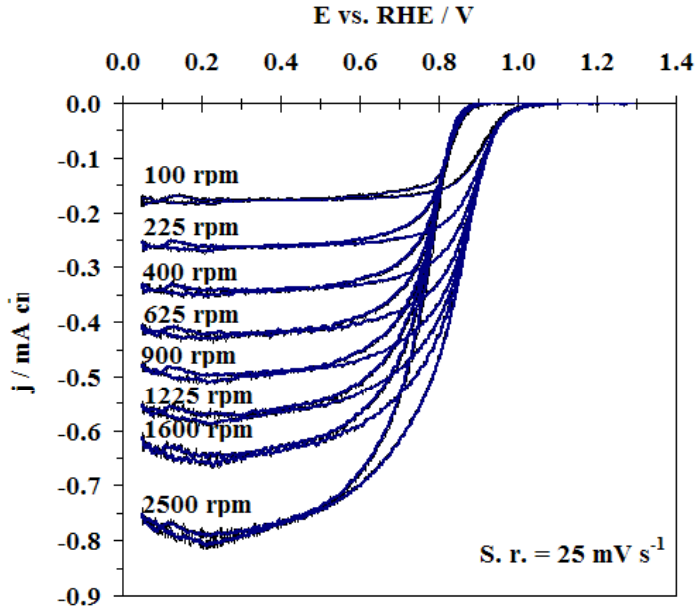
- **The test for mass transport control is that a plot of i_L vs $\omega^{1/2}$ is linear and intercepts the origin,**
- **$i_L \propto c$ and A,**
- ***D* may be determined (if unknown)**

Performing RDE experiments

The primary (disk) WE potential is swept back and forth across the formal potential of analyte. Usually, one sweeps between the standard electrode potential of the reaction and a region where other surface processes hinder the reaction of interest. In case of ORR:

$$O_2 + 4H^+ + 4e^- \rightarrow 2H_2O \qquad E^0 = 1.23V$$

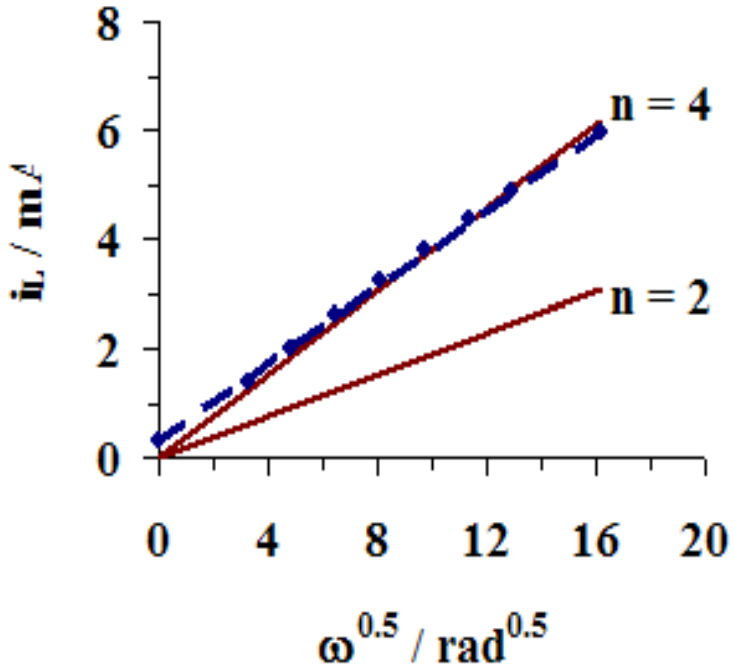
However, it differs from CV in that the working electrode is rotated at a certain speeds
Obtaining the family of such sinusoidal polarization curves is called as **Levich-study**



Levich plot for the ORR on a commercial Pt fuel cell catalyst

From the family of the reduction voltammograms, the limiting (Levich) currents can be determined as the height of the waves at the same chosen potential (0.4 V) and plotted against the oxygen supply.

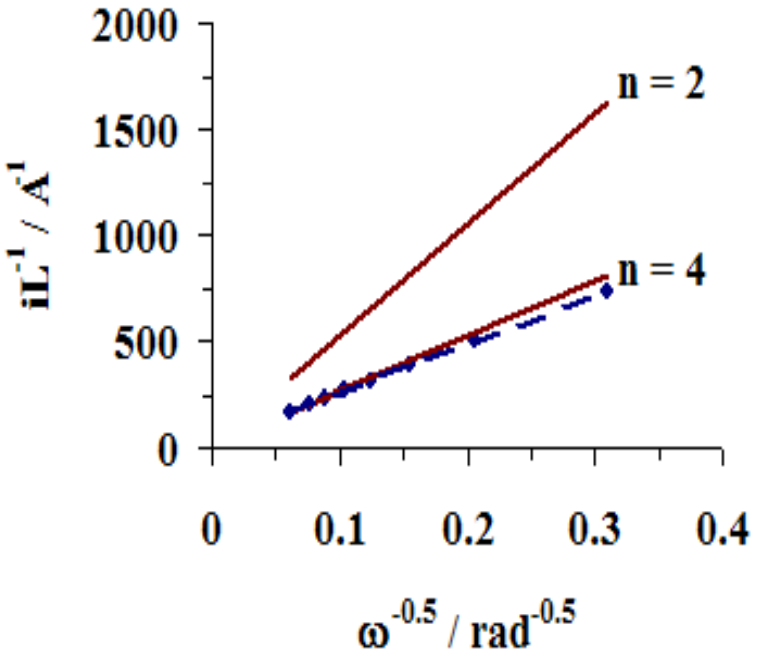
The Levich plot can also contain the **theoretical plots** for the water ($4e^-$) as well as the peroxide ($2e^-$) routes as calculated from the Levich-equation.



ORR is exclusively mass transport-controlled at 0.4 V and mainly proceeds via the four electron process (i.e. complete) on this catalyst.

The Koutecky-Levich approach for kinetics analysis

Data from the Levich-plot can be replotted in their reciprocal values to describe the non-limiting currents



Levich-Koutecky equation

$$\frac{1}{i} = \frac{1}{i_k} + \frac{1}{i_d} = \frac{1}{i_k} + \frac{1}{K\omega^{1/2}}$$

Kinetic current derived from Levich-Koutecky equation

$$i_k = \frac{i_d \cdot i}{i_d - i}$$

Recall the definition of kinetic current:

$$i_k = k\, n\, F\, A\, c\, \Gamma$$

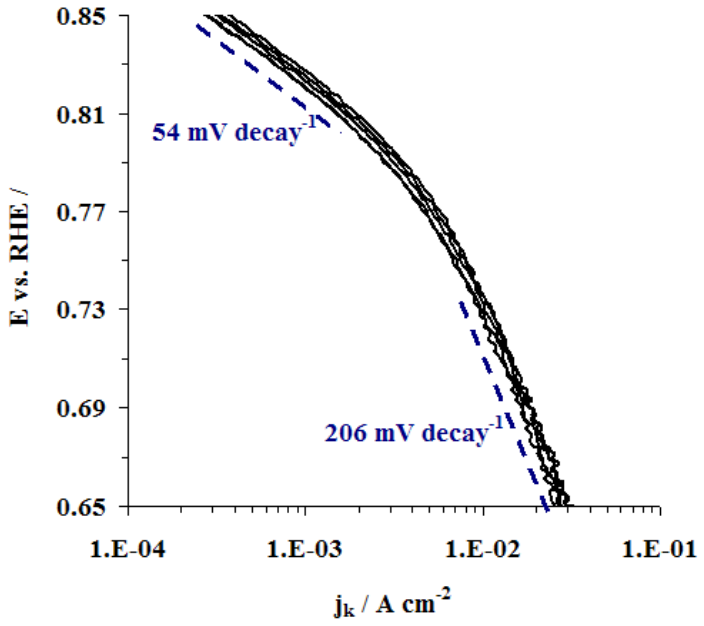
where Γ is the surface concentration of the analyte

Thus, the extrapolated intercept at $\omega^{-1/2} = 0$ ("infinite convection", $\Gamma = 0$) gives the rate constant (k)

Tafel (potential dependent) analysis of k enables determination of the transfer coefficient (α) as well

Obtaining the Tafel plot from RDE data

Using the RDE data and applying the Koutecky-Levich approach to derive the kinetic currents (here: current densities as $j_k = i_k / A$), one can also obtain information on the rate of the electrode processes



Two Tafel-slopes are seen for carbon supported Pt fuel cell catalysts, just as for Pt, according to ORR occurring on oxide covered and clean (double layer) conditions. The one at higher overpotentials is somewhat higher than that of obtained for well-defined Pt disk electrodes.

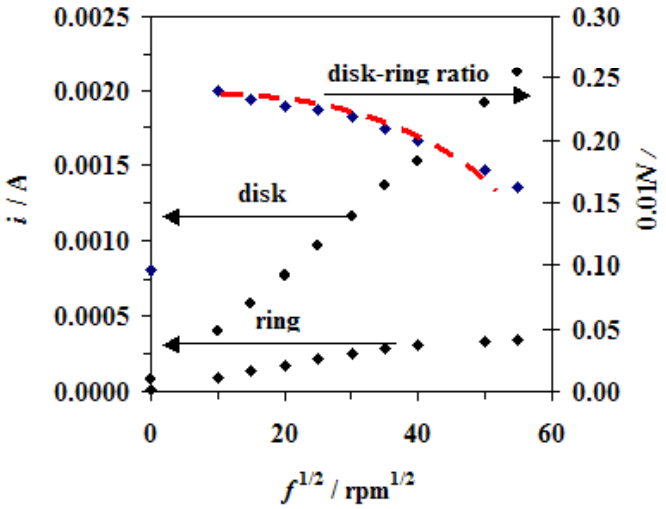
Toward a more detailed kinetics analysis – calibrating the RRDE

RRDE allows recording the ring currents while the ring electrode is held at constant electrode potential in parallel to the polarization of the disk electrode

It must be emphasized that not$_a$ ll the species formed at the disk will reach the ring; some of them will bypass the ring and leaves into the bulk of the solution. The % of the intermediates caught depends on the relative dimensions of the disk and the ring. The collection efficiency (***N***) is the fraction of a completely stable, solution free intermediate formed at the disk which is detected at the ring.

$$N\ (\%) = 100\ i_R / i_D$$

N can be determined experimentally by using a with a well-behaved reversible couple, e.g. ferricyanide/ferrocyanide redox system:



$$Fe(CN)_6^{3-} + e^- \rightarrow Fe(CN)_6^{4-}$$

$$Fe^{3+}(aq) + e^- \rightarrow Fe^{2+}(aq) \qquad E^0 = 0.77\ V$$

Learning about the intermediate – employing the RRDE setup

The ring electrode of RRDE *in situ* detects intermediates *at extremely low concentration*

Taking into account that the total disk current, I_D, is the sum of the O_2 reduction currents to water, I_{H2O}, and to H_2O_2, I_{H2O2}, and using the collection efficiency N as defined before

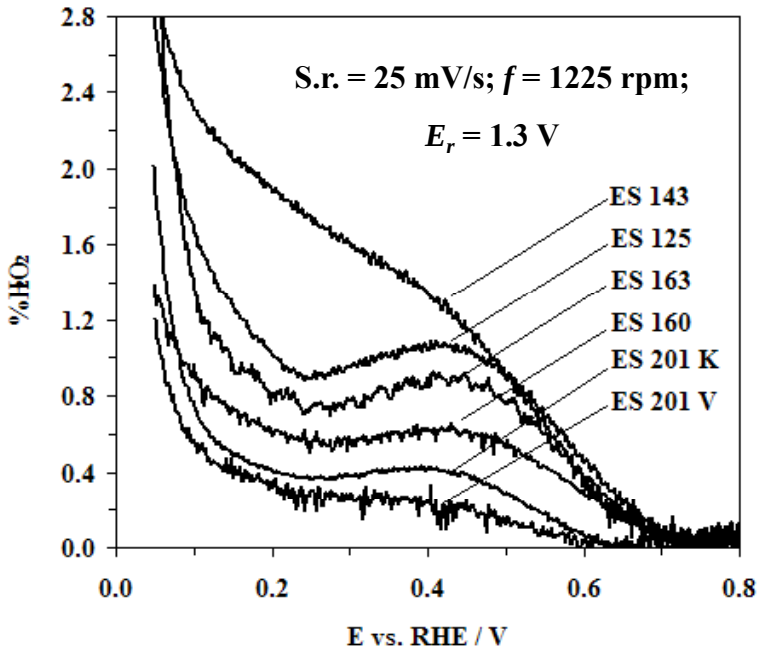
$$I_D = I_{H_2O} + I_{H_2O_2} \text{ with } I_{H_2O_2} = I_R N^{-1}$$

the fraction of H_2O_2 formation, X_{H2O2}, can be calculated from the molar flux rates of O_2:

$$\dot{n}_{O_2(4e-)} = I_{H_2O}/4F \text{ and } \dot{n}_{O_2(2e-)} = I_{H_2O_2}/2F$$

$$X_{H_2O_2} = \frac{\dot{n}_{O_2(2e-)}}{\dot{n}_{O_2(2e-)} + \dot{n}_{O_2(4e-)}} = \frac{2I_R/N}{I_D + I_R/N}$$

Comparison of the peroxide yields during ORR for different fuel cell catalysts



The extent and rate of hydrogen peroxide generation is detected from solutions containing with concentartions of femtomols!!! – **no other such analytical technique is available**