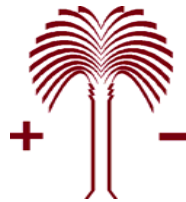


Novel Non-Precious Metals for PEMFC: Catalyst Selection Through Molecular Modeling and Durability Studies

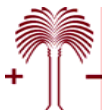


2005 DOE Hydrogen, Fuel Cells Infrastructure Technologies Program Review

Branko N. Popov
Department of Chemical Engineering
University of South Carolina,
Columbia, South Carolina 29208
May 24, 2005

This presentation does not contain any proprietary or confidential information

Project ID# FC15



Overview

Timeline

- Project Start Date
 - ✓ 31/9/2003
- Project End Date
 - ✓ 30/9/2007
- Percent Complete
 - ✓ 35%

Budget

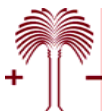
- Total Project Funding
 - ✓ DOE Share- \$ 1376.292 K
 - ✓ Contractor Share - \$351.207K
- FY 03: \$ 200K
- FY 04: \$ 125K
- FY 05: \$ 425K
- FY 06: \$ 395K
- FY 07: \$ 231.292K

Technical Barriers and Targets

- Electrode performance
 - ✓ Perform at least as good as the conventional Pt catalysts currently in use in MEAs
- Durability
 - ✓ 2000 hours operation with less than 10% power degradation
- Material Cost
 - ✓ cost at least 50% less as compared to a target of 0.2 g (Pt loading)/peak kW

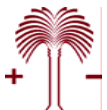
Partners / Collaborations

- Case Western University
 - ✓ Molecular Modeling
- Northeastern University
 - ✓ Structural Studies / Chalcogenides

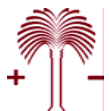
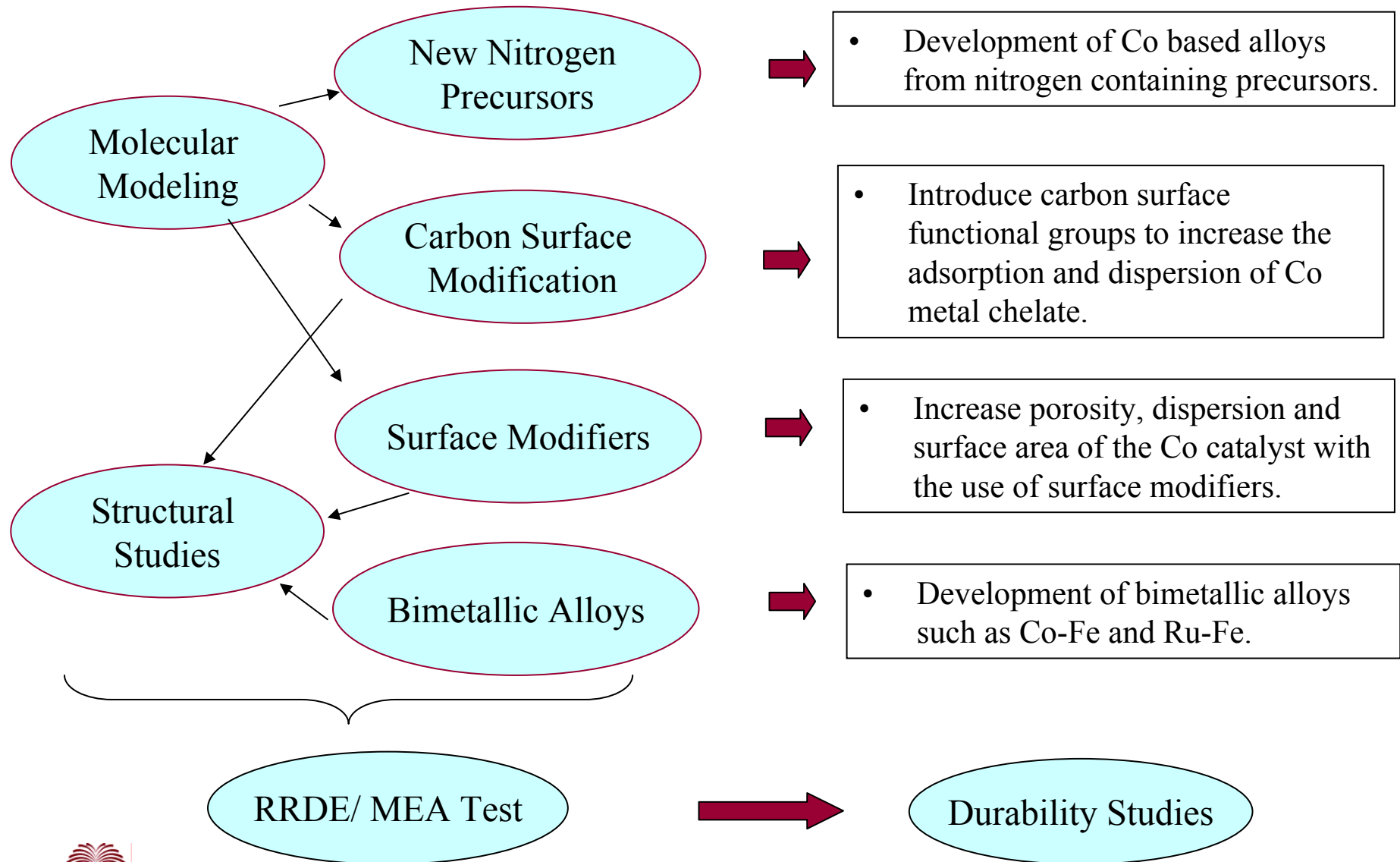


Objectives

- Develop transition metal supported catalysts for oxygen reduction using:
 - Low cost transition metal and nitrogen precursors
 - Modified carbon support
- Optimize number of the catalytic sites as a function of
 - Carbon pretreatment.
 - Chemical composition of catalyst.
 - Post treatment of catalyst.
- Improve understanding of reaction mechanism of oxygen reduction on non-precious catalysts through
 - Theoretical molecular modeling. (Case Western Reserve University)
 - Electrochemical characterization.
 - Structural studies (XPS, EXAFS, XANES). (North Eastern University)
 - Correlation between the catalyst composition, heat treatment and catalytic sites for oxygen reduction.
- Accomplish low cost catalyst through
 - Mass production methods.
 - Non precious metals.
 - Low cost precursors.
- Accomplish stable non precious catalysts with
 - High durability (corrosion resistant alloy catalysts).
 - Low peroxide generation.
 - High activity towards oxygen reduction.



Our Approach



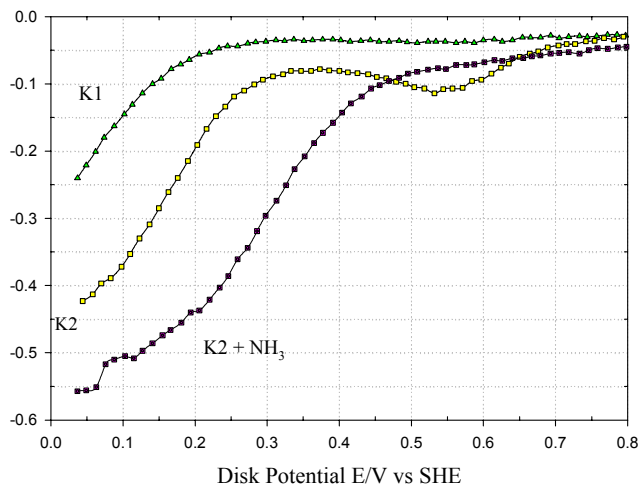
Accomplishments

- Metal free catalyst was developed with carbon surface modification.
 - Onset potential for oxygen reduction = 0.7 V vs. RHE.
 - FOUR electron pathway for ORR.
- Active Co-chelate /C catalysts was developed with the use of activated carbon
 - A methodology was developed to increase the active sites of the catalyst. Introduction of quinone- hydroquinone groups on the carbon surface increases the number of active sites by favoring the anchoring of Co chelate complexes on carbon substrate.
 - FOUR electron pathway for ORR.
- Active Co-chelate/ C catalyst was developed with the use of surface modifiers.
 - Two surface modifiers were identified (SM1 and SM2- USC product) to increase the activity of the non precious metal catalyst (Co, Fe and Co-Fe).
 - FOUR electron pathway for ORR.
- Ru based catalyst synthesized by our methodology has a performance equivalent to that of ETEK 20% Pt/C catalyst under RRDE test conditions.
- Bimetallic Ru-Co and Ru-Fe prepared by the methodology developed at USC shows performance comparable to that of ETEK 20% Pt/C catalyst under RRDE test conditions.



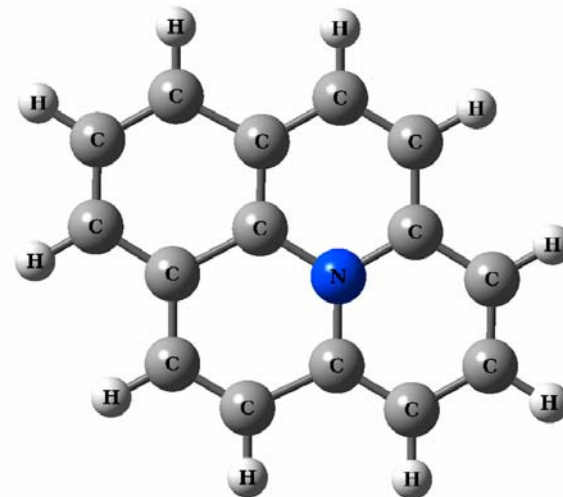
Development of Metal Free Catalyst

Modeling : Structure Model for Nitrogenated Carbon



- ✓ Introducing various oxygen and nitrogen groups on the surface of the carbon increases the activity towards oxygen reduction
- ✓ However, oxygen reduction is predominantly through TWO electron pathway.
- ✓ This agrees with the structure model for nitrogenated carbon.

Radical e^- is calculated to delocalize onto adjacent C atoms.



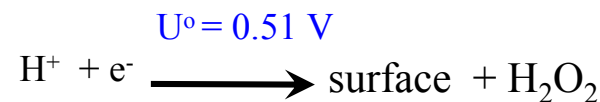
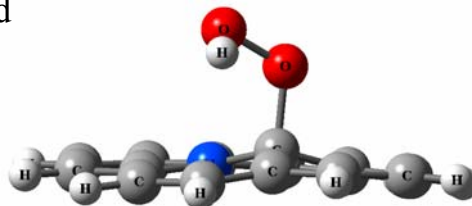
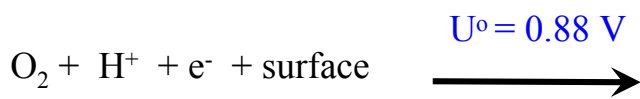
H bonds by 1.02 eV on N and $U^0 = -1.0$ V for the reaction



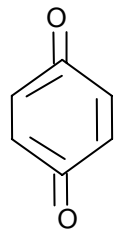
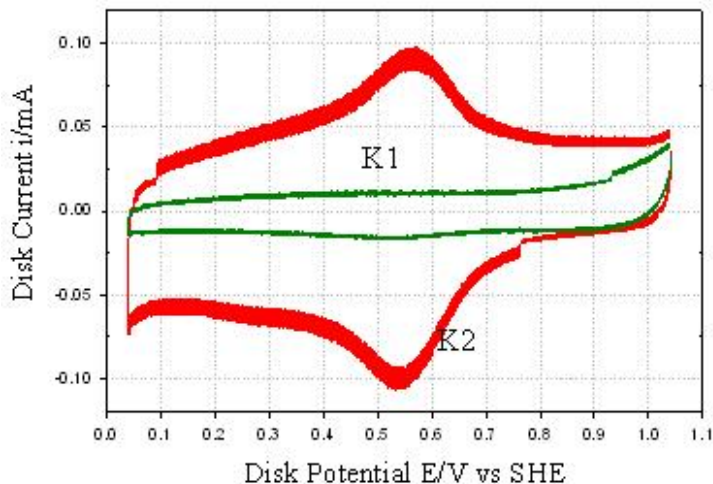
H bonds by 2.31 eV on C, and $U^0 = 0.2$ V.

This means H will be oxidatively removed from the surface to create a catalytically active radical site.

K1 – Un-Oxidized, K2 – Oxidized



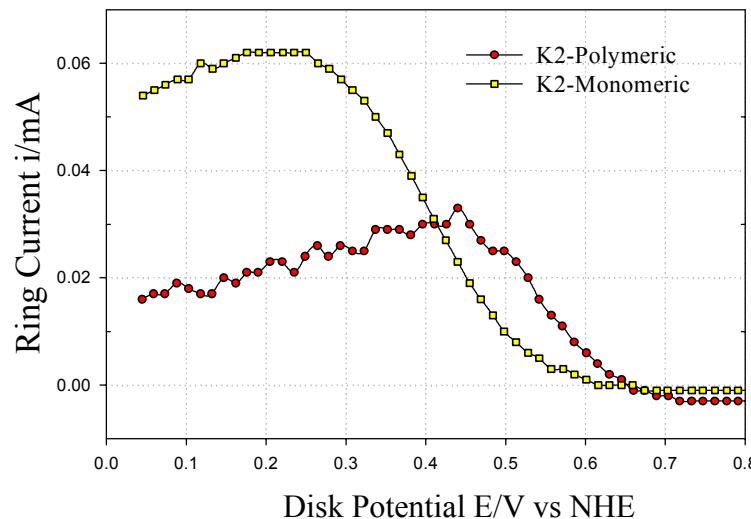
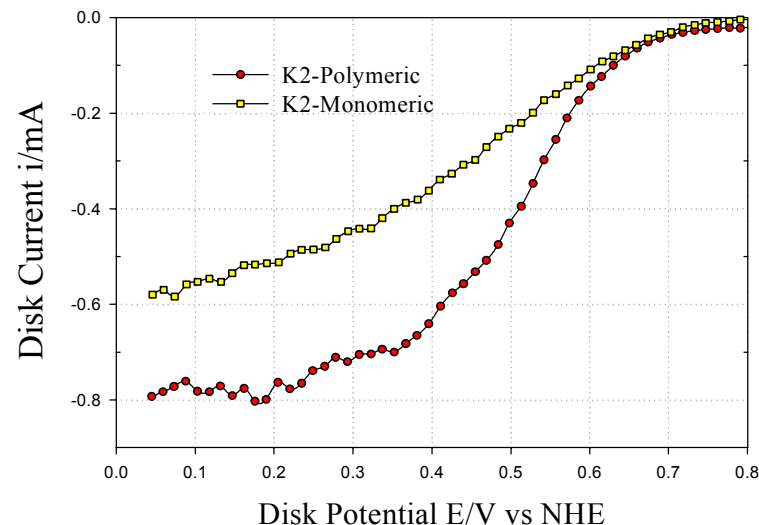
Development of Metal Free Catalysts



Quinone

K1-Unoxidized carbon

K2- Oxidized carbon



✓ Oxidation of carbon by HNO_3 introduces quinone groups on the carbon which favors nitrogen adsorption.

✓ Adsorption of monomeric nitrogen precursors on oxidized carbon

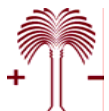
✓ Onset potential for ORR – 0.7 V vs. RHE

✓ TWO electron pathway for ORR

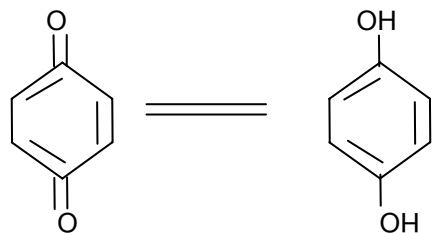
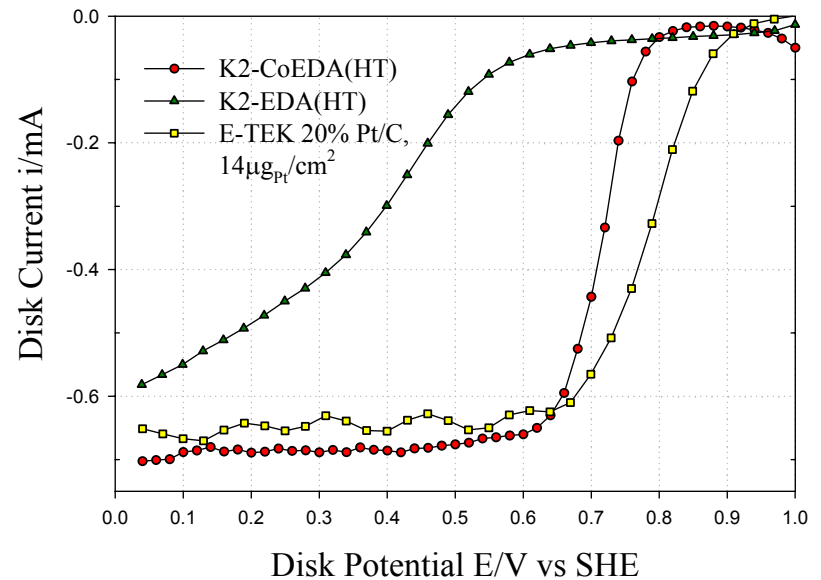
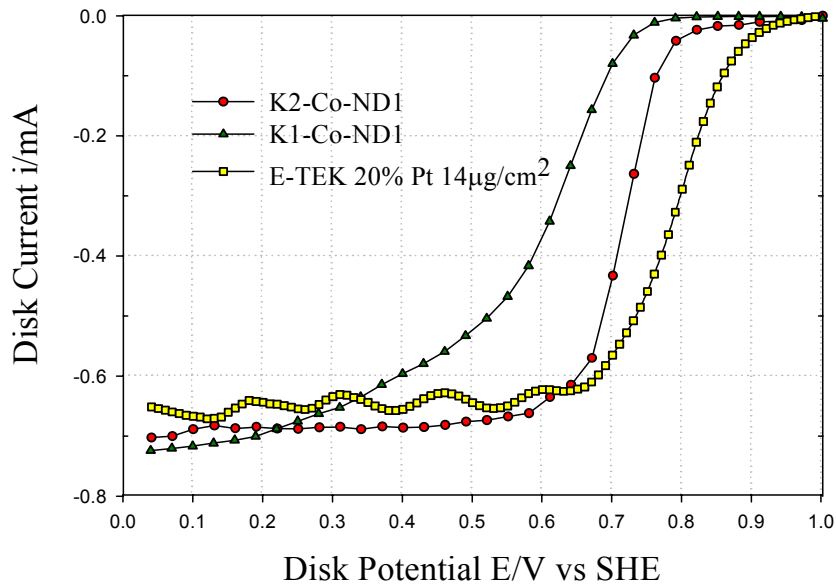
✓ Adsorption of polymeric nitrogen precursors in oxidized carbon

✓ Onset potential for ORR - 0.7 V vs. RHE

✓ FOUR electron pathway for ORR



Effect of Carbon Activation on Co-chelate/C Performance to Oxygen Reduction Reaction

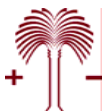


K1 – Un-Oxidized, K2 – Oxidized
ND – Chelating Agent

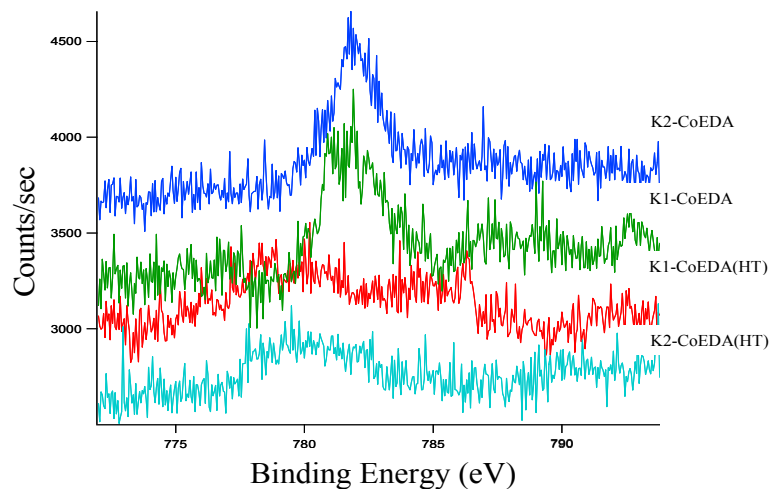
✓ Presence of quinone groups on carbon surface favors nitrogen adsorption.

✓ Introduction of Co in the catalyst structure increases the activity and shifts ORR mechanism from two electron to four electron.

✓ Developed chelate catalysts show less than 100 mV overpotential in comparison to ETEK 20% Pt/C

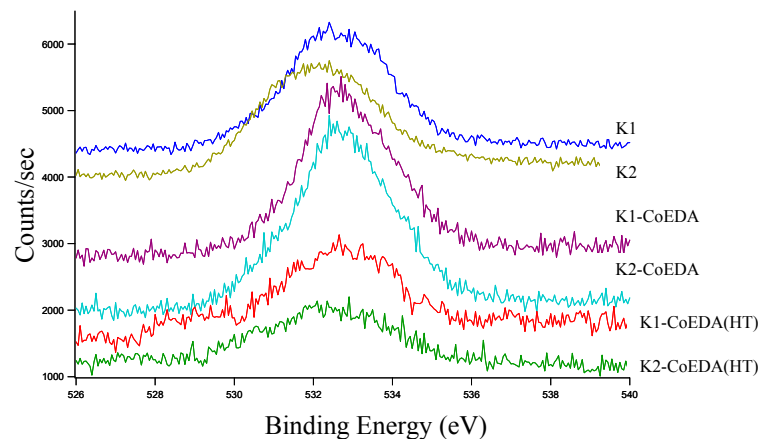


Investigating Relative Amounts of Oxygen Using XPS

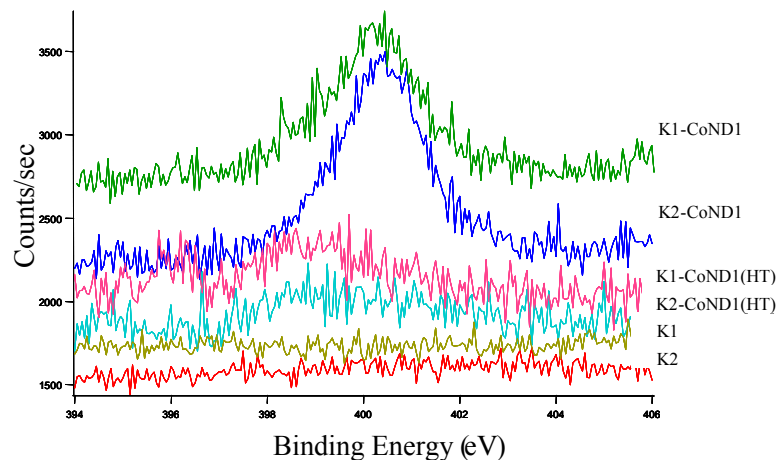


Co 2p Spectra

- ✓ The decrease in the intensity of Co peak can be attributed to the formation of a graphitic envelop around the transition metal with high temperature treatment
- ✓ Oxidation increases only the amount of quinone groups on carbon and not the total oxygen content.
- ✓ After heat treatment more amount of oxygen is retained in the catalysts dispersed on oxidized carbon. Thus quinone groups help in activity in addition to increasing dispersion.



O 1s Spectra



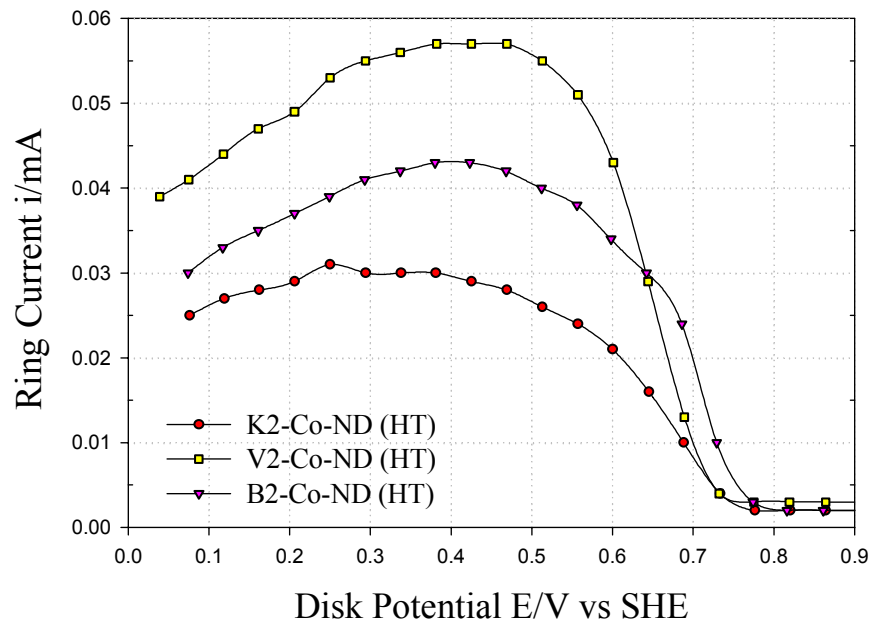
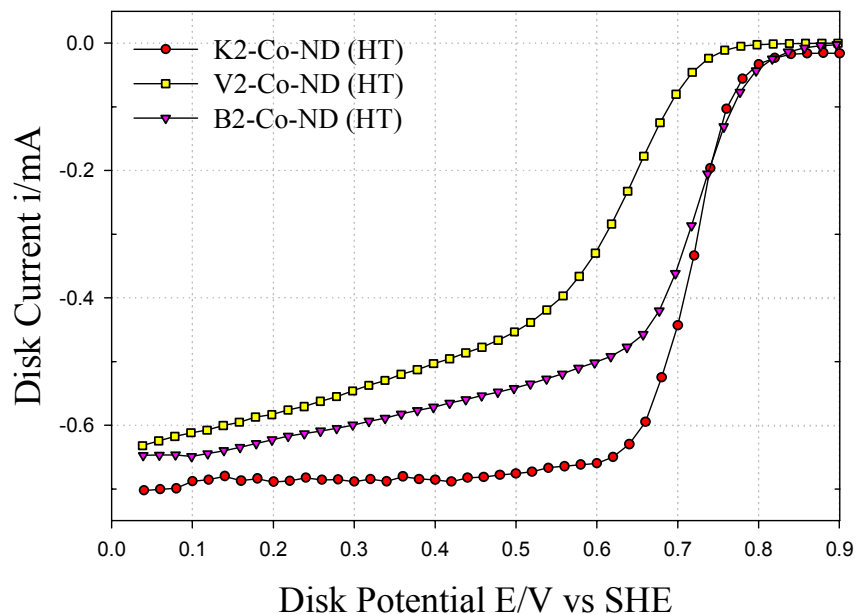
N 1s Spectra

K – Ketjen Black EC 300 J, V – Vulcan XC-72, B – Black Pearl 2000

1 – Un-Oxidized, 2 – Oxidized, ND – Chelating agent, HT – After heat treatment

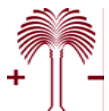


Activity to Oxygen Reduction Reaction of Co-chelate Loaded on Different Carbons



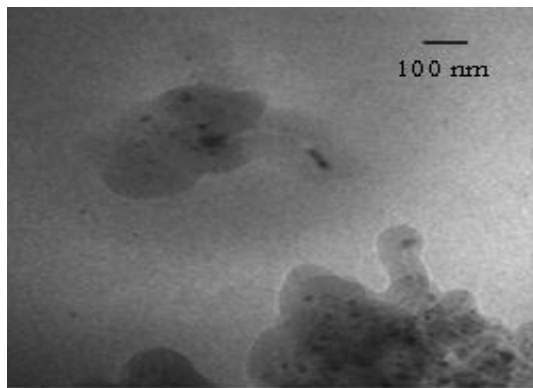
✓ Ketjen Black EC-300 J (K) with the highest mesoporous area shows the highest activity (highest disk and lowest ring currents)

Carbon	Area (m ² /g)	Micropores (m ² /g)	Mesopores (m ² /g)
Vulcan XC 72	254	118	100
Ketjen Black EC 300J	886	55	680
Black Pearl 2000	1500	720	540

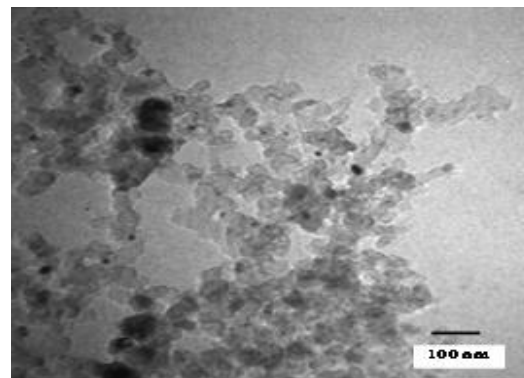


1 – Un-Oxidized, 2 – Oxidized, ND – Chelating agent

TEM image of Co-chelate Loaded on Different Carbons



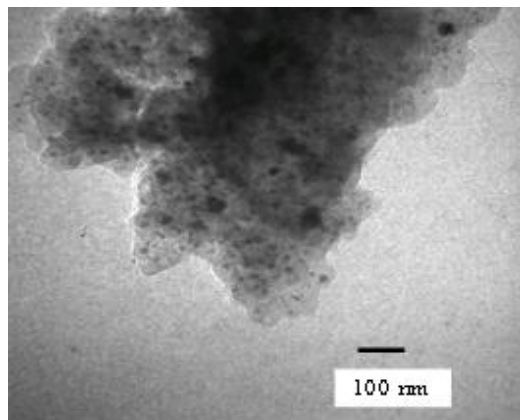
K2-Co-ND
(9.5 nm)



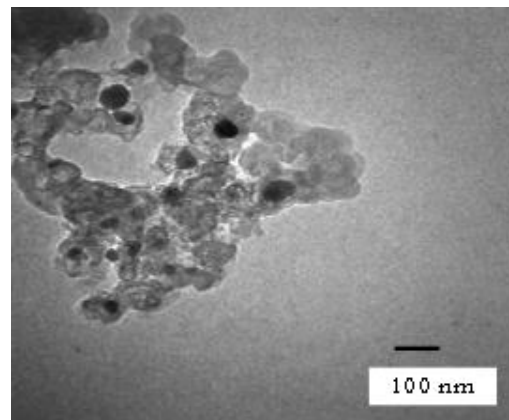
K1-Co-ND
(23.7 nm)

Co-chelate/Oxidized Ketjen Black EC 300 J

Co-chelate/Un-oxidized Ketjen Black EC 300 J



B2-Co-ND
(12.5 nm)



V2-Co-ND
(40 nm)

Co-chelate/Oxidized Black Pearl 2000

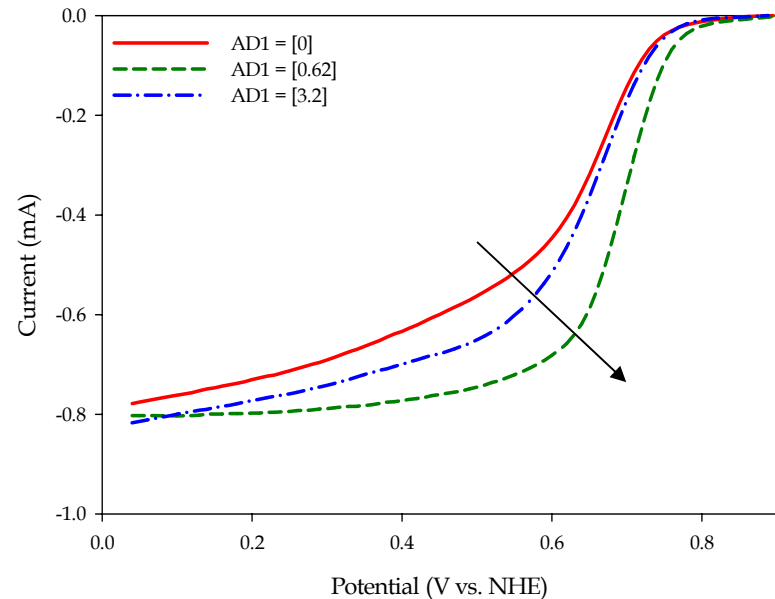
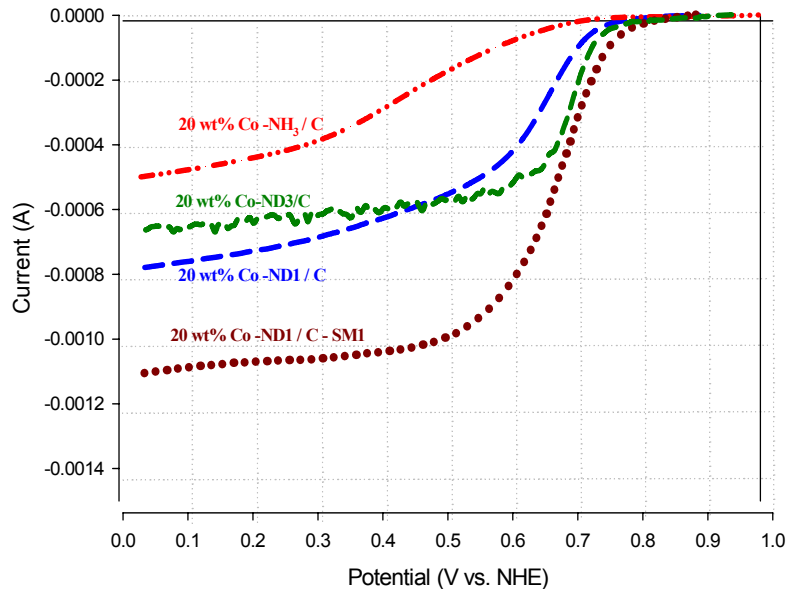
Co-chelate/Oxidized Vulcan XC-72



K – Ketjen Black EC 300 J, V – Vulcan XC-72, B – Black Pearl 2000

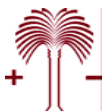
1 – Un-Oxidized, 2 – Oxidized, ND – Chelating agent

The Effect of Nitrogen Donors and Surface Modifier

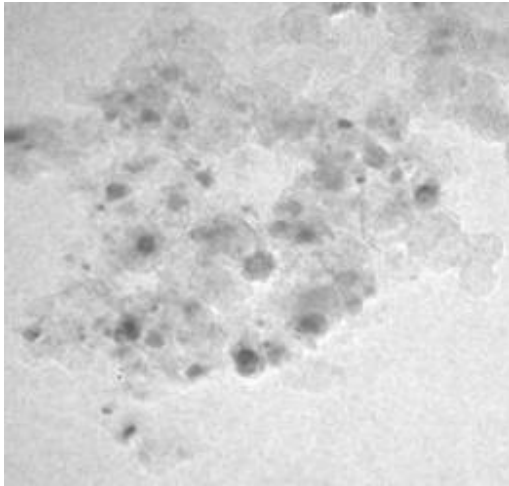


The scan rate is 5mV/s. Rotation rate 900 rpm in 0.5M H₂SO₄.

- ✓ The activity of the catalyst is dependent on the nitrogen donor used.
- ✓ Surface modifier increases the activity of the catalyst
 - ✓ Increases the dispersion.
 - ✓ Forms part of the catalytic site.

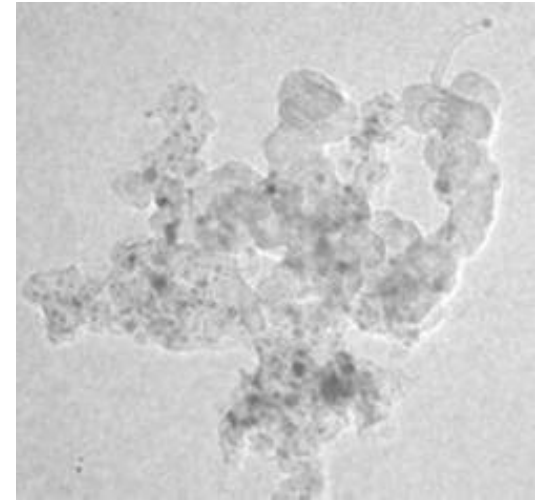


Effect of Surface Modifiers

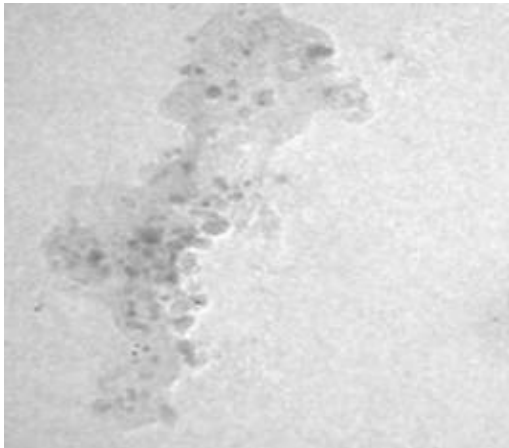


**SM1 = [0]
17 nm**

**SM1 = [0.62]
6 nm**

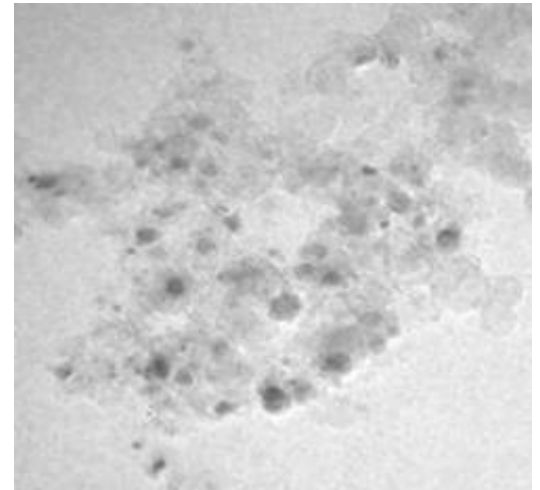



100 nm

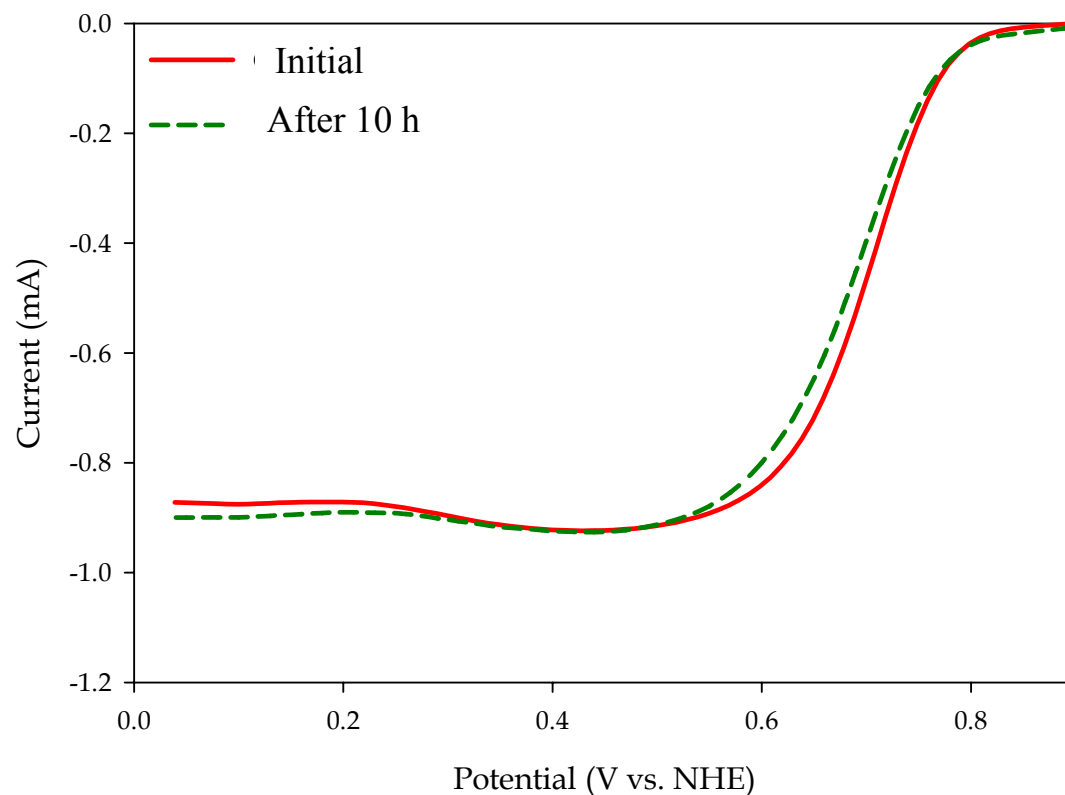


**SM1 = [3.2]
12 nm**

**SM1 = [46]
16 nm**



Stability Test for Co Catalyst in RRDE Test Conditions

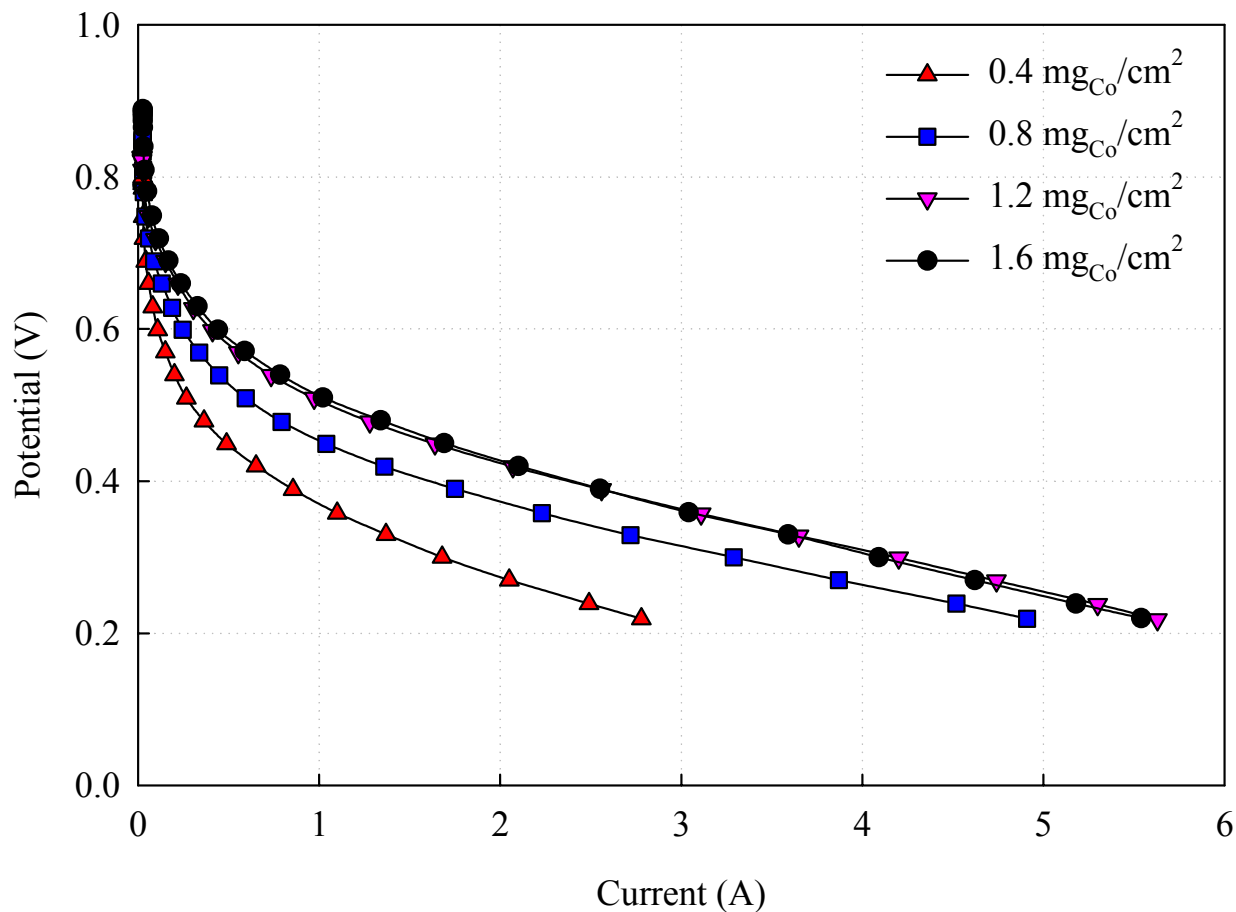


The scan rate is 5mV/s. Rotation rate 900 rpm in 0.5M H₂SO₄.

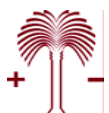


Performance Studies of Co-based Catalysts in Fuel Cell Station after 24 hrs

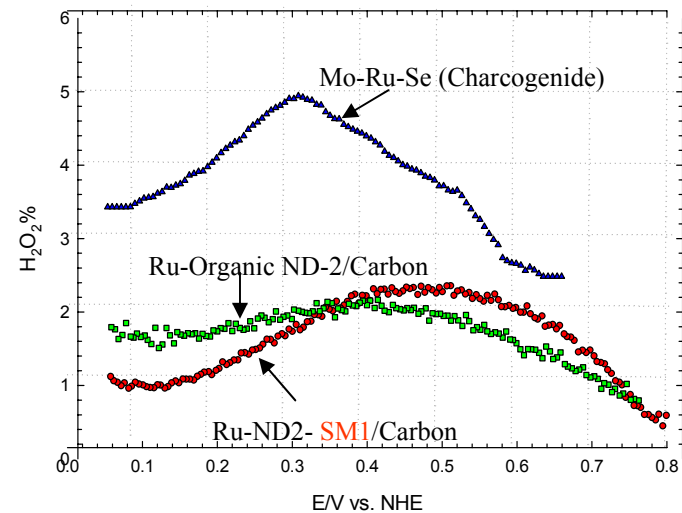
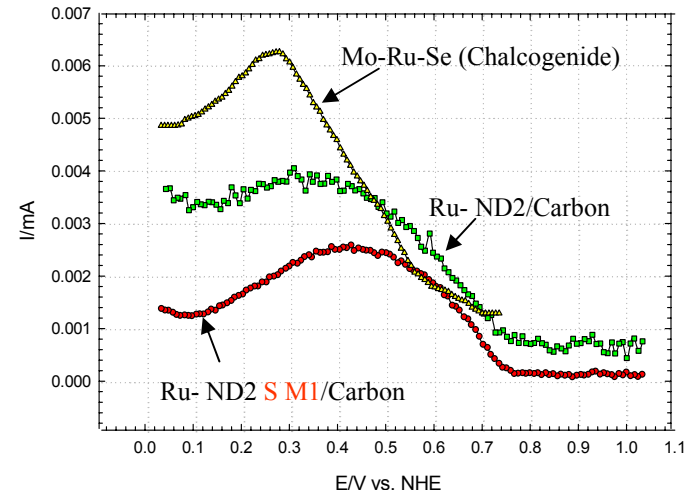
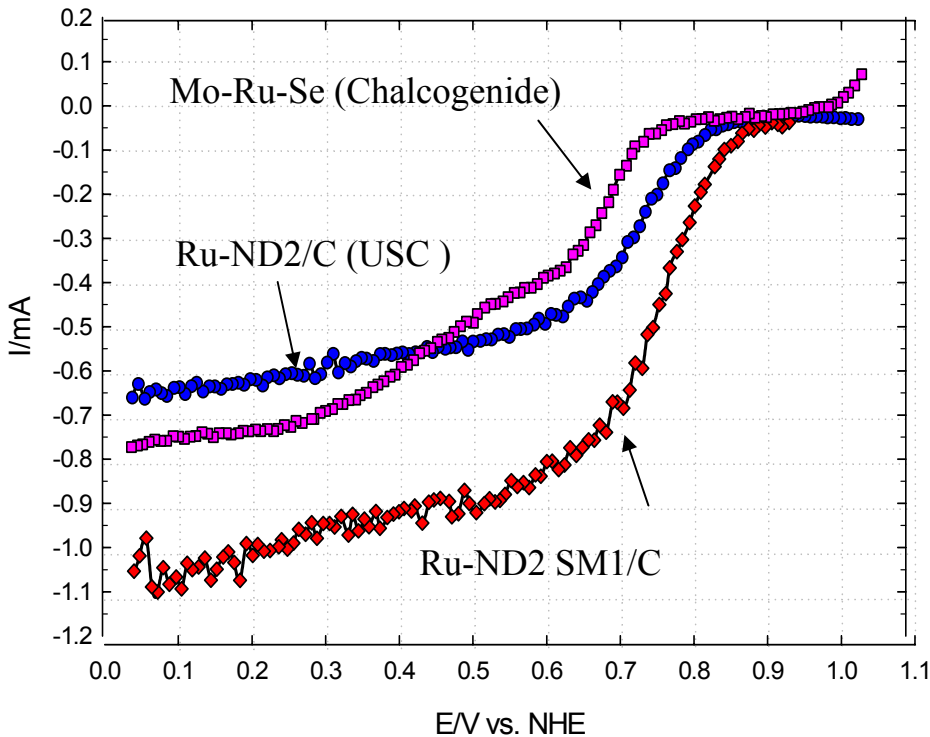
Anode: 0.4mg/cm² of 20wt% Pt/C



Operating Conditions: H₂/O₂, 75°C, 1atm, Nafion 112



Ru Chelate Catalyst for Oxygen Reduction Reaction



✓ Ru catalysts prepared by USC chelate method show improved activity than MoRuSe catalysts.

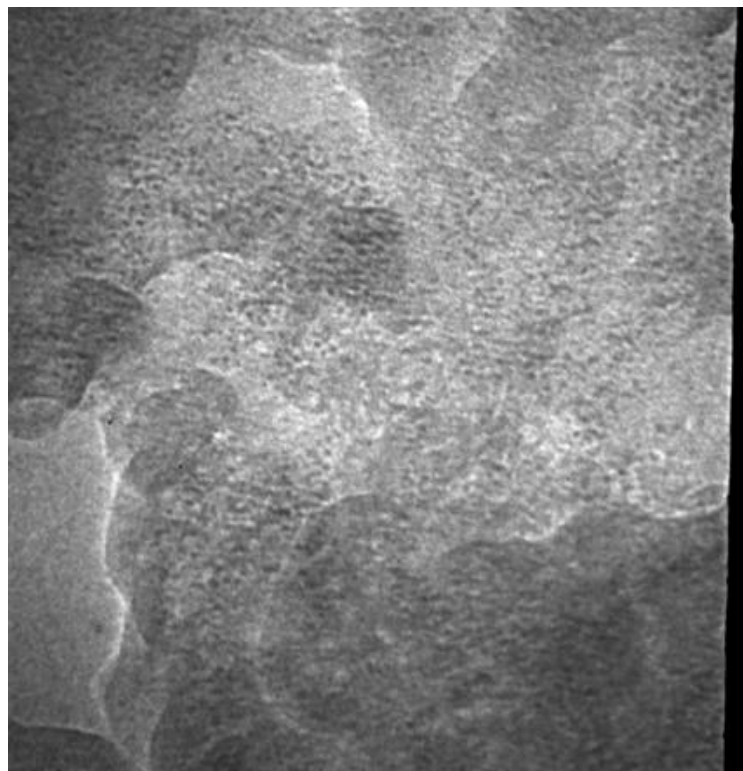
✓ % H_2O_2 produced is less than 2% for the synthesized catalysts.



ND: Nitrogen containing compound

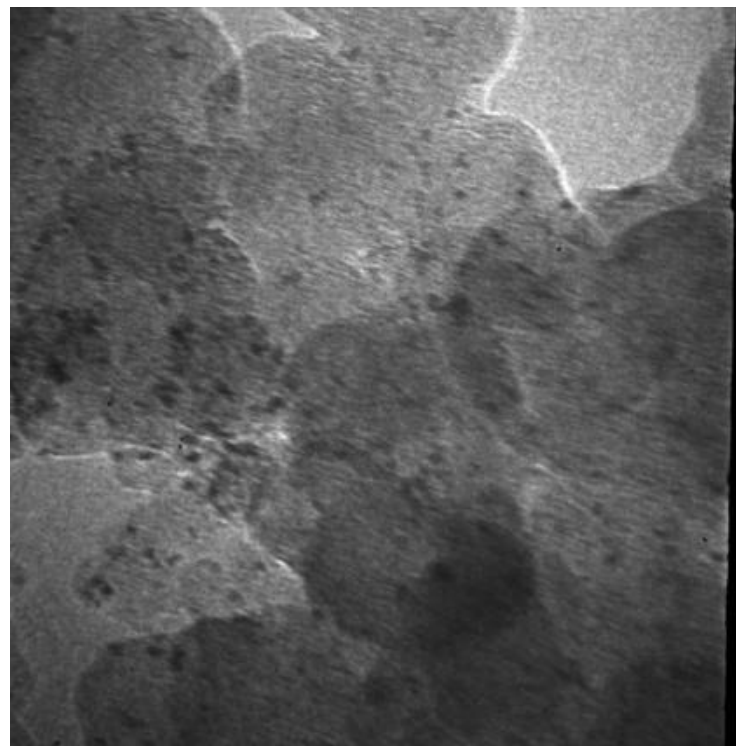
SM: Surface modifier

TEM Image of Ru Chelate and Chalcogenide Catalyst



File Name = Ru-400Ka.tif
Print Mag = 0x @ 0 in
Acquired Sep 29 2004 at 11:56 AM
TEM Mode =

20 nm
TEM Mag = 400000x



File Name = MoRuSe-400Kb.tif
tmv-kvssl
TMV-KVSSL
Print Mag = 0x @ 0 in
Acquired Jan 18 2005 at 7:19 PM
TEM Mode =

20 nm
HV=200kV
TEM Mag = 400000x

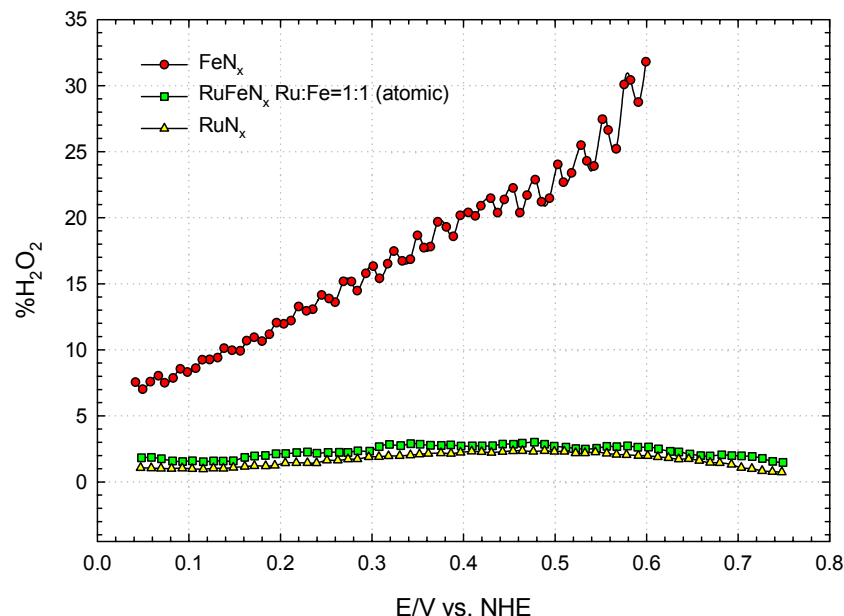
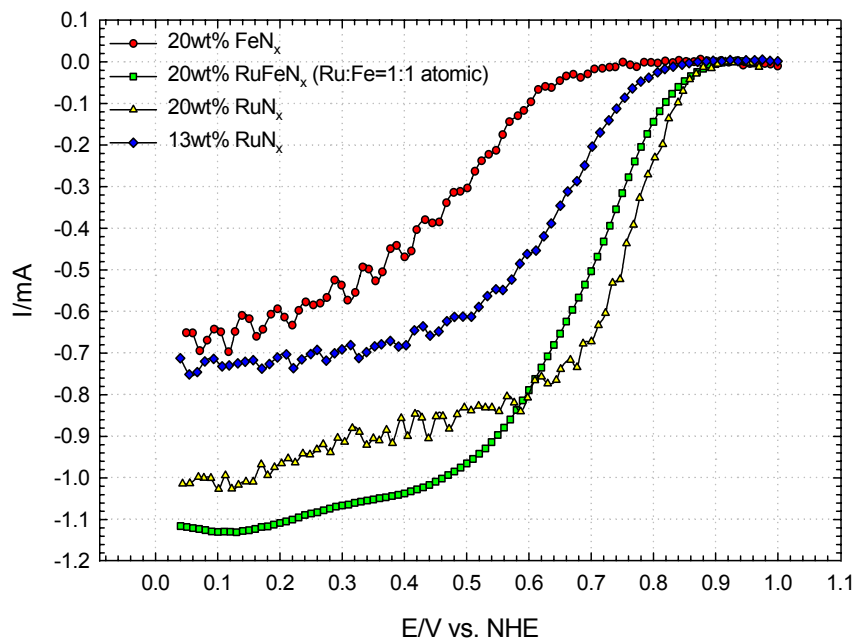


RuN_x

MoRuSe

Bimetallic Catalysts for Oxygen Reduction Reaction

RuFeN_x Catalysts for ORR



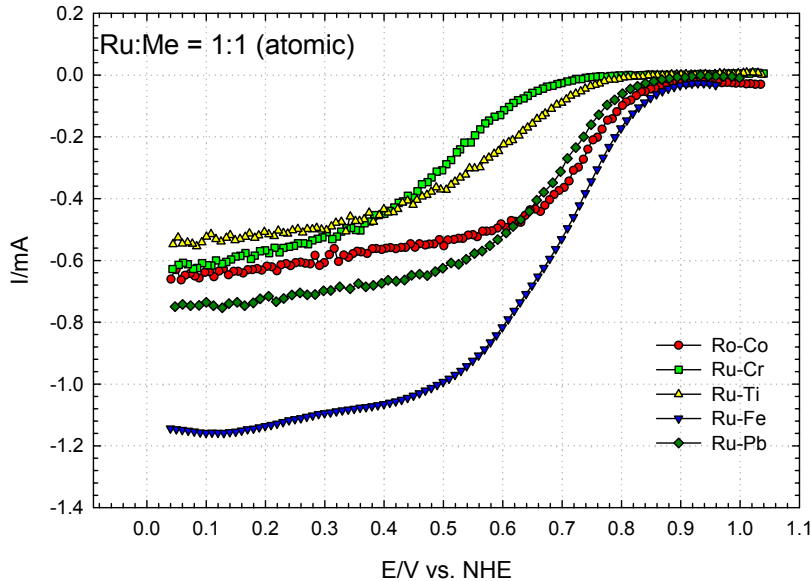
The scan rate is 5mV/s. Rotation rate 900 rpm in 0.5M H₂SO₄.

- ✓ Alloying 13wt% Ru with 7 wt% Fe show comparable performance to ETEK 20% Pt/C and 20%Ru/C.
- ✓ Synergistic effect between Ru and Fe is observed.



Bimetallic Catalysts for Oxygen Reduction Reaction

ORR - Various Bimetallic Catalysts

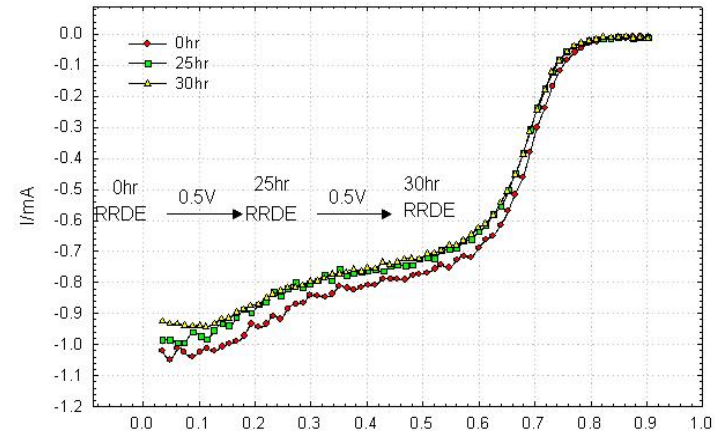


✓ Activity of Ru catalyst with alloying follow

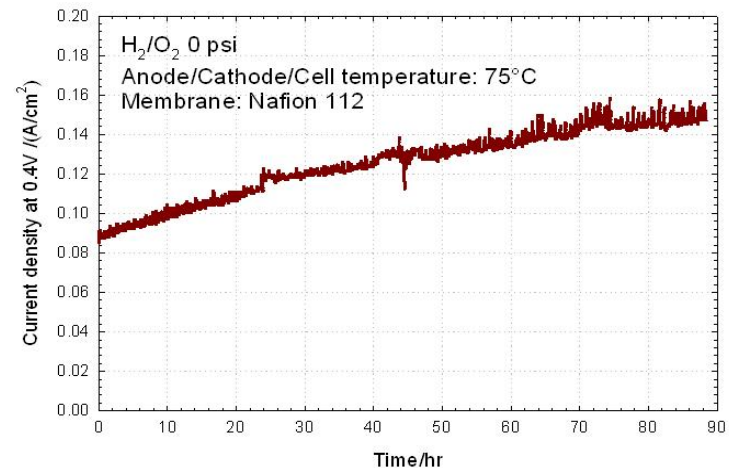
✓ Ru > RuFe > RuCo > Ru-Cr > Ru-Ti > Ru-Pb

✓ Ru and Ru-Fe catalysts show activity similar to ETEK 20% Pt/C.

Stability of RuCo Catalysts



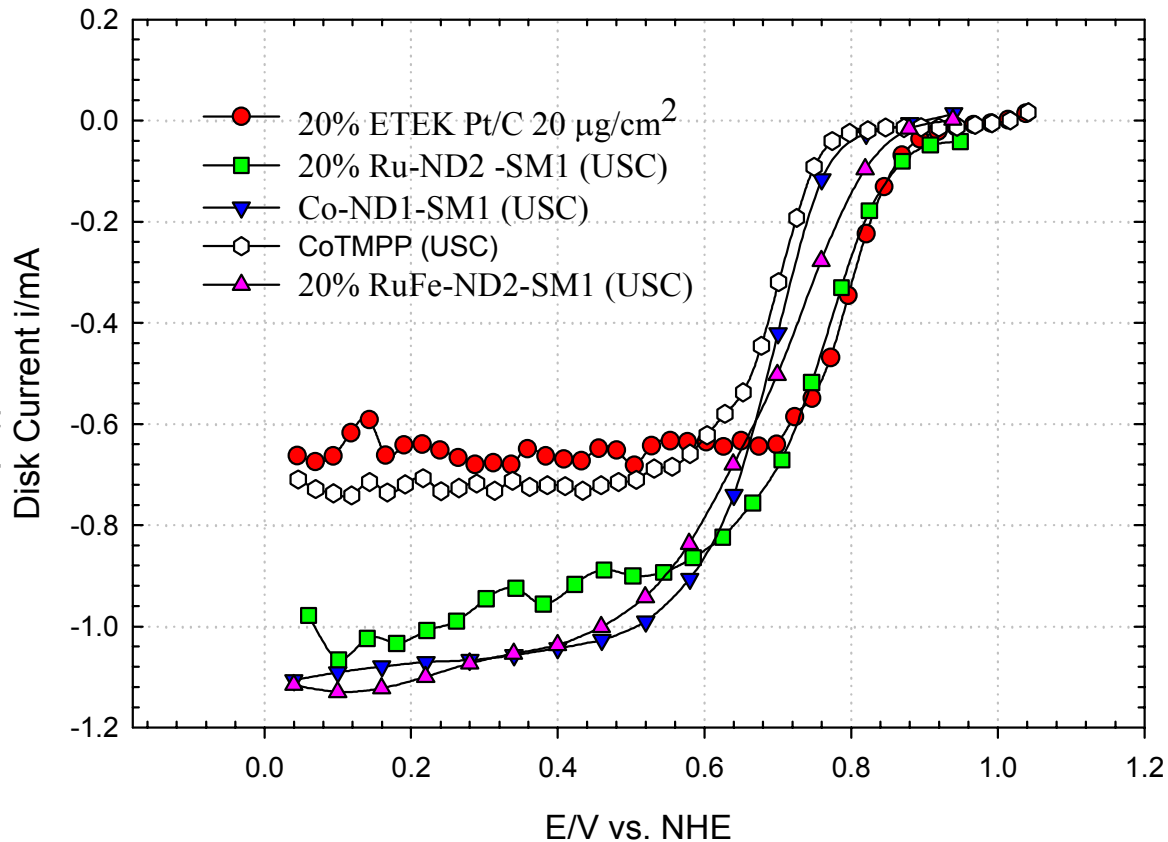
The scan rate is 5mV/s. Rotation rate 900 rpm
Electrolyte 0.5M H₂SO₄.



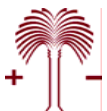
T_a - 77 °C, T_c - 75 °C, T_{cell} - 75 °C, 5 cm², Nafion112
Loading - 1.2 mg_{Ru}/cm², Ambient Pressure.



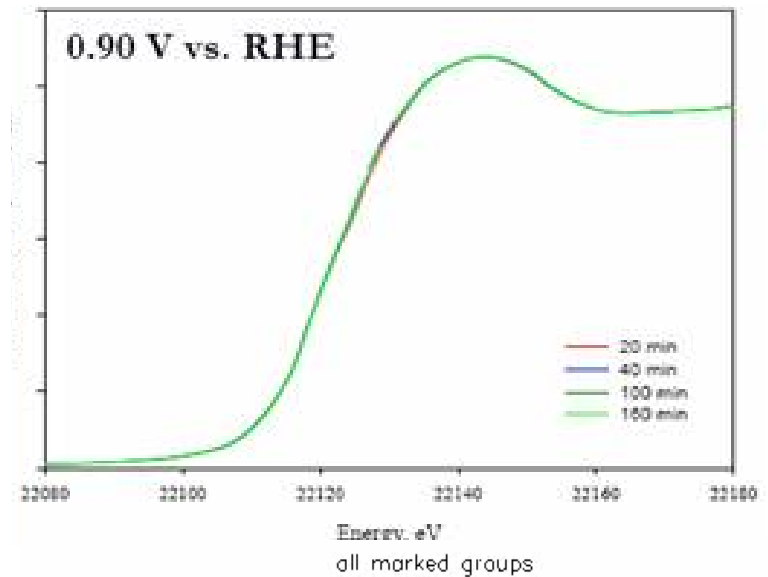
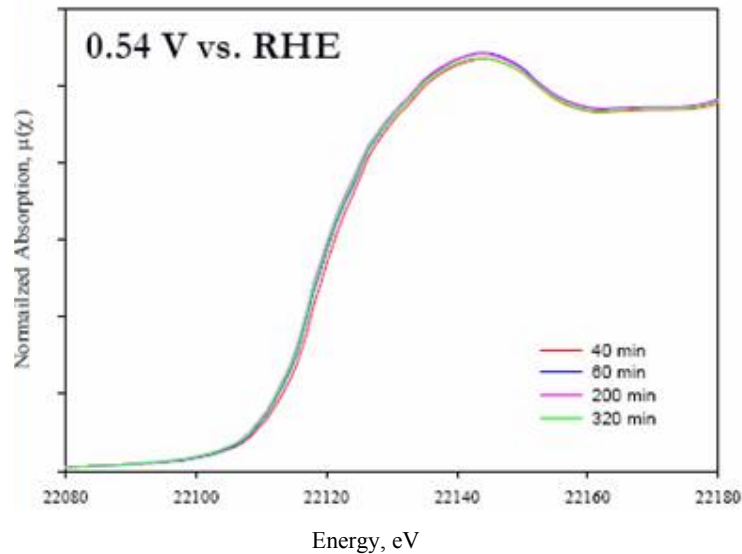
Comparison of Performance of USC Co and Ru Based Catalyst vs. Pt



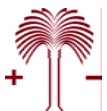
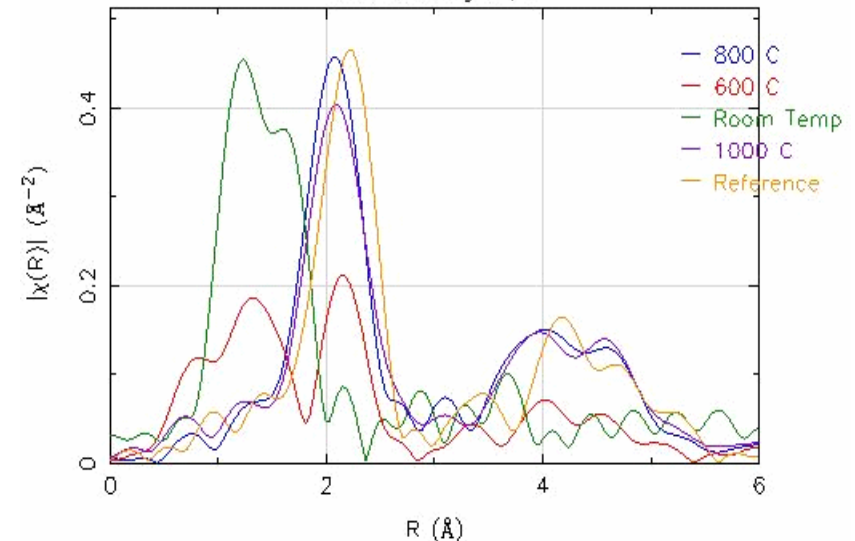
✓Ru catalysts prepared by USC chelate method with surface modifiers show performance close to that of 20% ETEK Pt/C catalysts



Initial *In-situ/Ex-situ* XAFS Results (NEU)

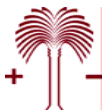


- In-situ XAFS studies to analyze the stability on Ru based catalysts
- Analyze the evolution of catalyst structure of Co and Fe catalyst with heat treatment.
- Develop cluster model to predict the structure of the active site.



Response to Reviewer's Comments

- Lack of Industrial Collaboration
 - USC has collaboration with Fuji Film Inc, Faraday Technologies which are complimentary to this research.
 - Northeastern University's collaboration with ETEK is complimentary to this research.
- Approach is a “Wish List”. Tasks listed are very large and difficult
 - Initial studies were primarily aimed at screening the catalysts.
 - Current research focuses on Co, Fe and Co-Fe bimetallic catalysts.
- NEU and CWRU don't seem actively engaged in the effort.
 - The project was at initial stages during the 2004 review program.
 - CWRU has been contributing to understand the role of nitrogenated species on the activity.
 - *In situ* and *ex-situ* XAFS studies are being conducted by NEU to analyze the catalyst structure and stability.



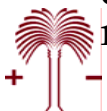
Future Work

Activity

- Enhancement of the intrinsic activity of Co based catalysts.
- Development of Fe chelate based catalysts.
- Development of Fe-Co chelate based catalysts.
- Effect of chain length and different surface functionalities on the ORR kinetics.
- Extensive material characterization/ structural analysis of the developed Co chelate catalyst - Attain insight on the nature of the active site.
- Search for new surface modifiers and carbon surface treatments to increase the number of active sites.

Stability

- Modify carbon surface functional groups to anchor chelate metal catalysts strongly.
- To increase the reversibility of the redox system for oxygen reduction.
- Use of Pressure / Temperature variants to increase the stability.
- Encapsulation of the catalyst in more stable materials such as carbide, nitride and zeolite.
- Extensive fuel cell testing to evaluate the stability of the catalyst



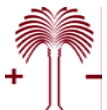
Publications and Presentations

Publications

1. N.P.Subramanian, S.P.Kumaraguru, H.Colon, B.N. Popov, “Studies on Co Based Electrocatalysts on Modified Carbon Substrates for PEMFC Applications”, Submitted to *J. Power Sources*.
2. N.P.Subramanian, H.Colon, S.P.Kumaraguru, B.N. Popov, “Development of Metal Free Catalysts for Oxygen Reduction”, submitted to *Carbon*

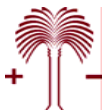
Presentations

- S. P. Kumaraguru, N. Subramanian, H. Colon, K. Hansung and B.N. Popov, “Novel Non Precious Metal Catalysts for PEMFC Applications”, *206th meeting of the Electrochem Soc.*, Honolulu, HI, October, 2004.
- N.P.Subramanian, S.P. Kumaraguru and B.N. Popov “Analysis of Carbon Substrates used in Non-Precious Metal Catalysts for Fuel Cell Applications”, *206th meeting of the Electrochem Soc.*, Honolulu, HI, October, 2004.



Hydrogen Safety

- All reactors are operated in a vented area.
- Hydrogen detector is placed near the hydrogen source.
- Reactors using high concentrations of hydrogen have additionally installed a burning flame to eliminate exhausting gas
- All the reactors have being design using leak-proof joints
- Ambient atmosphere pressures are used at all times in the reaction vessels and fuel cell stations
- Only personnel trained in how to operate the reactors and emergency procedures is allowed to use the reactor set-up
 - At least one person trained must present during runs in case of an emergency shutdown



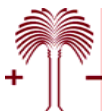
Safety Equipment



Furnace for Hydrogen Treatment
at High Temperature
and Safety Equipment



PEM Fuel Cell Dual Station
with a Hydrogen Sensor



Safety Questions for Hydrogen Review Program

- 1. What is the most significant hydrogen hazard associated with this project? Please be specific in your answer.**

The most significant hydrogen hazard is the fuel cell test station that we use to test the catalysts. However, the hydrogen flow rate used does not exceed 600 cm³/min.

- 2. What are you doing to deal with this hazard? Please list pertinent safety measures you are implementing and/or plan to implement.**

In order to prevent any accident safety features such as fail close H₂ valve, fail open N₂ valve, low voltage trip, low gas flow trip, high temperature alarm, and H₂ sensor with audible alarm are activated when the system is in operation. In addition, the system is positioned close to the hood in order to vent the used gas. Operation and emergency procedures are accessible in the case of an accident.

