

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



**Branko N. Popov, Swami Kumaraguru, Lingyun Liu,
Vijayadurga Nallathambi, Xuguang Li, Gang Wu, Jong-Won Lee,
Hector Colonmer and Nalini Subramanian**

**Center for Electrochemical Engineering
University of South Carolina, Columbia, SC 29208**

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Overview

Timeline

- Project Start Date
 - ✓ 9/30/2003
- Project End Date
 - ✓ 9/30/2007
- Percent Complete
 - ✓ 64%

Budget

- Total Project Funding
 - ✓ DOE Share- \$ 1376.292 K
 - ✓ Contractor Share - \$351.207K
- FY 05: \$ 400K
- FY 06: \$ 200K

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



Objectives

OVERALL:

To develop (i) non-precious metal and (ii) metal-free catalysts for PEMFC with high catalytic activity, selectivity and durability which perform as good as conventional Pt catalysts with a cost at least 50% less than a target of 0.2 g (Pt loading)/peak kW

SPECIFIC FOCUS FOR 2005 & 2006:

- ❑ **Non-precious metal chelate based catalysts**
 - **To develop Co and Co-X catalysts dispersed on high surface area carbon**
- ❑ **Metal free catalysts**
 - **To develop carbon-supported metal free CN-X and C-X nano-catalysts**



Approach

Co-based catalysts

- **Optimization of active reaction sites as a function of:**
 - (1) **Surface oxygen groups**
 - (2) **Carbon support**
 - (3) **Co loading**
 - (4) **N content**
 - (5) **Surface modifier**
 - (6) **Pyrolysis temperature**
 - (7) **Non-metallic additive “X”**
- **Fuel cell testing and stability**

Metal-free catalysts

- **Optimization of active reaction sites as a function of:**
 - (1) **Surface oxygen groups**
 - (2) **Nitrogen precursor**
 - (3) **Non-metallic additive “X”**
 - (4) **Pyrolysis temperature**
 - (5) **Porosity and pore size distribution**
- **Fuel cell testing and stability**



Technical Accomplishments

- ❑ Active Co/C catalysts were developed with the use of activated carbon, surface modifier and non-metallic additive “X”.
 - ❑ Carbon activation methodology was developed to increase the concentration of active sites of the Co-based catalyst.
 - ❑ Surface modifiers were used to increase the activity of the Co-based catalyst.
 - ❑ Onset potential as high as 0.82 V vs. SHE was obtained for Co-based catalysts.
 - ❑ Non-metallic additive “X” significantly decreased the amount of H₂O₂ produced during oxygen reduction.
 - ❑ FOUR electron pathway for ORR (< 5 % H₂O₂)

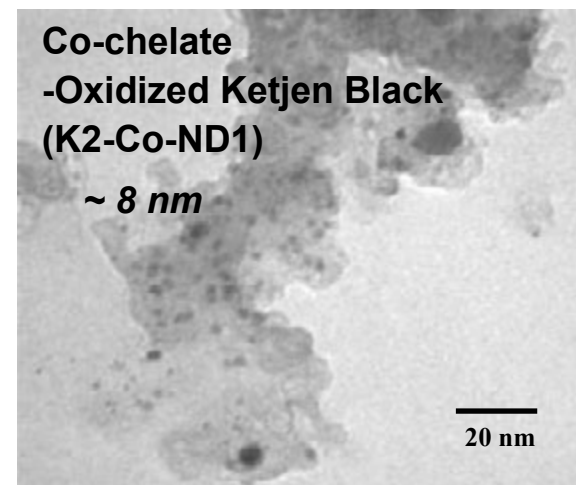
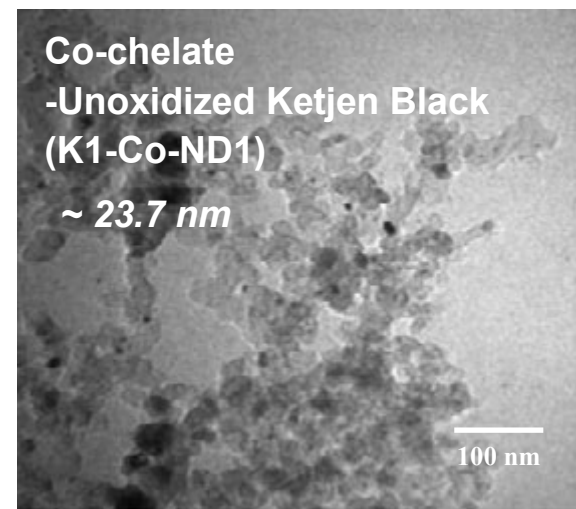
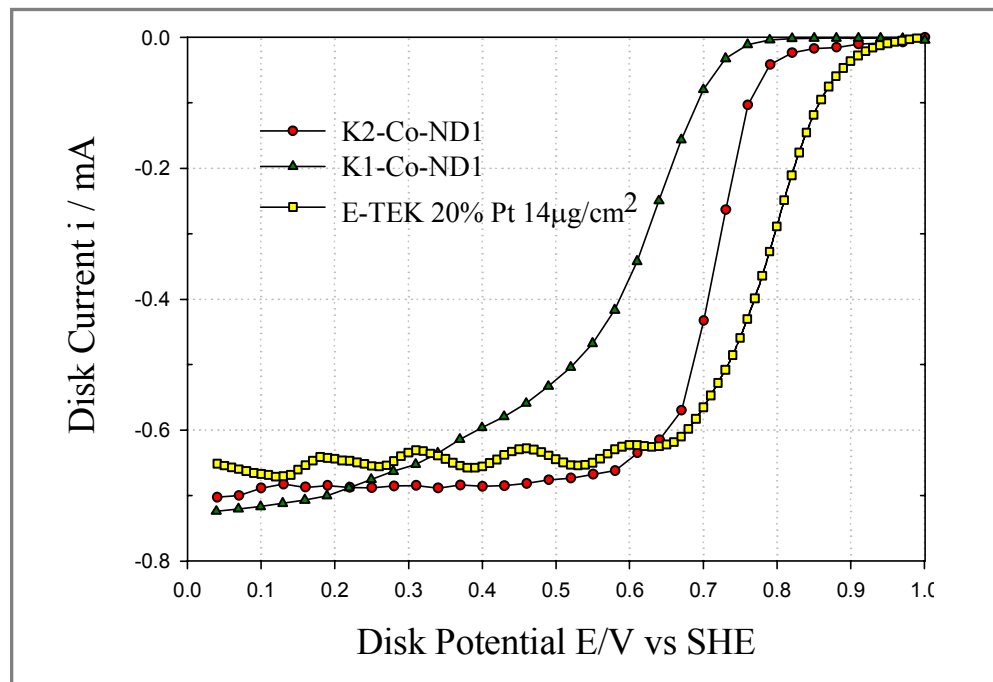
- ❑ Metal free catalysts (CN-X and C-X nano-catalysts) were developed.
 - ❑ Onset potential for oxygen reduction 0.8 V vs. SHE.
 - ❑ Peroxide generation less than 1 %.
 - ❑ FOUR electron pathway for ORR.



Development of Co-based Catalysts for PEMFC Applications



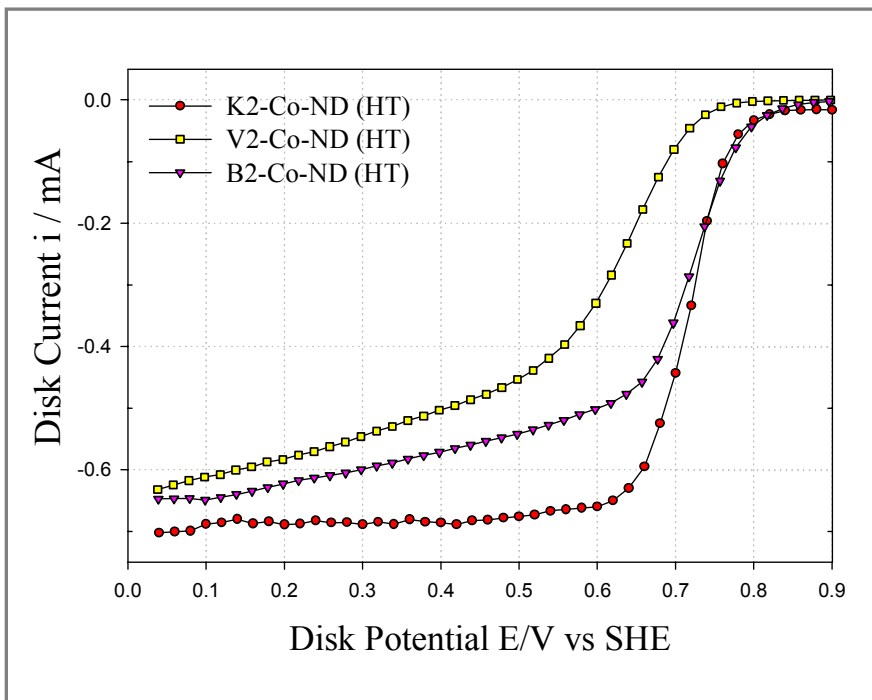
Optimization – (1) Effect of Surface Oxygen Group



- **HIGHLIGHT:** Presence of quinone groups on carbon surface favors nitrogen adsorption.
- Developed chelate catalysts show lower onset potential by about 100 mV in comparison to ETEK 20% Pt/C.



Optimization - (2) Effect of Carbon Support

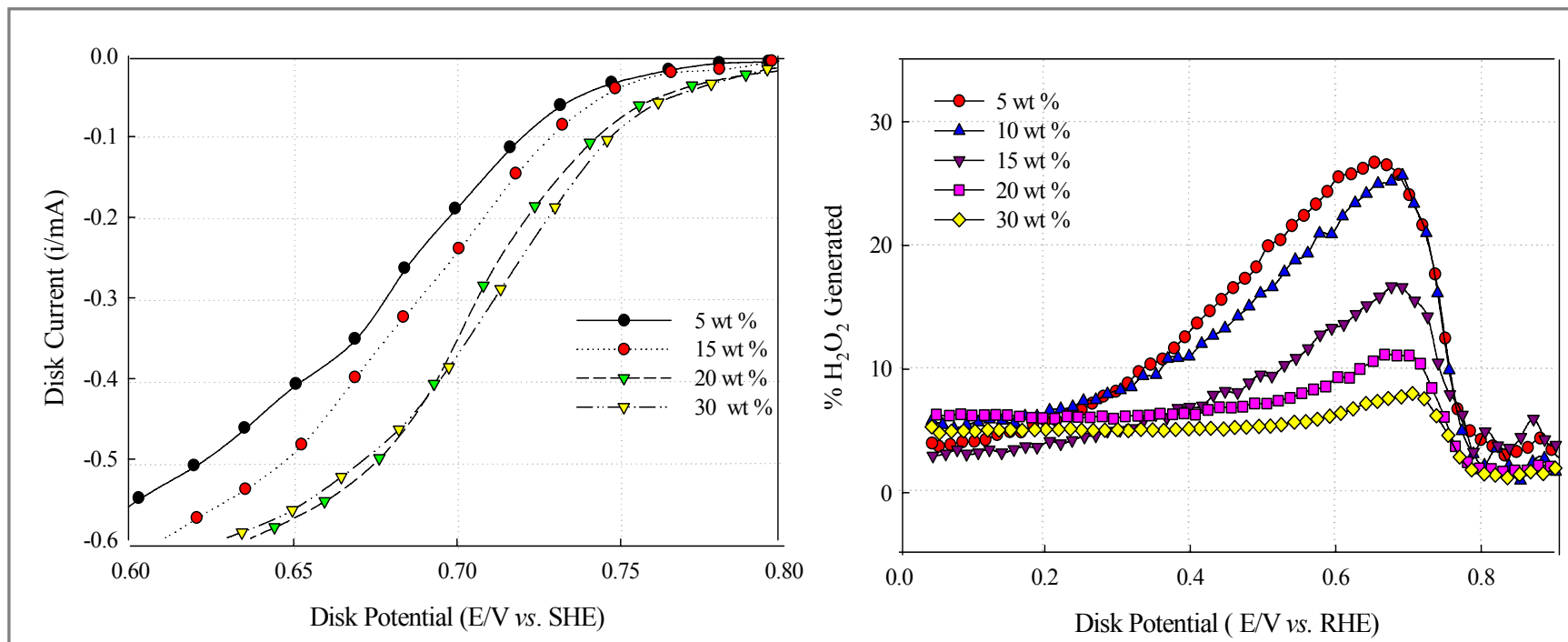


Carbon	Area (m ² /g)	Micro-pores (m ² /g)	Meso-pores (m ² /g)	Catalyst particle size (nm)
Vulcan XC 72	254	118	100	~ 40
Ketjen Black EC 300J	886	55	680	~ 8
Black Pearl 2000	1500	720	540	~ 12.5

- **HIGHLIGHT:** Ketjen black has higher mesoporous area than Vulcan and Black Pearl.
- Ketjen black leads to smaller particle size of catalysts and hence higher catalytic activity.



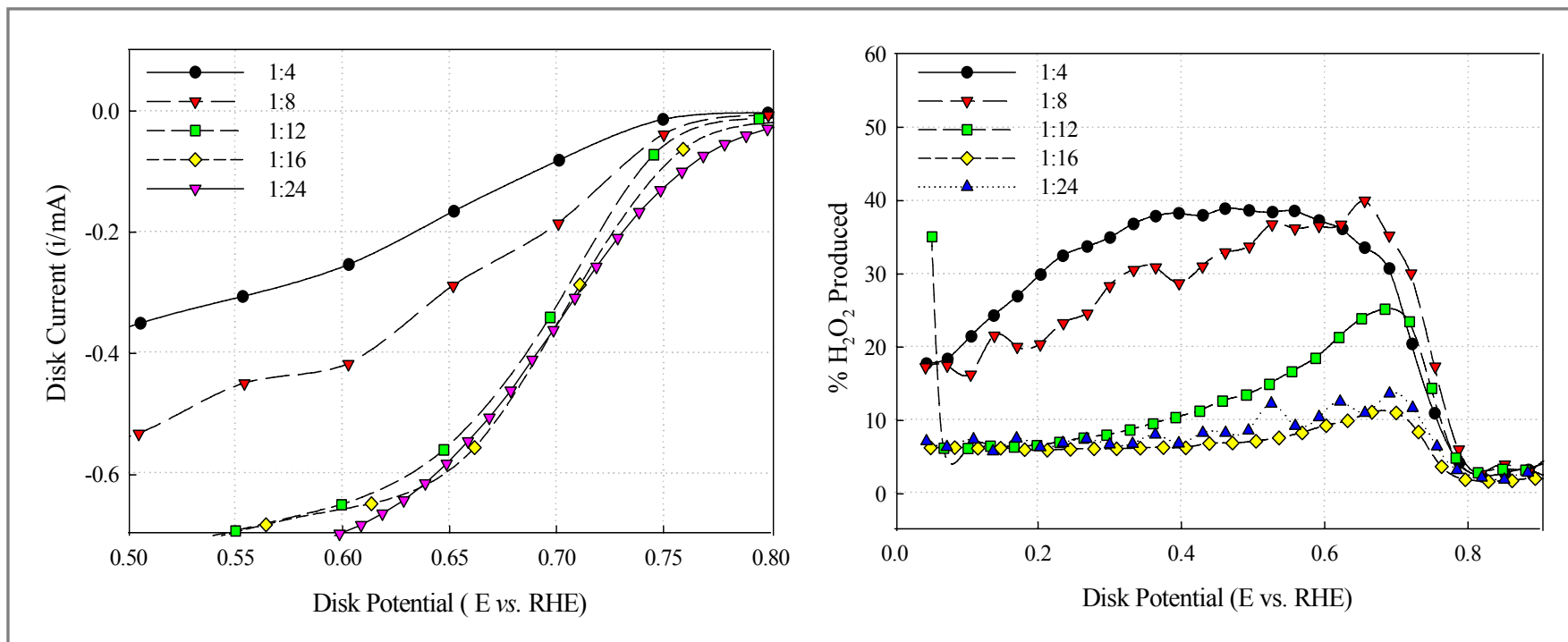
Optimization – (3) Effect of Co Loading



- **HIGHLIGHT:** Increase in Co loading decreases the overpotential toward oxygen reduction reaction by nearly 50 mV.
- Co loading on carbon has a huge influence on %H₂O₂ produced. %H₂O₂ is lower than 7% for 30 wt% Co loading at 0.7 V vs. NHE.



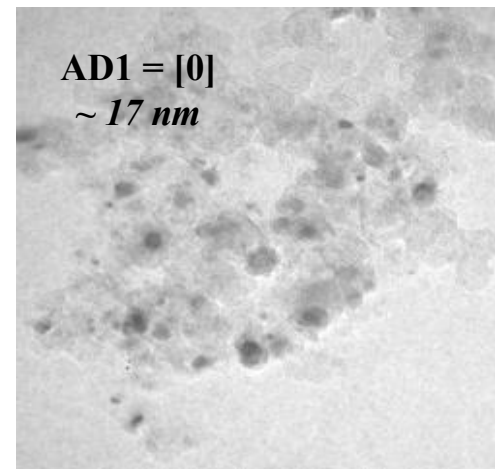
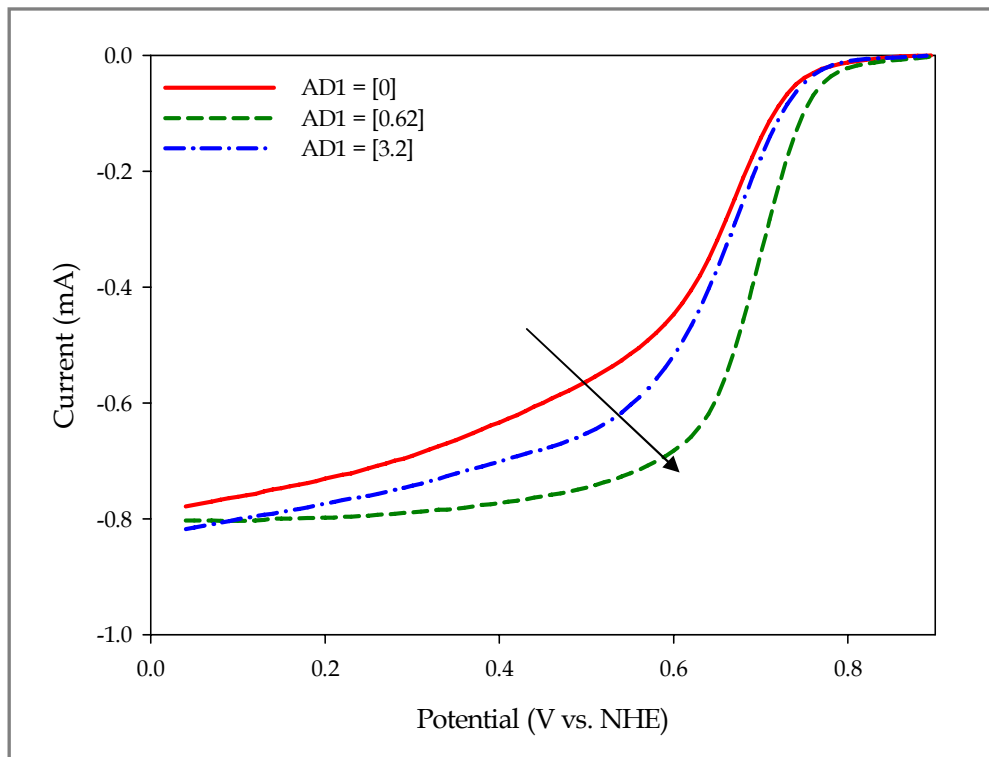
Optimization - (4) Effect of N Content



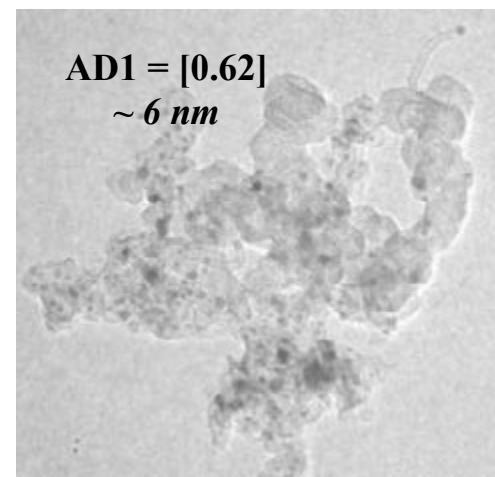
- **HIGHLIGHT:** Increase in nitrogen concentration increases the activity of the catalyst.
- %H₂O₂ produced decreases from 36 to 11% with increasing the nitrogen content.



Optimization - (5) Effect of Surface Modifier



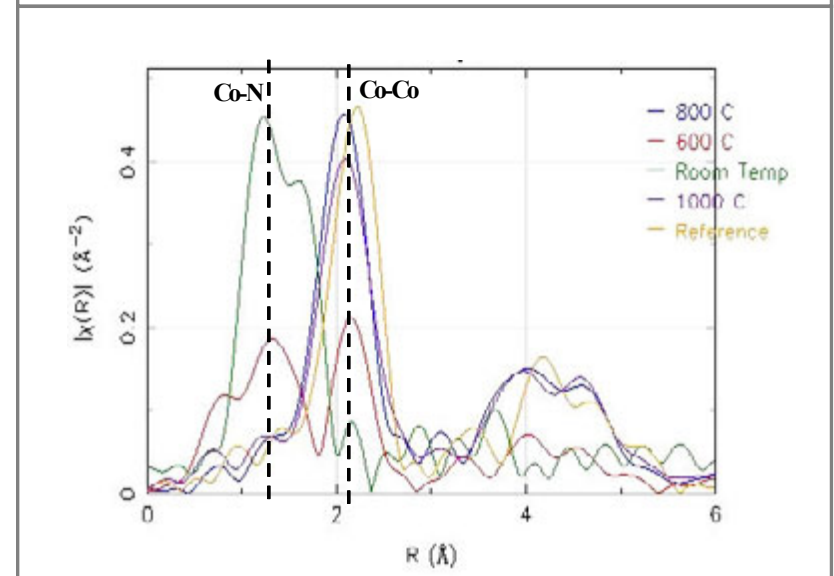
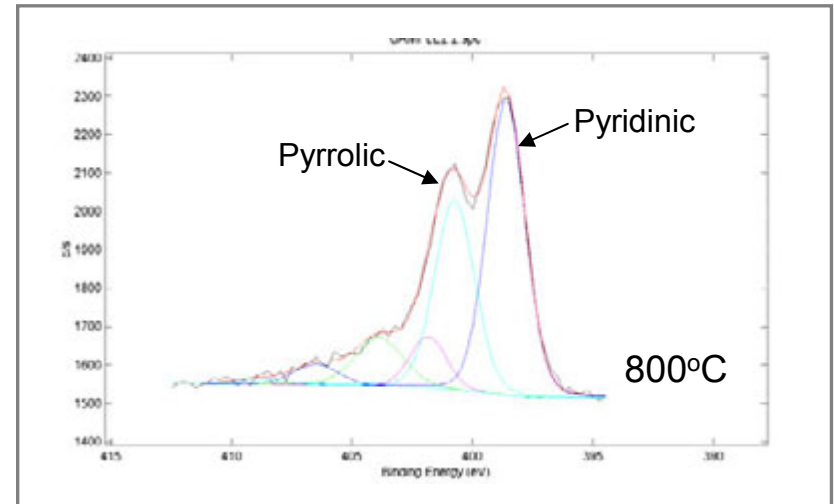
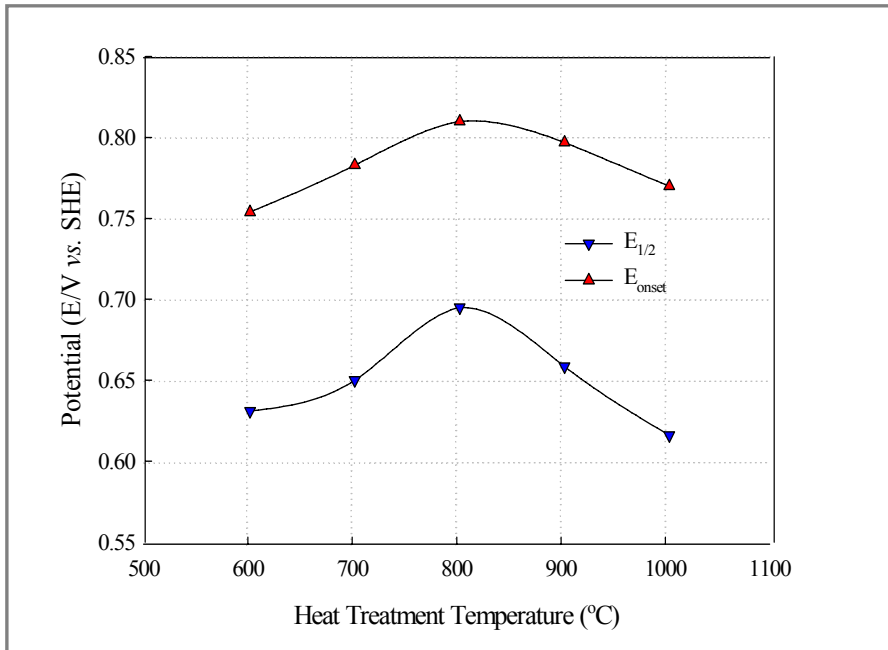
100 nm



HIGHLIGHT: Surface modifier increases the catalytic activity due to uniform dispersion of the catalyst particles.



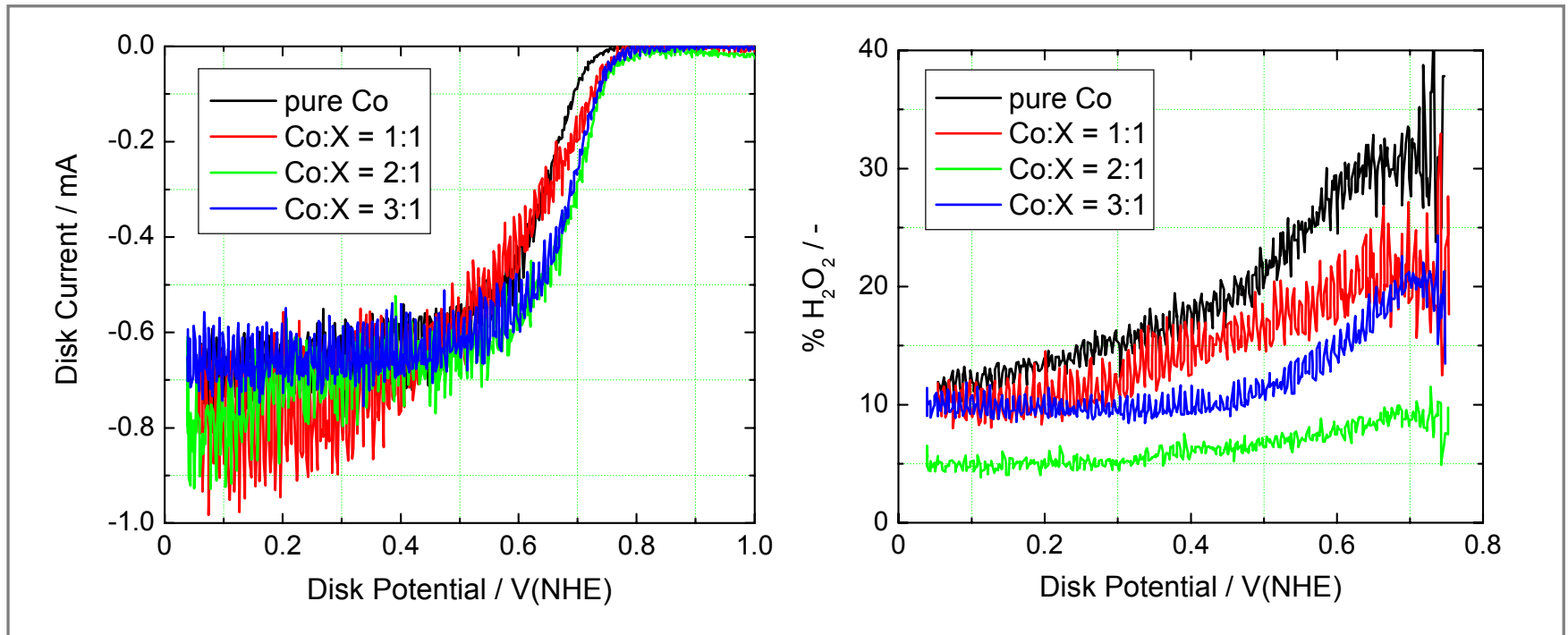
Optimization - (6) Pyrolysis Temperature



- **HIGHLIGHT:** Pyrolysis temperature was optimized to be 800 °C.
- **XPS:** Certain ratio of the pyridinic and pyrrolic N groups at 800 °C is associated with the enhanced catalytic activity.
- **EXAFS:** At 800 °C and beyond only Co-Co interaction is observed.



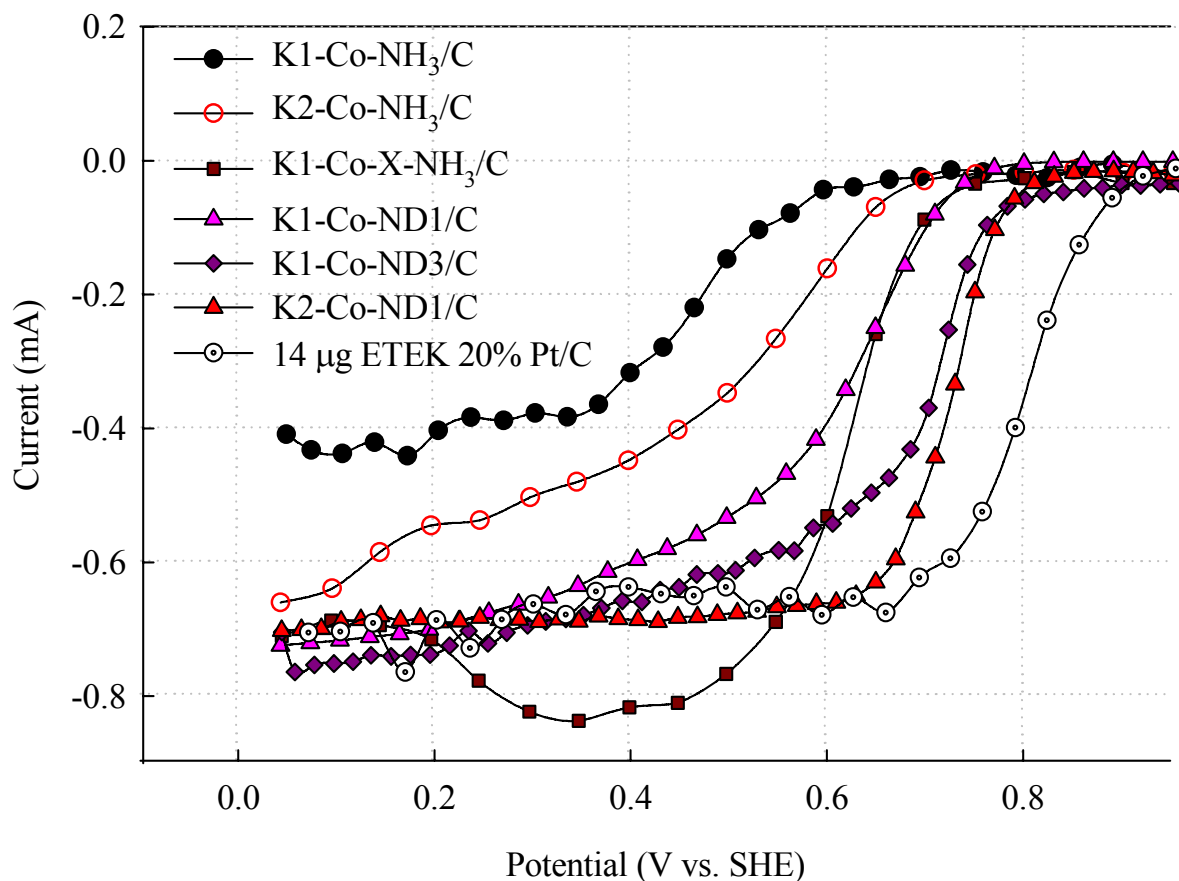
Optimization - (7) Non-Metallic Additive "X"



- **HIGHLIGHT:** Incorporation of non-metallic additive "X" with optimized concentration (Co:X = 2:1) increases both the catalytic activity and selectivity of the Co-catalyst.
- %H₂O₂ produced is lower than 5 % for the optimized Co-X catalyst below 0.5 V vs. NHE.



Progress in Co based Catalysts: Comparison with Pt/C

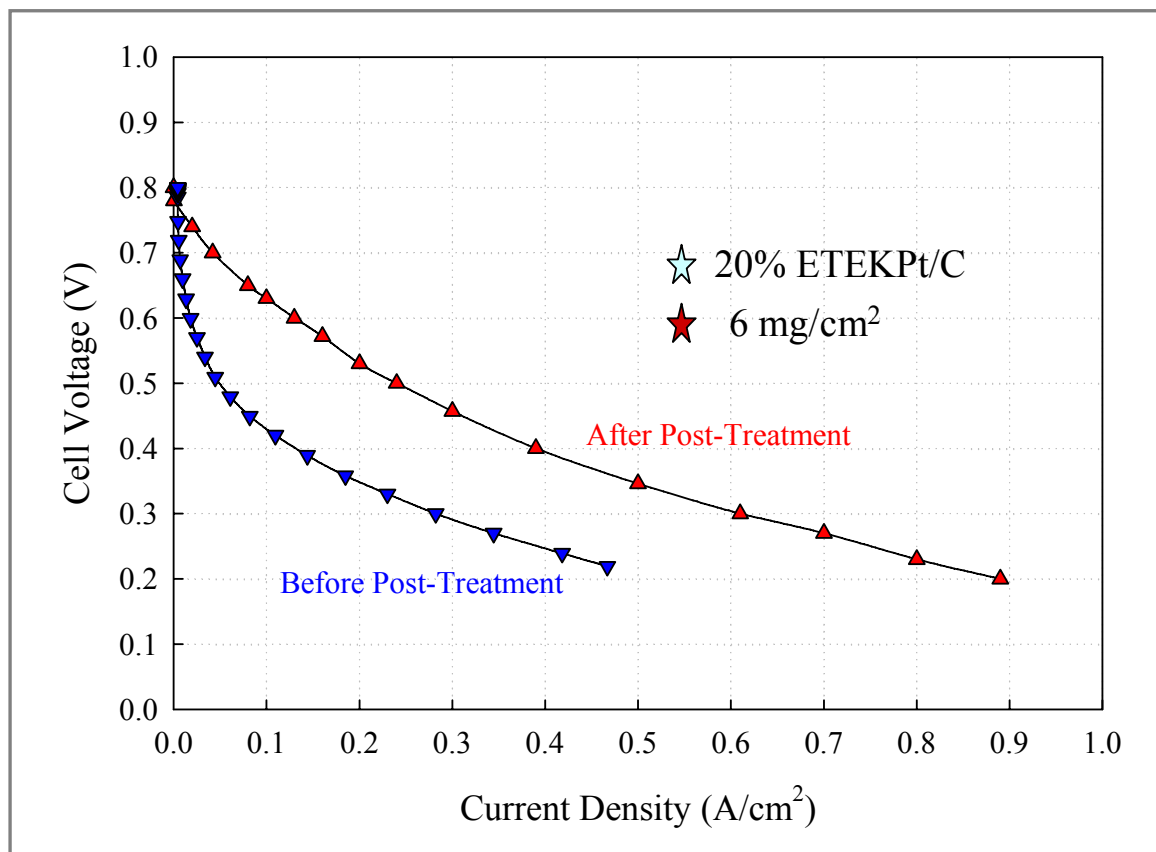


Catalyst	n	%H ₂ O ₂
	@ 0.5 V vs.SHE	
K1-Co-NH ₃ /C	2.9	50.3
K2-Co-NH ₃ /C	3.1	42.3
K2-Co-XNH/C	3.9	5.1
K1-Co-ND1/C	3.53	23.4
K2-Co-ND1/C	3.8	13
K1-Co-ND3/C	3.89	7%

- Co based catalysts show comparable performance with Pt/C catalysts under RRDE test conditions.
 - Onset potential for O₂ reduction – 0.82 V vs. SHE
 - FOUR electron pathway for ORR.
- Further research is aimed at decreasing the H₂O₂ production to 0 %.



Fuel Cell Test – Effect of Post-Treatment

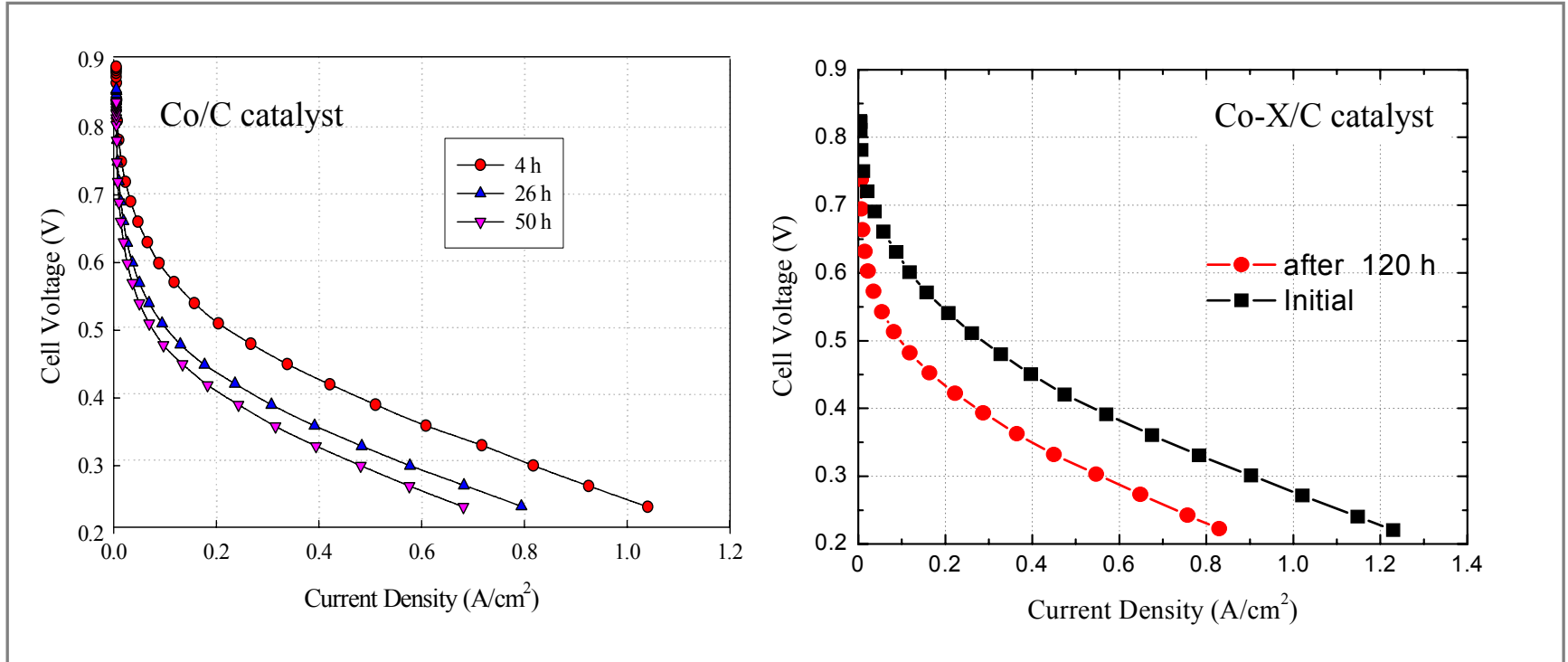


- **Anode:** 2 mg cm⁻² of ETEK 20% Pt/C
- **Cathode:** 2 mg cm⁻² of 20% Co-ND/C
- **Membrane:** Nafion 112
- **Operating conditions:**
(i) H₂/air; (ii) 15/30 psi;
(iii) 77/75 °C

- **HIGHLIGHT:** Significant increase in activity is observed with post treatment.
- Surface area of the catalyst increases due to the dissolution of inactive Co in the structure of the catalyst



Fuel Cell Test - Stability



HIGHLIGHT: Co-X catalyst shows better MEA performance and higher stability as compared with pure Co catalyst.

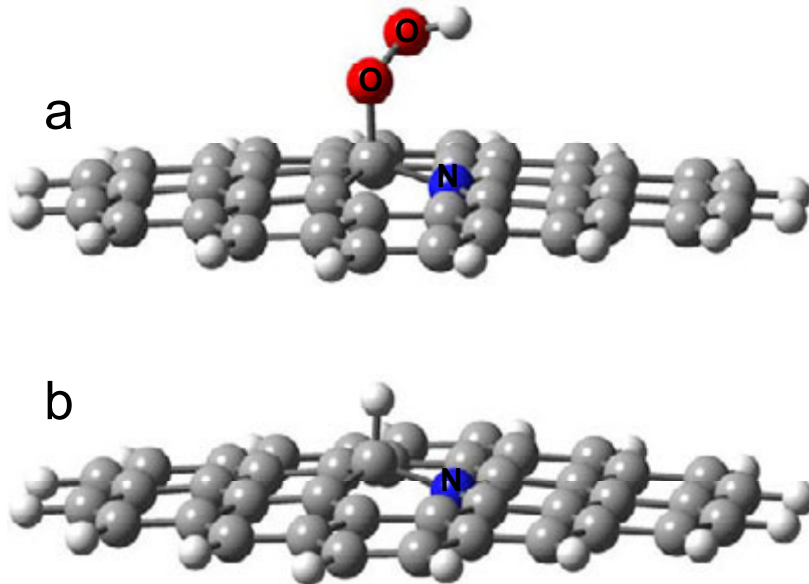


Development of Metal-Free Catalysts for PEMFC Applications



Molecular Modeling

Why is nitrogenated graphite active for oxygen reduction?



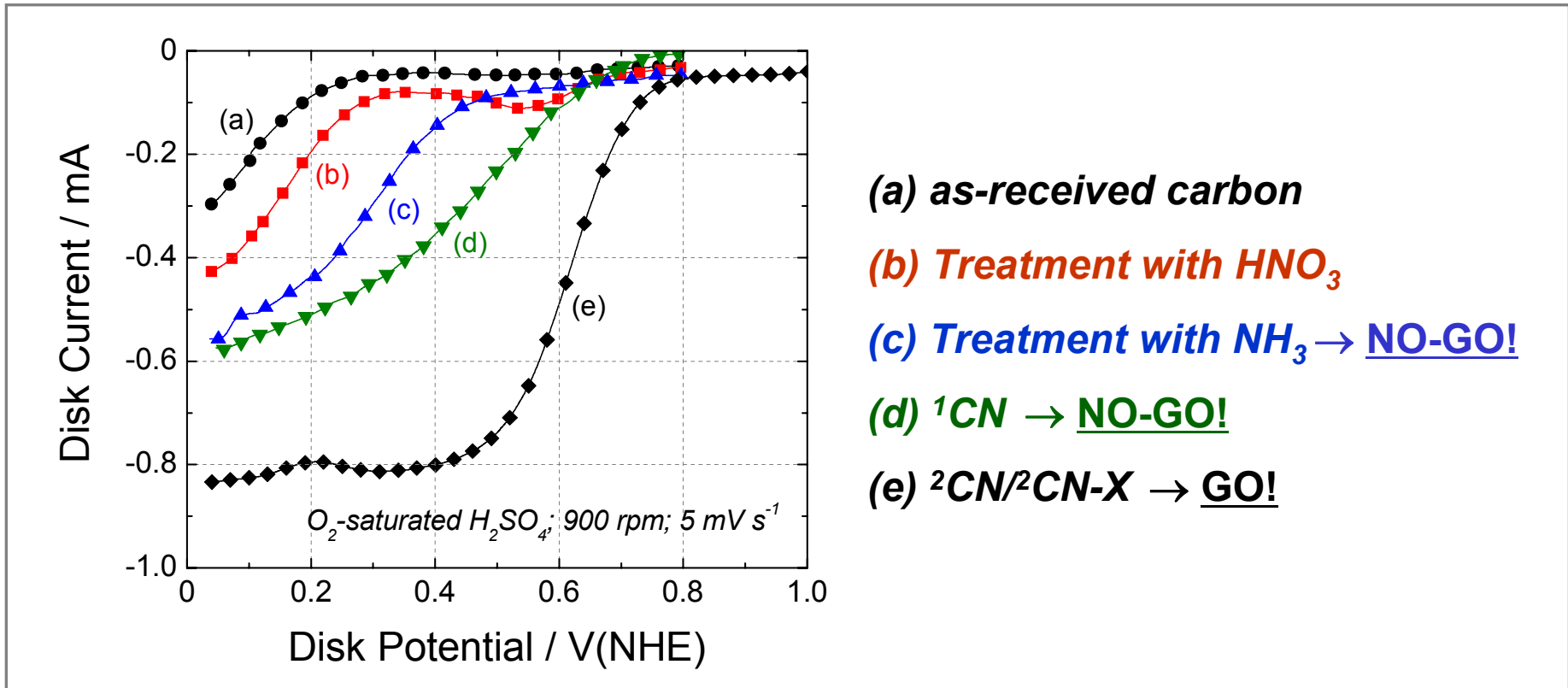
Substitutional N creates adjacent radical carbon adsorption sites that bond H weakly (2.24 eV) so that they are free at potentials >0.13 V. OOH bonds weakly (0.89 eV) to the radical carbon so that it forms from $O_2(\text{aq})$ reduction at 0.84 V and below. OOH(ads) is then reduced to $H_2O_2(\text{aq})$ at 0.55 V and below, matching the O_2 reduction current for nitrogenated Ketjen black.

H bonds to graphite edge sites more weakly, and is predicted to be removed at potentials >-0.08 V.

OOH also bonds to these sites more weakly, and is predicted to form from O_2 reduction at potentials <0.31 V. This matches the reduction curve for pure Ketjenblack.



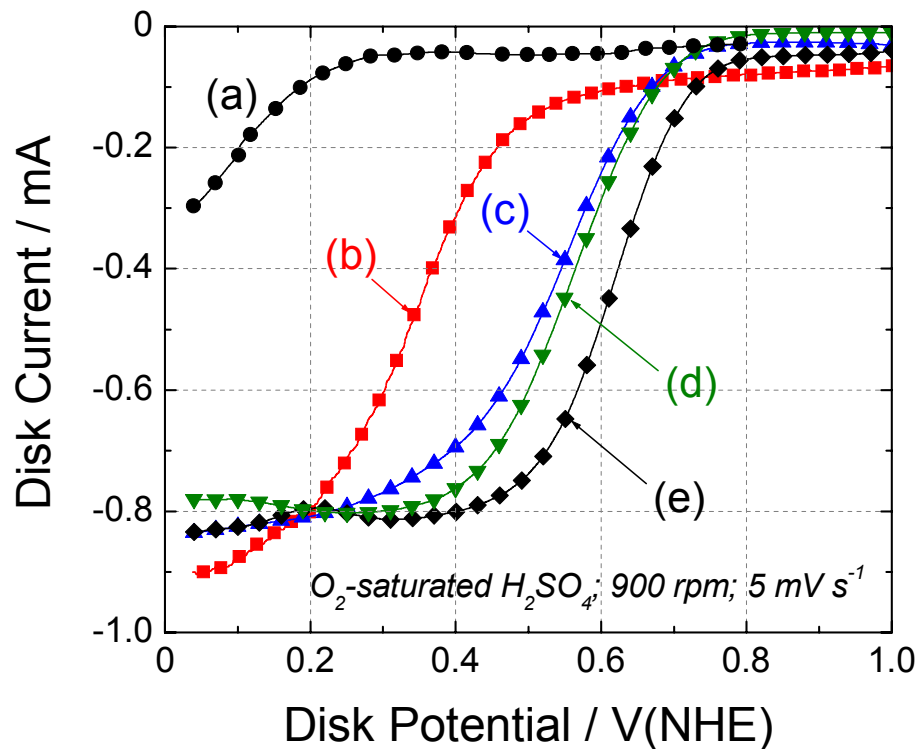
Research Progress



HIGHLIGHT: The USC methodology increased the onset potential for oxygen reduction by ca. 500 mV, as compared with the as-received carbon.



Supported CN & CN-X : Catalytic Activity



(a) as-received carbon

(b) ¹CN

(c) ²CN

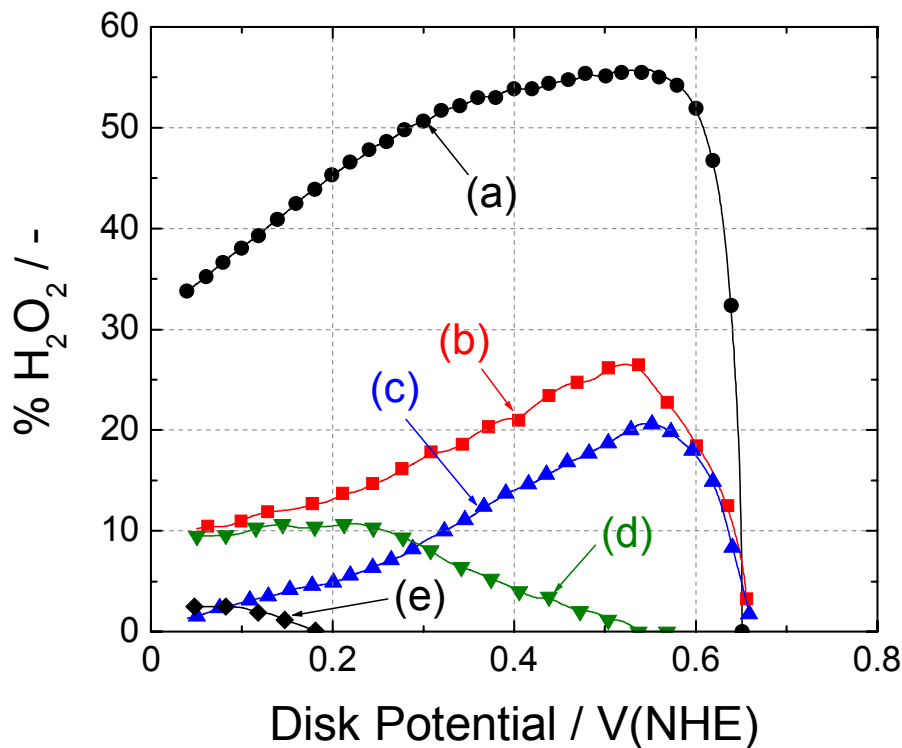
(d) ²CN-X

(e) ²CN/²CN-X

HIGHLIGHT: The USC-developed ²CN/²CN-X exhibited an onset potential as high as 0.8 V(NHE) and a well-developed limiting current.



Supported CN & CN-X : Catalytic Selectivity

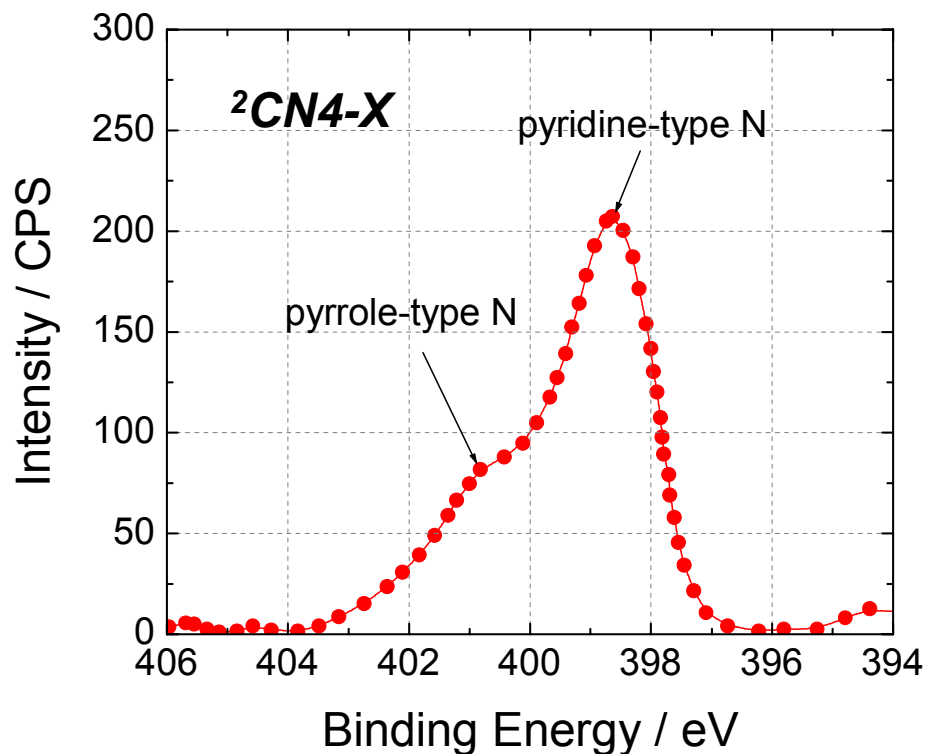


Catalyst	H_2O_2 at 0.5 V
(a) $^1\text{CN1}$	56%
(b) $^2\text{CN2}$	28%
(c) $^2\text{CN3}$	19%
(d) $^2\text{CN4}$	3%
(e) $^2\text{CN4-X}$	0%

HIGHLIGHT: The USC-developed $^2\text{CN4-X}$ catalyzes oxygen reduction to water via four-electron transfer with no H_2O_2 production.



Catalytic Active Sites



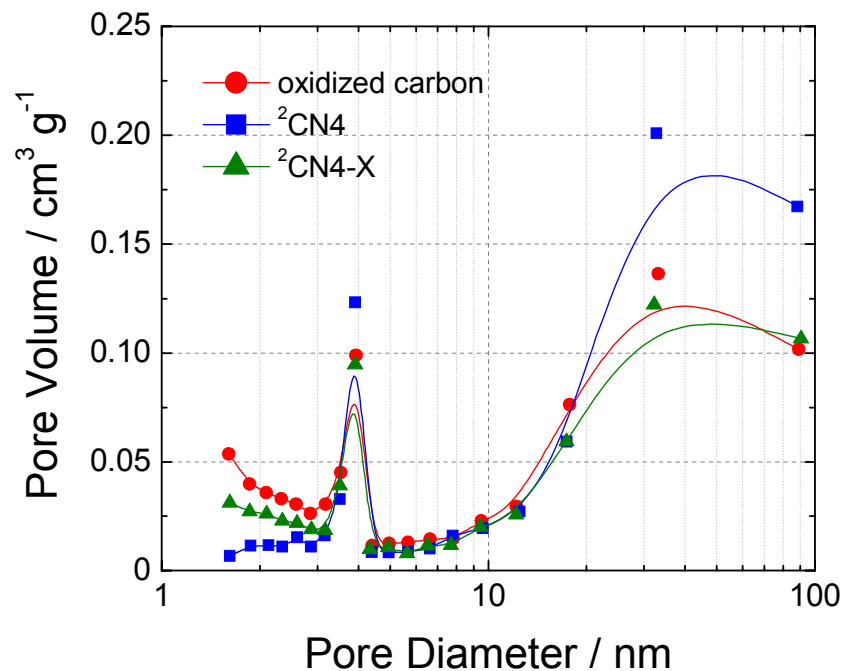
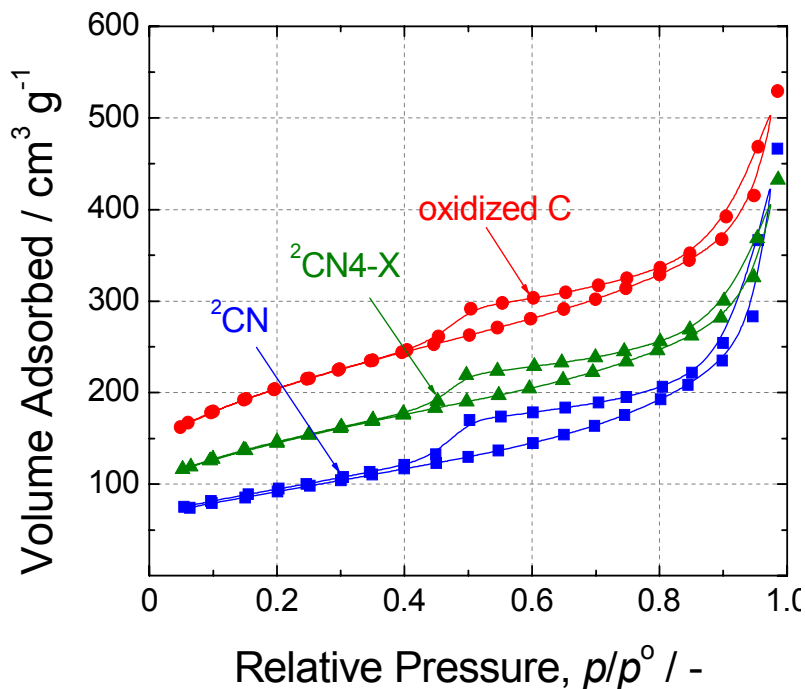
X-ray photoelectron spectroscopy

<i>N type</i>	<i>binding energy (eV)</i>
<i>pyridinic</i>	<i>ca. 398.2</i>
<i>nitrile</i>	<i>ca. 399.8</i>
<i>pyrrolic</i>	<i>ca. 400.9</i>
<i>graphitic</i>	<i>ca. 403.6</i>

HIGHLIGHT: High-temperature pyrolysis led to the formation of pyridine-type nitrogen which is believed to be active for oxygen reduction.



Porous Structure (BET) Analysis

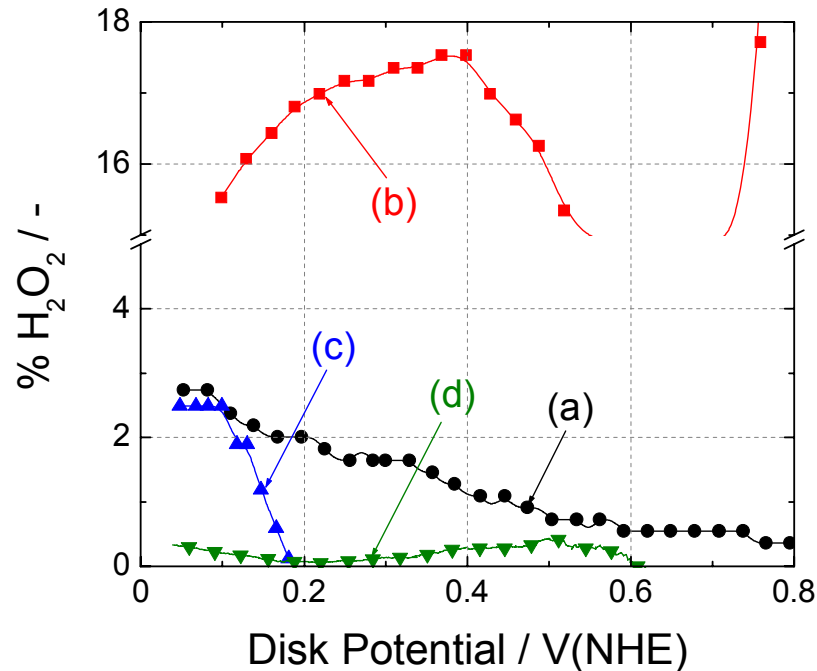
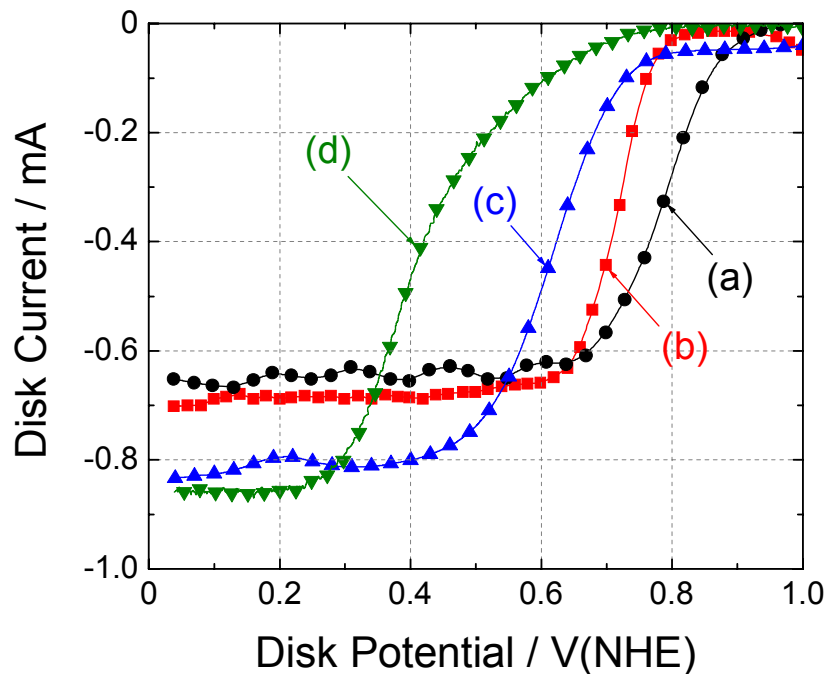


sample	surface area (m ² g ⁻¹)	average pore diameter (nm)
oxidized C	694.3	4.71
² CN4	321.4	8.97
² CN4-X	496.2	5.39

HIGHLIGHT: Larger surface area of ²CN4-X resulted in higher catalytic activity.



Activity & Selectivity - Comparison with Metal Catalysts



(a) 19.1 wt% Pt-C; (b) 20 wt% Co-ND1-C; (c) $^2\text{CN4-X1}$; (d) $^3\text{C-X2}$

HIGHLIGHT: The metal free catalysts show moderate catalytic activities, but they exhibit higher selectivity for oxygen reduction to water, when compared with the Pt- and Co-catalysts.



Future Work

NON-PRECIOUS Co-BASED CATALYST

- ❑ To further increase the catalytic selectivity for oxygen reduction:**
 - i) Incorporation of non-metallic additive “X” in the Co/carbon nanocluster***

- ❑ To perform the durability study on the optimized Co catalyst in RRDE and fuel cells and understand the degradation mechanism**

- ❑ To increase the catalyst durability**
 - i) Synthesis of Co catalysts doped with X and Cr using a procedure developed at USC***
 - ii) Synthesis of Co and Co-X catalysts loaded on graphitized carbon***



Future Work

METAL FREE CATALYST

- ❑ Further to increase the catalytic activity and selectivity for oxygen reduction**
 - i) Optimization of metal free C-X nanocatalyst***
 - ii) Use of different carbon black supports***
 - iii) Synthesis of “unsupported” catalyst with high mesoporous area by using template method***

- ❑ To perform the durability study on the optimized metal free catalyst in RRDE and fuel cells, and understand the degradation mechanism**

- ❑ To increase the catalyst durability**
 - i) Synthesis of metal free catalysts loaded on graphitized carbon***
 - ii) Encapsulation of metal free catalysts with ZrO₂***



Summary

- ❑ **Objective:** Develop (i) non-precious metal and (ii) metal-free catalysts for PEMFC which perform as good as conventional Pt catalysts
- ❑ **Approach:** Optimize the active reaction sites to increase the catalytic activity and stability using USC-developed methodology
- ❑ **Technological Accomplishments and Progress:** Demonstrated high catalytic activity (0.8 – 0.85 V vs. SHE) and selectivity (0 – 5 % H₂O₂) for Co-based and metal free catalysts
- ❑ **Collaborations:** Active partnership with Case Western Reserve University and Northeastern University
- ❑ **Proposed future research:** (i) Optimize MEA performance with the Co-based metal and metal-free catalysts, and (ii) increase catalyst stability



Response to Reviewer's Comments

- Objectives appear to include everything on a wish list.
 - Current research focuses on increasing the number of catalytic active sites and selectivity for Co-based and metal free catalysts.
- It is unlikely the PI will be able to accomplish low cost catalyst through mass production methods at a university.
 - The objective is to develop the synthesis procedure for Co-based and metal free catalysts with low cost precursors which can be easily upgraded for mass production.
- Catalyst stability and durability should be addressed.
 - Preliminary results indicate that the incorporation of non-metallic additive “X” improved the catalyst stability under fuel cell test conditions.
 - Current research focuses on the catalyst stability under accelerated durability test (ADT) and fuel cell test conditions.



Publications and Presentations

Publications

1. H. Kim, B.N. Popov, "Development of Novel Method for Preparation of PEMFC Electrodes", *Electrochem. Solid-State Lett.*, 7 (2004) A71.
2. H. Kim, N.P. Subramanian and B.N. Popov, "Preparation of PEM Fuel Cell Electrodes Using Pulse Electrodeposition", *J. Power Sources*, 138 (2004) 14.
3. H.R. Colón-Mercado and B.N. Popov, "Stability of Platinum Based Alloy Cathode Catalysts in PEM Fuel Cells", *J. Power Sources*, 155 (2006) 253.
4. R. Sidik, A. Anderson, N.P. Subramanian, S.P. Kumaraguru and B.N. Popov, "O₂ Reduction on Graphite and Nitrogen-Doped Graphite: Experiment and Theory" *J. Phys. Chem. B*, 110 (2006) 1787.
5. R. Sidik and A. Anderson, "Co₉S₈ as a Catalyst for Electroreduction of O₂: Quantum Chemistry Predictions", *J. Phys. Chem*, 110 (2006) 936.
6. N.P. Subramanian, S.P. Kumaraguru, H.R. Colón-Mercado, B.N. Popov, "Studies on Co Based Electrocatalysts on Modified Carbon Substrates for PEMFC Applications", *J. Power Sources*, in press.
7. L.Liu, H. Kim, J.-W.Lee and B.N. Popov "Development of Novel Ru-based Catalysts for Oxygen Reduction Reaction", *J. Electrochem. Soc.*, submitted.
8. S.P. Kumaraguru, N.P. Subramanian, H.R. Colón-Mercado, M. Curran and B.N. Popov "Fe-based catalysts for PEMFC Applications", under preparation.

Presentations

1. 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.
2. B.N. Popov, "Novel Non Precious Metal Catalysts for PEMFC Applications", *206th meeting of the Electrochem Soc.*, Honolulu, HI, October, 2004.
3. 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.
4. L. Liu and B.N. Popov, "Highly Active Ru-Chelate Catalysts for Oxygen Reduction Reaction", *1st Symposium on Manufacturing of MEAs for Hydrogen Applications*, Dayton, OH, August, 2005.
5. S.P.Kumaraguru, M.Curran and B.N.Popov, "Non Noble Metal Catalysts for Oxygen Reduction Reaction", *208th meeting of the Electrochem Soc.*, Los Angeles, CA, October, 2005.

