

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

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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

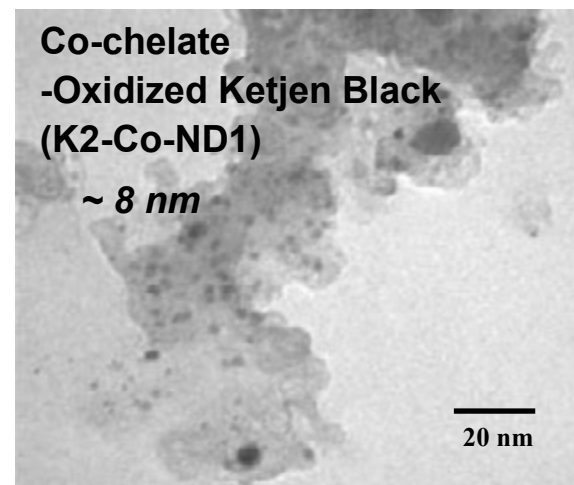
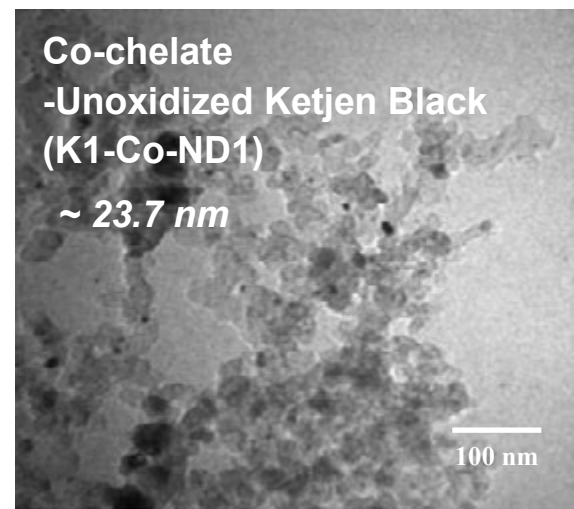
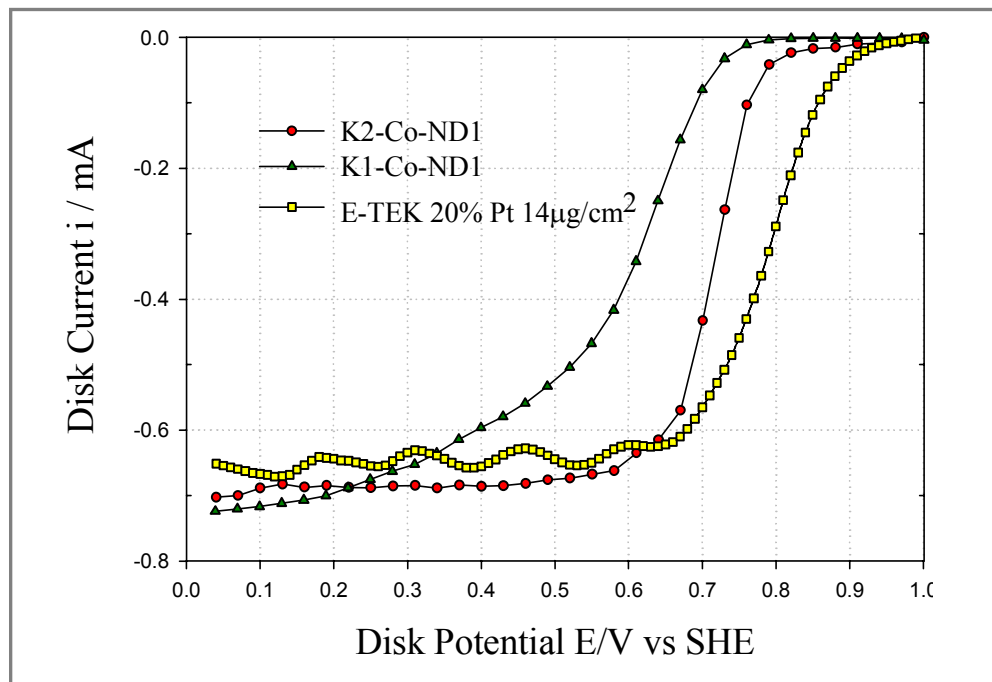
- ❑ Active Co/C catalysts were developed with the use of activated carbon, surface modifier and non-metallic additive “X”.
  - ❑ Carbon activation methodology was developed to increase the concentration of active sites of the Co-based catalyst.
  - ❑ Surface modifiers were used to increase the activity 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 H<sub>2</sub>O<sub>2</sub> produced during oxygen reduction.
  - ❑ FOUR electron pathway for ORR (< 5 % H<sub>2</sub>O<sub>2</sub>)
  
- ❑ 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*



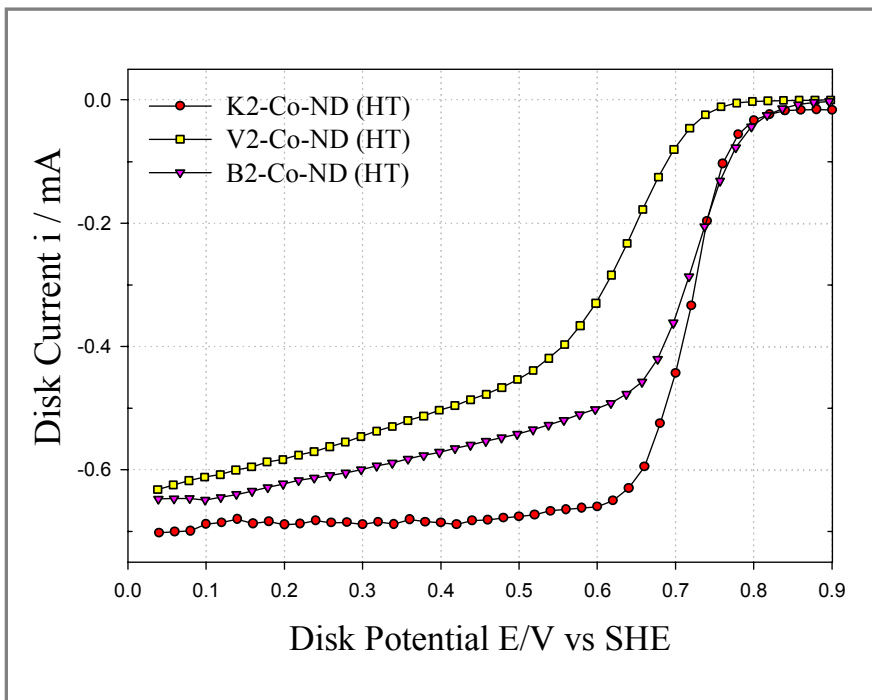
# Optimization – (1) Effect of Surface Oxygen Group



- **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



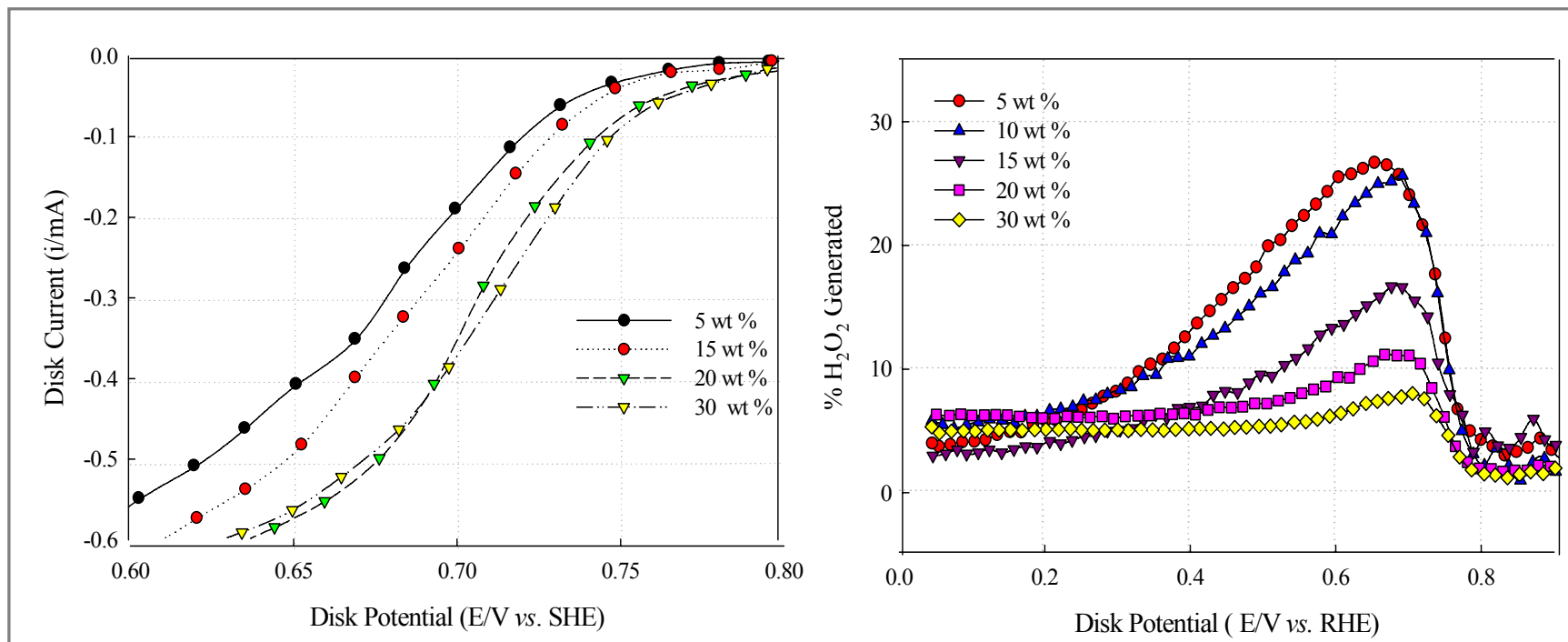
Carbon	Area (m <sup>2</sup> /g)	Micro-pores (m <sup>2</sup> /g)	Meso-pores (m <sup>2</sup> /g)	Catalyst particle size (nm)
Vulcan XC 72	254	118	100	~ 40
Ketjen Black EC 300J	886	55	680	~ 8
Black Pearl 2000	1500	720	540	~ 12.5

- **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.





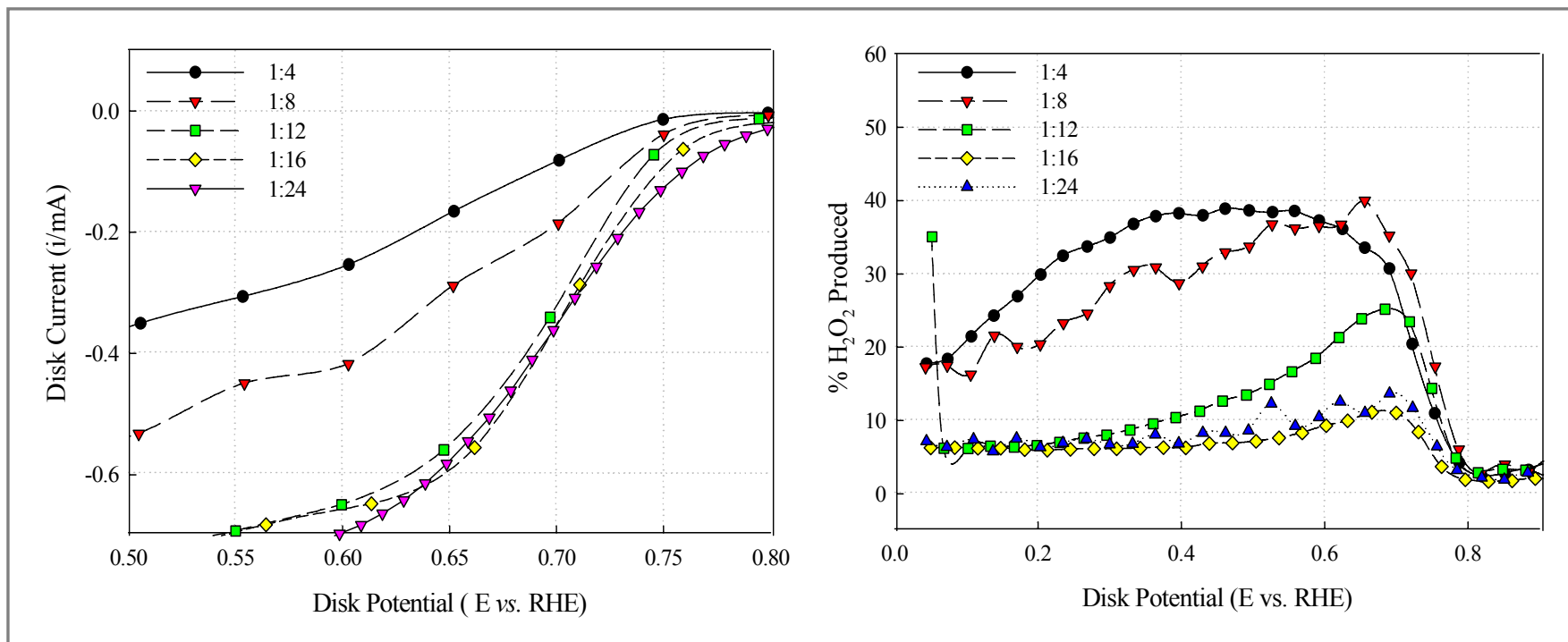
# Optimization – (3) Effect of Co Loading



- **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 %H<sub>2</sub>O<sub>2</sub> produced. %H<sub>2</sub>O<sub>2</sub> is lower than 7% for 30 wt% Co loading at 0.7 V vs. NHE.



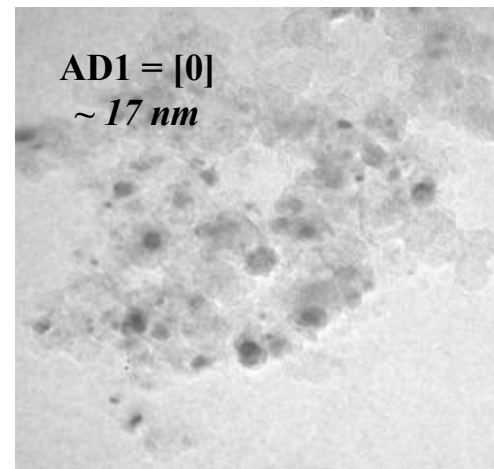
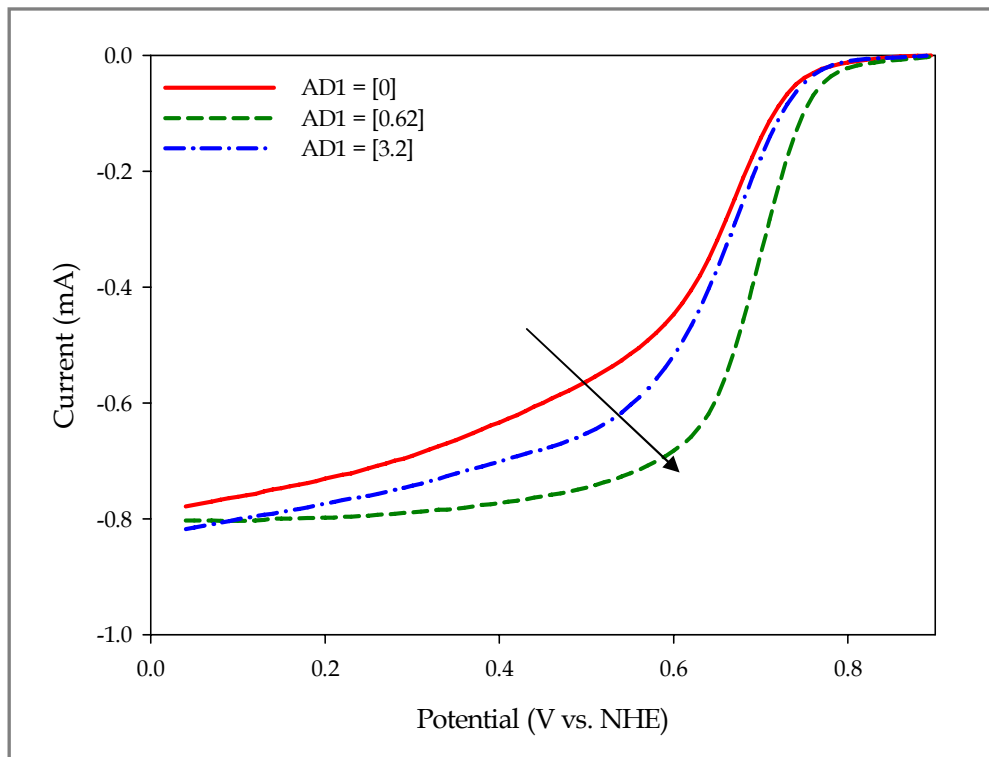
# Optimization - (4) Effect of N Content



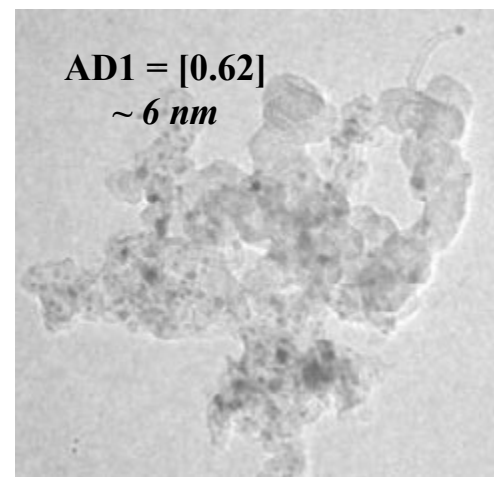
- **HIGHLIGHT:** Increase in nitrogen concentration increases the activity of the catalyst.
- %H<sub>2</sub>O<sub>2</sub> produced decreases from 36 to 11% with increasing the nitrogen content.



# Optimization - (5) Effect of Surface Modifier



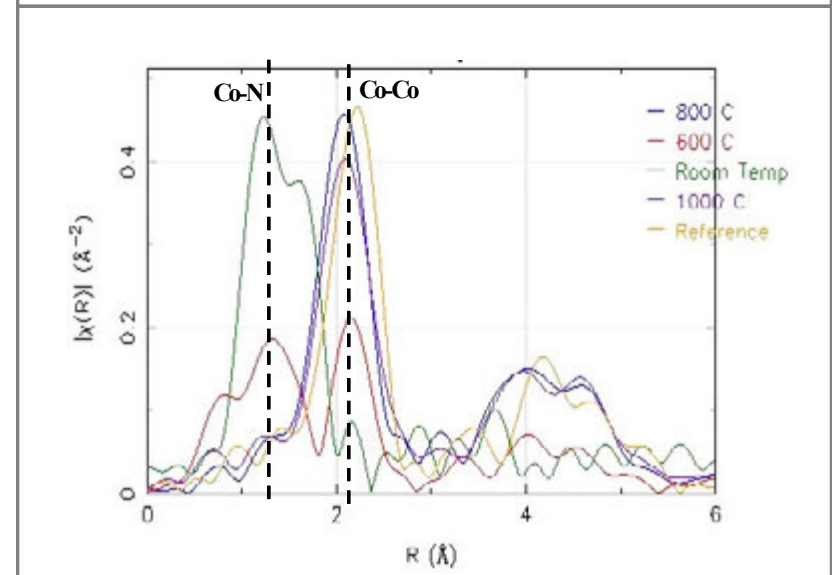
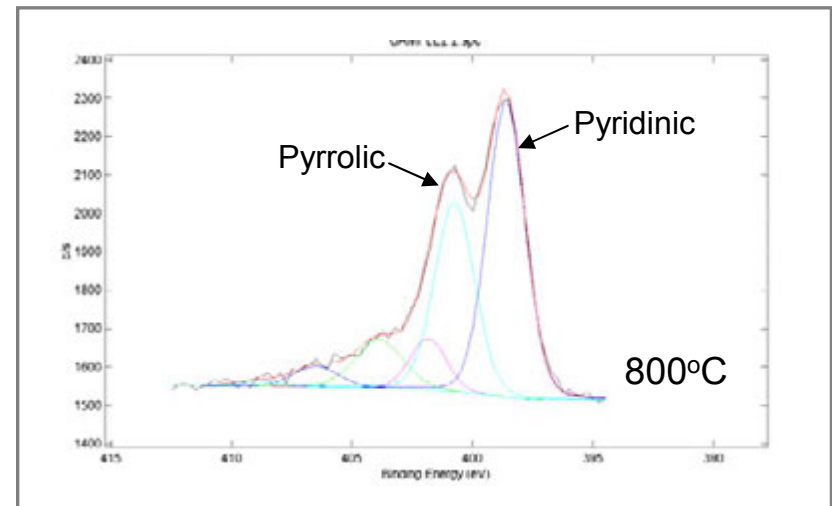
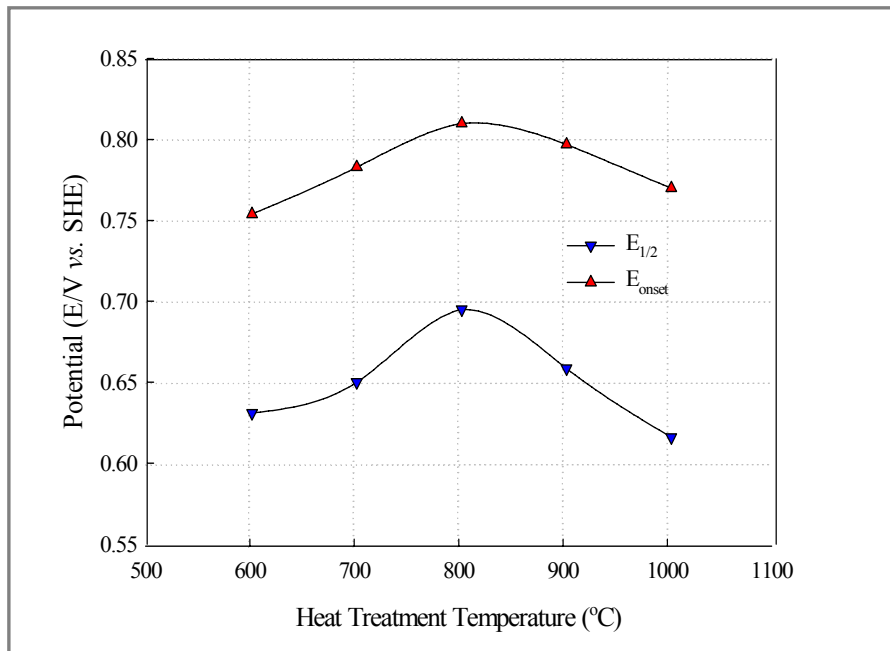
100 nm



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



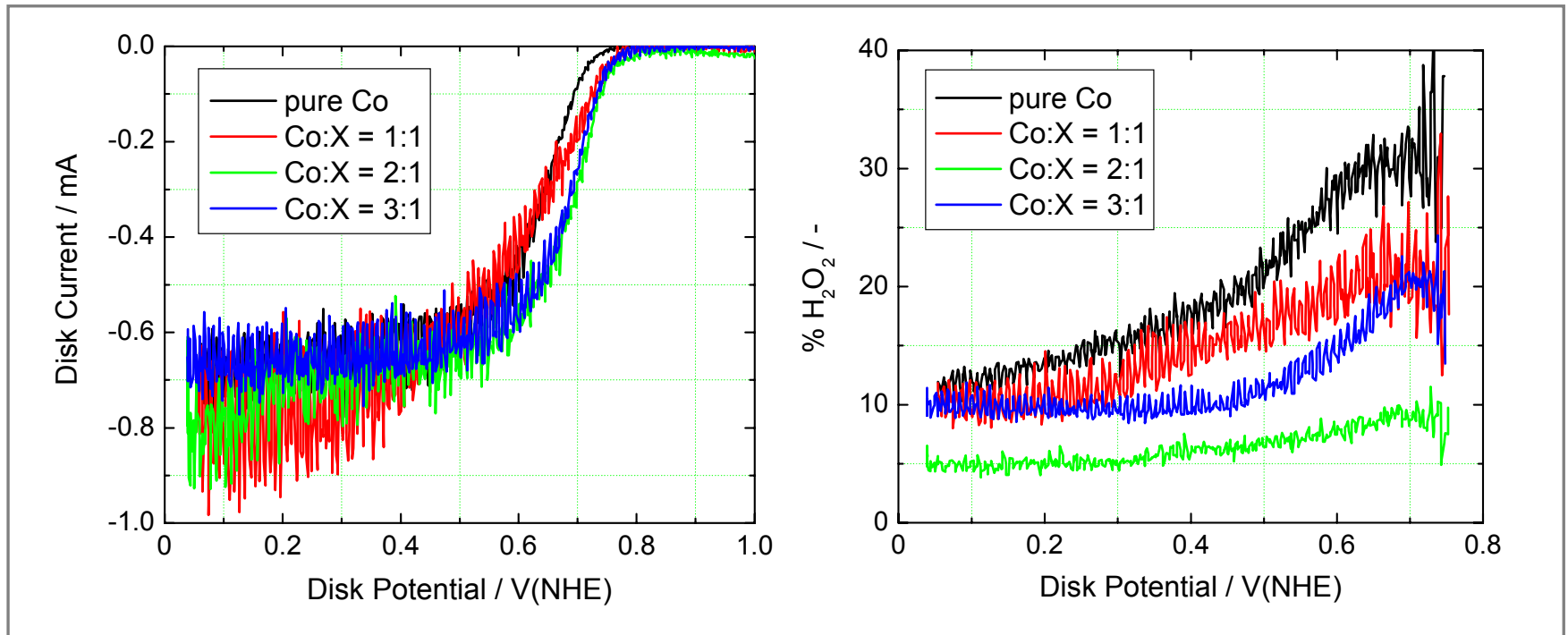
# Optimization - (6) Pyrolysis Temperature



- **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.



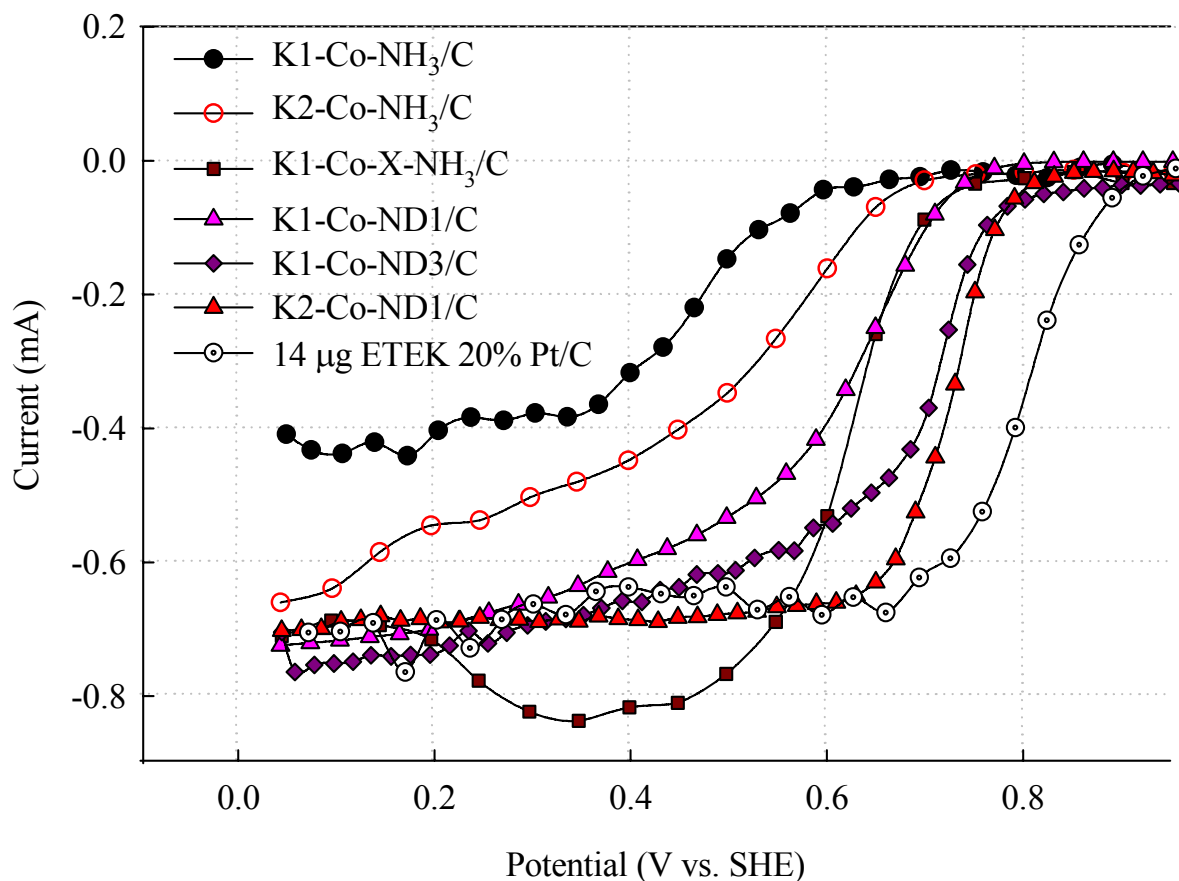
# Optimization - (7) Non-Metallic Additive "X"



- **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.
- %H<sub>2</sub>O<sub>2</sub> 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

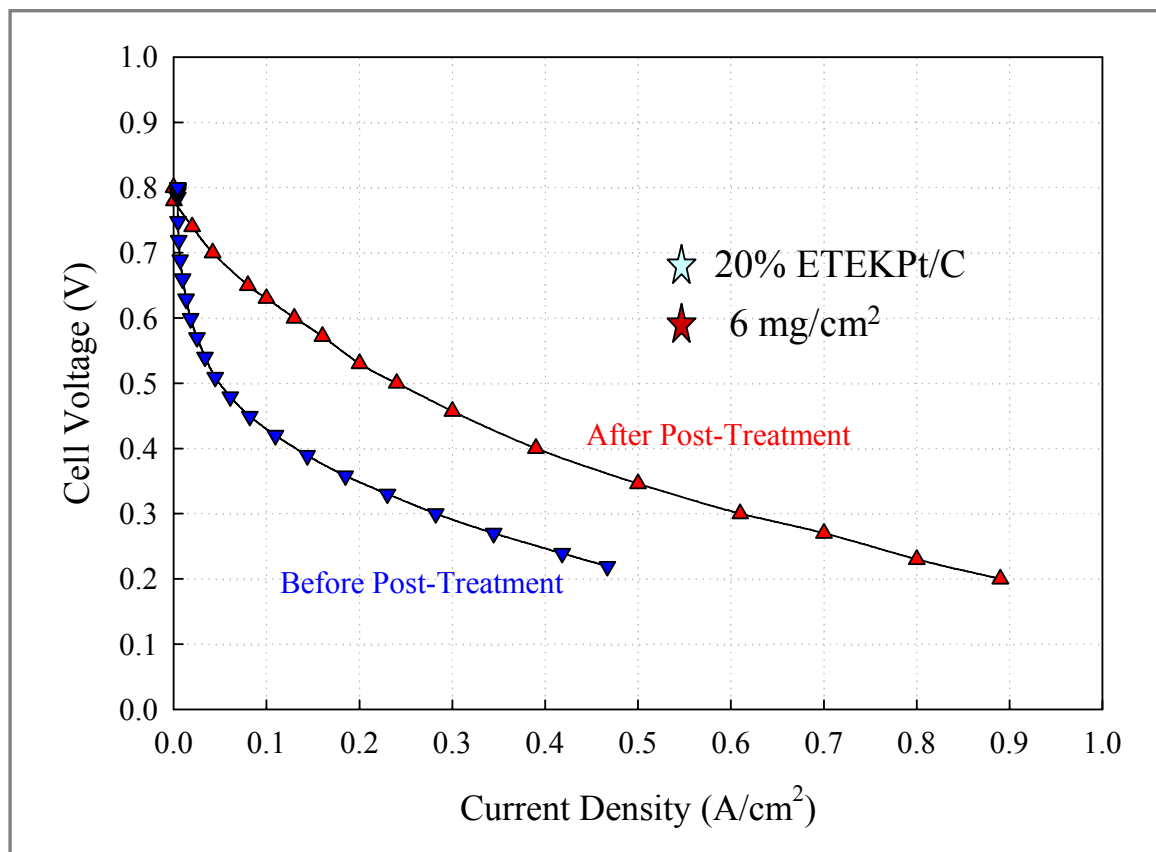


Catalyst	n	%H <sub>2</sub> O <sub>2</sub>
	@ 0.5 V vs.SHE	
K1-Co-NH <sub>3</sub> /C	2.9	50.3
K2-Co-NH <sub>3</sub> /C	3.1	42.3
K2-Co-XNH/C	<b>3.9</b>	<b>5.1</b>
K1-Co-ND1/C	3.53	23.4
K2-Co-ND1/C	3.8	13
K1-Co-ND3/C	<b>3.89</b>	<b>7%</b>

- Co based catalysts show comparable performance with Pt/C catalysts under RRDE test conditions.
  - Onset potential for O<sub>2</sub> reduction – 0.82 V vs. SHE
  - FOUR electron pathway for ORR.
- Further research is aimed at decreasing the H<sub>2</sub>O<sub>2</sub> production to 0 %.

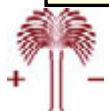


# Fuel Cell Test – Effect of Post-Treatment

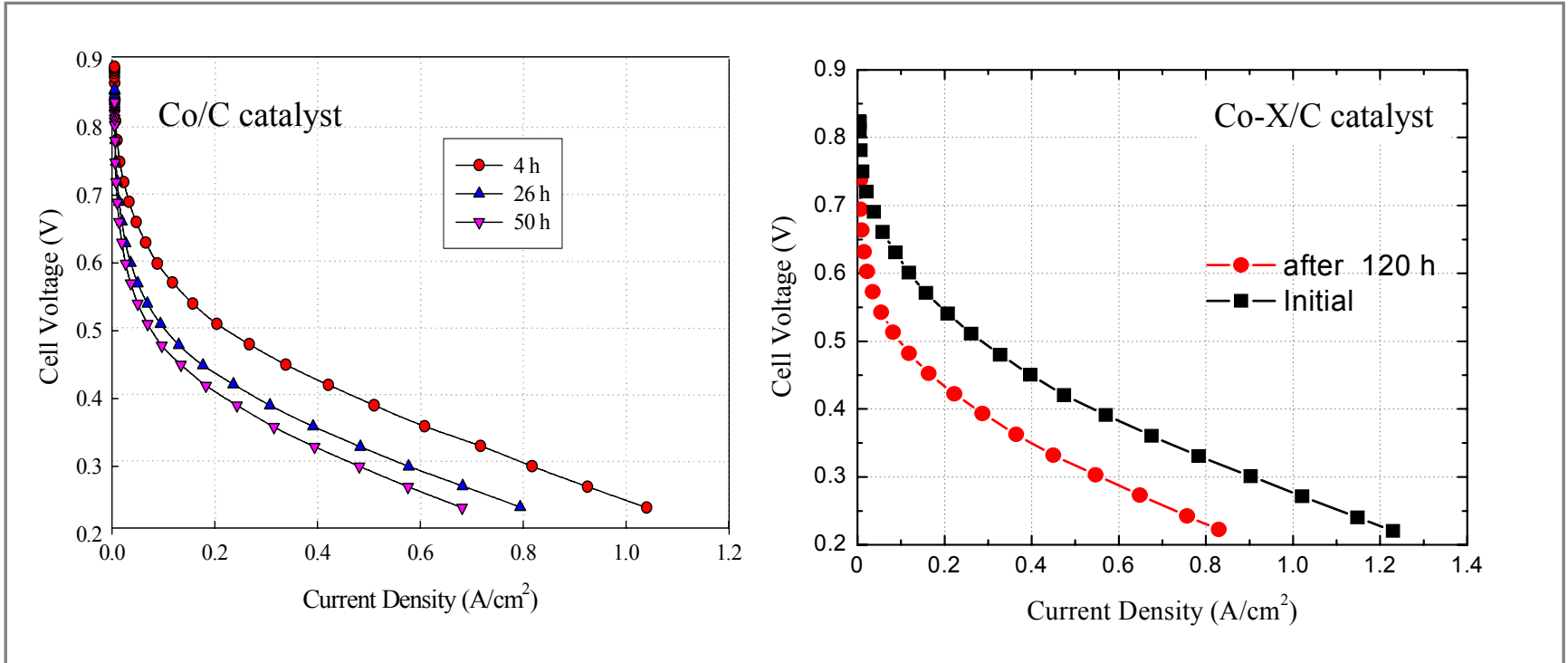


- **Anode:** 2 mg cm<sup>-2</sup> of ETEK 20% Pt/C
- **Cathode:** 2 mg cm<sup>-2</sup> of 20% Co-ND/C
- **Membrane:** Nafion 112
- **Operating conditions:**  
(i) H<sub>2</sub>/air; (ii) 15/30 psi;  
(iii) 77/75 °C

- **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.***



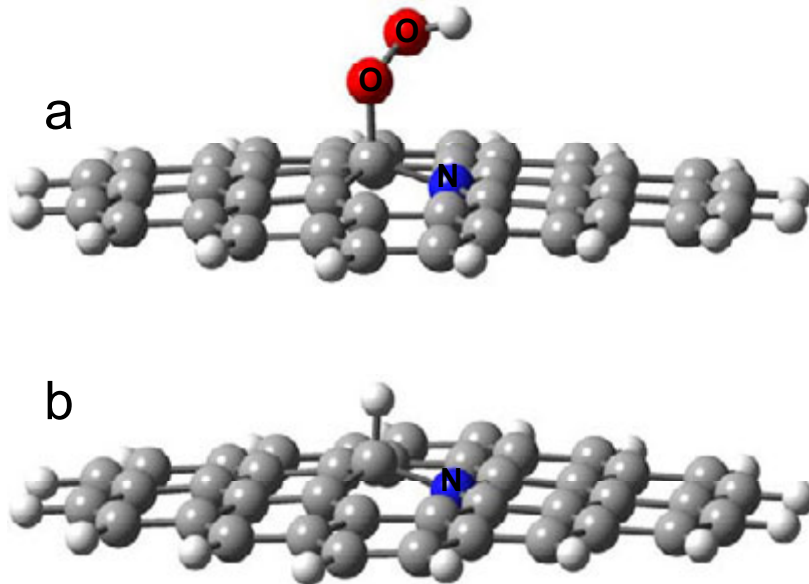


# *Development of Metal-Free Catalysts for PEMFC Applications*



# Molecular Modeling

Why is nitrogenated graphite active for oxygen reduction?



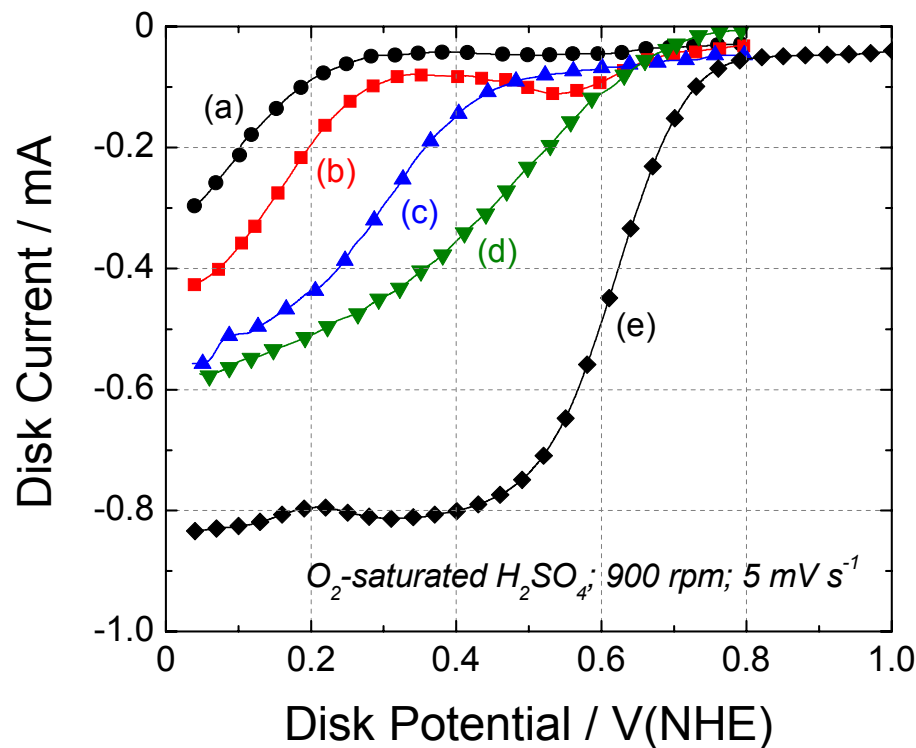
Substitutional N creates adjacent radical carbon adsorption sites that bond H weakly (2.24 eV) so that they are free at potentials  $>0.13$  V. OOH bonds weakly (0.89 eV) to the radical carbon so that it forms from  $O_2(\text{aq})$  reduction at 0.84 V and below. OOH(ads) is then reduced to  $H_2O_2(\text{aq})$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



(a) *as-received carbon*

(b) *Treatment with HNO<sub>3</sub>*

(c) *Treatment with NH<sub>3</sub>* → NO-GO!

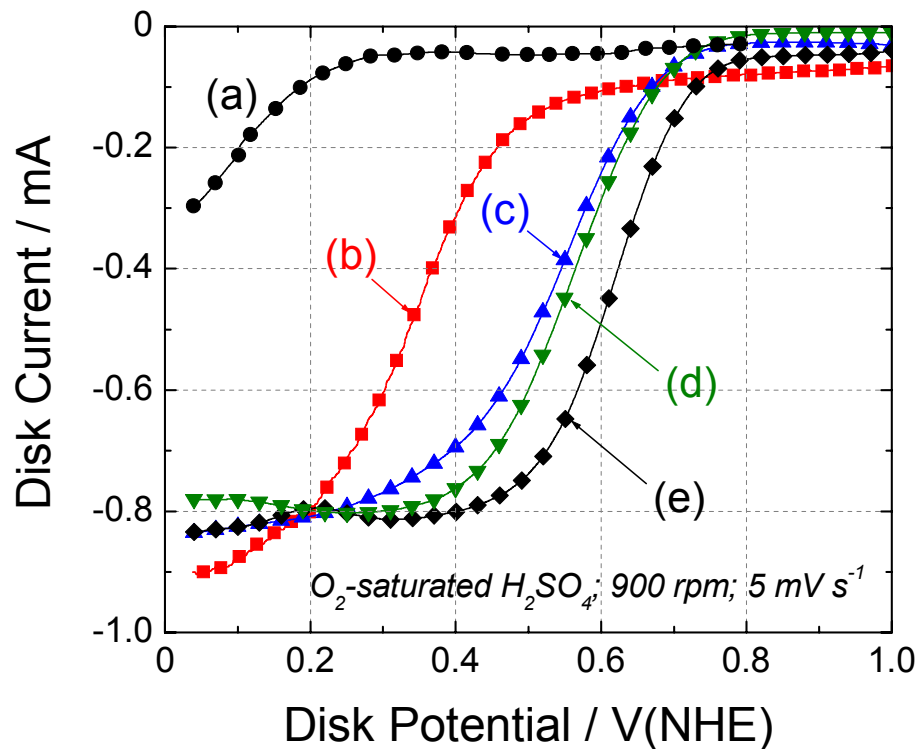
(d) <sup>1</sup>CN → NO-GO!

(e) <sup>2</sup>CN/<sup>2</sup>CN-X → GO!

**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) <sup>1</sup>CN

(c) <sup>2</sup>CN

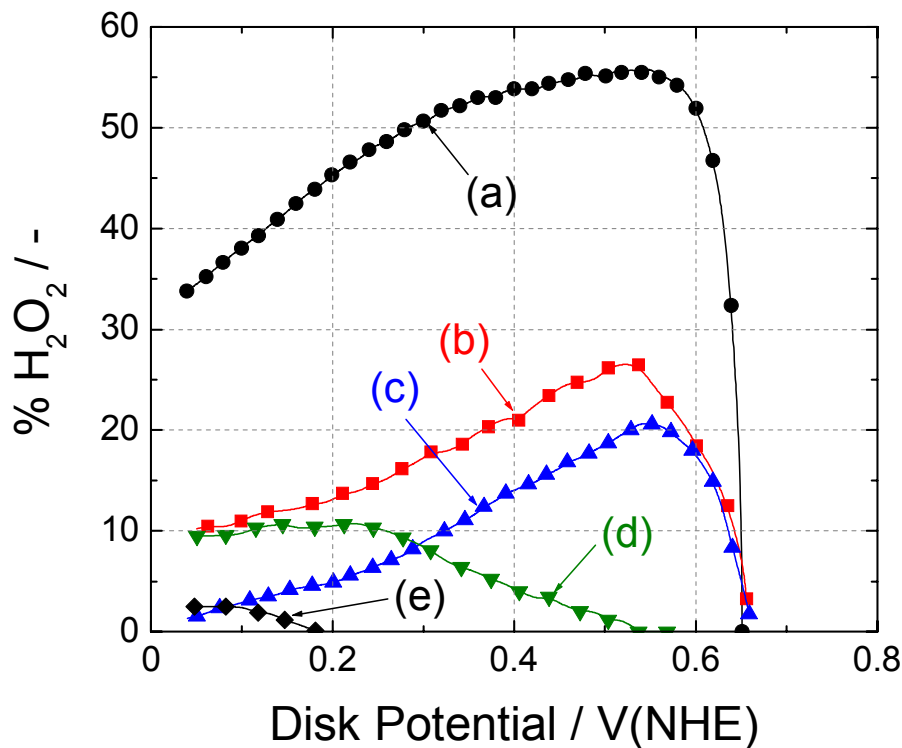
(d) <sup>2</sup>CN-X

(e) <sup>2</sup>CN/<sup>2</sup>CN-X

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



# Supported CN & CN-X : Catalytic Selectivity

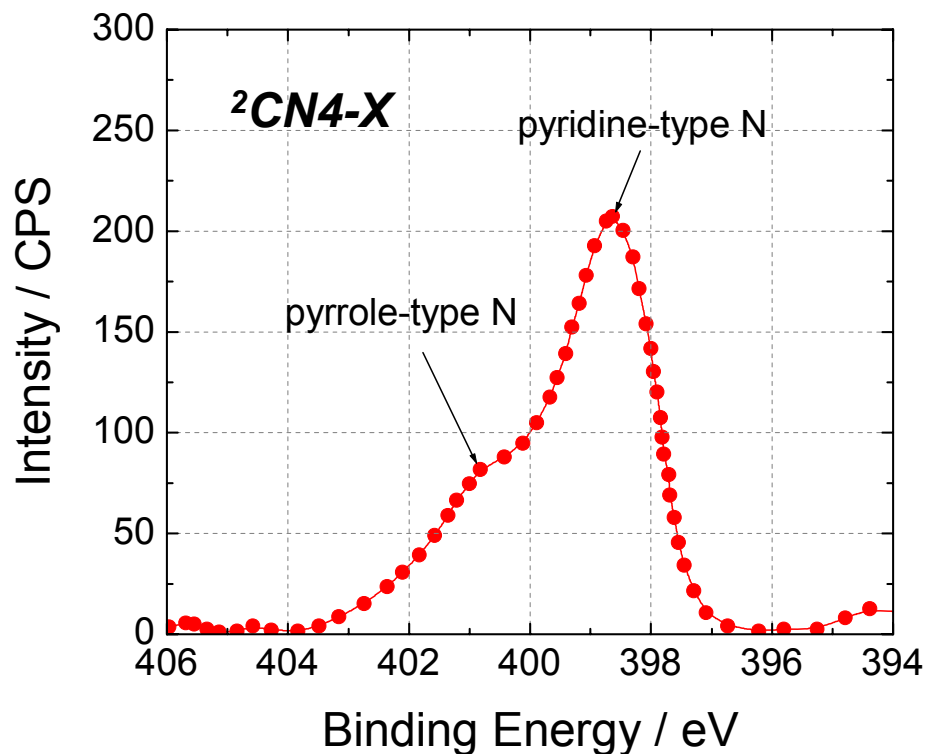


Catalyst	$\text{H}_2\text{O}_2$ at 0.5 V
(a) $^1\text{CN1}$	56%
(b) $^2\text{CN2}$	28%
(c) $^2\text{CN3}$	19%
(d) $^2\text{CN4}$	3%
(e) $^2\text{CN4-X}$	0%

**HIGHLIGHT:** The USC-developed  $^2\text{CN4-X}$  catalyzes oxygen reduction to water via four-electron transfer with no  $\text{H}_2\text{O}_2$  production.



# Catalytic Active Sites



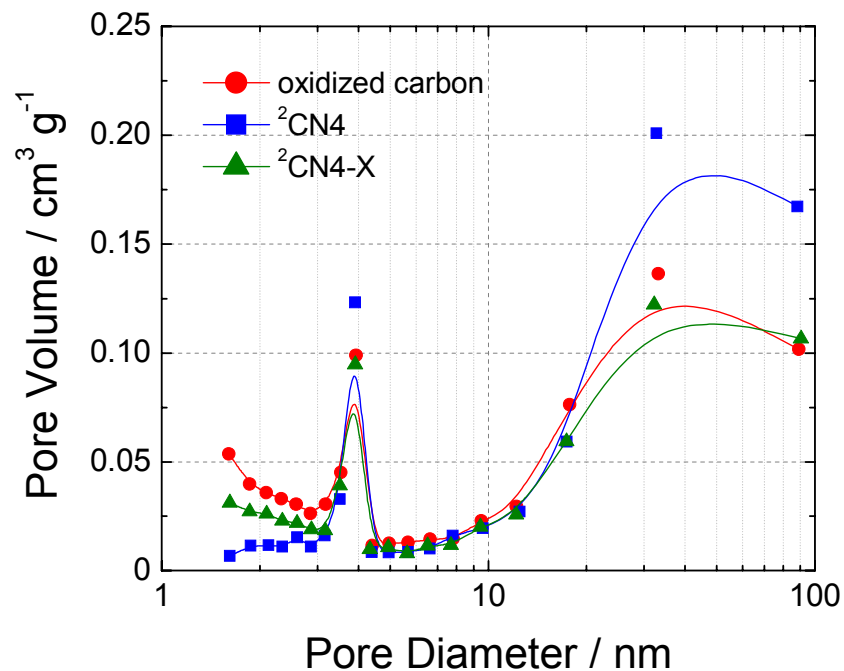
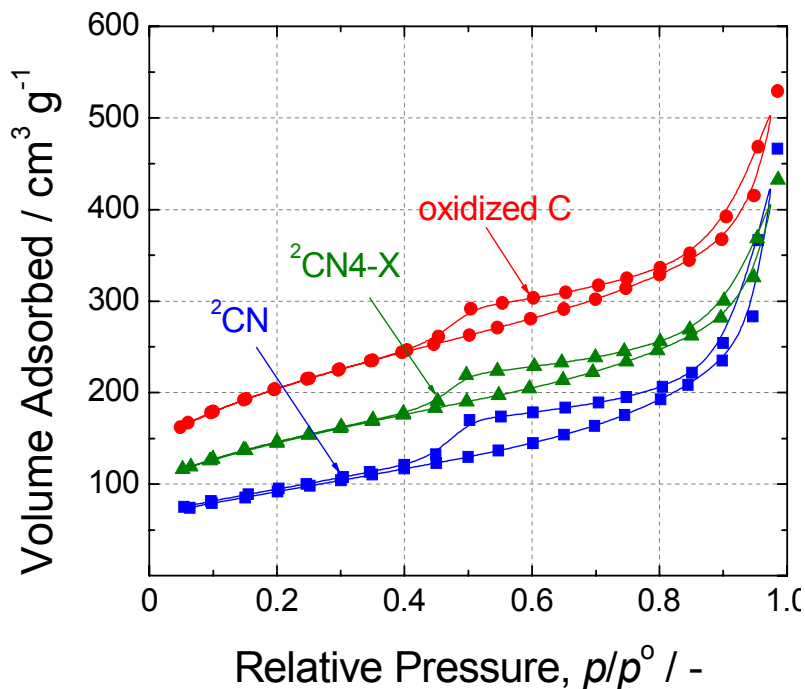
## *X-ray photoelectron spectroscopy*

<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

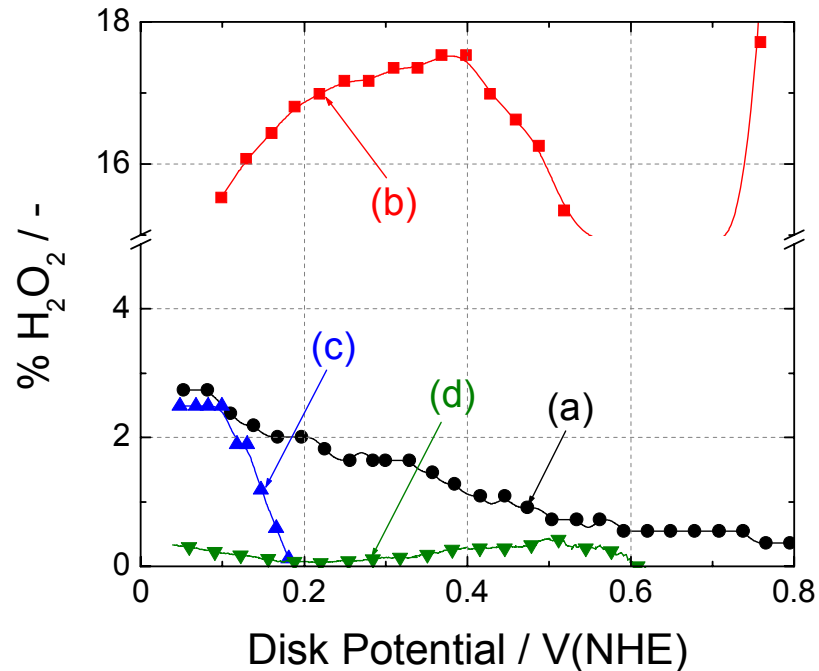
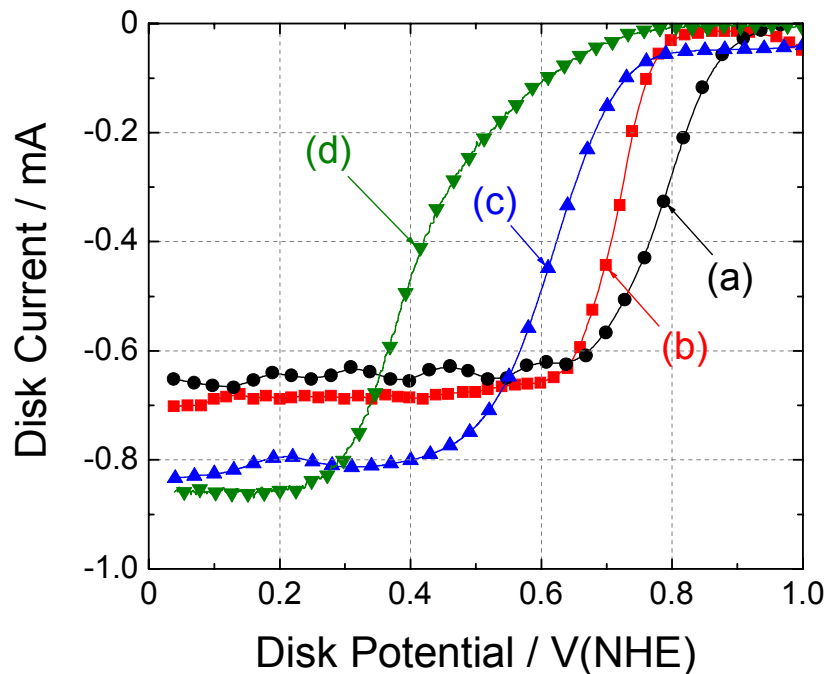


sample	surface area (m <sup>2</sup> g <sup>-1</sup> )	average pore diameter (nm)
oxidized C	694.3	4.71
<sup>2</sup> CN4	321.4	8.97
<sup>2</sup> CN4-X	496.2	5.39

**HIGHLIGHT:** Larger surface area of <sup>2</sup>CN4-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) <sup>2</sup>CN4-X1; (d) <sup>3</sup>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 ZrO<sub>2</sub>***



# 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 % H<sub>2</sub>O<sub>2</sub>) 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

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- 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, "O<sub>2</sub> Reduction on Graphite and Nitrogen-Doped Graphite: Experiment and Theory" *J. Phys. Chem. B*, 110 (2006) 1787.
5. R. Sidik and A. Anderson, "Co<sub>9</sub>S<sub>8</sub> as a Catalyst for Electroreduction of O<sub>2</sub>: 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", *206<sup>th</sup> meeting of the Electrochem Soc.*, Honolulu, HI, October, 2004.
2. B.N. Popov, "Novel Non Precious Metal Catalysts for PEMFC Applications", *206<sup>th</sup> 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", *206<sup>th</sup> 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", *1<sup>st</sup> 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", *208<sup>th</sup> meeting of the Electrochem Soc.*, Los Angeles, CA, October, 2005.

