

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

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University of South Carolina

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Project ID:  
FCP15

# Project Overview

## Timeline

- Project Start Date - 9/30/2003
- Project End Date - 9/30/2008
- Percent Complete - 90%

## Technical Barriers and Targets

- **Electrode performance**  
Perform at least as well as the conventional Pt catalysts currently in use in MEAs
- **Durability**  
2,000 hours operation with less than 10% power degradation
- **Material Cost**  
Cost at least 50% less as compared to a target of 0.2 g of Pt / peak kW

## Partners / Collaborations

- **Case Western Reserve University**
  - Molecular Modeling
- **Northeastern University**
  - Structural Studies



# Project Objective

## OVERALL:

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

## SPECIFIC FOCUS:

2003 - 2004

### Transition metal-chelate catalysts

- Catalyst screening
  - Mo-Ru-Se/C, Ru-N/C, Ru-Fe-N/C, Co-N/C, Fe-N/C, Cr-N/C, Cu-N/C, Ni-N/C
- Specific focus
  - Ru-N/C, Ru-Fe-N/C, Co-N/C

2005

### Carbon-based metal-free catalysts

- Surface modification of porous carbon with:
  - (i) oxygen functional group
  - (ii) nitrogen functional group
  - (iii) non-metallic additive "X"

2006 - 2008

### Carbon composite catalysts

- Use of metal-free catalysts as a catalyst support
- "Metal-catalyzed pyrolysis" to increase the number of active sites
- Chemical post-treatment
- Fuel Cell and stability testing according to DOE test protocol



# Technical Accomplishments

- ❑ Highly active carbon-based metal-free catalysts were developed.
  - ❑ Carbon activation methodology was developed to synthesize metal-free catalyst with surface functional groups.
  - ❑ Onset potential as high as 0.82 V vs. SHE was obtained.
  - ❑ No H<sub>2</sub>O<sub>2</sub> generation (FOUR electron pathway for ORR).
- ❑ Highly active carbon composite catalysts were developed.
  - ❑ Metal-free catalyst was used as a catalyst support to increase the activity and selectivity.
  - ❑ Metal-catalyzed pyrolysis process was developed to increase the concentration of active sites and the stability.
  - ❑ The post-heat-treatment and chemical treatment were optimized.
  - ❑ FOUR electron pathway for ORR.
  - ❑ 10% performance degradation in fuel cell after 480 h of continuous operation.
- ❑ Accelerated corrosion test for Pt catalysts on different supports
  - ❑ 15% loss in catalyst activity was observed after 50 h testing.



# Specific Focus on Carbon-Based Catalysts (FY 2005 - 2008)

**OVERALL OBJECTIVE:** To develop highly active carbon-based catalyst with:

- active reactions sites with strong Lewis basicity ( $\pi$  electron delocalization) to facilitate reductive  $O_2$  adsorption
- nano-structured graphitic carbon with high stability

## **Carbon-based metal-free catalyst (MFC)**

### **Optimization of active reaction sites**

**as a function of:**

- (1) **surface oxygen groups**
- (2) **nitrogen content and precursor**
- (3) **carbon support**
- (4) **porosity and pore size distribution**
- (5) **pyrolysis temperature**
- (6) **non-metallic additive "X"**

## **Carbon composite catalyst**

**The following steps were performed to**

**develop carbon composite catalyst:**

- (1) **Use of metal-free catalyst as a catalyst support**
- (2) **Metal-catalyzed pyrolysis to increase the number of active sites**
- (3) **Chemical post-treatment**

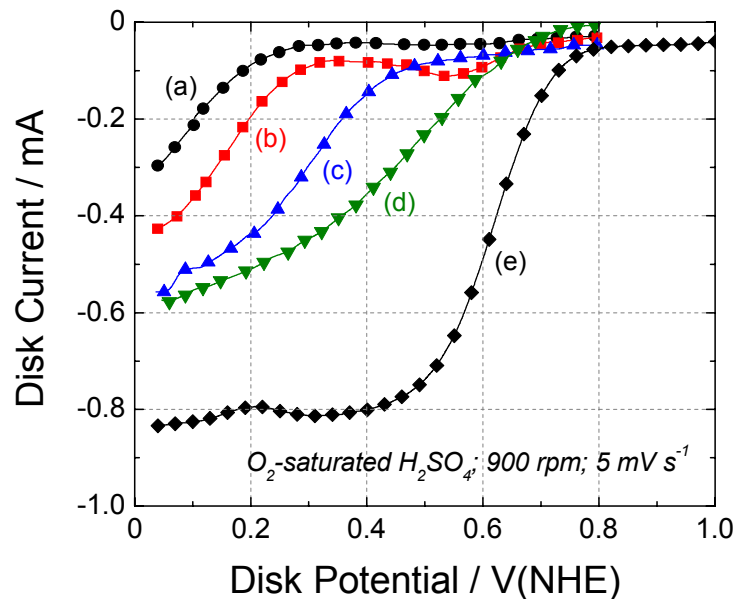
## **Durability test**

**The following catalysts were tested**

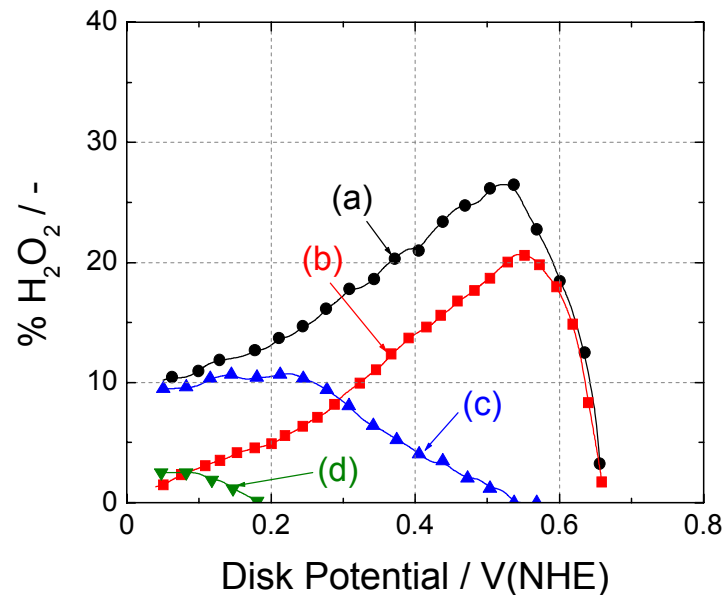
- (1) **Pt/CC1**
- (2) **Pt/CC2**



# Carbon-Based Metal-Free Catalysts



(a) as-received carbon; (b) Treatment with  $HNO_3$ ;  
 (c) Treatment with  $NH_3$ ; (d) USC Methodology - 1;  
 (e) USC Methodology - 2

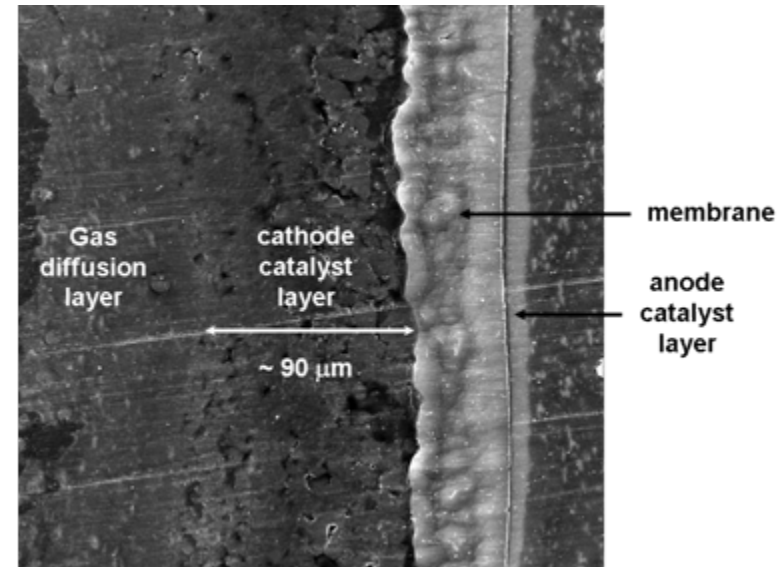
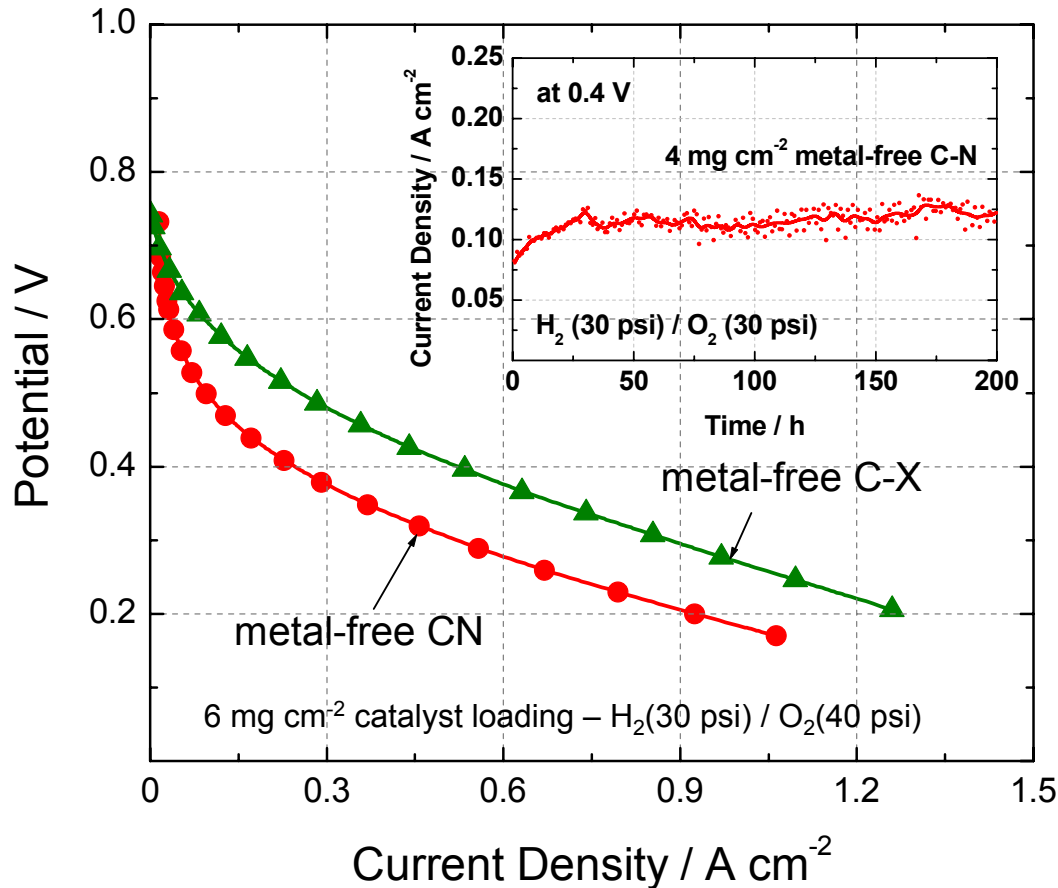


(a) MFC-1; (b) MFC-2;  
 (c) MFC-3; (d) MFC-4

- HIGHLIGHT:** The USC methodology increases the onset potential for oxygen reduction by ca. 500 mV, as compared with the as-received carbon.
- The USC-developed “MFC-4” catalyzes oxygen reduction to water via four-electron transfer with no  $H_2O_2$  production (above 0.2 V vs. NHE).



# Carbon-Based Metal-Free Catalysts

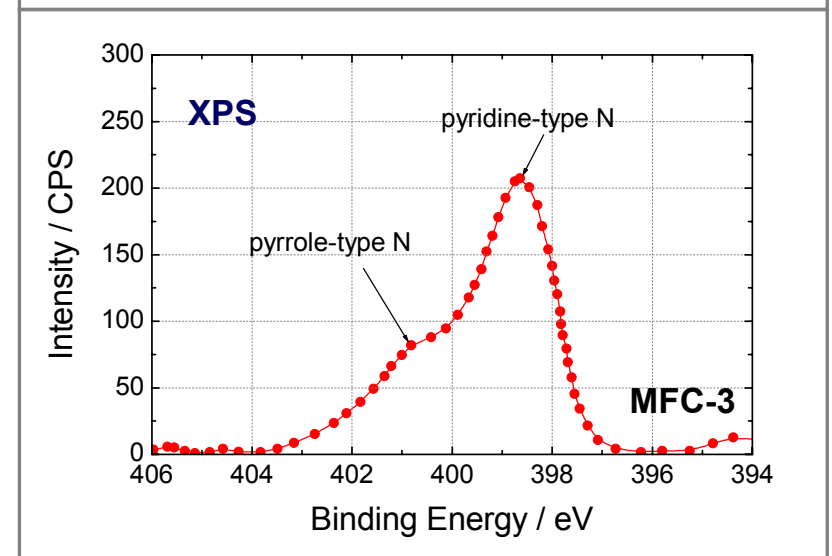
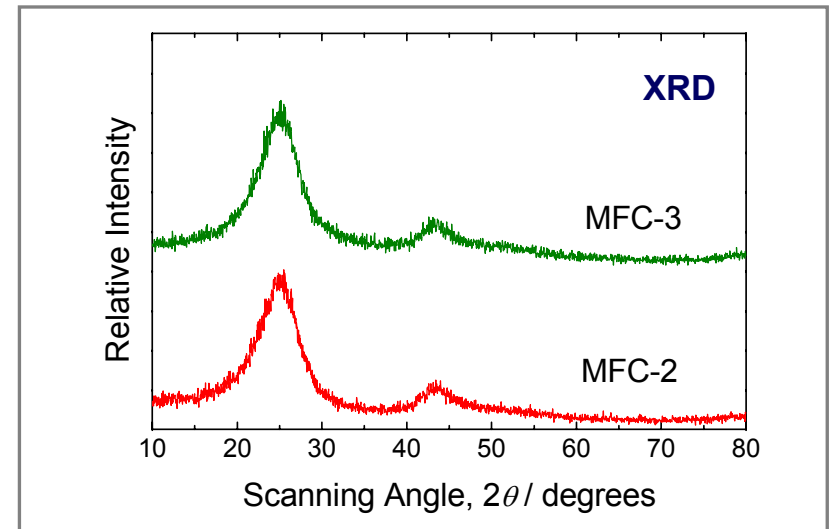
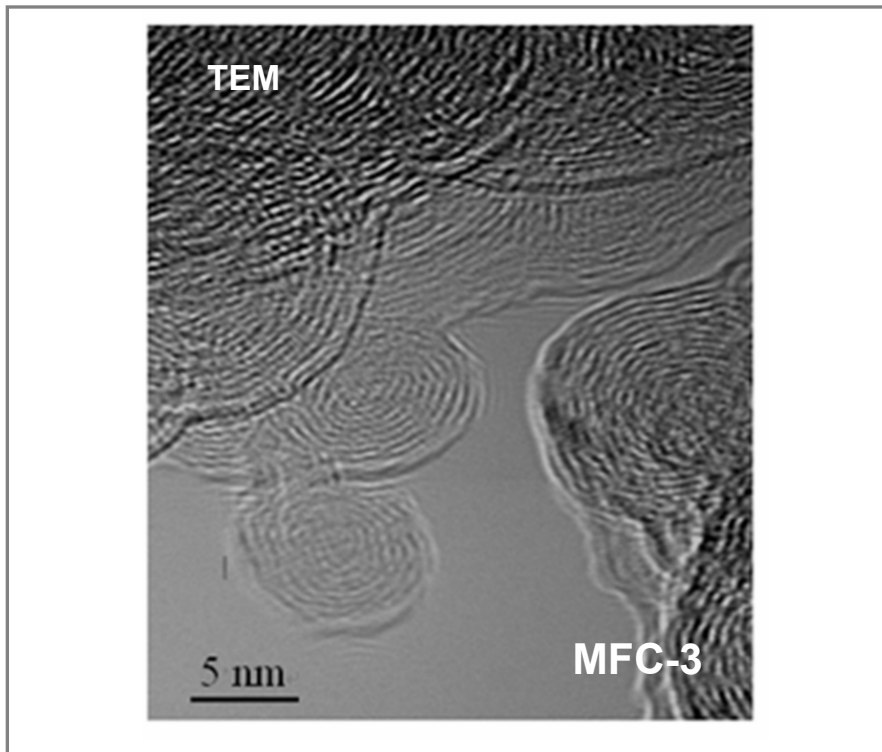


Cross-section of MEA with the metal-free C-X cathode catalyst.

- **Anode:** 2 mg cm<sup>-2</sup> of ETEK 20% Pt/C
- **Membrane:** Nafion™ 112
- **Operating temperature:** 77 °C (H<sub>2</sub>); 75 °C (O<sub>2</sub>); 75 °C (cell)



# Carbon-Based Metal-Free Catalysts

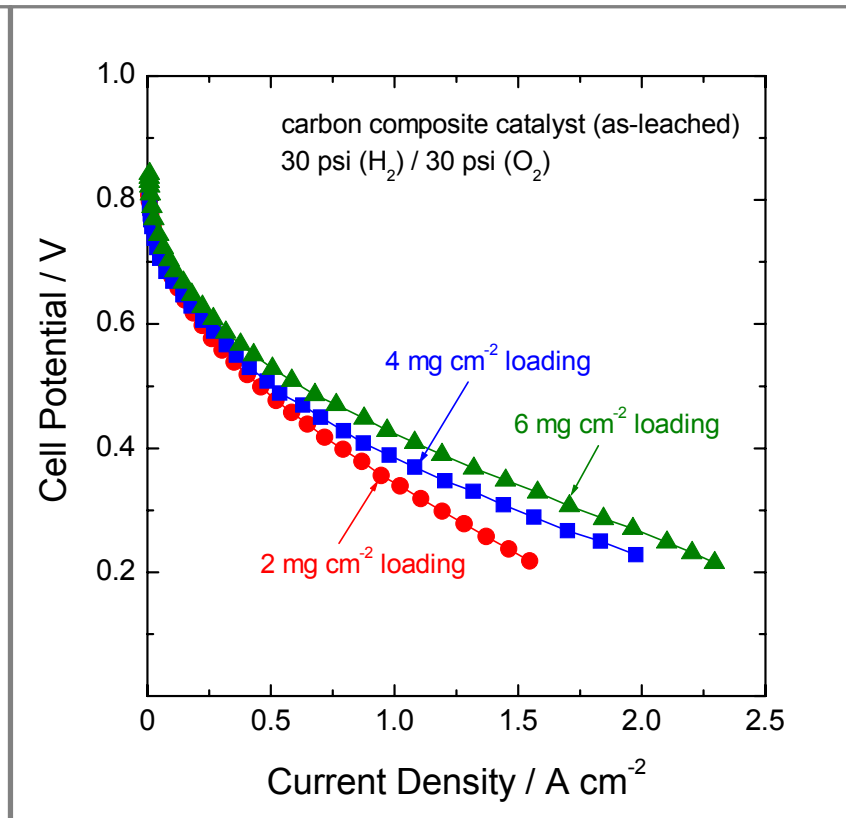
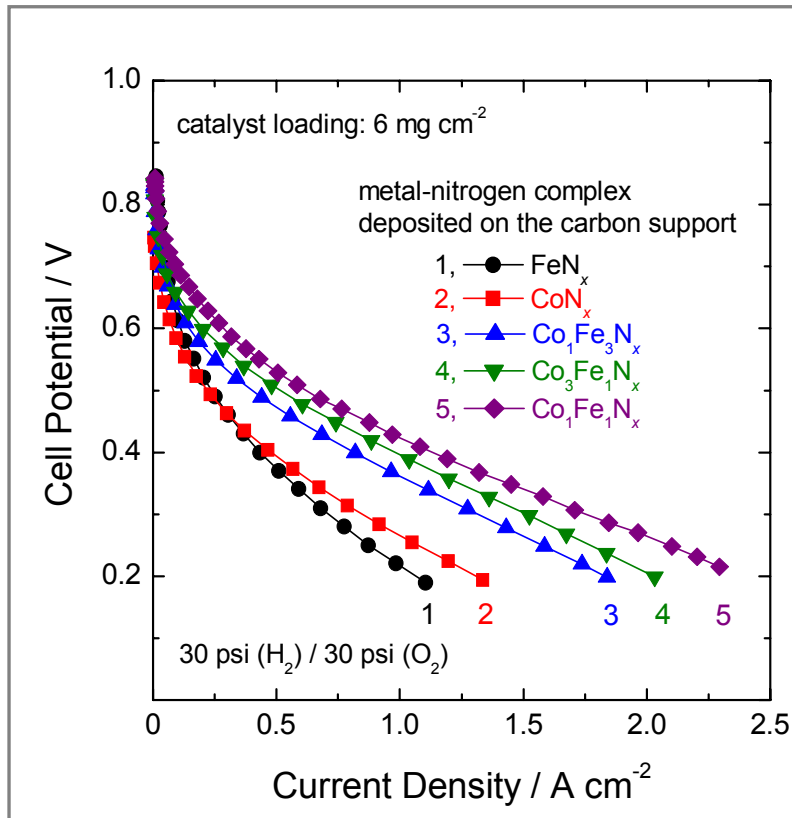


- **HIGHLIGHT: TEM & XRD:** No metallic elements in the synthesized catalysts.
- **XPS:** High-temperature pyrolysis leads to the formation of pyrrole- and pyridine-type nitrogen.





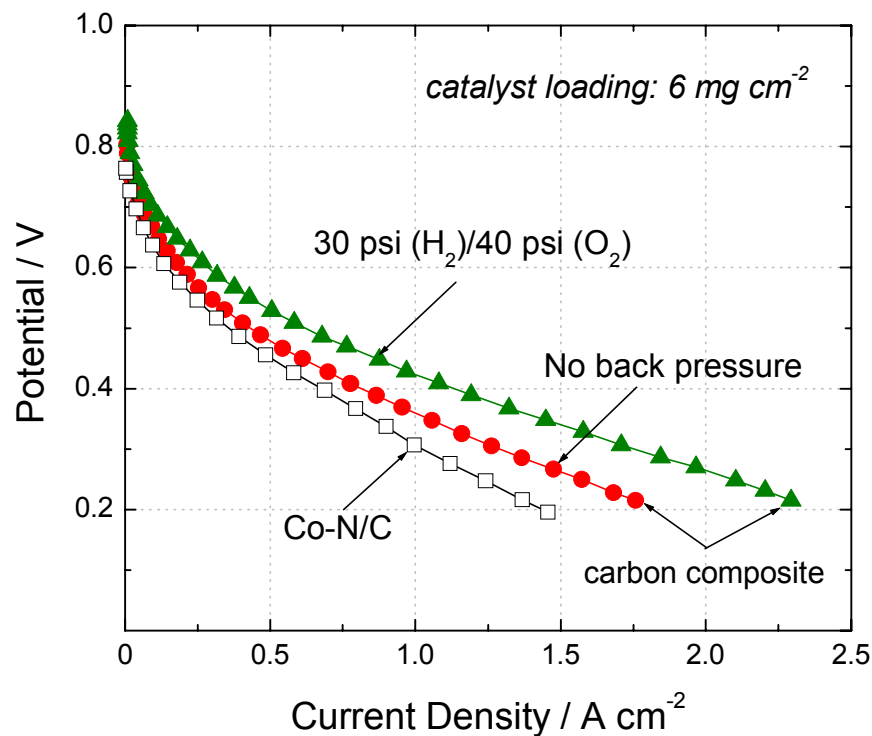
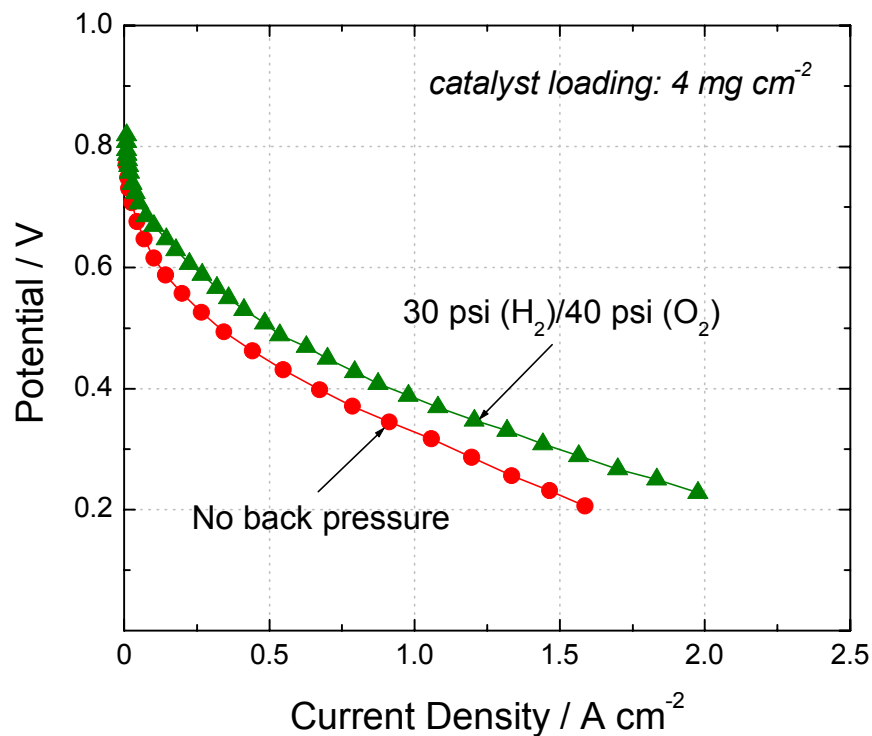
# Carbon Composite Catalysts



- **HIGHLIGHT:** Co-Fe-N complex showed improved activity when compared to Co-N and Fe-N catalysts.
- $Co_1Fe_1N_x$  showed maximum fuel cell performance at  $6\ mg\ cm^{-2}$  catalyst loading.



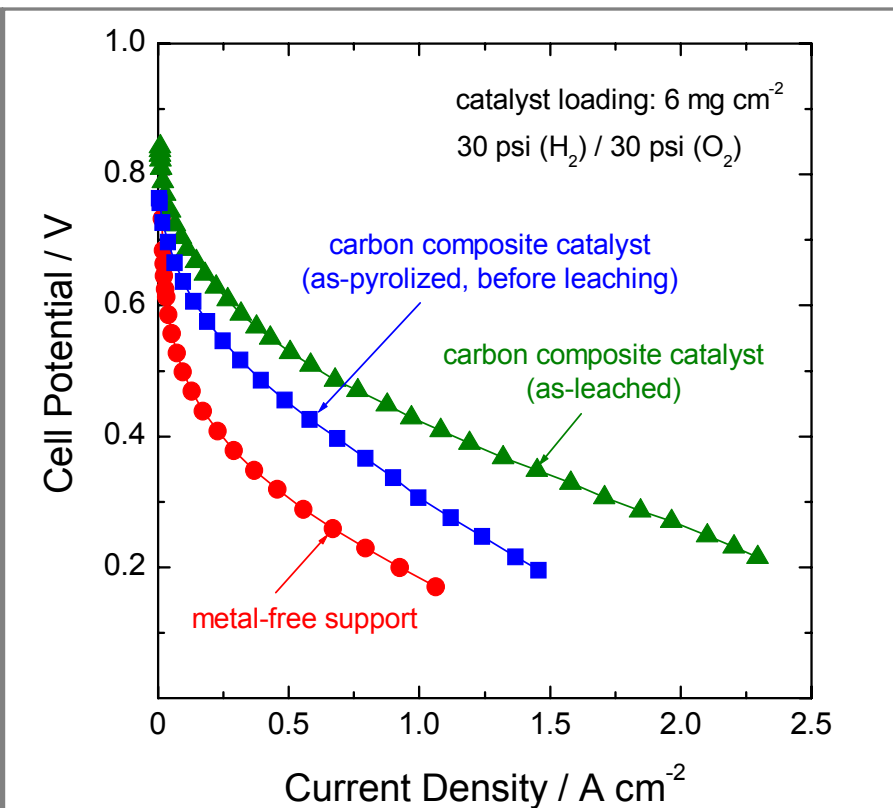
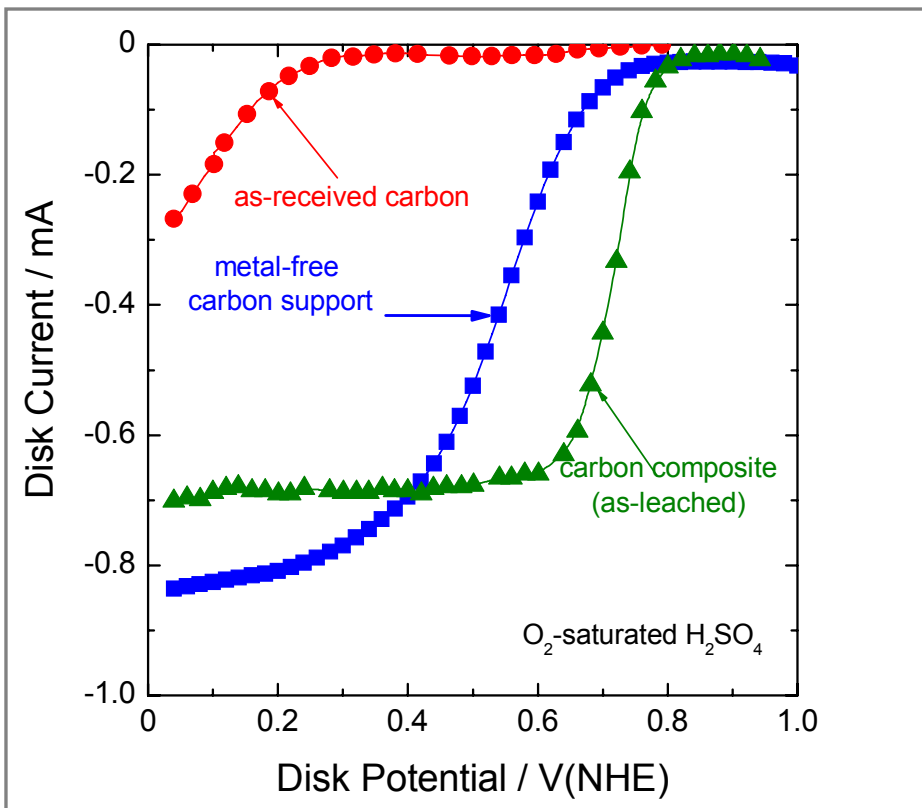
# Carbon Composite Catalysts



- **Anode:** 2 mg cm<sup>-2</sup> of E-TEK 20% Pt/C (0.4 mg cm<sup>-2</sup> Pt)
- **Cathode:** 4 or 6 mg cm<sup>-2</sup> of carbon composite catalyst
- **Membrane:** Nafion™ 112
- **Operating temperature:** 77 °C (H<sub>2</sub>); 75 °C (O<sub>2</sub>); 75 °C (cell)



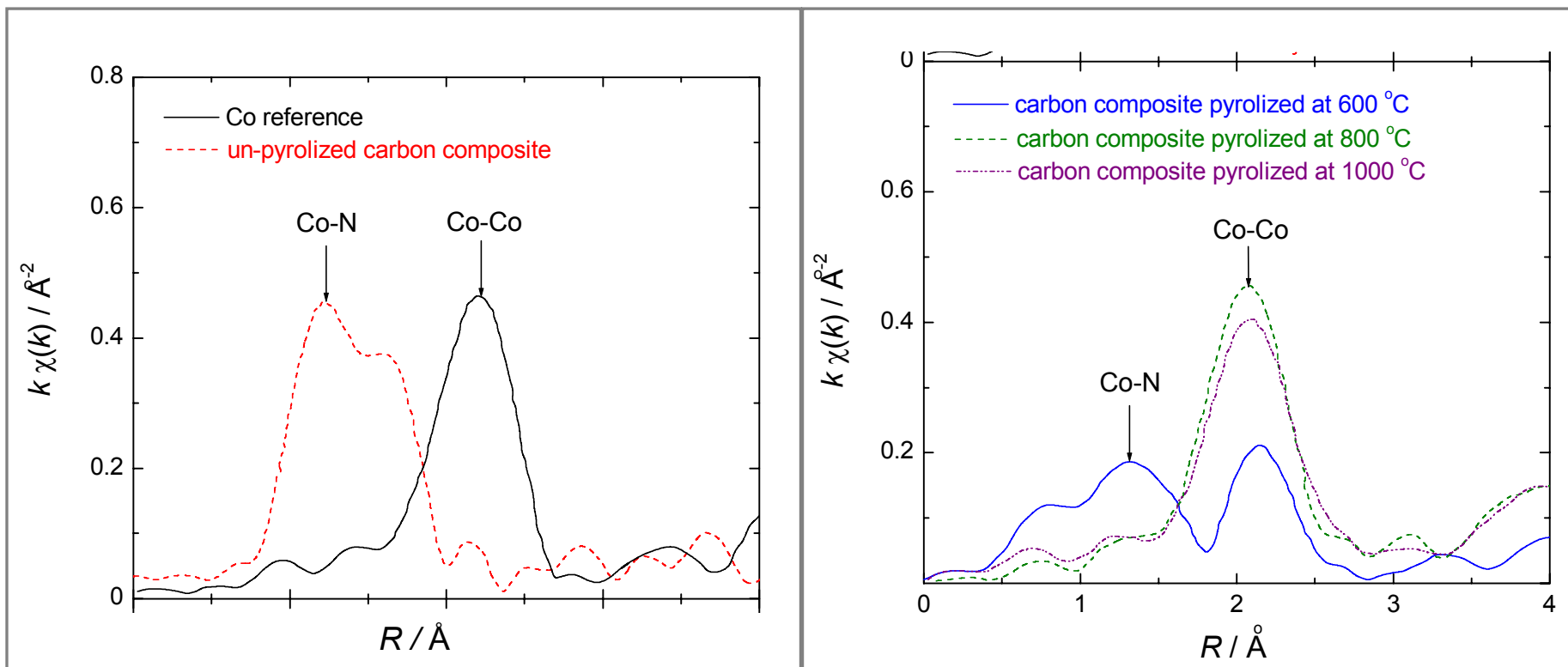
# Metal-Free and Carbon Composite Catalysts – A Comparison



- **HIGHLIGHT:** Metal-nitrogen complexes are responsible for the activity.
- Chemical leaching increases the activity.



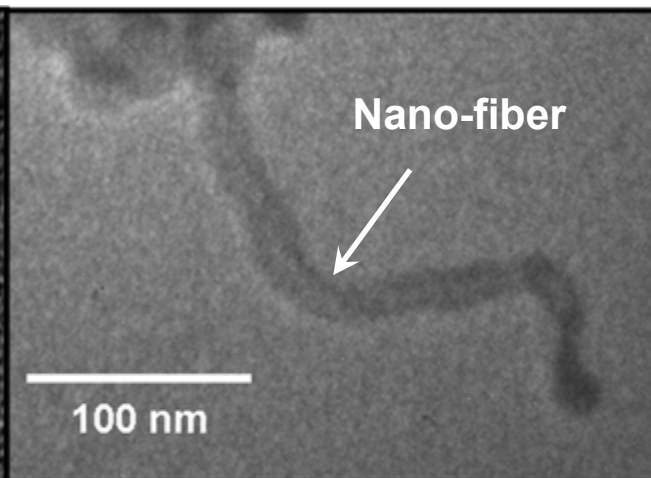
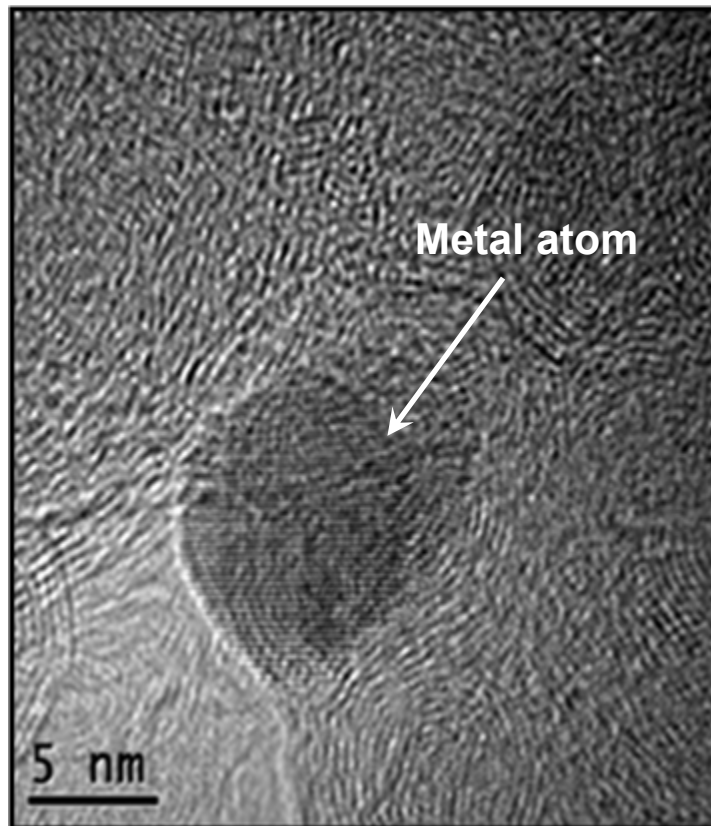
# Carbon Composite Catalysts



- **HIGHLIGHT: Metal-N complex is not responsible for ORR activity**
- **Un-pyrolyzed catalyst shows only Co-N peak**
- **Co-Co peak intensity increases with increase in pyrolysis temperature**
- **CoN<sub>x</sub> complex decomposes above 800 °c**
- **Co-Co peak is Predominantly observed above 800 °C**



# Carbon Composite Catalysts



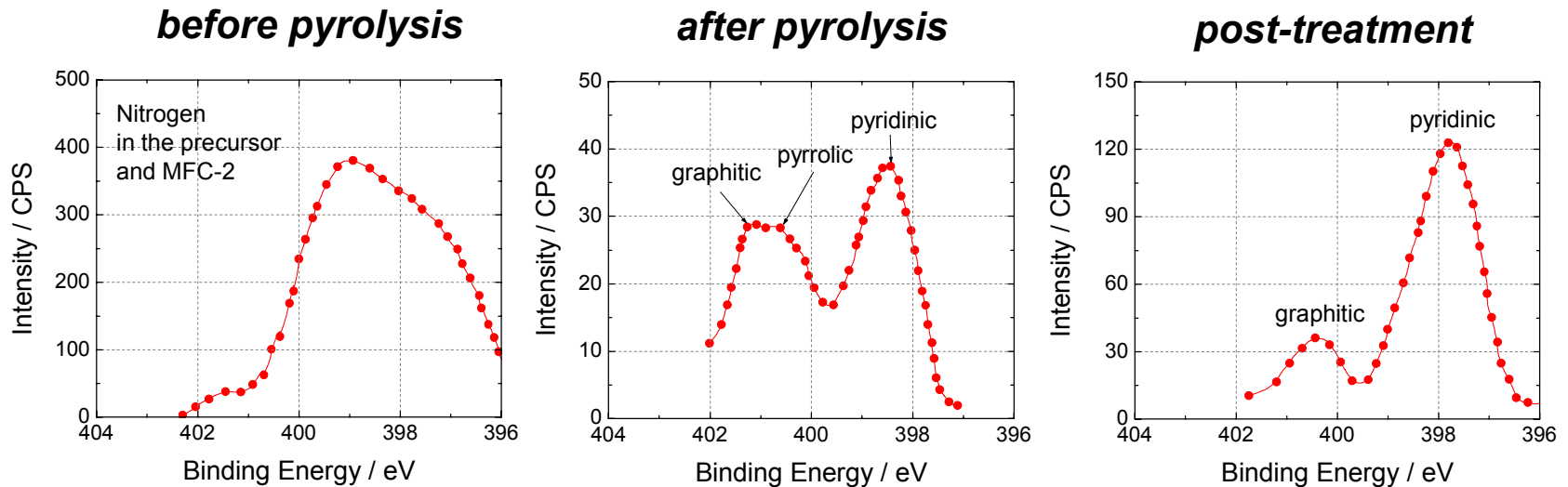
Surface concentration determined by XPS

C	O	N	Co	Fe
94.86	1.26	3.88	-	-

- **HIGHLIGHT:** Metal atoms are covered with several graphitic layers.
- Nanostructured fiber of graphitic carbon was formed as a result of metal-catalyzed pyrolysis.
- No metal traces were detected on the surface of carbon composite catalyst.



# Carbon Composite Catalysts



**Potential**

**Current density (A cm<sup>-2</sup>)**

**0.7 V**

**0**

**0.03 with ~15% H<sub>2</sub>O<sub>2</sub>**

**0.05 with ~1.5% H<sub>2</sub>O<sub>2</sub>**

**0.4 V**

**0.3 with ~ 37% H<sub>2</sub>O<sub>2</sub>**

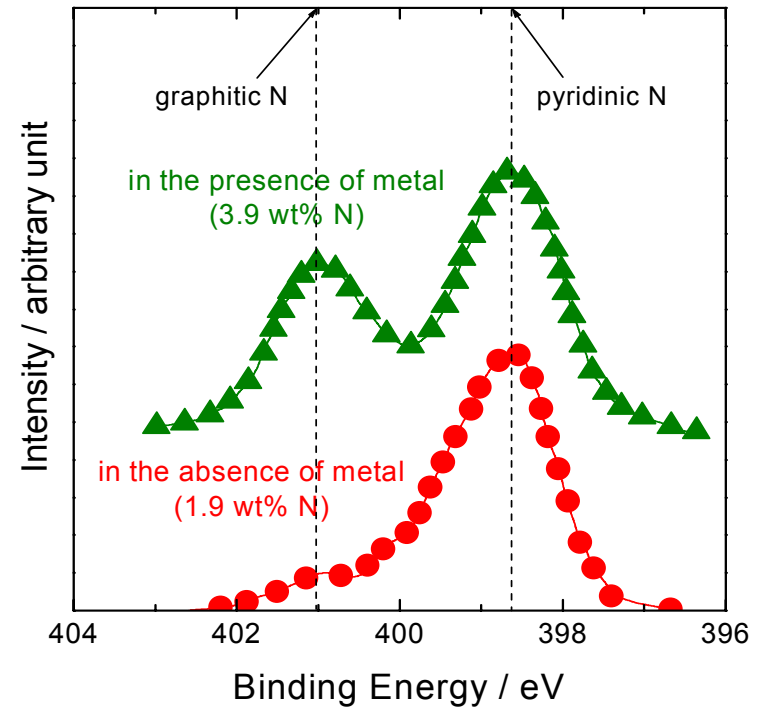
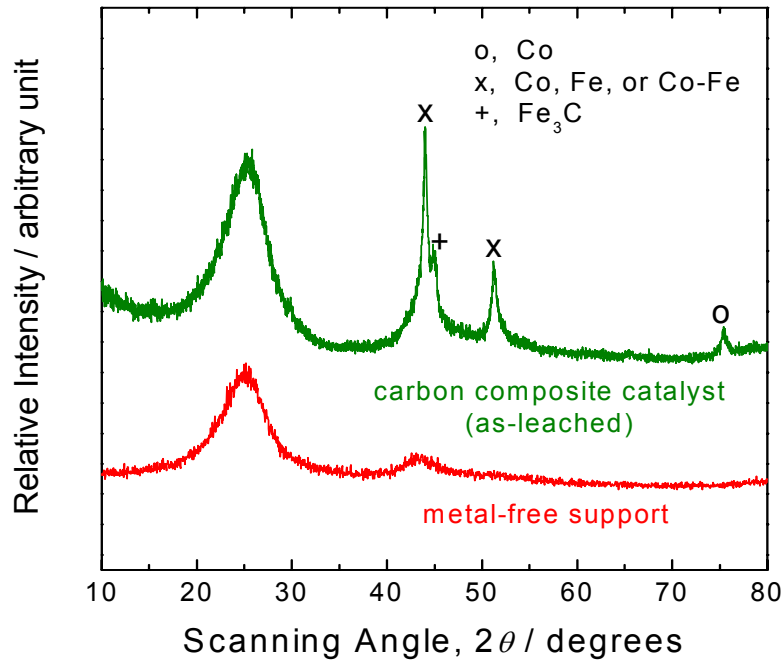
**0.7 with ~ 10% H<sub>2</sub>O<sub>2</sub>**

**0.9 with ~1.5% H<sub>2</sub>O<sub>2</sub>**

- **HIGHLIGHT:** High-temperature pyrolysis increases the Lewis basicity due to the increased concentration of pyridine-type nitrogen, and incorporates the nitrogen into graphitic structures which increases the stability.
- **Post-treatment** increases the concentration of pyridinic-type nitrogen while removing pyrrolic-type nitrogen.

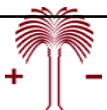


# Carbon Composite Catalysts

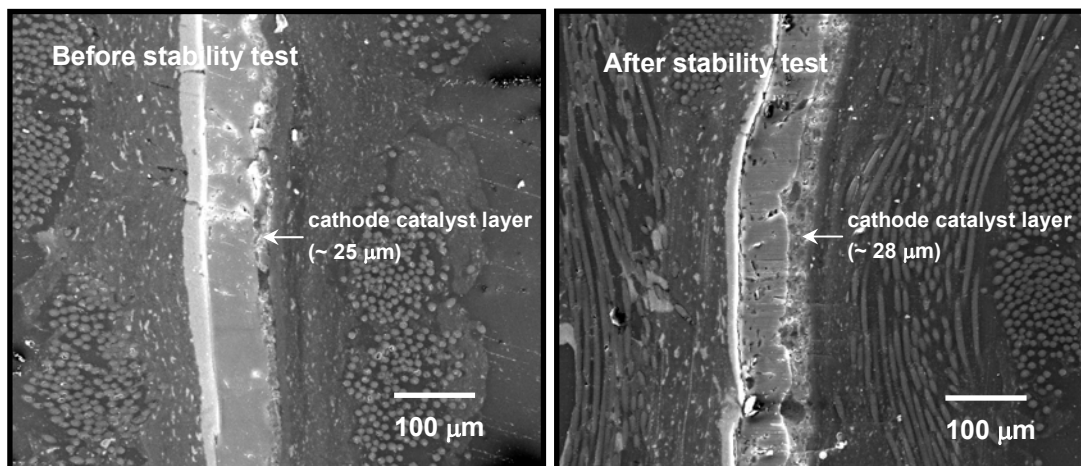
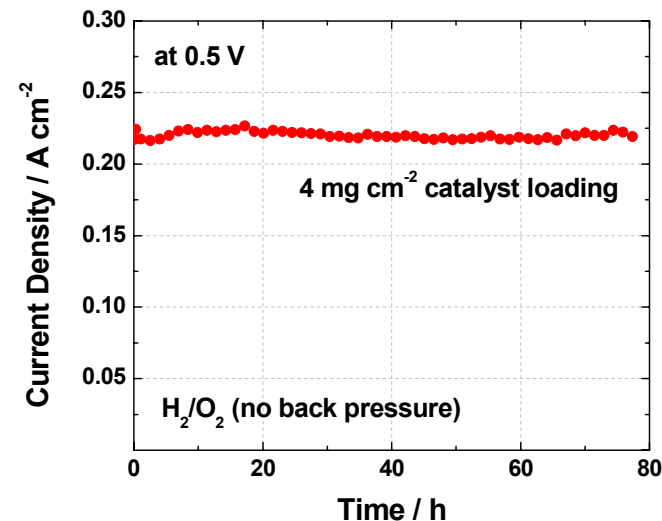
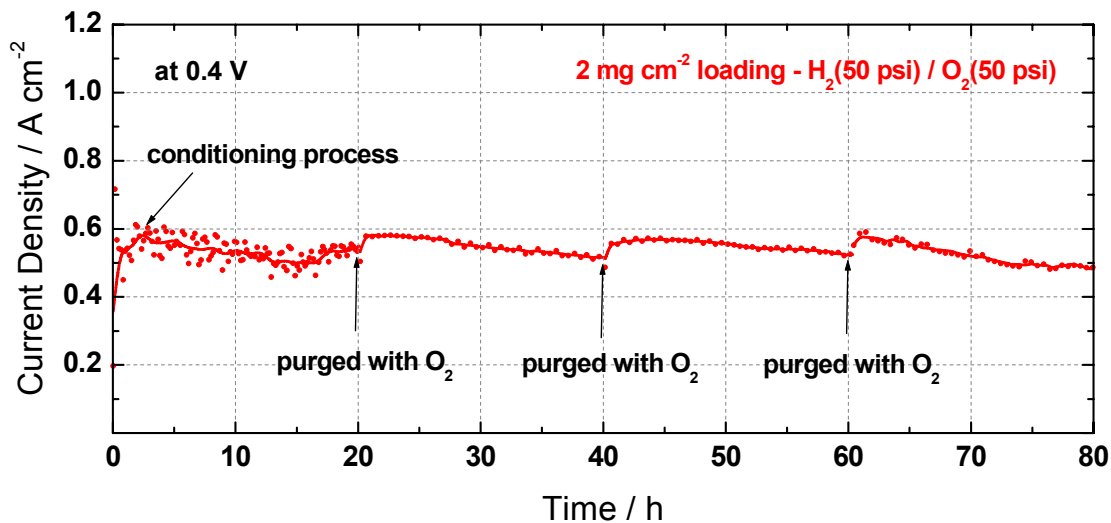


Analytical technique		Concentration (wt.%)	
		Co	Fe
ICP-MS	Before leaching	10.4	9.6
	After leaching	4.6	1.41
XPS	After leaching	0	0

- **HIGHLIGHT: Transition metal increases the  $\text{N}_2$  content**
- **Fe and Co contents decreased after leaching**
- **Chemical leaching removes surface metal particles only**
- **Metal particles are encased within the carbon structure**



# Carbon Composite Catalysts – Durability Study



- **HIGHLIGHT:** No significant degradation of the catalyst is observed.

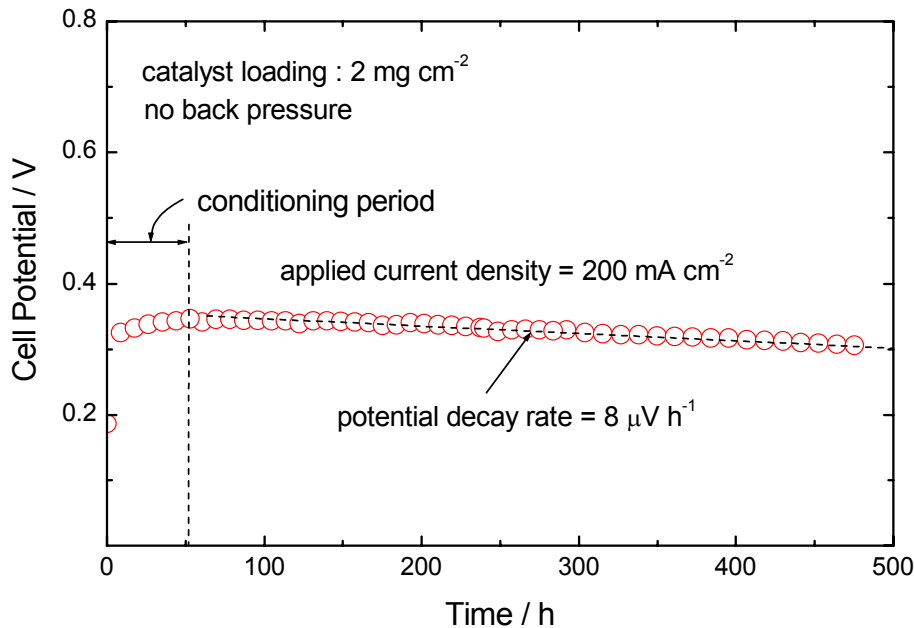
- Water management should be optimized.

Cross-section of MEA with the carbon composite cathode catalyst (2 mg cm<sup>-2</sup>) before and after stability test for 80 h

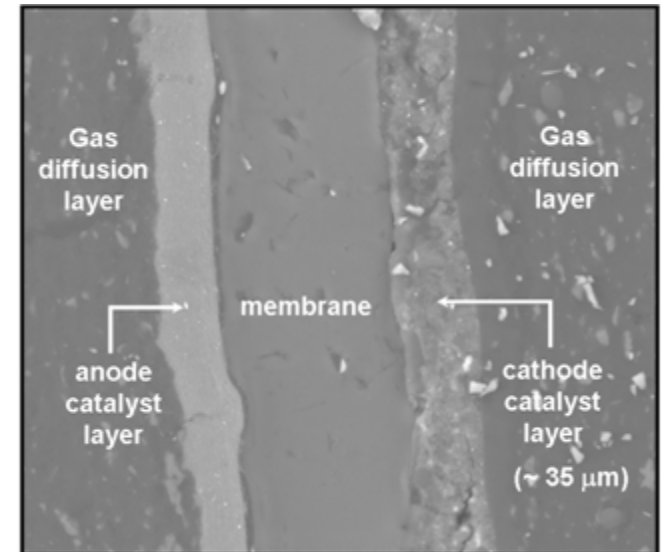
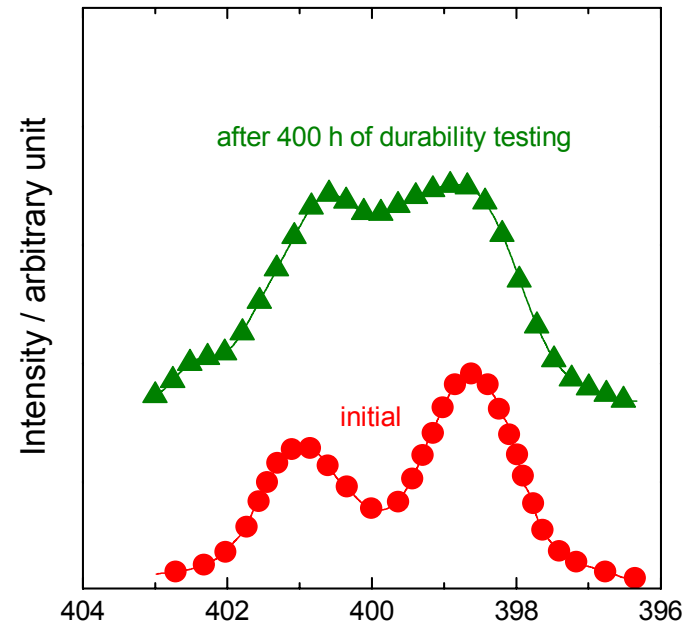




# Carbon Composite Catalysts – Durability Study

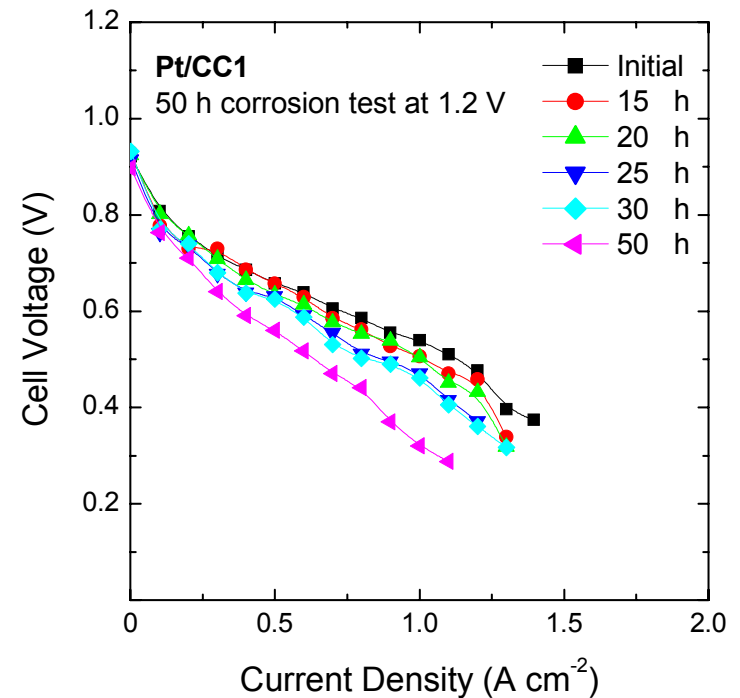


- **HIGHLIGHT:** Approximately 10% performance decrease over 480 h.
- Catalytically active nitrogen functional groups remain stable during long-term operation.
- Thick catalyst layer causes water management problem during operation.



# Accelerated Corrosion Test of Different Supports

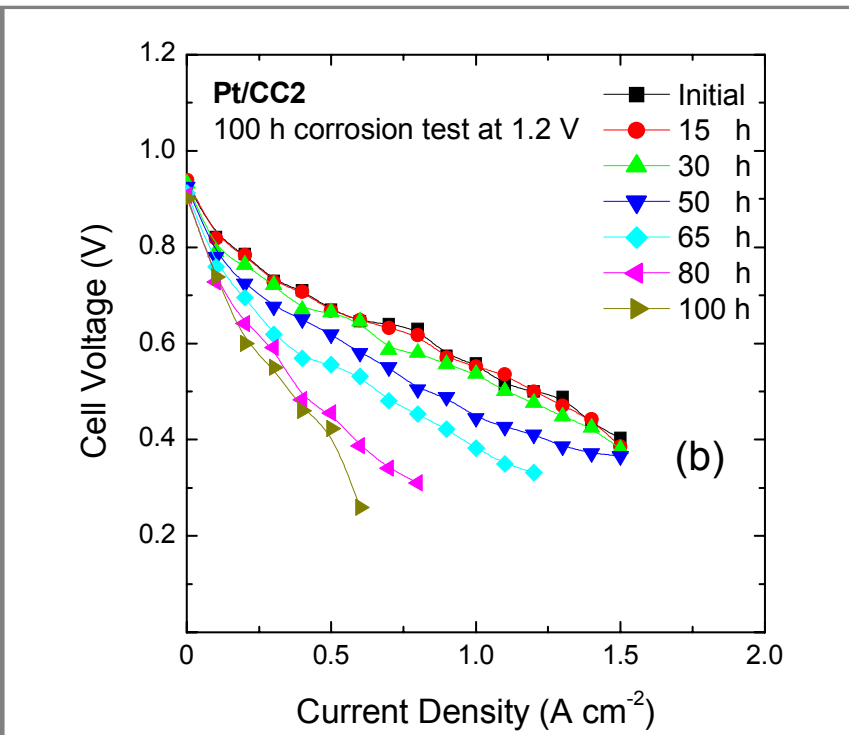
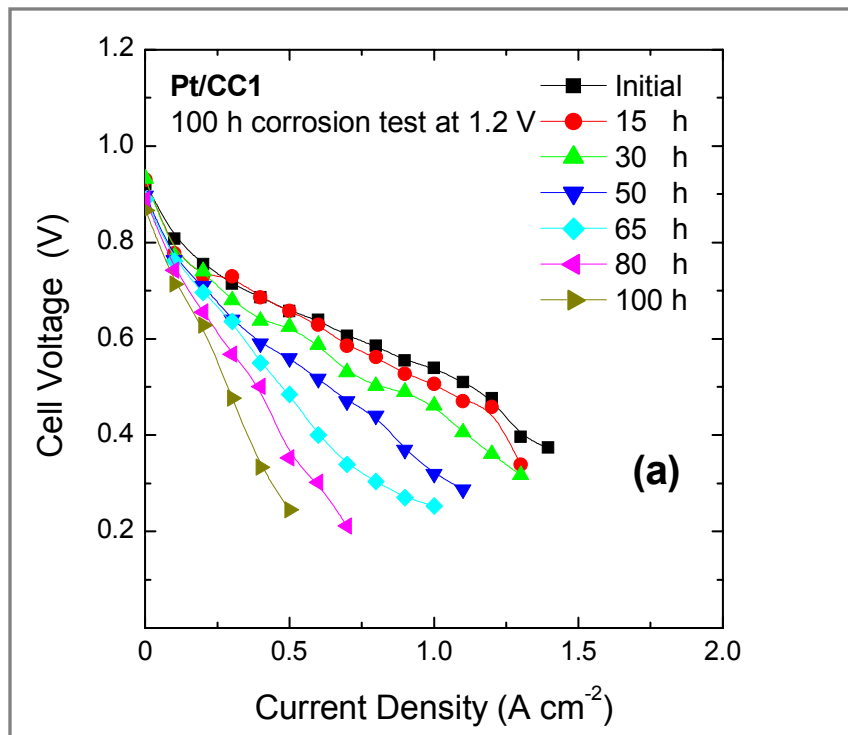
- Fuel cell start-up,
- Measure polarization curve under H<sub>2</sub>/air (Relative humidity, RH = 50 %),
- apply 1.2 V at 80 °C under H<sub>2</sub>/N<sub>2</sub> (RH = 100 %) for 15 hrs,
- Measure polarization curve under H<sub>2</sub>/air (RH = 50 %),
- Apply 1.2 V at 80 °C under H<sub>2</sub>/N<sub>2</sub> (RH = 100 %) for 5 hrs or more and
- Repeat procedure of (iv) and (v).



Corrosion time	Pt/CC1		GM catalyst	
	%E <sub>loss</sub> @ 0.5A cm <sup>-2</sup>	%E <sub>loss</sub> @ 1.0A cm <sup>-2</sup>	%E <sub>loss</sub> @ 0.5A cm <sup>-2</sup>	%E <sub>loss</sub> @ 1.0A cm <sup>-2</sup>
15 h	0	6.3	0.9	2.7
20 h	3.5	6.7	1.1	3.1
25 h	3.9	12.8	2.7	7.1
30 h	4.9	14.7	6.7	11.5
50 h	14.8	40.8	36	N/A



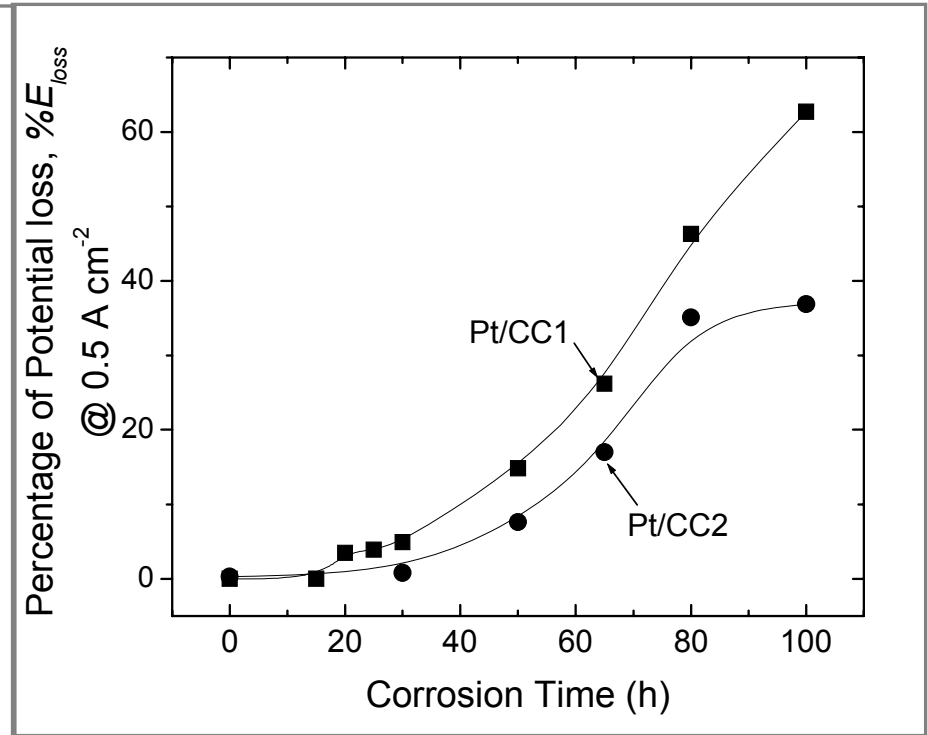
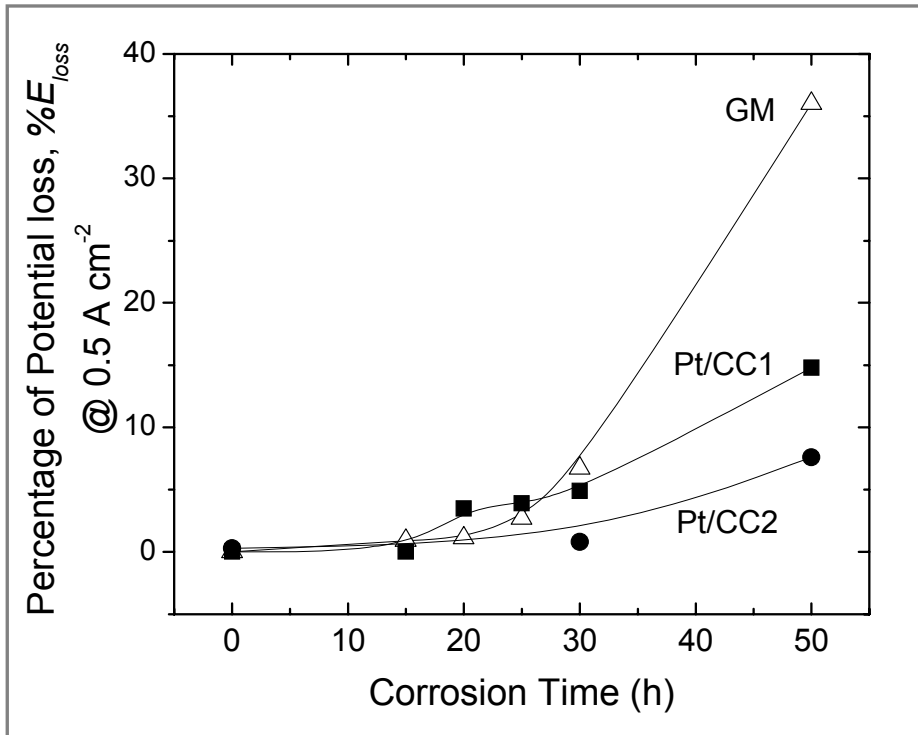
# Accelerated Corrosion Test of Different Supports



- **HIGHLIGHT:** Pt/Carbon composite 2 (Pt/CC2) performs better than GM catalyst
- Pt/CC2 shows lower degradation than Pt/CC1 and GM catalyst
- Multilayer structure of Pt/CC2 modifies the carbon surface and lowers carbon corrosion



# Accelerated Corrosion Test of Different Supports



•**HIGHLIGHT:** Slower decrease in catalytic activity (7.6 – 14.8%) than GM catalyst (36%) at 0.5 Acm<sup>-1</sup> when polarized at 1.25 V.



# Future Work

- To further improve the durability of carbon composite catalysts by controlling hydrophobicity of catalyst layer and by increasing the activity and by reducing the catalyst layer thickness.
- To eliminate the water flooding of USC developed non-platinum catalyst.
- To increase the fuel cell durability by optimizing the MEA preparation conditions – including (i) Nafion loading on the catalyst layer, (ii) calendaring process of the catalyst layer, (iii) hot-pressing load, etc.
- To develop low Pt loading cathode by using carbon composite catalysts as novel supporting materials.



# Summary

- ❑ **Objective:** Develop carbon-based metal-free catalysts and carbon composite catalysts for PEMFC which perform as well 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 (0.82 – 0.85 V vs. SHE), selectivity (0 – 1 % H<sub>2</sub>O<sub>2</sub>) and stability (for 80 h) for carbon-based catalysts.
- ❑ **Collaborations:** Active partnership with Case Western Reserve University and Northeastern University. Northeastern University was unable to prepare stable Co chalcogenide catalysts.
- ❑ **Proposed future research:** Optimize MEA performance and stability with the carbon composite catalysts by improving water management and low Pt loading catalyst using carbon composite as support.

