

## V.E.2 Novel Non-Precious Metal Catalysts for PEMFC: Catalyst Selection through Molecular Modeling and Durability Studies

Branko N. Popov

University of South Carolina  
301 Main Street  
Columbia, SC 29208  
Phone: (803) 777-7314; Fax: (803) 777-8265  
E-mail: popov@enr.sc.edu

DOE Technology Development Manager:  
Nancy Garland

Phone: (202) 586-5673; Fax: (202) 586-9811  
E-mail: Nancy.Garland@ee.doe.gov

DOE Project Officer: Reg Tyler

Phone: (303) 275-4929; Fax: (303) 275-4753  
E-mail: Reginald.Tyler@go.doe.gov

Technical Advisor: John Kopasz

Phone: (630) 252-7531; Fax: (630) 972-4405  
E-mail: kopasz@cmt.anl.gov

Contract Number: DE-FC36-03GO13108

Subcontractors:

- Dr. Alfred B. Anderson, Case Western Reserve University, Cleveland, OH
- Dr. Sanjeev Mukerjee, Northeastern University, Boston, MA

Start Date: September 30, 2003

Projected End Date: March 31, 2008

### Objectives

- Synthesize carbon-based metal-free catalysts and carbon composite catalysts for the oxidation reduction reaction (ORR).
- Optimize catalytic active reaction sites as a function of carbon support, surface oxygen groups, nitrogen content, surface modifiers, pyrolysis temperature, porosity, and the concentration of the non-metallic additive "X" in the catalyst matrix.
- Evaluate catalyst stability under various conditions to demonstrate the potential of carbon-based catalysts to substitute conventional Pt catalysts currently used in membrane electrode assemblies (MEAs).

### Technical Barriers

This project addresses the following technical barriers from the Fuel Cells section of the Hydrogen, Fuel Cells and Infrastructure Technologies Program

Multi-Year Research, Development and Demonstration Plan:

- (A) Durability
- (B) Cost
- (C) Performance

### Technical Targets

- Non-Pt catalyst activity per volume of supported catalyst (Year 2010):  $>130 \text{ A cm}^{-3}$  (stack) at 0.8 V<sub>IR-free</sub>
- Cost: at least 50% less than a target of 0.2 g (Pt loading)/peak kW
- Durability:  $>2,000$  h operation with less than 10% power degradation

### Accomplishments

- Carbon-based metal-free catalysts
  - Accomplished the catalytic activity as high as  $1.3 \text{ A cm}^{-2}$  at 0.2 V for  $6 \text{ mg cm}^{-2}$  catalyst loading in the fuel cell.
  - No irreversible loss of catalytic activity during 200 h of continuous operation.
- Metal-free CN-X and C-X catalysts
  - Optimized "catalyzed pyrolysis" conditions to increase the concentration of the active reaction sites.
  - Accomplished the catalytic activity as high as  $2.0 \text{ A cm}^{-2}$  at 0.2 V for  $4 \text{ mg cm}^{-2}$  catalyst loading in the fuel cell.
  - No irreversible loss of catalytic activity during 80 h of continuous operation.



### Introduction

Currently Pt and Pt alloys are widely used as cathode catalysts in proton exchange membrane fuel cells (PEMFCs) because of their high catalytic activity and selectivity as well as high corrosion resistance. In the last few years, several transition metal compounds such as macrocycle-based metal porphyrin systems, chevre phase-type compounds and other transition metal chalcogenides have been proposed as selective catalysts for the ORR. However, significant increase in activity and stability of the catalyst is still essential for PEMFC applications. The objective of this project is to

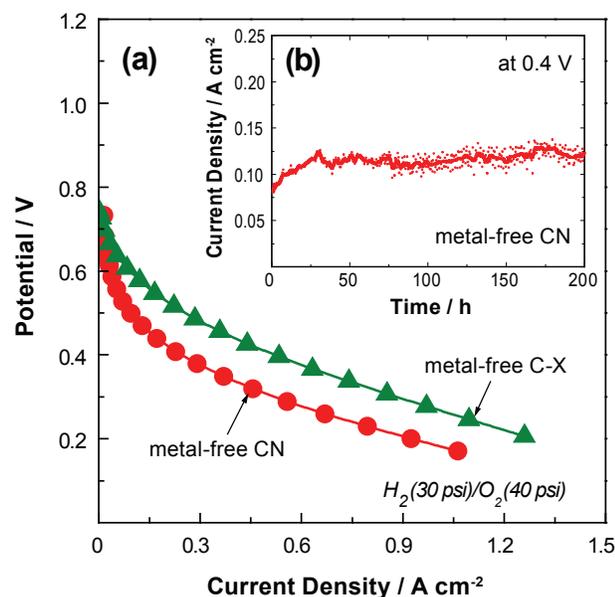
develop highly active and stable carbon-based metal-free catalysts and carbon composite catalysts with strong Lewis basicity ( $\pi$  electron delocalization) to facilitate the ORR.

## Approach

Carbon-based metal-free catalysts were synthesized by modifying the surface functional groups on the porous carbon black with low-cost organic precursors. The active reaction sites for the ORR were optimized as a function of: (i) carbon support, (ii) surface oxygen groups, (iii) nitrogen content, (iv) pyrolysis temperature, (v) porosity, (vi) pore size distribution and (viii) the concentration of the non-metallic additive “X”. As a next step, highly active carbon composite catalysts were developed using a metal-free catalyst as a catalyst support through catalyzed pyrolysis, followed by chemical post-treatments.

## Results

Figure 1(a) presents the fuel cell performance with a loading of  $6 \text{ mg cm}^{-2}$  of the metal-free CN and C-X catalysts. Here, C, N and X stand for carbon, nitrogen and non-metallic additive, respectively. The tests were run at  $75^\circ\text{C}$  with  $\text{H}_2$  and  $\text{O}_2$  using the back pressures of 30 and 40 psi, respectively. Ohmic potential drop was not compensated for in the measurement. For the metal-free C-X catalyst, the current density was measured to be  $1.3 \text{ A cm}^{-2}$  at 0.2 V. Figure 1(b) shows the current transient measured at 0.4 V for a stability test of the fuel cell loaded with  $4 \text{ mg cm}^{-2}$  of the metal-free C-N catalyst.



**FIGURE 1.** (a) Fuel Cell Performance of the Metal-Free CN and C-X Catalysts, and (b) Stability Test Data for the CN Catalyst

The result shows an initial increase of current density to ca.  $0.12 \text{ A cm}^{-2}$  and then a steady-state current profile without showing performance degradation for up to 200 h.

The carbon composite catalyst was developed using a metal-free catalyst as a catalyst support through catalyzed pyrolysis followed by chemical post-treatments. In this process the pyrolysis in the presence of transition metals facilitates and stabilizes the incorporation of nitrogen within the graphene matrix. The nature of nitrogen functional groups was identified using XPS at each synthesis step: (i) before “catalyzed pyrolysis”, (ii) after “catalyzed pyrolysis”, and (iii) after chemical post-treatment, and the results are summarized in Table 1 along with the fuel cell performance. The current density and the amount of  $\text{H}_2\text{O}_2$  were determined at 0.4 V in a fuel cell and an rotating ring disk electrode (RRDE), respectively.

The activity and selectivity gradually increased after pyrolysis and after chemical post-treatment. X-ray photoelectron spectroscopy (XPS) data obtained before pyrolysis show only nitrogen functional groups in the N-precursor. High-temperature pyrolysis results in the formation of pyridinic, pyrrolic and graphitic nitrogen groups. Chemical post-treatment increases the relative concentration of pyridinic nitrogen, while removing pyrrolic nitrogen. XPS results indicate that high-temperature pyrolysis combined with chemical post-treatment increases the concentration of pyridine-type nitrogen resulting in the increased Lewis basicity, and

**TABLE 1.** Catalytic Activity, Selectivity and XPS Spectrum at Each Synthesis Step of Carbon Composite Catalyst

Step	Current Density ( $\text{A cm}^{-2}$ )	% $\text{H}_2\text{O}_2$	XPS
Before Pyrolysis	0	-	500 Nitrogen in the precursor
After Pyrolysis	0.32	5	40 graphitic pyrrolic pyridinic
After chemical post-treatment	0.88	0.5	120 graphitic pyridinic

incorporates the nitrogen into graphitic structures that increases the stability.

The catalyzed pyrolysis process was optimized to increase the concentration of active reaction sites for ORR and their stability. Figure 2(a) illustrates the fuel cell performance of carbon composite catalysts prepared under different pyrolysis conditions. The cathode catalyst loading was  $4 \text{ mg cm}^{-2}$ , and the tests were run with  $\text{H}_2$  (30 psi) and  $\text{O}_2$  (30 psi). Figure 2(b) presents the stability test data measured by applying 0.4 V at an ambient pressure. The optimized carbon composite catalyst (“procedure – C”) showed the current density of  $2.0 \text{ A cm}^{-2}$  at 0.2 V (Figure 2(a)), and exhibited a steady-state current profile after 15 h (Figure 2(b)).

Figure 3 shows the current transient (stability test performance) measured on the carbon composite catalyst as a function of time. The cathode catalyst

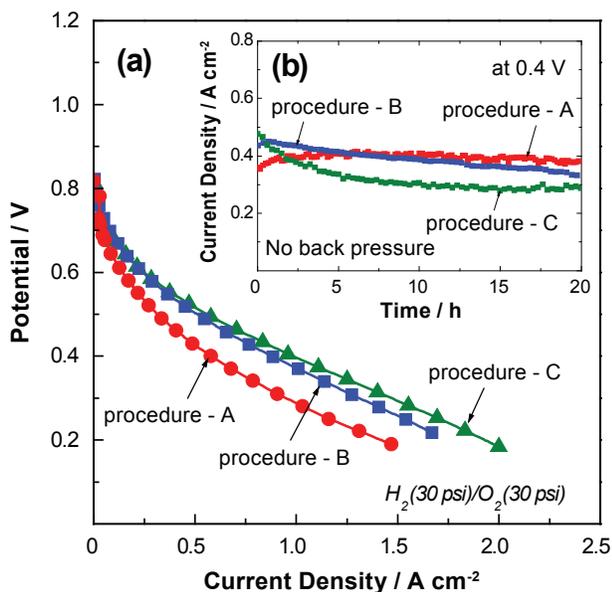


FIGURE 2. (a) Fuel Cell Performance and (b) Stability Test Data of the Carbon Composite Catalysts Prepared Under Different Pyrolysis Conditions

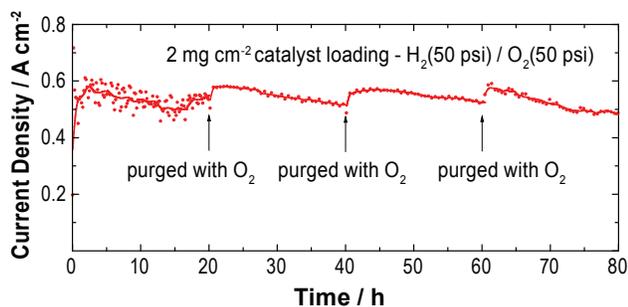


FIGURE 3. Typical Stability Test Data for the Carbon Composite Catalyst

loading was  $2 \text{ mg cm}^{-2}$ , and the tests were run using  $\text{H}_2$  (50 psi) and  $\text{O}_2$  (50 psi). As indicated in the figure, the cathode compartment was periodically purged with  $\text{O}_2$  gas during test, in order to remove liquid water accumulated inside the MEA. The result shows an initial increase of current density to ca.  $0.6 \text{ A cm}^{-2}$ , followed by a slight decay with time. The fuel cell performance was fully recovered upon  $\text{O}_2$  purging, which indicates that an ineffective water management is responsible for a slight performance loss of the PEMFC, and no irreversible loss of catalytic activity occurs.

Best performing catalysts are being tested under a variety of conditions – including (i) gas flow rate, (ii) back pressure, (iii) cell temperature, (iv) humidification temperature, and (v) gas diffusion layer, and advances in water management are being made. As an example, Figure 4 presents the stability test data obtained at 0.5 V for the carbon composite catalyst. The test was run at an ambient pressure for the cathode catalyst loading of  $4 \text{ mg cm}^{-2}$ . Note that no performance degradation was observed for 80 h of continuous operation without an  $\text{O}_2$  purging step.

### Conclusions and Future Directions

Carbon-based metal-free catalysts were synthesized by modifying the surface functional groups on the porous carbon black with low-cost organic precursors. Further, carbon composite catalysts were developed using a metal-free catalyst as a catalyst support through catalyzed pyrolysis followed by chemical post-treatments. Materials characterization studies indicated that the nature of nitrogen functional groups on the

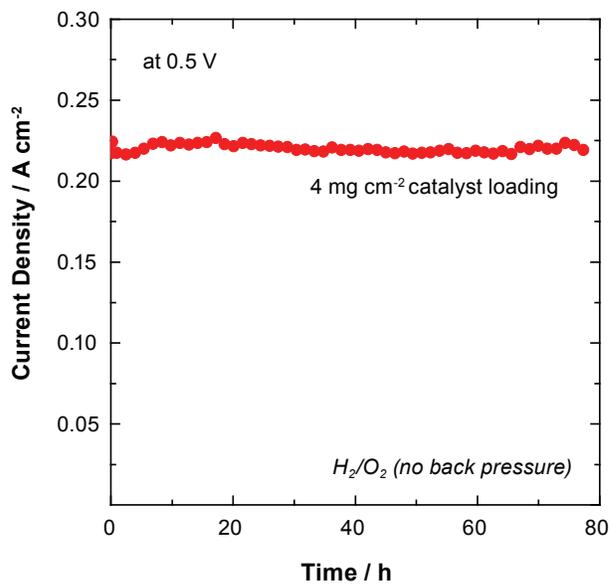


FIGURE 4. Stability Test Data of PEMFC with The Carbon Composite Catalyst Performed Without Intermittent  $\text{O}_2$  Purging Steps

carbon surface and the carbon nanostructures play a critical role in the activity and stability of carbon-based catalysts. The catalytic activities as high as  $1.3 \text{ A cm}^{-2}$  ( $6 \text{ mg cm}^{-2}$  loading) and  $2.0 \text{ A cm}^{-2}$  ( $4 \text{ mg cm}^{-2}$  loading) at  $0.2 \text{ V}$  were obtained for the metal-free and carbon composite catalysts, respectively, in the fuel cell, and no irreversible activity loss was observed.

## Future Directions

### University of South Carolina

- To improve water management by controlling hydrophobicity of catalyst layer and by reducing catalyst layer thickness.
- To increase the fuel cell durability by improving the integrity of the carbon composite catalyst layer in MEA.
- To reduce the MEA resistance.

### Northeastern University and Case Western Reserve University

- No additional work.

## Special Recognitions & Awards/Patents Issued

1. Crystal Flame Innovation Award in Research from FuelCell South was presented to Dr. Popov's research group for research work in the field of non-precious catalyst development and preparation thin film assemblies with nano-structured catalysts and the development of the pulse deposition technique for preparation of membrane electrode assemblies.

## FY 2007 Publications/Presentations

1. H.R. Colón-Mercado, B.N. Popov, "Stability of Platinum Based Alloy Cathode Catalysts in PEM Fuel Cells," J. Power Sources, 155 (2006) 253.
2. R. Sidik, A. Anderson, N.P. Subramanian, S.P. Kumaraguru, B.N. Popov, "O<sub>2</sub> Reduction on Graphite and Nitrogen-Doped Graphite: Experiment and Theory," J. Phys. Chem. B, 110 (2006) 1787.
3. R. Sidik, 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.
4. 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, 157 (2006) 56.
5. L. Liu, J.-W. Lee, B.N. Popov, "Development of Ruthenium-Based Bimetallic Electrocatalysts for Oxygen Reduction Reaction," J. Power Sources, 162 (2006) 1099.
6. S.P. Kumaraguru, N.P. Subramanian, H. Colon and B.N. Popov, "Non-noble Metal Catalysts for Oxygen Reduction Reaction in Acidic Media," ECS Trans., 1 (2006) 27.
7. L. Liu, B.N. Popov, "Highly Active Ruthenium Based Catalysts for Oxygen Reduction Reaction," ECS Trans., 1 (2006) 41.
8. L. Liu, H. Kim, J.-W. Lee, B.N. Popov, "Development of Novel Ruthenium-Based Catalysts for Oxygen Reduction Reaction," J. Electrochem. Soc., 154 (2007) A123.
9. E. Vayner, R.A. Sidik, A.B. Anderson, B.N. Popov, "Theoretical Study of Co<sub>8</sub>Se<sub>9</sub> as a Catalyst for O<sub>2</sub> Electro Reduction," J. Phys. Chem, accepted for publication.
10. G. Wu, J.-W. Lee, B.N. Popov, "Nitrogen-Containing Carbon Composite Catalyst for Oxygen Reduction in PEM Fuel Cell," J. Electrochem. Soc., submitted.
11. G. Wu, X. Li, J.-W. Lee, B.N. Popov, "Effect of Te on the Catalytic Activity and Selectivity of Co-N/C for Oxygen Reduction," J. Electrochem. Soc., submitted.
12. "Highly Active Carbon-Based Catalysts for PEM Fuel Cells", 210<sup>th</sup> Meeting of the Electrochem Soc., Cancun, Mexico, October, 2006. (contributed)
13. "Highly Active Carbon-Based Catalysts for PEM Fuel Cells", 2006 Annual AIChE Meeting, San Francisco, CA, November, 2006. (contributed)