V.C.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@engr.sc.edu

DOE Technology Development Manager:
Amy Manheim
Phone: (202) 586-1507; Fax: (202) 586-9811
E-mail: Amy.Manheim@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: Walt Podolski
Phone: (630) 252-7558; Fax: (630) 972-4430
E-mail: podolski@cmt.anl.gov

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

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Objectives

- Synthesis of novel non-precious metal electrocatalysts and metal-free electrocatalysts with similar activity and stability as Pt for the oxygen reduction reaction (ORR).
- Optimization of catalytic active reaction sites as a function of carbon support, presence of surface oxygen groups, nitrogen content, surface modifiers, pyrolysis temperature, porosity, pore size distribution and the concentration of the non-metallic additive "X" in the catalyst matrix.

Technical Barriers

This project addresses the following technical barriers from the Fuel Cells section (3.4.4.2) of the Hydrogen, Fuel Cells and Infrastructure Technologies Program Multi-Year Research, Development and Demonstration Plan:

(A) Durability

(B) Cost

(C) Electrode Performance

Technical Targets

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

Accomplishments

- Non-precious Co-X/C catalysts
  - Increased the concentration of active reaction sites by using carbon activation methodology.
  - Obtained the onset potential for ORR as high as 0.87 V normal hydrogen electrode (NHE).
  - Decreased the H_2O_2 amount to a level lower than 5% by incorporating non-metallic additive "X" (FOUR electron pathway for ORR).
  - Obtained the catalytic activity as high as 165 A cm^{-3} at 0.3 V (no voltage drop compensation) in the fuel cell.
- Metal free CN-X and C-X catalysts
  - Obtained the onset potential for ORR as high as 0.8 V(NHE).
  - Decreased the H_2O_2 amount to zero (FOUR electron pathway for ORR).
  - Obtained the catalytic activity as high as 100 A cm^{-3} at 0.3 V (no voltage drop compensation) in the fuel cell.

Introduction

Currently Pt and Pt alloys are widely used as cathode materials in polymer electrolyte 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 the macrocycle-based metal porphyrin system, chevrel phase-type compounds and other transition metal chalcogenides have been proposed as selective

catalysts for the ORR [1-3]. However, significant increase in activity and stability of the catalyst is still essential for PEMFC applications.

In this project, non-precious Co-based catalysts and metal free carbon-based catalysts for the ORR have been synthesized through low-cost mass production methods. The goal of this project is to demonstrate the potential of the non-precious metal and metal-free catalysts to perform at least as good as conventional Pt catalysts currently in use in MEAs with a cost at least 50% less than a target of 0.2 g (Pt loading)/peak kW and with durability > 2,000-hr operation with less than 10% power degradation. The performance of the synthesized catalysts has been evaluated based on three main criteria: (i) activity towards ORR, (ii) selectivity for four-electron reduction (percent H_2O_2 produced) and (iii) fuel cell performance.

Approach

This project aims at synthesizing novel non-precious metal catalysts and metal-free catalysts with similar activity and selectivity as Pt for ORR. The active reaction catalytic sites and selectivity were optimized by optimizing (i) carbon support, (ii) surface oxygen groups, (iii) nitrogen content, (iv) surface modifiers, (v) pyrolysis temperature, (vi) porosity, (vii) pore size distribution and (viii) the concentration of the non-metallic additive "X" in the catalyst matrix.

Results

Three different types of electrocatalysts for ORR were synthesized: (i) Co-based catalyst doped with X additive (Co-X), (ii) metal free CN-X, and (iii) C-X catalysts. The Co-X catalyst was prepared by refluxing stoichiometric amounts of Co and X salts, N-donor and carbon black powders (Ketjen) in non-aqueous media, followed by pyrolysis at high temperatures. The CN-X and C-X catalysts were synthesized by modifying the surface functional groups on the porous Ketjen black with organic N-precursors and "X" element, followed by high-temperature pyrolysis.

Figure 1 shows polarization curves of un-doped Co catalyst and Co-X catalyst measured using a rotating ring disc electrode (RRDE) technique. The experiments were performed in 0.5 M H_2SO_4 solution saturated with oxygen at a rotation rate of 900 rpm. The Co-X catalyst shows an onset potential for ORR as high as 0.87 V(NHE), i.e. the increase in the catalytic activity by about 100 mV, as compared with the un-doped Co catalyst. For the Co-X catalyst, the Co concentration was determined to be less than 2.5 wt% measured using x-ray photoelectron spectroscopy (XPS) which is much lower than that in the conventional metal catalyst. This suggests that the metal-free CN-X or C-X catalyst can be synthesized by doping a very small amount of Co-N, resulting in improved activity and selectivity of the metal-free catalysts.

Figure 2 presents polarization curves for metal-free CN-X and C-X catalysts measured by RRDE. For comparison, the curve measured on the as-received Ketjen black is also shown in Figure 2. The as-received carbon does not show any catalytic activity towards

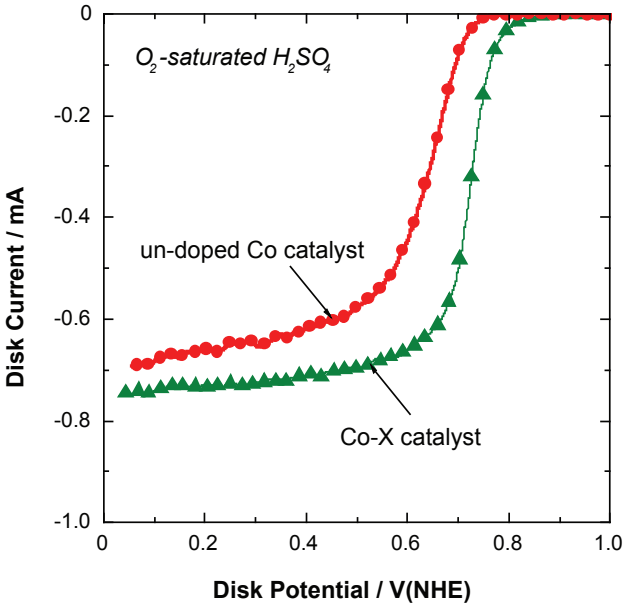

FIGURE 1. Polarization Curves of Un-Doped Co Catalyst and Co-X Catalyst Measured by RRDE

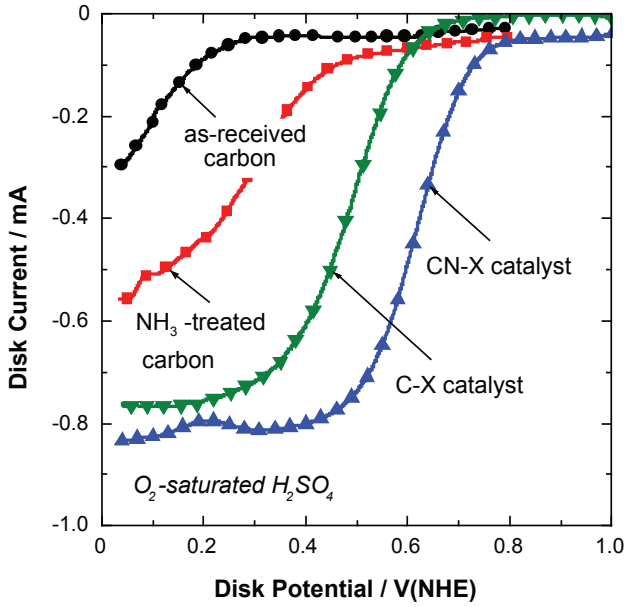

FIGURE 2. Polarization Curves of Metal-Free CN-X and C-X Catalysts Measured by RRDE

ORR. A remarkable increase in the catalytic activity has been achieved with the introduction of nitrogen groups and the "X" additive. The CN-X and C-X catalysts synthesized by novel University of South Carolina (USC) methodologies with organic N-precursors show improved performance when compared with the conventional NH_3-treated carbon. The optimized CN-X catalyst exhibits an onset potential for ORR as high as 0.8 V(NHE) and also a well-defined diffusion limiting current which is only observed in Pt-based catalysts.

Figure 3 illustrates the percentages of H_2O_2 produced on three different electrocatalysts (Co-X, CN-X and C-X) during ORR. The amount of H_2O_2 determined from the Pt catalyst is given in Figure 3. Generally, the Co-based catalyst generates more than 20% H_2O_2 at 0.5 V(NHE); however, the Co-X catalyst developed at USC produces only 5% H_2O_2 at the same potential range, indicating the increased selectivity towards four-electron reduction with the incorporation of "X". The optimized CN-X catalyst catalyzes ORR via four-electron pathway with producing no H_2O_2 at 0.5 V(NHE). Notice that Pt catalyst generates 1 to 2% H_2O_2.

The nature of the nitrogen functional groups on the metal-free CN-X catalyst was identified using XPS. Figure 4 shows typical XPS spectra of the nitrogen atom (N) 1s region for the CN-X catalyst. Two dominant peaks are observed at 398.7 and 400.8 eV which can be assigned to pyridinic N and pyrrolic N, respectively. The pyridinic N possesses one lone pair of electrons in addition to the one electron donated to the conjugated π bond system [4]. The pyridinic N group was detected from the surfaces of Co-X and C-X catalysts as well. Our characterization study suggests that the pyridinic N facilitates reductive O_2 adsorption without the irreversible formation of oxygen functionalities, thereby enhancing the catalytic activity and selectivity towards ORR.

Figure 5 compares the fuel cell performances of different electrocatalysts. The supported catalyst

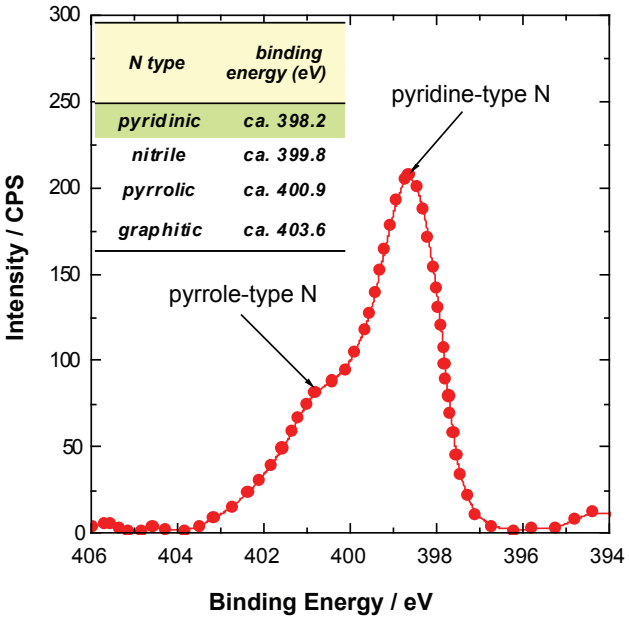

FIGURE 4. XPS Spectra of N 1s Region for the CN-X Catalyst

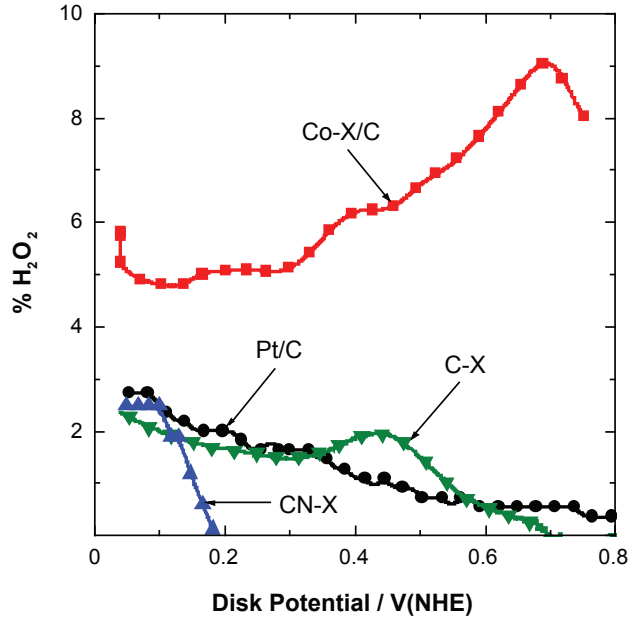

FIGURE 3. Percentages of H_2O_2 Produced on Different Electrocatalysts: Pt, Co-X, CN-X and C-X

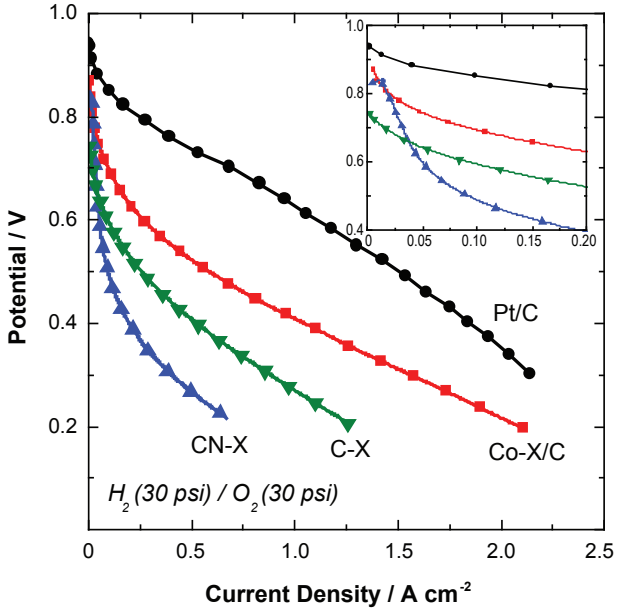

FIGURE 5. Fuel Cell Performance of Different Electrocatalysts: Pt, Co-X, CN-X and C-X

loadings were maintained at 6 mg cm^{-2} for the cathode and 2 mg cm^{-2} (Pt) for the anode, and the tests were run at 75°C with H_2(30 psi)/O_2(30 psi). No voltage drop compensation was made during the measurement. The fuel cells tested using Co-X and CN-X catalysts exhibit the open circuit potential (OCP) higher than 0.8 V, as shown in the inset. The Co-X catalyst shows the current density of 1.6 A cm^{-2} at 0.3 V in comparison with 2.1 A cm^{-2} for the Pt catalyst. The current densities for CN-X and C-X catalysts were measured to be ca. 0.4 and 0.9 A cm^{-2}, respectively, at 0.3 V. The catalytic activities normalized with respect to the volume of supported catalyst (A cm^{-3}) were summarized at different cell potentials as listed in Table 1.

TABLE 1. Catalytic Activities per Volume of Supported Catalyst (A cm^{-3}) at Different Cell Potentials

Catalyst	Catalytic activity per volume of supported catalyst, A cm^{-3}				
	0.7 V	0.6 V	0.5 V	0.4 V	0.3 V
Co-X/C	8	30	60	110	165
CN-X	0.3	6	16	34	63
C-X	2	9	28	59	98

Figure 6 presents the back scattered electron images of the cross-section of MEAs prepared using the metal-free C-X catalyst. The image clearly shows that the catalyst layer is about 90 μm thick, which is much thicker than the conventional Pt catalyst layer (~10 μm). This result indicates that the fuel cell with the metal-free catalyst may have higher mass transport limitation in the catalyst layer. The future work will be focused on improving the fuel cell performance by reducing the catalyst layer thickness and the ohmic potential drop of MEA.

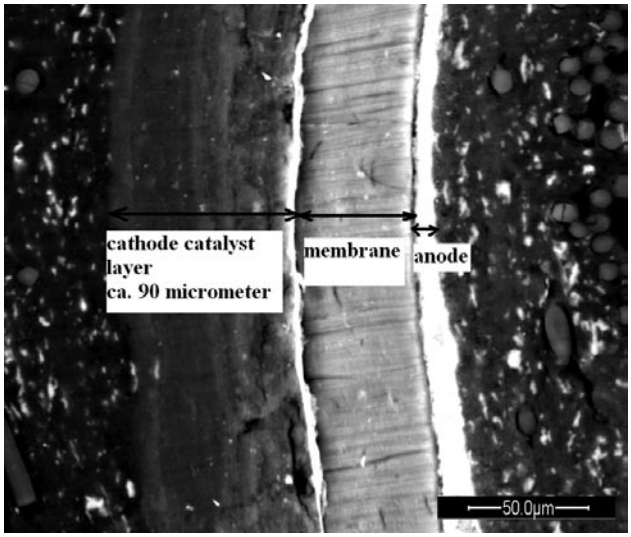

FIGURE 6. Back Scattered Electron Images of the Cross-Section of MEAs Prepared Using the Metal-Free C-X Catalyst

Conclusions and Future Directions

Non-precious Co-based catalysts and metal-free carbon-based catalysts with high activity (0.8 to 0.87 V(NHE)) and selectivity (0 to 5% H_2O_2) for the ORR have been synthesized using low-cost precursors. The increased activity and selectivity for ORR were attributed to the pyridinic N group on the catalyst surface. The fuel cell performance was determined using the novel electrocatalysts synthesized in this project, and the catalytic activities as high as 165 and 100 A cm^{-3} at 0.3 V were obtained for the Co-X and C-X catalysts.

Future Directions

University of South Carolina

- Synthesize the "unsupported" metal-free CN-X and C-X catalysts with high mesoporous area by using the template method.
- Further improve fuel cell performance by optimizing the catalyst layer thickness/porous structures and reducing the MEA resistances.
- Perform the durability study in the RRDE and fuel cells and understand the degradation mechanism.
- Improve the durability of the Co-X catalyst by doping Cr using a procedure developed at USC.
- Increase the durability by loading the metal-free CN-X and C-X catalysts on graphitized carbon.

Northeastern University

- Study the structure-property relation of the catalysts.
- Attain correlation of corrosion data with the electrochemical data.
- Study the role of dopants on the electrochemical stability and activity.

Case Western Reserve University

- Continue study of H_2O_2 formation on nitrided graphite.
- Continue calculation of the coverage dependent adsorption energies for H_2O, OH and O_2 on various sites of Co_9S_8.

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 2006 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_2 Reduction on Graphite and Nitrogen-Doped Graphite: Experiment and Theory", J. Phys. Chem. B, 110 (2006) 1787.

3. R. Sidik, A. Anderson, "Co_9S_8 as a Catalyst for Electroreduction of O_2: 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, H. Kim, J.-W.Lee, B.N. Popov, "Development of Novel Ru-based Catalysts for Oxygen Reduction Reaction", J. Electrochem. Soc., submitted.

6. S.P.Kumaraguru, M.Curran, B.N.Popov, "Non Noble Metal Catalysts for Oxygen Reduction Reaction", 208th meeting of the Electrochemical Society, Los Angeles, CA, October, 2005 (contributed).

7. L.Liu, B.N. Popov, "Novel Ru Chelate Catalysts for Oxygen Reduction Reaction", 208th meeting of the Electrochemical Society, Los Angeles, CA, October, 2005 (contributed).

8. S.P. Kumaraguru, B.N. Popov, "Development of Non Precious Metal Catalysts for PEMFC Cathodes", Graduate Symposium, USC, June 2005.

9. B.N. Popov, "Overview of Fuel Cell Research at CEE", FuelCell South Annual Conference, May 2005, Columbia, SC (invited).

10. L. Liu, 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 (contributed).

11. S.P. Kumaraguru, N. Subramanian, H.R. Colón-Mercado, H. Kim, B.N. Popov, "Novel Non Precious Metal Catalysts for PEMFC Applications", 206th meeting of the Electrochemical Society, Honolulu, HI, October, 2004 (contributed).

12. N.P. Subramanian, S.P. Kumaraguru, B.N. Popov, "Analysis of Carbon Substrates used in Non-Precious Metal Catalysts for Fuel Cell Applications", 206th meeting of the Electrochemical Society, Honolulu, HI, October, 2004 (contributed).

13. S.P. Kumaraguru, B.N. Popov, "New Electrocatalysts for PEM Fuel Cells", SERMACS, Durham, NC, November, 2004 (invited).

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