

## V.E.7 Non-Platinum Bimetallic Cathode Electrocatalysts

Deborah J. Myers (Primary Contact),  
Xiaoping Wang, Nancy Kariuki, Suhas Niyogi,  
and Jennifer Mawdsley

Argonne National Laboratory  
9700 S. Cass Avenue  
Argonne, IL 60439  
Phone: (630) 252-4261; Fax: (630) 252-4176  
E-mail: Myers@cmt.anl.gov

DOE Technology Development Manager:  
Jason Marcinkoski

Phone: (202) 586-7466; Fax: (202) 586-9811  
E-mail: Jason.Marcinkoski@hq.doe.gov

Technical Advisor: John Kopasz

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

Subcontractors/Partners:

- William A. Goddard, III, California Institute of Technology, Pasadena, CA
- Clemens Heske, University of Nevada, Las Vegas, NV
- John R. Regalbuto, University of Illinois, Chicago, IL
- Karren L. More, Oak Ridge National Laboratory, Oak Ridge, TN
- Piotr Zelenay, Los Alamos National Laboratory, Los Alamos, NM

Project Start Date: January 1, 2007

Project End Date: December 31, 2010

### Objectives

Develop a non-platinum cathode electrocatalyst for polymer electrolyte fuel cells with the following attributes to meet DOE's technical targets:

- Promotes the direct four-electron reduction of oxygen with high electrocatalytic activity (comparable to that of Pt).
- Chemically compatible with the acidic polymer electrolyte.
- Stable at high potentials and to potential cycling.
- Low cost.

### 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

This project is addressing the following 2010 DOE technical targets for electrocatalysts:

- Activity: 0.44 A/mg Pt or 720  $\mu\text{A}/\text{cm}^2$  @ 0.9 V
- Durability: 5,000 h @ 80°C, <40% electrochemical area loss
- Cost: \$8/kW, 0.3 mg platinum group metal (PGM)/ $\text{cm}^2$

**TABLE 1.** Current Status of Progress towards Meeting the DOE Technical Target for Catalyst Oxygen Reduction Activity

Supported Metal System	Pd	Pd-Cu	Pt (E-Tek)	DOE 2010 target
ORR Activity at 0.9V, 23°C (mA/mg metal)	3.8	16.0	131.0	440



### Approach

The goal of this project is to reduce the cost and improve the durability of polymer electrolyte fuel cell power systems by replacing the platinum-containing cathode electrocatalyst with alternative materials. Our approach to achieving this goal is to develop non-platinum noble metal-base metal bimetallics. Based on the effect of the electronic configuration of a metal on oxygen reduction reaction (ORR) kinetics, as described by the Nørskov and Hammer theory [1], and on the known ability of one component of an alloy to affect the electronic configuration of another [2], we have chosen a series of bimetallic alloys. The candidate metals for the bimetallic alloys have been chosen such that there is preferential segregation of the catalytically active, noble metal to the surface of the alloy particles [3], with the bulk of the particle comprised mainly of an inexpensive base metal selected for its ability to alter the electronic properties of the surface metal [2] to make them more like the desirable electronic properties of Pt<sub>3</sub>Co [4]. This approach addresses the DOE durability, cost, and performance technical barriers by altering oxophilicity of the catalyst to prevent oxidation-related degradation, lowering the PGM loading by replacing PGM in the electrocatalyst particle core with a base metal, and by modifying surface electronic properties to enhance ORR activity.

## Accomplishments

This year we are studying palladium-base metal systems, with the focus of our efforts thus far being on palladium-copper bimetallics. Palladium and copper precursors were deposited on high surface area carbon, Vulcan XC-72R, by co-impregnation from aqueous solutions of the metal nitrates. Carbon-supported Pd-Cu has also been made by a colloidal technique. Following deposition on the carbon, the metals or metal nitrates were heat-treated in a reducing atmosphere (dilute or pure hydrogen) in order to reduce the precursors to metals and to promote the formation of bimetallic compounds or solid solutions. We have studied the effect of the ratio of Pd to Cu and post-deposition heat treatment temperatures on the ORR activity of carbon-supported catalysts. The heat treatment temperature range, 300 to 800°C, was chosen based on temperature-programmed reduction studies, which showed both palladium and copper to be fully reduced at 300°C. Materials characterization by X-ray diffraction and transmission electron microscopy showed that the degree of alloying of the two metals and the size of the nanoparticles depended strongly on the heat treatment temperature and on the palladium to copper ratio. As shown in Table 2 and Figure 1, higher heat treatment temperatures resulted in higher degrees of alloying, larger particle sizes, and narrower particle size distributions. In addition to formation of a face-centered cubic solid solution, line-compound (PdCu) formation was observed at processing temperatures of 600°C and above for Pd to Cu ratios of 1:3 and 1:1.

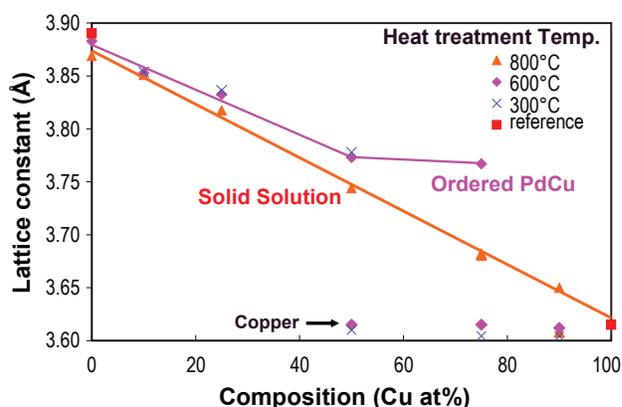
- The thin-film rotating disk electrode (RDE) technique was used to determine the room temperature ORR activity of the carbon-supported bimetallic electrocatalysts [5]. As shown in Figure 2, the ORR activity was strongly dependent on the post-deposition heat treatment temperature and on the Pd to Cu ratio. The highest ORR activity was observed for the bimetallic Pd:Cu atomic ratios

**TABLE 2.** Particle Size and Particle Size Distribution for the Pd-Cu/C Catalysts as a Function of Palladium to Copper Ratio and Post-Deposition Heat Treatment Temperature

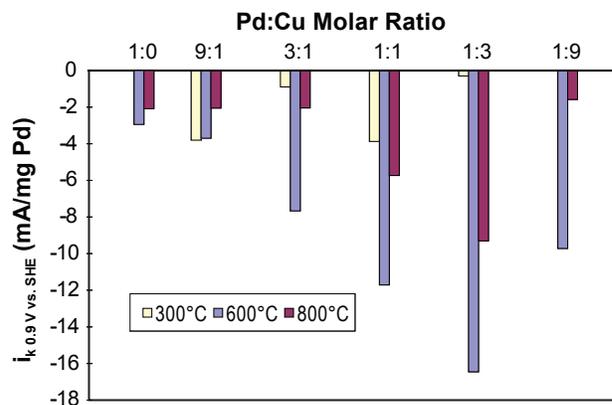
Pd: Cu Molar Ratio	Particle size (nm)		
	300°C	600°C	800°C
1:9	10.8 ± 2.1	17.2 ± 3.3	46.3 ± 11.2
1:3	8.1 ± 2.8	23.3 ± 8.3	55.0 ± 14.5
1:1	6.1 ± 1.6	21.0 ± 5.1	69.8 ± 18.1
3:1	9.1 ± 3.3	21.8 ± 5.5	68.3 ± 10.7
9:1	6.5 ± 1.8	21.9 ± 4.9	73.5 ± 15.4

of 1:1 and 1:3 heat treated at 600°C, which showed ORR activities five to six times higher than carbon-supported palladium alone. These two compositions exhibited formation of the PdCu line compound, indicating that the ordered phase is desirable for enhanced ORR kinetics.

- The best performing catalysts, prepared by impregnation, exhibited much larger nanoparticle diameters (~23 nm) and broader size distributions (mean standard deviation of 8.3 nm) than desired (2-4 nm). In addition, the impregnation method resulted in an inhomogeneous composition distribution. It is believed that the ORR activity of Pd-Cu can be further improved by better control of the alloy phase composition and the nanoparticle size. To achieve these goals, alternative synthetic routes, utilizing colloids and strong electrostatic adsorption, are being pursued. Using the colloidal technique, we have succeeded in decreasing the particle size of the carbon-supported palladium-



**FIGURE 1.** Extent of Solid Solution and Line Compound Formation for the Pd-Cu/C Catalysts as a Function of Palladium to Copper Ratio and Post-Deposition Heat Treatment Temperature



**FIGURE 2.** Oxygen Reduction Activity of Pd-Cu/C Catalysts at 0.9 V and 23°C as a Function of Palladium to Copper Ratio and Post-Deposition Heat Treatment Temperature

copper alloys to  $3.4 \pm 1.7$  nm prior to and  $7.7 \pm 2.0$  nm after heat treatment to remove the capping agent. We are investigating alternative methods for removing the capping agent in order to limit particle growth during this step in the synthesis procedure.

### FY 2007 Publications/Presentations

1. Nancy N. Kariuki, Xiaoping Wang, and Deborah J. Myers, "Palladium-Base Metal Nanoparticles as Cathode Electrocatalysts for Polymer Electrolyte Membrane Fuel Cells," 211<sup>th</sup> Meeting of the Electrochemical Society, Chicago, IL, May 8-11, 2007.

### References

1. B. Hammer and J. Nørskov, *Adv. In Catalysis*, Vol. 45 (2000).
2. A. Ruban, B. Hammer, P. Stoltze, H. L. Skriver, and J. K. Nørskov, *J. Mol. Catal. A* 115 (1997) 421.
3. A. V. Ruban, H. L. Skriver, and J. K. Nørskov, *Phys Rev. B*, **59** (24) (1999) 15995.
4. B. S. Mun, M. Watanabe, M. Rossi, V. Stamenkovic, N.M. Markovic, P.N. Ross, Jr., *J. Chem. Phys.*, **123** (2005) 204717.
5. T. J. Schmidt and H. A. Gasteiger, "Chapter 22: Rotating thin-film method for supported catalysts," in *Hanbook of Fuel Cells – Fundamentals, Technology and Applications*, Vol. 2 Electrocatalysis, W. Vielstich, H. A. Gasteiger, A. Lamm, eds., John Wiley & Sons, New York, 2003.