

V.C.6 Non-Platinum Electrocatalysts

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Start Date: October 2002

Projected End Date: September 2006

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 (3.4.4.2) of the Hydrogen, Fuel Cells and Infrastructure Technologies Program Multi-Year Research, Development and Demonstration Plan:

- (B) Cost
- (C) Electrode performance

Technical Targets

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

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

Current Status of Progress Towards Meeting the DOE Technical Target for Catalyst Activity

Supported metallic system	Iridium-Based			Palladium-Based		DOE 2010 target at 0.9 V
	Ir	Ir base metal	Base metal	Pd	Pd base metal	
Oxygen reduction activity at 0.8 V (mA/mg metal)	0.02	0.065	0.003	8.4	36.6	440

Accomplishments

- Synthesized and tested two metal center-polymeric systems
 - Oxygen reduction reaction (ORR) activity at <0.6 V, stable over 3 days of testing
- Synthesized, tested, and characterized one Ir-based bimetallic system (nine compositions)
 - ORR mass activity increased three-fold by addition of base metal to iridium
- Synthesized one Pd-based bimetallic system (five compositions); testing and characterization is underway
 - ORR mass activity increased by more than a factor of four by addition of base metal to palladium
 - Highest ORR mass activity of 36 mA/mg at 0.8 V
- Completed characterization and testing of three Au-based bimetallic systems

Introduction

The objective of this work is to develop non-platinum cathode catalysts for polymer electrolyte fuel cells. The high cost of platinum is one of the main barriers to commercialization of polymer electrolyte fuel cell power systems. A major portion of the overall platinum loading is required on the cathode due to the relative slow kinetics of the oxygen reduction reaction (ORR). In the past decade, there have been significant advances in reducing the platinum metal loading of both the anode and the cathode. However, any further significant cost reductions will require replacing platinum, especially in the cathode layer, with less expensive but active and stable electrocatalytic materials.

Approach

Our approach to developing non-platinum cathode electrocatalysts involves two systems: (1) bi-metallic base metal-noble metal systems and (2) metal centers attached to electron-conducting polymer backbones. The choice of metals for the bi-metallic systems is based on surface energy calculations by Ruban et al., [1] giving the propensity of one metal to segregate to the surface of a bi-metallic combination. We are studying systems where the Ruban et al. calculations show that the minor noble metal component will tend to segregate to the surface of a particle with a predominantly base metal core to form a protective layer. Examples of the noble metals are gold, iridium, and palladium. The base metal component was chosen to modify the d-band center of the noble metal, making it more “Pt-like”. We are also investigating the use of metal centers attached to electron-conducting polymer backbones to allow precise control of the spacing between the metal centers and to promote high catalyst utilization by having an electronic conductor in close proximity to the reaction site. The oxygen reduction kinetics of the candidate materials are determined using the thin-film rotating ring-and-disk electrode technique. This technique allows determination of the reaction kinetic parameters (exchange current density and transfer coefficient) independent of mass-transfer effects [2].

Results

This year we studied gold, iridium, and palladium alloyed with base metals. The alloys were prepared in the form of nano-particles deposited on high surface area carbon powder (Vulcan XC-72R) using impregnation or deposition techniques from metal nitrates. The molar ratio of noble metal to base metal was varied from 9:1 to 1:9. Following deposition, the catalysts were heat-treated in a reducing atmosphere at temperatures ranging from 300 to 800°C. The iridium alloys were also soaked in perchloric acid electrolyte for several days in order to determine the stability of the material under acidic conditions. X-ray diffraction analyses of the bimetallic samples showed that alloys had been formed. Transmission electron microscopic analyses indicated that the particle sizes of the samples were comparable at a mean particle diameter of 4 nm. The rotating disk electrode technique was used to evaluate the ORR activity of the catalysts in oxygen-saturated perchloric acid electrolyte at room-temperature.

The highest ORR activity for the iridium system was seen for a catalyst with an iridium to base metal ratio of 3:1 that had been heat treated to 400°C and pre-treated in perchloric acid electrolyte. The data of Figure 1 compares the ORR activity of this catalyst as compared to iridium and the base metal alone. These data show

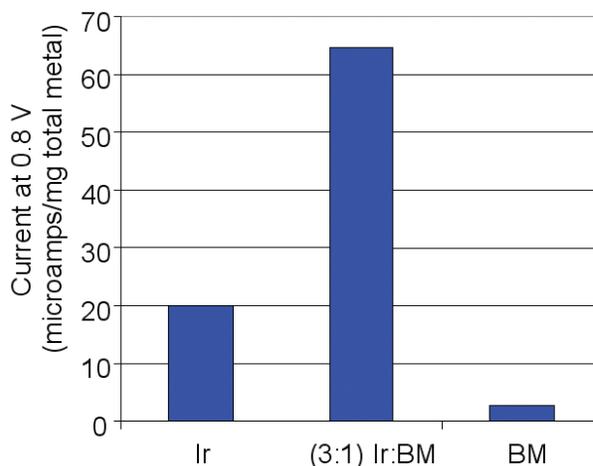


FIGURE 1. Oxygen Reduction Mass Activity for Carbon-Supported Nano-Particles of Iridium, a Base Metal, and an Alloy of Iridium and the Base Metal With an Atomic Ratio of 3 Ir:1 Base Metal

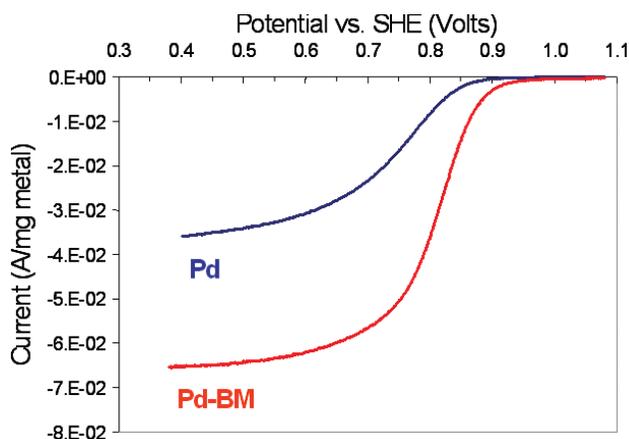


FIGURE 2. Oxygen Reduction Mass Activity for Carbon-Supported Nano-Particles of Palladium and a Palladium-Base Metal Alloy

that alloying with the base metal enhances the activity of the iridium and cannot be explained by the mere addition of the ORR activities of the two metals. As shown in Figure 2, the addition of a base metal to palladium was found to increase its ORR activity, with a 100 mV shift of the onset potential to 930 mV.

Conclusions and Future Directions

Conclusions

- Nano-particle base metal alloys of iridium and palladium have been formed using solution-phase deposition techniques
- Iridium and palladium-based alloys systems have higher ORR activity than iridium or palladium alone

- The ORR activity of the bimetallic systems is strongly influenced by the ratio of noble to base metal and the catalyst preparation and processing conditions (e.g., acid treatment and heat treatment temperature)

Future Work

- Determine the ORR mechanism ($2e^-$ or $4e^-$ transfer) for the iridium and palladium-based systems
- Prepare and test the ORR activity of additional bimetallic systems identified
- Prepare core-shell bimetallic nano-particles by colloidal and strong electrostatic adsorption synthesis
- Determine surface composition of bimetallic nano-particles using infrared spectroscopy
- Fabricate and test a membrane-electrode assembly using newly-developed electrocatalysts

FY 2006 Publications/Presentations

1. "Polymer Electrolyte Fuel Cell Cathode Electrocatalysts", Xiaoping Wang, Romesh Kumar, and Deborah J. Myers, Poster and Abstract, 2005 Fuel Cell Seminar, Palm Springs, CA, November 14-18, 2005.

References

1. A.V. Ruban, H.L. Skriver, and J.K. Nørskov, *Phys Rev. B*, **59** (24) (1999) 15995.
2. T.J. Schmidt and H.A. Gasteiger, "Chapter 22: Rotating thin-film method for supported catalysts" in Handbook of Fuel Cells – Fundamentals, Technology and Applications, Vol. 2 Electrocatalysis, W. Vielstich, H.A. Gasteiger, A. Lamm, eds., John Wiley & Sons, 2003.