

V.E.4 Non-Platinum Bimetallic Cathode Electrocatalysts

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

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

DOE Technology Development Manager:
Nancy Garland

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

Subcontractors:

- 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

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- Varying Pd to base metal ratio, annealing temperature, and annealing atmosphere.
- Characterizing oxygen reduction reaction (ORR) activity, surface composition, and electronic structure.

Technical Barriers

This project addresses the following technical barriers from the Fuel Cells section of the Fuel Cell 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: \$5/kW, 0.3 mg platinum group metal (PGM)/ cm^2 .

Objectives

- Overall objective:
 - Develop a non-platinum cathode electrocatalyst for polymer electrolyte membrane fuel cells (PEMFCs) with the following attributes to meet DOE's technical targets for electrocatalyst activity, durability, and cost:
 - Promotes the direct four-electron reduction of oxygen with high electrocatalytic activity (0.44 A/mg Pt or 720 $\mu\text{A}/\text{cm}^2$ @ 0.9 V).
 - Chemically compatible with the acidic polymer electrolyte.
 - Stable at high potentials and to potential cycling (5,000 h @ 80°C, <40% electrochemical area loss).
 - Low cost (\$5/kW).
- Specific objectives for Fiscal Year (FY) 2010:
 - Prepare/characterize model systems (bulk electrodes) and nano-particles of Pd-Mo, Pd-Re, Pd-Ta, and Pd-W binaries and Pd-Cu-Mo, Pd-Cu-W, Pd-Cu-Re, Pd-Cu-Ta, and Pd-Cu-Ni ternaries:

Accomplishments

- Calculated the ORR energetics for Pd and Rh alloys and the effect of water solvent on these energetics.
- Calculated the effect of adsorbed oxygen on surface segregation energies of Pt and Pd alloys.
- Determined the effect of annealing temperature and atmosphere on the ORR activity of twenty-one bi-metallic and tri-metallic Pd bulk electrodes; highest ORR activity enhancement with alloying was 2.1x (Pd_3Mo).
- Synthesized and characterized the structure, oxidation state, particle size, and ORR activity of nano-particles in the Pd-W, Pd-Mo, Pd-Re, and Pd-Ni-Cu systems.
- Achieved a nano-particle ORR activity enhancement with alloying of 3.4x with an (ORR activity of 680 mA/mg Pd at 0.8 V and room temperature for a $\text{Pd}_{18}\text{Ni}_{18}\text{Cu}_{64}$ alloy).
- Determined valence band structure of highest activity bi-metallic Pd alloys (PdMo and PdCu).



Introduction

The platinum-based cathode electrocatalyst is a major contributor to the cost of PEMFC power systems [1,2]. The goal of this project is to develop active and stable non-platinum noble metal-base metal alloy ORR electrocatalysts to expand the availability of effective materials beyond Pt alloys and thereby reduce the cost of the cathode electrocatalyst.

Approach

Our approach to developing non-platinum noble metal PEMFC cathode electrocatalysts is to utilize noble metal-base metal alloys. The function of the base metal is to decrease the loading of the noble metal and to modify its valence band structure to make it more Pt-like in its bonding with ORR reactants, intermediates, and products. The choice of noble metal and base metal combinations are based on calculated valence band or “d-band center” shifts of the noble metal in noble metal-base metal alloys and on the tendency of the noble metal to segregate to the surface of the alloys [3-7].

Two project tasks guide the choice of alloy systems: (1) computational studies of preferred catalyst atomic structures, electronic structures, d-band centers, and preferred reaction pathways and activation energies and (2) model system (bulk electrode) fabrication and characterization. Favorable alloy systems are fabricated as high-surface-area-carbon-supported nano-particles using co-impregnation, colloidal, and strong-electrostatic adsorption techniques. The nano-particles are characterized by a variety of spectroscopic, microscopic, and electrochemical techniques to determine composition, phase structure, particle size, electronic structure, and ORR activity and stability.

Results

Computational Results

This year’s computational effort focused on the change in the energetics of the ORR on Pd and Rh with alloying, the effect of water solvent on these energetics, and the change in the alloys’ noble metal segregation energies in the presence of adsorbed O. The alloys studied, Pd₃W, Pd₃Mo, Pd₃Re, Pd₃Ta, Rh₃Co, and Rh₃Fe, were those with calculated d-band centers close to that of Pt and favorable energies for noble metal surface segregation, as detailed in last year’s report [8].

As shown in Figure 1, the ORR may proceed through various adsorbates and pathways. The binding energies of each of the potential ORR adsorbates and the activation energies of the reaction steps were determined using periodic quantum mechanic calculations on four-layer noble metal or noble metal-base metal alloy slabs. The trends determined from these calculations were:

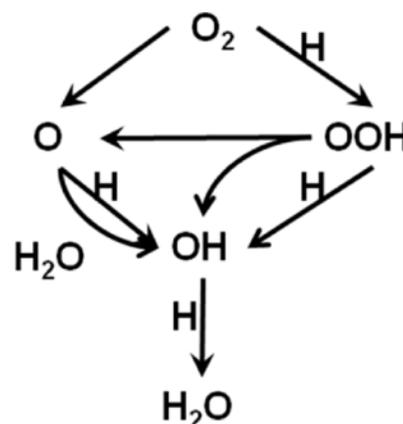


FIGURE 1. Potential Pathways for the Oxygen Reduction Reaction

- Alloying Pd decreases the binding energy of H, O, O₂, and H₂O₂ and increases the binding energy of OH, OOH, and H₂O.
- Alloying Rh increases the binding energy of OH.
- Alloying Pd decreases the barriers for H₂O formation and O hydration (two key steps in the ORR).
- Alloying Rh increases the barriers for H₂O formation and O hydration.

The presence of water solvent was found to alter the barriers for the ORR steps, thus modifying the preferred reaction pathway and overall reaction barrier. For Pd and Pd alloys the favored pathway in the gas phase is through OOH formation, OOH dissociation, O hydration, and HOH formation. In water solvent, the favored pathway is through the steps of O₂ dissociation, OH formation, and HOH formation. On Rh and Rh alloys the preferred steps in the gas phase are O₂ dissociation, O hydration, and HOH formation, whereas in the presence of water O₂ dissociation is followed by OH and HOH formation. The overall ORR barrier is reduced when alloying Rh with Co and increased when alloying with Fe. All Pd alloys showed lower overall barriers than Pd alone.

The computational studies of noble metal surface segregation energies for two Pt alloys (Pt₃Co and Pt₃Ni) and ten Pd alloys (Pd₃Au, Pd₃Cu, Pd₃Ir, Pd₃Mo, Pd₃Os, Pd₃Re, Pd₃Rh, Pd₃Ru, Pd₃Ta, and Pd₃W) showed that only Pd₃Ir and Pd₃Os segregate both in the absence and presence of adsorbed O. The alloys Pd₃Mo, Pd₃Re, Pd₃Ta, and Pd₃W were found to be extremely non-segregating in presence of adsorbed O, indicating that elimination of oxygen during the heat treatment/annealing step of alloy preparation is crucial and also a potential source of instability of the alloy materials during the ORR.

Experimental Results

This year's experimental efforts focused on the synthesis and characterization of bulk alloys and nano-particles of the Pd binary alloys Pd-Mo, Pd-W, Pd-Re, and Pd-Ta. These systems were identified last year as having favorable valence band energies, palladium surface segregation energies, and bonding characteristics with ORR reactants, intermediates, and products [7]. We also studied ternary systems based on the palladium-copper binary system to further enhance its activity and stability [8-10].

Model Systems

Ingots of 21 different compositions in six Pd alloy systems were fabricated by arc-melting. To promote surface segregation of Pd, the ingots were annealed at temperatures between 600 and 1,500°C in atmospheres of 3.5-3.7% H₂/He, 1% H₂/Ar, 100 ppm H₂/Ar, or Ar. The ingots' ORR activity and the effect of annealing temperature and atmosphere on the activity were determined using cyclic voltammetry in a quiescent oxygen-saturated aqueous electrolyte. Using this method, the figure of merit for activity is the half-peak potential of the oxygen reduction current peak.

These studies showed that annealing Pd alloys promotes surface segregation of Pd, as evidenced by Pd-like voltammetry in deaerated electrolyte and positive shifts in the ORR half-peak potential (i.e., enhanced ORR activity). The degree of Pd segregation depended on the annealing environment and temperature, the oxophilicity of the base metal, and the Pd to base metal

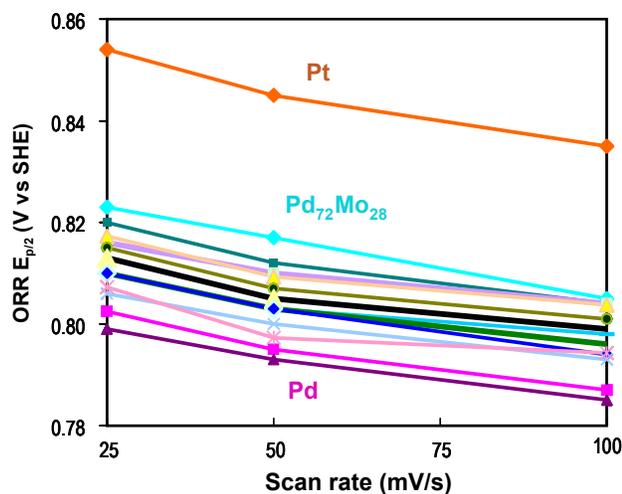


FIGURE 2. Half-peak potential (vs the standard hydrogen electrode, SHE) for the oxygen reduction reaction in aqueous acidic electrolyte as a function of potential scan rate for annealed Pd, Pd alloy, and Pt ingots. Half-peak potential and ORR activity were found to decrease in the order: Pt > Pd₇₂Mo₂₈ > Pd₉₅Re₅ > PdCu > Pd₉Mo > Pd₄W > PdCu₂ > Pd₃W > Pd₉₈Ta₂ > Pd₃Cu > PdCu₃ > Pd₃Re > Pd > Pd₅₃Mo₄₇.

ratio. Of the 21 Pd alloy ingots tested, the Pd₇₂Mo₂₈ alloy showed the highest enhancement of ORR activity with an increase in ORR half-peak potential of 22 mV compared to Pd alone, but 28 mV lower than that of Pt. A 22 mV shift in half-peak potential translates to a 2.1x ORR activity enhancement assuming a Tafel slope of 68 mV/dec (Figure 2).

X-ray photoelectron characterization of the Pd₇₅Mo₂₅ alloy showed that Mo modifies the Pd valence band, extending the density of states (DOS) to higher binding energies as reflected in a d-band center shift of 0.38 eV (Figure 3). Compared to Pt, Pd₇₅Mo₂₈ lacks DOS near the Fermi energy and at >4 eV binding energy. These missing states may explain the lower ORR activity, however further studies are needed to determine the involvement of various states in the ORR.

Nano-Particles

High-surface-area carbon-supported nano-particles of Pd-W, Pd-Mo, Pd-Re, and Pd-Ni-Cu alloys were synthesized using colloidal and strong-electrostatic adsorption (Pd-W and Pd-Mo), co-impregnation (Pd-Re), and colloidal techniques (Pd-Ni-Cu). The atomic ratios of Pd to base metal of the various systems are listed in Table 1. X-ray diffraction confirmed the formation of alloys in all cases. In addition to the alloy, the Pd-Mo system also contained an additional molybdenum carbide

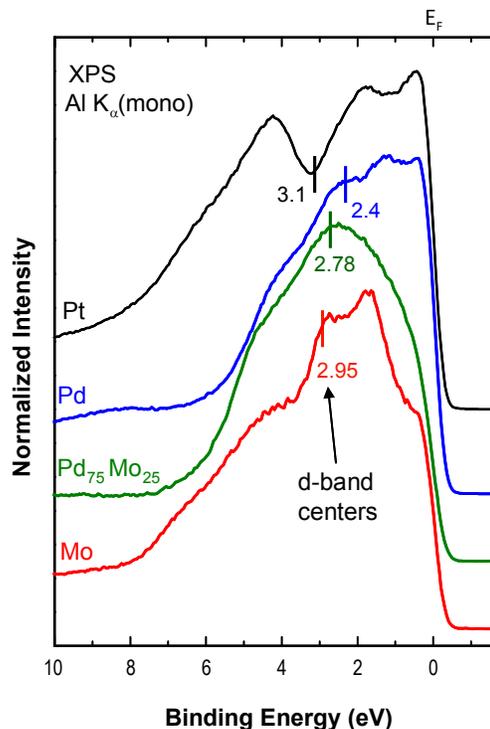


FIGURE 3. Valence band DOS and corresponding d-band centers for Pd, Mo, Pt, and Pd₃Mo showing that alloying Pd with Mo modifies the valence band DOS and shifts the d-band center toward that of Pt.

phase was detected for the Pd-Mo system. Oxygen reduction reaction activity was determined using the rotating disk electrode (RDE) technique and aqueous acidic electrolyte. The highest ORR activities achieved for each system are summarized in Table 1. Of the systems studied, only Pd-Ni-Cu showed enhanced ORR mass activity. X-ray photoelectron spectroscopy analyses indicated that the inhibition of ORR activity for the binary alloy nano-particles may be due to the presence of base metal oxides on the nano-particle surfaces.

TABLE 1. Summary of palladium alloy nano-particle catalysts synthesized this year and the highest mass (i_m) and area-specific (i_s) ORR activities achieved in each of the alloy systems. The atomic ratio of Pd to base metal and the post-deposition heat treatment resulting in the highest ORR activities are shown in parentheses.

System	Pd:BM (at. ratio)	$i_m@0.8\text{ V}$ (mA/mg Pd)	$i_s@0.8\text{ V}$ ($\mu\text{A}/\text{cm}^2$)
Pd-W	75:25, 50:50, 8:92, 15:85, 26:74, 42:58	93 (75:25@800°C)	830 (75:25@700°C)
Pd-Mo	90:10, 72:28 55:45, 10:90 14:76, 18:82, 26:74	138 (55:45@700°C)	600 (55:45@700°C)
Pd-Re	95:5, 75:25, 50:50, 33:67, 25:75	150 (3:1@300/450°C)	820 (1:1@ 300,450°C)
Pd-Ni-Cu	18:18:64	680 (550°C)	nd
Pd	100	200	nd

nd = not determined

Conclusions and Future Directions

Computational studies of the energetics of the ORR on Pd, Rh, and base metal alloys of Pd and Rh indicated that alloying Pd with Mo, W, Ta, or Re should increase ORR activity. Alloying Rh with Fe should decrease ORR activity and alloying with Co should increase activity. Experimental studies of the ORR activity of Pd alloy ingots showed that alloying with Re, Cu, W, and Mo at a 3:1 atomic ratio of Pd to base metal does enhance the ORR activity of Pd. The ORR activity increased in the order: $\text{Pd}_3\text{Re} < \text{Pd}_3\text{Cu} < \text{Pd}_3\text{W} < \text{Pd}_3\text{Mo}$, with Pd_3Mo showing an area-specific activity enhancement of 2.1x versus Pd alone. Valence band characterization of Pd_3Mo showed that Mo modifies the valence band of Pd, extending the density of states to higher binding energies. Though the overall d-band center of Pd is shifted toward that of Pt upon alloying with Mo, the valence band of Pd_3Mo lacks states near the Fermi energy and at higher binding energies (>4 eV). Future efforts will focus on alloying Pd with other binary and ternary combination of base metals to mimic Pt's density of states to further enhance the ORR activity of Pd.

Future work:

- Perform RDE studies on bi- and tri-metallic model systems (bulk electrode ingots) that showed the highest ORR activities in quiescent electrolyte experiments.
- Determine the surface composition and valence band structure as a function of annealing temperature and atmosphere, using X-ray photoelectron spectroscopy, for these model systems.
- Continue synthesis of nano-particles of most promising compositions identified in model system and computational studies, with goal of achieving base metal oxide-free surfaces.
- Expand surface segregation calculations to include other noble metal:base metal ratios, ternaries, and effect of annealing atmosphere.
- Study segregation effect for binary and ternary systems in the presence of different adsorbed species on the surface.
- Study ternary systems, such as Pd-Cu-Mo, Pd-Cu-W, Pd-Cu-Re, Pd-Cu-Ta, Pd-Cu-Ni with varying Pd to base metal ratios to enhance the activity and stability of highest activity binary system identified to date.
- Continue determining alloy electronic structures using DOS spectra and perform detailed analysis of how the electronic structures affect ORR activity.

FY 2010 Publications/Presentations

Publications

1. Y. Sha, T.H. Yu, Y. Liu, B.V. Merinov, and W.A. Goddard, III "Theoretical Study of Solvent Effects on the Platinum-Catalyzed Oxygen Reduction Reaction" *J. Phys. Chem. Lett.* **2010**, 1, 856-861.
2. T. H. Yu, Y. Sha, B.V. Merinov, and W.A. Goddard, III "Improved Non-Pt Alloys for the Oxygen Reduction Reaction at Fuel Cell Cathodes Predicted from Quantum Mechanics" *J. Phys. Chem. C*, **2010**, 114, 11527-11533.
3. N.N. Kariuki, X. Wang, J.R. Mawdsley, M.S. Ferrandon, S.G. Niyogi, J.T. Vaughney, and D.J. Myers, "Colloidal Synthesis and Characterization of Carbon-Supported Pd-Cu Nanoparticle Oxygen Reduction Electrocatalysts", *Chem. Mater.* **2010**, 22, 4144- 4152.
4. Ph.D. thesis: Timo Hofmann, "Spectroscopic Investigation of Pd-Cu Bimetallic Systems for PEM Fuel Cell Catalysts", UNLV, Dec., 2009.

Presentations

1. D. Myers, "Non-Platinum Cathode Electrocatalysts and Platinum Electrocatalyst Degradation in Polymer Electrolyte Fuel Cells", Indiana University-Purdue University at Indianapolis, IN, April 15, 2010. (Invited)

2. W.A. Goddard, "Multiparadigm simulations toward new catalysts and membranes for fuel cells and batteries" 239th ACS National Meeting, San Francisco, CA, 2010.
3. T. Hofmann, "Spectroscopic Investigation of Pd - Cu Bimetallic Systems for PEM Fuel Cell Catalysts", 2010 Southern Nevada Math & Science Conference (Southern Nevada Science Teachers Association), Las Vegas, NV, Jan. 23, 2010.
4. N. Kariuki, X. Wang, S. Niyogi, J. Mawdsley, D. Myers, T. Hofmann, Y. Zhang, and C. Heske, "Pd-Cu ORR Electrocatalysts: A Correlation of Structure, Activity, and Stability", International Energy Agency Annex XXII Fall 2009 Workshop, Argonne, IL, Nov.13, 2009.
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2. J. Sinha, "Direct Hydrogen PEMFC Manufacturing Cost Estimation for Automotive Applications", 2010 U.S. Department of Energy (DOE) Hydrogen Program and Vehicle Technologies Program Annual Merit Review and Peer Evaluation Meeting, Washington, D.C., June 7-11, 2010.
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