

V.C.6 Non-Platinum Bimetallic Cathode Electrocatalysts

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Objectives

- Develop a non-platinum cathode electrocatalyst for polymer electrolyte fuel cells 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 $\mu\text{A}/\text{cm}^2$ at 0.9 V).
 - Chemically compatible with the acidic polymer electrolyte.
 - Stable at high potentials and to potential cycling (5,000 h at 80°C, <40% electrochemical area loss).
 - Low cost (\$5/kW).

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) Electrode Performance

Technical Targets

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

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

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

Supported Metal System	Pd	Pd-Cu	Pt (E-Tek)	DOE 2010 Target (at 80°C)
Oxygen Reduction Reaction (ORR) Activity at 0.9V, 23°C (mA/mg PGM)	4.7	60	97	440

Accomplishments

The following accomplishments were realized this year:

- Calculated preferred reaction pathways and barriers for two possible O₂ reduction reaction mechanisms on slabs of pure metals using density functional theory:
 - Dissociative mechanism through -OH formation.
 - Associative mechanism through -OOH formation.
- Calculated reaction force field potentials for Pd and Pd-Cu.
- Determined effect of Pd particle size (1.2 to 20 nm) on ORR kinetics:
 - 5 nm particle size shows highest ORR mass activity.
- Synthesized and characterized a series of Pd-Cu, Pd-Ni, Pd-Fe via co-impregnation; determined the effect of Pd to base metal ratio, post-deposition heat treatment temperature and atmosphere, and acid treatment.
- Developed strong electrostatic adsorption technique for Pd-Co and achieved Co core-Pd shell structure.
- Developed colloidal technique for Pd-Cu; synthesized and characterized a series of colloidal Pd-Cu catalysts.
- Determined that Cu modifies the valence band density of states of Pd.

- Achieved factor of 3.75 improvement in ORR activity of Pd-Cu/C catalyst by using alternative colloidal technique.
- Achieved ORR mass activity of approximately 75% that of commercial Pt/C with Pd-Cu/C catalyst (@800 mV).



Introduction

This project is aimed primarily at reducing the cost of the polymer electrolyte fuel cell cathode catalyst by replacing platinum with less expensive metals, while also meeting or exceeding the catalyst durability and performance targets. The objective is to develop non-platinum ORR electrocatalysts that promote the direct four-electron reduction of oxygen at high rates to meet the DOE cost and performance targets, while also stabilizing the non-platinum metals against dissolution in the acidic fuel cell environment.

Approach

The project's approach to meeting the cost, durability, and performance targets is to develop base metal-noble metal alloy nanoparticles with a minor noble metal content, to lower cost, and with the noble metal forming a surface skin to protect the primarily base metal particle core against dissolution in the acidic electrolyte. The initial base metal-noble metal combinations were chosen based on theoretical calculations predicting the tendency of the noble metal component to segregate to the surface of the alloy [1]. The base metal is also chosen to modify the valence band or d-band structure of the surface noble metal to make it more Pt-like in its bonding with oxygen and the ORR intermediates [2-4]. The durability of the noble metals, which tend to be less stable than platinum, is being addressed by shifting the valence band structure of the noble metals, thus decreasing the oxophilicity of the noble metal and imparting stability against dissolution [5].

The project's approach includes two tasks aimed at guiding the synthetic efforts, one computational and one experimental. Computational studies are being used to guide the choice of particle composition (i.e., noble metal to base metal ratio and noble metal and base metal identity) providing the desired physical structure, electronic structure, and bonding characteristics with oxygen and site-blocking intermediates. Well-controlled and characterized model systems of bulk polycrystalline alloys with the desired core-skin composition are being used to verify the concept of modifying the valence band structure of noble metals with base metals, to correlate with the computational results, and to guide the choice of nanoparticle composition. Carbon-

supported bimetallic nanoparticles are being fabricated by co-impregnation, colloidal, and strong electrostatic adsorption techniques. The co-impregnation technique is used for quick screening of the catalyst compositions, but results in relatively large and poly-disperse nanoparticles. The colloidal and strong-electrostatic adsorption techniques are used to form small, mono-disperse particles of the most promising noble metal-base metal compositions and ratios resulting from the co-impregnation screening. Spectroscopic techniques are being used to determine that the desired nanoparticle bulk and surface composition have been obtained. The oxygen reduction activities of the nanoparticles are being screened using the thin-film rotating ring-disk technique (TF-RDE) [6] and the nanoparticle stabilities are screened using potentiostatic and potential cycling in non-adsorbing electrolyte. Materials showing oxygen reduction activity and stability meeting the DOE goals will be incorporated into membrane-electrode assemblies and their short and long-term performance under accelerated test conditions will be determined.

Results

The specific objective this past year was to synthesize and evaluate the oxygen reduction activity, stability, and electronic structure of nanoparticles of the palladium alloy systems. We have synthesized high-surface-area-carbon-supported nanoparticle catalysts in four Pd-base metal systems (Cu, Ni, Fe, and Co) and Pd alone using the co-impregnation, colloidal, and strong electrostatic adsorption techniques. The effects of noble metal to base metal ratio, post-deposition heat treatment temperature, and hydrogen content in the heat treatment atmosphere were evaluated. Temperature-programmed reduction experiments were performed to determine the temperatures at which the catalyst components are reduced, in the case of the co-impregnated samples, or the temperature at which the organic capping agent is removed, in the case of the colloidal technique. Using the strong electrostatic adsorption technique, the effect of Pd precursor type, either anionic or cationic, and the effect of carbon support type, either as-received or oxidized Vulcan carbon or BP2000 was also studied.

As was discussed in last year's annual report, the oxygen reduction activity of the Pd-Cu catalysts prepared by the co-impregnation technique strongly depends on the Pd to Cu molar ratio and on the heat treatment temperature. For this system and using this preparation method, the highest ORR activity was measured for the catalyst with a nominal palladium to copper molar ratio of 1:3, heat treated at 600°C. To test the stability of this material and to remove any unalloyed copper, this catalyst was treated in dilute perchloric acid for 3-6 days. This treatment improved the ORR mass activity (per mass Pd) of this catalyst by 30%. This year we performed detailed characterization of the acid-treated

Pd:Cu 25:75 catalyst prepared by co-impregnation, which showed the highest area-specific ORR activity of all the Pd-Cu catalysts studied ($129 \mu\text{A}/\text{cm}^2$ at 900 mV). The characterization showed that this catalyst consists of 3.7 wt% Pd and 1.0 wt% Cu or 68 mol% Pd and 32 mol% Cu (via inductively-coupled plasma-atomic emission spectroscopy), has a particle size of 21.5 ± 7 nm (transmission electron microscopy), and has a face-centered cubic $\text{Pd}_{49}\text{Cu}_{51}$ alloy core with a Pd-rich surface (X-ray diffraction and X-ray photoelectron spectroscopy). X-ray absorption fine-structure analyses at both the Pd and Cu K-edges were consistent with catalyst structure of a 2-3 monolayer thick, oxidized Pd-rich layer on a $\text{Pd}_{49}\text{Cu}_{51}$ alloy core. These analyses provide a guide for the desired structure of Pd-Cu nanoparticles with high area-specific ORR activity. The goal is to maintain this particle structure while reducing particle size in order to enhance the ORR mass activity.

The focus of the synthetic effort in the Pd-Cu system this year was to use the colloidal technique to form smaller and more uniform particles of the most promising Pd-Cu alloys as determined in the co-impregnation screening studies. As shown in the electron micrographs of Figure 1 and as summarized in Table 2, the colloidal technique provides complete alloying of Pd and Cu at lower temperatures than the co-impregnation technique which results in smaller particles and narrower particle size distribution. Using the TF-RDE technique, the ORR activity was determined for all the Pd-Cu catalysts prepared by the co-impregnation and colloidal techniques and an alternative colloidal technique in which the viscosity of the deposition media was increased. The kinetic current for the ORR as a function of potential and normalized to the weight of PGM, is shown in Figure 2 for the Pd-Cu catalysts developed in this project and for two commercial catalysts, 20 wt% Pd on Vulcan carbon and 20 wt% Pt also on Vulcan carbon (E-Tek). Also indicated in Figure 2 are the mean metal particle sizes. As these results show, the addition of copper to palladium increases the ORR mass activity of palladium by a factor of four. With the most active Pd-Cu catalyst, synthesized by the alternative colloidal technique, we have achieved approximately 75% the mass activity of Pt with a slightly larger particle size of 3.3 nm compared to 2.3 nm for Pt. The TF-RDE results show that the half-wave potential for ORR is shifted by more than 70 mV by the addition of Cu to Pd, approaching the half-wave potential measured for the commercial Pt/C at identical PGM loading. To determine the source of the enhanced ORR activity of the Pd-Cu catalysts, the valence band structures of these catalysts were determined using monochromated X-ray photoelectron spectroscopy. The valence band structure of the Pd:Cu 25:75 nanoparticles, prepared by the co-impregnation, colloidal, and alternative colloidal techniques are compared to the valence band structure of Pd, Cu, and

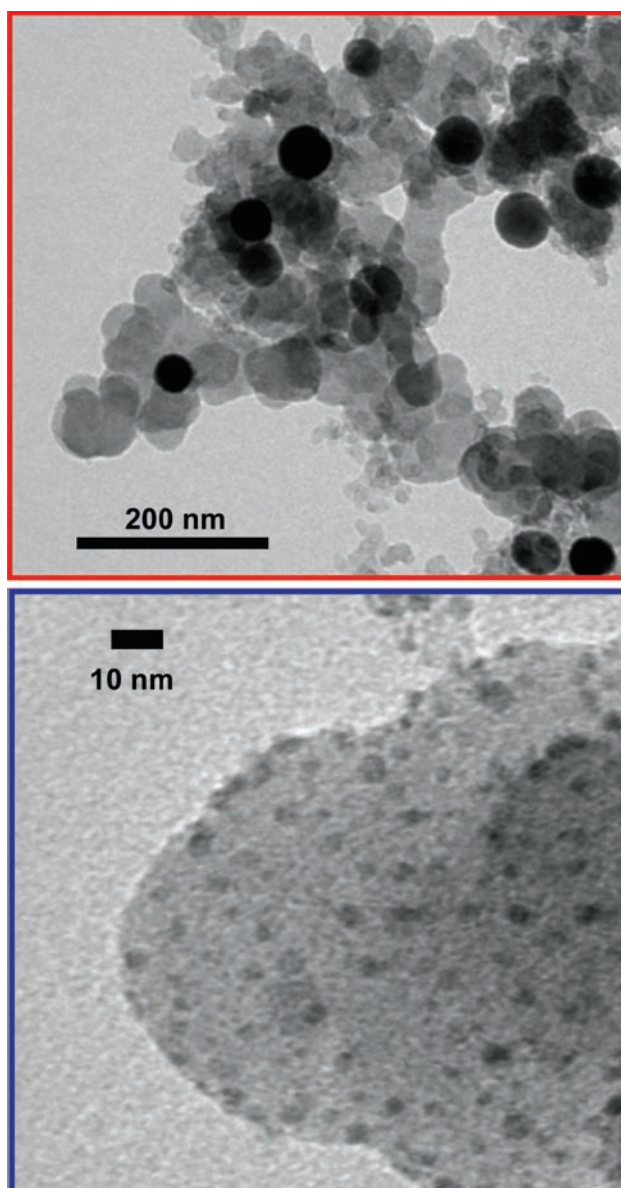


FIGURE 1. Transmission electron micrographs of Vulcan carbon-supported nanoparticles of Pd-Cu formed by the co-impregnation technique and heat treated at 800°C (top) and by the colloidal technique and heat treated at 300°C (bottom).

TABLE 2. Comparison of the Composition Control and Nanoparticle Size and Size Distribution Obtained with the Colloidal and Co-Impregnation Techniques

Technique, nominal moles Pd: moles Cu, heat treatment temperature	Nanoparticle composition (mol% Cu)	Nanoparticle size (nm)
Colloidal, 50:50, 500°C	50.7 ± 5.8	10.0 ± 2.5
Colloidal, 25:75, 500°C	75.2 ± 2.9	7.0 ± 1.0
Impregnated, 25:75, 800°C	67.5 ± 8.9	55.0 ± 14.5
Impregnated, 25:75, 600°C	47.5 ± 10.7	23.3 ± 8.3

Pt foils in Figure 3. As shown in this figure, the Pd-Cu nanoparticles have a strongly modified valence band structure compared to Pd and Cu foils and the addition of Cu shifts the Pd density of occupied valence band states toward that of Pt.

This past year, we synthesized a series of Pd-Ni carbon-supported nanoparticle catalysts using the co-impregnation technique with Pd to Ni molar ratios ranging from 90:10 to 10:90 and determined the effect of heat treatment temperature and atmosphere. To summarize these results, we found that Ni substitutes into the Pd lattice and that the ORR activity correlates with the extent of this substitution. The highest ORR activity for the 700°C treated catalysts was observed for the catalyst with a Pd to Ni molar ratio of 25:75. The overall highest ORR activity observed for Pd-Ni was for the catalyst with a Pd to Ni molar ratio of 50:50 heat-treated at 500°C. This past year we also studied the Pd-Fe system by varying the Pd:Fe molar ratio from 75:25 to 30:70 and heat-treated from 450 to 620°C. Unlike the Pd-Cu and Pd-Ni systems, it was found that there is less of a dependence of the ORR activity on the Pd to base metal ratio. The highest ORR activity was observed for the catalyst with a Pd to Fe molar ratio of 75:25, consistent with published results, [7] and heat treated at 620°C.

A summary of the highest ORR activities observed for each of the systems studied this year, is shown in Figure 4. The addition of Ni resulted in a factor of 1.4 enhancement in the ORR mass activity of Pd, Fe resulted in a factor of 2.5 enhancement, and Cu a factor of 3.6 enhancement. An evaluation of the kinetic parameters of the palladium-based catalysts at room temperature, using TF-RDE and rotating ring-disk electrode experiments, showed that the number of electrons transferred in the ORR is 4.1 ± 0.1 , the Tafel slope ranged

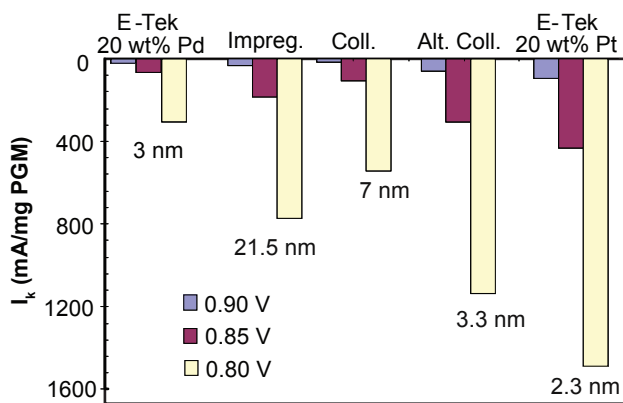


FIGURE 2. Room-temperature oxygen reduction activities (normalized to PGM loading) of Vulcan carbon-supported Pd:Cu 1:3 nanoparticle catalysts compared to commercial 20 wt% Pd and 20 wt% Pt (E-Tek). Mean particle sizes, as determined by transmission electron microscopy, are indicated.

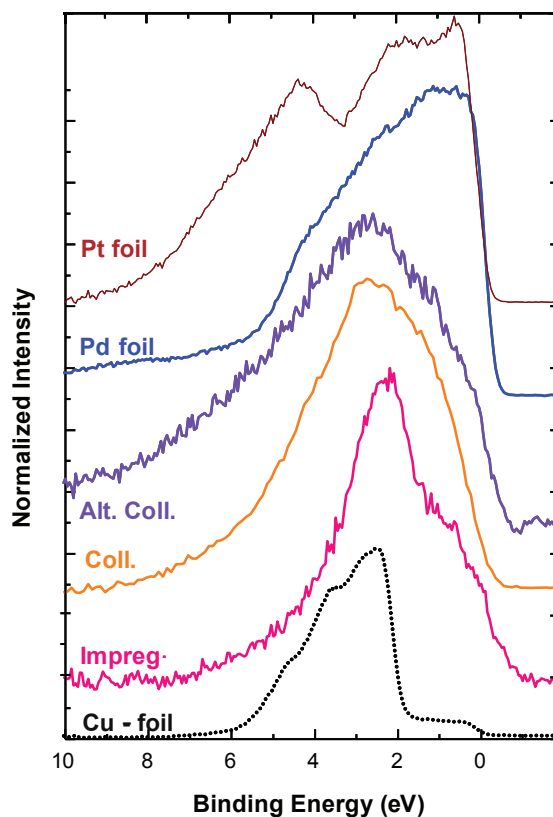


FIGURE 3. Valence band spectra of Vulcan carbon-supported Pd:Cu (25:75 molar ratio) nanoparticles prepared by the impregnation (impreg.), colloidal (coll.), and alternative colloidal (alt. coll.) techniques. Shown for comparison are the spectra for Pt, Pd, and Cu-foils.

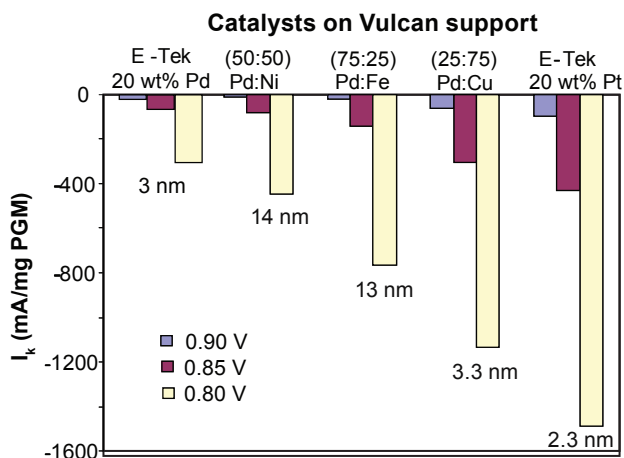


FIGURE 4. Room-temperature oxygen reduction activities (normalized to PGM loading) of Vulcan carbon-supported Pd:Ni (50:50 molar ratio), Pd:Fe (75:25), and Pd:Cu (25:75) nanoparticle catalysts compared to commercial 20 wt% Pd and 20 wt% Pt (E-Tek). Mean particle sizes, as determined by transmission electron microscopy, are indicated.

from 55 ± 1 mV/dec (Pd-Cu) to 66 ± 2 mV/dec (Pd-Fe), and the percent conversion of oxygen to hydrogen peroxide at 0.2 V was $< 0.07\%$. These parameters are very similar to those observed for Pt and Pt-based catalysts [8].

Conclusions and Future Directions

Conclusions

- The ORR mass activity of Pd nanoparticles is dependent on the Pd nanoparticle size (1.2 to 20 nm tested), with the highest activity observed for the 5 nm particles.
- The ORR kinetics of the Pd-Cu, Pd-Fe, and Pd-Ni catalysts are dependent on the Pd to base metal molar ratio and the heat treatment temperature, with the highest ORR mass activities seen for Pd:Cu 25:75, Pd:Fe 75:25, and Pd:Ni 50:50.
- The addition of copper, iron, and nickel enhances the ORR mass activity of Pd by a factor of 3.6, 2.5, and 1.4, respectively, achieving up to 75% the mass activity (normalized to PGM content only) of commercial Pt/C with Pd-Cu₃/C.
- The Pd-Cu alloys have a higher average binding energy of electrons in the valence band compared to Pd alone, with the shift in energy being toward the average binding energy of electrons in Pt's valence band. The valence band structure of the Pd-Cu alloy nanoparticles is highly dependent on synthetic procedure.
- Periodic quantum mechanical slab calculations for the two possible gas phase oxygen reduction reaction mechanisms (associative and dissociative) show:
 - For the associative mechanism, leading through OOH formation, the rate-determining step on Pt, Pd, and Cu is H₂O formation and the relative barriers are Cu > Pd > Pt.
 - For the dissociative mechanisms, leading through OH formation, the rate-determining step on Pd is H₂O formation and on Pt and Cu is OH formation and the relative barriers are Cu >> Pt > Pd.

On-Going Work and Future Directions

- Computational analyses:
 - Determine energetics, including barriers, for dissociative and associative ORR mechanisms on Pd-Cu slabs.
 - Study surface segregation in Pd-Cu alloy slabs using quantum mechanics and in nanoparticles using large-scale molecular dynamics (ReaxFF).
 - Investigate solvation and coverage effects for the ORR on Pd and Pd-Cu alloys.

- Fit ReaxFF to the cathode chemical reaction energies and perform simulations of cathode reactions on Pd-Cu nanoparticles.
- Model systems and nanoparticle characterization:
 - Study effect of annealing, determine surface segregation, and measure ORR activity on Pd-Cu model system.
 - Prepare and characterize Pd on Ni, Pd on Fe, Cu on Pd, Ni on Pd, and Fe on Pd model systems.
 - Perform depth-dependent electronic structure characterization using tunable synchrotron radiation.
- Nanoparticle fabrication, activity, and stability characterization:
 - Prepare significant quantities of most active Pd-Cu catalyst for membrane-electrode assembly testing.
 - Deposit Pd shell on Pd-Cu alloys prepared by colloidal technique.
 - Develop the colloidal technique for PdNi, PdFe, and PdCo alloys and the strong-electrostatic adsorption technique for PdNi, PdFe, and Pd-Cu.
 - Determine stability of all Pd alloys to potential cycling.
 - Characterize Rh-based alloys fabricated by co-impregnation.

Special Recognitions & Awards/Patents Issued

1. Deborah J. Myers, Xiaoping Wang, Nancy N. Kariuki, "Non-Platinum Bimetallic Polymer Electrolyte Fuel Cell Catalysts"; Patent Pending.

FY 2008 Publications/Presentations

1. X. Wang, N. Kariuki, J.T. Vaughey, J. Goodpaster, R. Kumar, and D.J. Myers, "Bimetallic Pd-Cu Oxygen Reduction Electrocatalysts", *J. Electrochem. Soc.*, (2008) B602.
2. N.N. Kariuki, X. Wang, S. Niyogi, J. Mawdsley, and D.J. Myers, "Composition-Controlled Synthesis of Bimetallic Palladium-Copper Nanoparticles for Fuel Cell Electrocatalysis", 213th Meeting of the Electrochemical Society, May, 2008, Abstract No. 306.
3. N. Kariuki, D.J. Liu, D.J. Myers, S. Niyogi, X. Wang, and J. Yang, "Bimetallic palladium cathode electrocatalysts & new MEA concept development" LANL-NEDO-FC-Cubic Workshop, Tokyo, Japan, October 30, 2007 (invited presentation).
4. D.J. Myers, "Fundamental Studies of Platinum Electrocatalyst Degradation and Non-Platinum Bimetallic Cathode Electrocatalysts", Plug Power, Latham, NY, August 10, 2007 (invited presentation).

5. D. J. Myers, X. Wang, N. Kariuki, S. Niyogi, J. Mawdsley, and R. Kumar, "Non-Platinum Bimetallic Cathode Electrocatalysts", IEA-AFC Annex XVI Spring 2007 Workshop, Helsinki, Finland, June 8, 2007.
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10. Y. Sha, T. Yu, B.V. Merinov, A.C.T. van Duin, W.A. Goddard, "Mechanisms and Rates for the Oxygen Reduction Reaction on Non-Platinum PEMFC Catalysts from First-Principles-based Modeling", Fuel Cell Seminar, San Antonio, Texas, 2007.

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