

## V.E.4 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  $\mu\text{A}/\text{cm}^2$  @ 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).

### 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: \$5/kW, 0.3 mg platinum group metal (PGM)/ $\text{cm}^2$ .

### Accomplishments

- Synthesized and determined the oxygen reduction reaction (ORR) activity of palladium-cobalt, rhodium-cobalt, and rhodium-iron alloy nanoparticle systems.
- Highest room temperature nanoparticle ORR specific and mass activity achieved:
  - 95  $\mu\text{A}/\text{cm}^2$  (900 mV; room temperature); 2,420  $\mu\text{A}/\text{cm}^2$  (800 mV; room temperature) for Pd:Cu 1:1 by co-impregnation; 20 nm.
  - 0.06 A/mg Pd for Pd:Cu 1:3 by alternative colloidal; 3.3 nm (900 mV; room temperature)
- Scaled up synthesis of  $\text{Cu}_3\text{Pd}$  electrocatalyst and tested electrocatalyst in membrane electrode assembly (MEA).
- Developed capability to calculate the full valence band structure of pure metals and alloys and correlated the calculated structure of Pt, Pd, and Pd-Cu alloys with experimentally-determined structure.
- Using computational studies, identified several Pd alloys favoring noble metal surface segregation.
- Identified several non-Pt systems having d-band centers similar to Pt's (as a first approximation for choice of systems with desirable electronic structures).
- Fabricated model systems of binary and ternary Pd alloys identified as promising in computational effort.



### Introduction

A major contributor to the cost of an automotive polymer electrolyte membrane fuel cell system is the platinum-based cathode electrocatalyst. The goal of this project is to reduce the cost of the cathode catalyst by replacing platinum with less expensive alloys, while also meeting or exceeding the catalyst durability and performance targets.

## 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 or stabilizing the primarily base metal particle core against dissolution in the acidic electrolyte. The initial choice of base metal-noble metal combinations was based on published theoretical calculations predicting the tendency of the noble metal component to segregate to the surface of a base metal substrate and on the ability of the base metal to modify the electronic properties of the noble metal, as reflected by a shift of the weighted average energy of occupied d-band states (i.e., the "d-band center") toward that of Pt [1-4]. The durability of the candidate noble metals (Pd, Rh, and Ir), which tend to be less stable in acidic environments than platinum, is being addressed by shifting the valence band energy of the noble metals, thus decreasing the oxophilicity of the noble metal and imparting stability against dissolution [5-7].

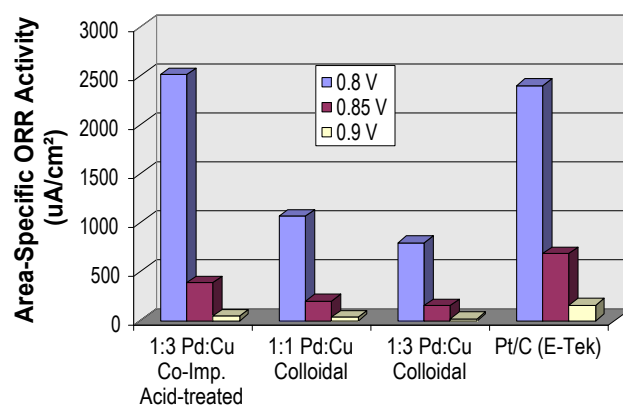
The project's approach includes: (1) computational and model system (pure metals and bulk alloys) studies to guide the choice of systems and noble metal to base metal ratio, (2) nanoparticle fabrication and characterization (ORR activity, particle size, composition, and electronic structure), (3) MEA fabrication and testing, and (4) post-test characterization. Carbon-supported bimetallic nanoparticles are being fabricated by co-impregnation, colloidal, and strong electrostatic adsorption techniques. The co-impregnation technique is used for screening of the catalyst compositions, resulting 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 catalyst compositions identified in the co-impregnation screening studies. Spectroscopic techniques are 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) [8,9] and the nanoparticle stabilities are screened using potentiostatic and potential cycling measurements in non-adsorbing perchloric acid electrolyte, mimicking the fuel cell ionomer (perfluorosulfonic acid). Materials showing promising ORR reduction activity and stability are incorporated into MEAs and their short and long-term performance determined under accelerated test conditions.

## Results

This year we synthesized high-surface-area carbon-supported nanoparticles in the palladium-copper, palladium-cobalt, rhodium-cobalt, and rhodium-iron

systems and determined the effect of noble to base metal ratio and post-deposition heat treatment temperature and atmosphere on ORR activity. The highest ORR activity observed for the rhodium-iron system was 37 mA/mg Rh and 53  $\mu\text{A}/\text{cm}^2$  with a rhodium to iron atomic ratio of 1:1, heat treated at 500°C in 100% hydrogen (@ 0.8 V, room temperature, TF-RDE results). The highest ORR activity for the rhodium-cobalt system was 275 mA/mg Rh and 290  $\mu\text{A}/\text{cm}^2$  (@ 0.8 V, room temp., TF-RDE results) for a catalyst with a rhodium to cobalt atomic ratio of 1:9, heat treated in 4% hydrogen at 300°C and 700°C, respectively. These results show that both iron and cobalt increase the ORR activity of rhodium, but the absolute ORR area-specific and mass activities are far below those of platinum.

This year we also determined the area specific activities for the most promising palladium-copper nanoparticle catalysts, using the hydrogen adsorption/desorption region of the baseline voltammograms to determine the electrochemically-active surface area [9]. As shown in Figure 1, the palladium-copper catalyst with a nominal palladium to copper atomic ratio of 1:3, prepared by the co-impregnation method, heat treated at 600°C, and acid-treated in perchloric acid, showed an area-specific ORR activity comparable to that of commercial platinum (@0.8 V, room temperature, TF-RDE results). Detailed morphological, compositional, and structural characterization of this catalyst by a variety of techniques (electron microscopy, energy-dispersive X-ray emission spectroscopy, X-ray diffraction, and X-ray absorption spectroscopy) showed this catalyst to be comprised of 21.5  $\pm$  7 nm particles with palladium-copper alloy cores (49:51 Pd to Cu atomic ratio), surrounded by a palladium-rich shell. The large particle size of this catalyst relative to that of the commercial Pt catalyst (2.3 nm) means a larger fraction of the noble metal resides in the interior of the particle and does not

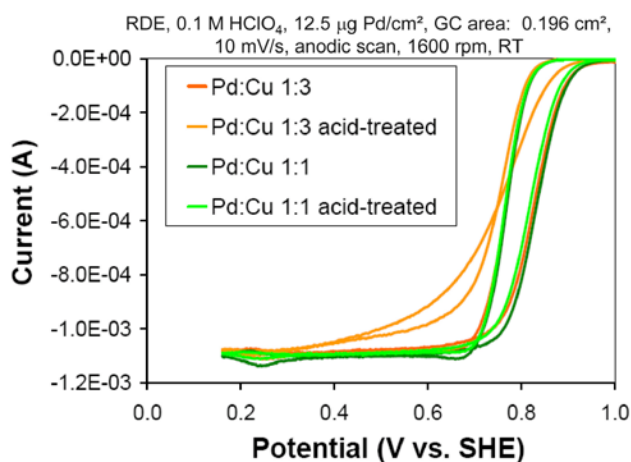


**FIGURE 1.** Room temperature area-specific oxygen reduction reaction activity for Pd-Cu nano-particle catalysts compared to commercial Pt/C (BASF/E-Tek).

participate in the ORR reaction, thus decreasing the catalyst's mass activity. In order to achieve higher mass activities, we attempted to make smaller particles of this same composition and structure, using the colloidal technique to form a 1:1 Pd:Cu core and depositing a palladium shell on this core. The colloidal technique resulted in reduced metal particle sizes of 7-10 nm, but also reduced mass and area-specific ORR activities (Figure 1). We are currently exploring if the reduced area-specific activity results from a particle size effect, as is seen for Pt catalysts [9], or from a different atomic structure. All attempts at deposition of a shell of Pd on both the 1:1 and 1:3 PdCu cores lowered both the mass and area-specific ORR activities of these catalysts.

The stability of the colloidal palladium-copper nanoparticle catalyst with 1:1 and 1:3 Pd:Cu atomic ratios was tested by determining their ORR activity, using TF-RDE, before and after soaking in 0.6 M perchloric acid for three days. As shown in Figure 2, the ORR activity of the 1:1 catalyst was unchanged by treatment for three days in 0.6 M perchloric acid, whereas the 1:3 catalyst showed a dramatic loss of ORR activity. This is attributed to the ability of the 1:1 catalyst to form a stable Pd-rich protective surface, whereas the high copper content of the 1:3 catalyst results in destruction of the structure when leaching copper (as verified by X-ray diffraction analysis). The 1:3 catalyst was also found to be unstable in the fuel cell environment. Testing of the 1:1 catalyst in a membrane-electrode assembly is underway.

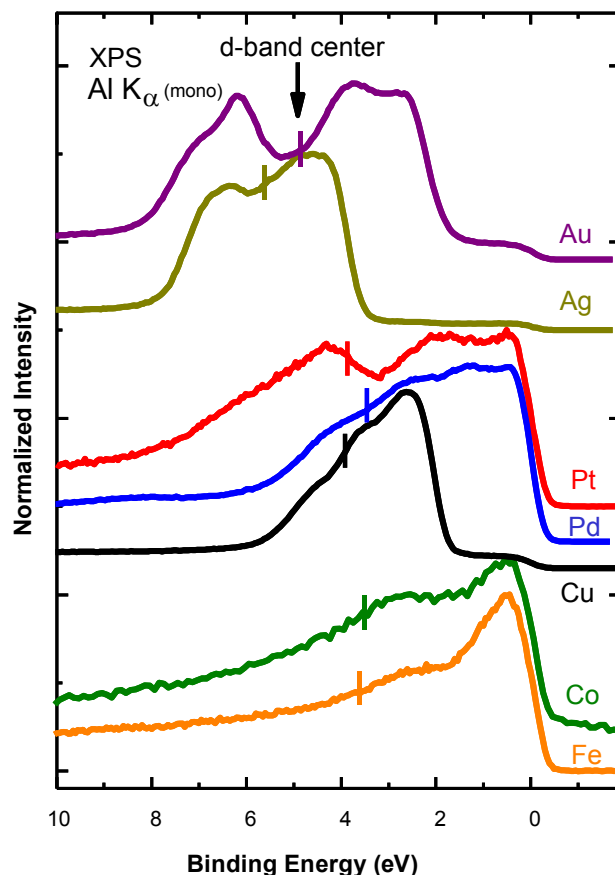
In the model system characterization task, the University of Nevada, Las Vegas, has determined the valence band structure of a number of base and noble metal foils using Al  $K\alpha$  X-ray photoelectron spectroscopy. These spectra, shown in Figure 3, illustrate that all of the metals have distinct valence



**FIGURE 2.** Rotating disk electrode results in oxygen-saturated room temperature perchloric acid for Pd:Cu 1:1 and Pd:Cu 1:3 (atomic ratios) synthesized by the colloidal technique before and after acid treatment.

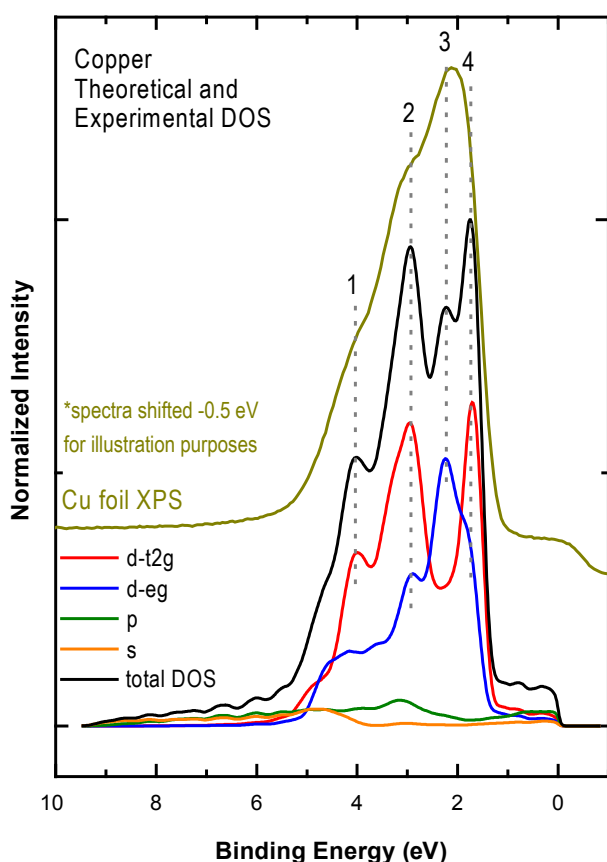
band structures. The vertical bars in Figure 3 indicate the calculated “d-band center” of the respective metals, which has been considered to influence the bonding of oxygenated species to metals and their resulting ORR activity [1-4]. From these data, it can be seen that copper and platinum have similar “d-band center” positions, despite the fact that the actual d-band structures are very different. Likewise, these two metals differ immensely in their bond strength with oxygen and also in their ORR activity [10]. This finding indicates the need for an overall evaluation of the valence band structure rather than using the simplified reduction to the “d-band center” as a figure of merit.

In the computational aspect of the project, the California Institute of Technology is using first principles theory and computation to determine the valence band structure, preferred atomic structures and adsorption sites, ORR reaction pathways and barriers on various metals and metal alloy systems. They calculated the surface segregation energies and “d-band centers” for Pt, Pd, and Rh alloyed with metals in the atomic number range between Sc and Zn (26 systems), Y and Cd (28 systems), and Ta and Hg (21 systems). This survey showed that palladium alloys with molybdenum,



**FIGURE 3.** Density of states in the valence band for select metal foils and calculated d-band centers.

rhodium, tantalum, or tungsten show favorable segregation of palladium to the surface of the alloy and “d-band centers” approximating that of platinum. However, as mentioned above, the entire valence band structure, its influence on the bond strength with oxygen and oxygenated species, and the complete energetics of the ORR must be determined for these and other alloys. Toward this end, the complete valence band structure for Pt, Pd, Cu, and CuPd, and Cu<sub>3</sub>Pd have been determined. As an example, the calculated contributions of the individual wave functions to the valence band structure of copper are shown in Figure 4. This type of calculation and its verification, by comparison with experimentally-determined valence band structures, are the first steps toward analysis of the individual contributions to valence band structures and involvement of these states in the oxygen reduction reaction. This in turn will result in the ability to better predict which non-platinum systems should show ORR activities comparable or higher than the platinum-based catalysts.



**FIGURE 4.** Calculated individual wave functions, calculated total valence band density of states (summation of individual wave functions), and experimentally-determined valence band density of states for copper.

## Conclusions and Future Directions

### Conclusions

- Copper modifies the valence band structure and ORR activity of palladium. The extent of the modification of the ORR activity is correlated with the extent of downshift of the valence band density of states.
- Palladium-copper alloy nanoparticles (21 nm), made by the co-impregnation technique, have comparable area-specific ORR activity at 0.8 V to that of platinum.
- Smaller palladium-copper alloy nanoparticles (7-10 nm) made by the colloidal technique have lower area-specific ORR activity.
- d-band center alone does not adequately reflect the valence band structure (density of states as a function of energy) and bond strength of oxygen with metals; the entire spectral distribution must be analyzed.
- Palladium alloyed with molybdenum, rhodium, tantalum, or tungsten shows favorable segregation of palladium to the surface of the alloy and “d-band centers” approximating that of platinum (as a first approximation - entire valence band density of states must be determined).

### Future Directions

#### Computational Analyses

- Based on density functional theory calculations, determine complete energetics for the ORR on Pd-Mo, Pd-Re, Pd-Ta, and Pd-W alloys.
- Continue to determine alloy electronic structures using density of states analysis.
- Investigate solvation effect for the ORR on Pd-based alloys.
- Continue developing reactive force field large-scale molecular dynamic calculations reactive force field for the ORR on relevant alloys.

#### Model Systems

- Characterize ingots 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 with varying Pd to base metal ratios:
  - Determine ORR activity, electronic structure, and surface composition as a function of annealing temperature.

### Nanoparticle Fabrication, Activity, and Stability Characterization

- Test of Pd:Cu 1:1 nanoparticle catalyst activity and stability in MEA.
- Synthesis of alloy and core/shell Pd-Cu, Pd-Mo, and Pd-W catalysts using strong-electrostatic adsorption technique.
- Fabricate Pd-Cu-M ternaries and Pd-M binaries using colloidal techniques.

### 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 2009 Publications/Presentations

1. “Bimetallic Palladium-Base Metal Nanoparticle Oxygen Reduction Electrocatalysts”, X. Wang, N.N. Kariuki, S. Niyogi, M. Smith, D.J. Myers, T. Hofmann, Y. Zhang, M. Bär, and C. Heske, Proceedings of the Electrochemical Society (ECS), 2008 Fall Meeting, Honolulu, HI, ECS Transactions 16, 109-119 (2008).
2. “Bimetallic Palladium-Base Metal Nanoparticle Oxygen Reduction Electrocatalysts”, X. Wang, N.N. Kariuki, S. Niyogi, M. Smith, D.J. Myers, T. Hofmann, Y. Zhang, M. Bär, and C. Heske, 214<sup>th</sup> ECS Meeting, October 12–17, Honolulu, Hawaii, 2008.
3. “First-Principles-based Modeling of Non-Platinum Catalysts for Oxygen Reduction Reaction”, Y. Sha, T. Yu, B.V. Merinov, A. van Duin, and W.A. Goddard III, 214<sup>th</sup> ECS Meeting, October 12–17, Honolulu, Hawaii, 2008.
4. “First-Principles-based Modeling of Improved Pt Alloy Catalysts”, T. Yu, Y. Sha, B.V. Merinov, A. van Duin, W.A. Goddard III, and P. Shirvanian, 214<sup>th</sup> ECS Meeting, October 12–17, Honolulu, Hawaii, 2008.
5. “A Rational Method to Prepare Supported Metal Catalysts,” J.R. Regalbuto, Spring AIChE Meeting, Salt Lake City, March, 2009 (invited).

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