

V.C.4 Low Pt Loading Fuel Cell Electrocatalysts

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Objectives

- Explore a novel class of electrocatalysts for O₂ reduction consisting of Pt monolayers on *noble metal - non-noble metal core-shell* nanoparticles.
- Demonstrate the stability of Pt mixed metal monolayer (Pt₈₀Ir₂₀/Pd/C) and Pt/Au/Ni/C electrocatalysts in fuel cell tests. Further tests of PtRu₂₀ anode electrocatalyst.
- Scale up synthesis involving displacement of a Cu monolayer.
- Further reduce noble metal content: Pd-alloy and NbO₂ supports.
- Address the problem of Pt dissolution under potential cycling regimes.
- Test the effects of Au clusters on the stability of Pt.

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:

- (A) Durability
- (B) Costs
- (C) Electrode performance

Technical Targets

Performance Parameter	Units	2005	2010	2015
Precious metal loading	g/kW	2.7	0.3	0.2
Durability with cycling	Hr	2,000	5,000	5,000

Accomplishments

- Novel class of electrocatalysts developed: Pt monolayer on *noble metal - non-noble metal core-shell* nanoparticles.
 - Performance of 0.14 g/kW meets the target for 2010 of 0.15 g/kW.
 - Pt mass activity: 20x increase; noble metal mass activity: 5x increase.
- Scale-up of the electrocatalysts' synthesis to 1 g/batch was accomplished.
- Au clusters (submonolayer) were shown to have a pronounced stabilization effect on Pt under potential cycling regimes.
- Pd₂Co and Pd₃Fe have activities similar to that of Pt; methanol tolerance of Pd₂Co was confirmed in a fuel cell test at Los Alamos National Laboratory (LANL).
- NbO₂ is a promising support for Pt monolayer catalysts.

Introduction

Despite the remarkable advances achieved recently, certain deficiencies in fuel cell technology still need to be addressed, particularly the inadequate efficiency of energy conversion and the high Pt content of electrocatalysts. Both problems are connected to the rather slow electrocatalytic O₂ reduction reaction (ORR) at fuel cell cathodes. We demonstrated in this project that a very promising way to resolve these difficulties can be based on new types of electrocatalysts that have high activities and very low Pt monolayer contents. Their Pt mass activities are about an order of magnitude higher than those of commercial electrocatalysts. Following is described the latest in the development of these electrocatalysts.

Approach

Our approach to solving the problems of slow kinetics of the ORR and a high Pt content has been

to design electrocatalysts that have sub-monolayer or monolayer amounts of Pt on a surface of suitable metal or alloy nanoparticles. This approach facilitated enhancing the activity of Pt and, at the same time, a considerable reduction of its loading. Enhanced activity of Pt can be a consequence of a low coordination of Pt atoms; tensile strain in the Pt monolayer on a suitable substrate, which causes an upshift of the d-band center of Pt; and electronic (ligand) effects. The electrodeposition of Pt monolayers on metal or alloy nanoparticles was accomplished using our method of galvanic displacement of a Cu monolayer.

Results

A new class of O_2 electrocatalysts consists of Pt monolayers deposited on the surfaces of carbon-supported non-noble metal – noble metal core-shell nanoparticles. These core-shell nanoparticles were formed by segregating the atoms of the noble metal onto the nanoparticles' surfaces at elevated temperatures. The noble metal shell protects the non-noble core from contact with the electrolyte. A Pt monolayer (ML) was deposited by galvanic displacement of a Cu monolayer deposited at underpotentials (Figure 1). The mass activities of several electrocatalysts investigated, e.g., Pt/Pd/Co₅, are more than an order of magnitude higher than those of commercial Pt/C electrocatalysts. Geometric effects in the Pt monolayer and the effects of PtOH coverage, revealed by electrochemical, x-ray diffraction and x-ray absorption spectroscopy data, appear to be the sources of the enhanced catalytic activity (Figure 2).

The initial phase of the fuel cell test of the Pt mixed metal monolayer (Pt₈₀Ir₂₀/Pd/C) electrocatalyst shows a remarkable stability of the polarization curve.

Durability and CO tolerance of the Brookhaven National Laboratory anode PtRu₂₀/C electrocatalyst was confirmed in a 2,400 h test at Plug Power Corporation. The performance of 0.063 g_{Pt}/kW meets the 2010 target of 0.15 g/kW, i.e., 1/2 of 0.3 g/kW (Ru not counted). Compared to a commercial membrane electrode assembly (0.6 mg Pt/Ru/cm²), it has higher activity for the oxidation of clean H₂ but slightly lower activity for the reformat. The Pt loading was only 0.022 mg_{Pt}/cm².

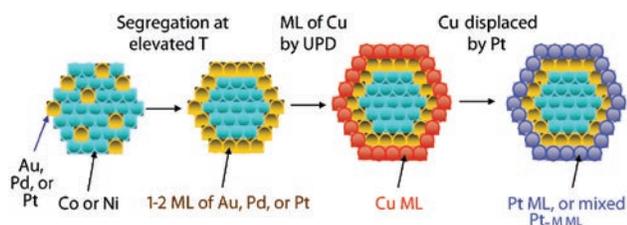


FIGURE 1. Model for the Synthesis of Pt ML Electrocatalysts on Non-Noble Metal-Noble Metal Core-Shell Nanoparticles

One issue regarding Pt monolayer electrocatalysts is the possibility of scaling up the synthesis involving displacement of a Cu monolayer. In collaboration with the team from Battelle Memorial Institute, we scaled up the synthesis to 1 g per batch. Further increase of the productivity is not considered a difficult task.

To further reduce the noble metal content in low Pt loading electrocatalysts, a new electrocatalyst was synthesized by depositing a small amount of Pt (monolayer-level) on carbon-supported niobium oxide nanoparticles (NbO₂ or Nb₂O₅). The Nb₂O₅ and NbO₂ nanoparticles were prepared by the sol-gel method. The average diameters of the nanoparticles determined by transmission electron microscope (TEM) and x-ray diffraction (XRD) were ca 11 nm. Voltammetry tests demonstrated that both the Pt/NbO₂/C and Pt/Nb₂O₅/C electrocatalysts (5 μg_{Pt} cm⁻²) showed higher Pt mass-specific activity for the ORR than a commercial Pt/C electrocatalyst (see Figure 3). The results indicate

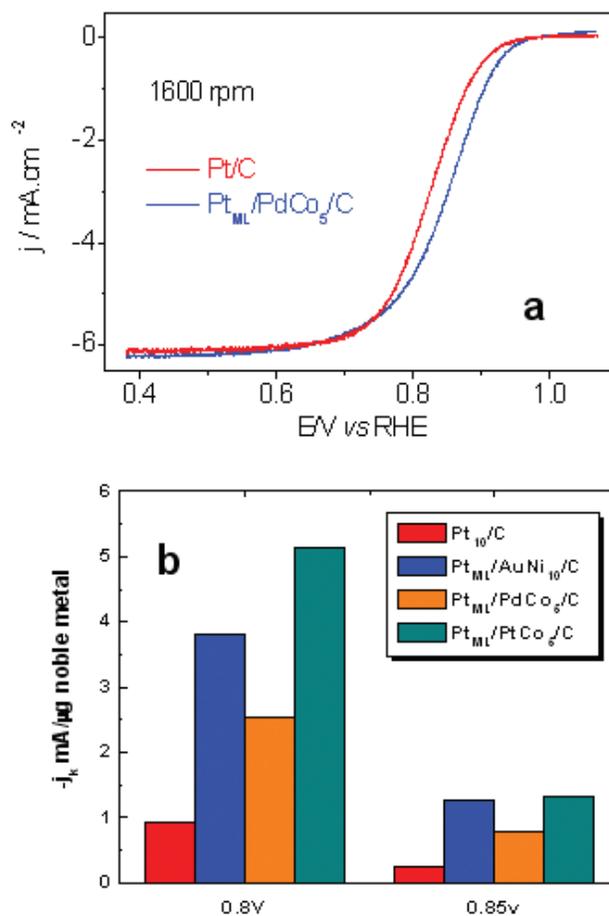


FIGURE 2. (a) The ORR on a Pt ML electrocatalyst on carbon-supported PdCo₅ core-shell nanoparticles in 0.1M HClO₄. Sweep rate 10 mV/s; room temperature. (b) Total noble metal mass activity of Pt ML electrocatalysts on several core-shell nanoparticles indicated in the graph compared with a commercial Pt/C electrocatalyst.

that the niobium oxides can adequately support Pt, which could further reduce the noble metal content in electrocatalysts for the ORR.

We now report on a new electrocatalyst that does not contain Pt; it consists of Pd-Fe alloy nanoparticles. Pd is considerably less expensive than Pt, but less active for the ORR. Our previous work on Pd alloy electrocatalysts demonstrated that PdCo/C nanoparticles are very active for the ORR. Pd-Fe/C electrocatalysts with a molar ratio of Pd:Fe ranging from 1:1 to 4:1 were prepared by thermal treatment of the mixture of Pd/C nanoparticles and FeCl₃ solution. From the phase diagram, we deduced that the ordered Pd₃Fe (L1₂-type) phase with a face centered cubic (fcc) structure is favored in the composition range of 65-85 atomic % Pd at 500°C. The highest ORR activity is obtained for a 0.273-nm Pd-Pd bond distance, i.e., highly compressed Pd (Figure 4). The density functional theory (DFT) calculations indicate that compression of a Pd lattice in PdFe alloys will downshift the d-band center and thus decrease its reactivity. Pd is a relatively reactive metal. Therefore, decreasing the activity of Pd could lower the blocking effect of O₂, O/OH, O₂⁻ and H₂O₂ by weakening their bonding to Pd, resulting in an enhanced ORR activity.

Resolving the problem of Pt dissolution under potential cycling regimes is of critical importance for the application of fuel cells in electric vehicles. We report an unexpected but very interesting effect of a submonolayer of Au clusters that causes a pronounced stabilization of Pt under a potential cycling regime. The Au nanoclusters were obtained by displacement

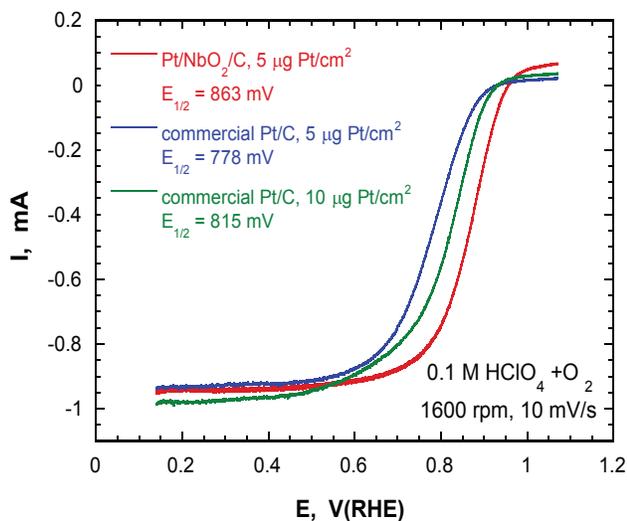


FIGURE 3. The ORR on a Pt adlayer electrocatalyst on carbon-supported NbO₂ nanoparticles compared with Pt/C in 0.1M HClO₄. Sweep rate 10 mV/s. Pt loadings are given in the graph.

of a monolayer of Cu underpotentially deposited on Pt nanoparticles. We demonstrated for a Pt(111) surface that a pseudomorphic layer of Au restructures into 3D and 2D clusters upon potential excursion to 1 V. Thus, it is likely that on Pt nanoparticles, at potentials of the ORR, Au forms clusters rather than a uniform monolayer. The impact of gold nanoclusters on the initial electrocatalytic activity of Pt for oxygen reduction is insignificant, while the stability of the modified Pt electrocatalyst under the accelerated fuel cell testing conditions is greatly improved. Thirty thousand potential cycles from 0.6 to 1.1 V at 25°C in O₂-saturated solution cause a significant degradation of the commercial Pt/C electrocatalyst (40 mV loss in E_{1/2} and 45% loss in active surface area). The same electrocatalyst covered by Au clusters under the same potential cycling regime is not affected (Figures 5a and 5b). The charge for deposited Au is equivalent to 2/3 of a monolayer, but the effective blocking of Pt surface by Au was not determined. A delayed oxidation of Pt nanoparticles covered with Au in comparison to the oxidation of Pt nanoparticles without Au coverage was seen from *in situ* x-ray absorption near-edge spectroscopy measurements. This may be one reason for the increased stability of the modified surface.

Conclusions and Future Directions

1. A novel class of electrocatalysts has been developed: Pt monolayer on *noble metal - non-noble metal core-shell* nanoparticles. Its performance of 0.14 g/kW meets the target for 2010 of 0.15 g/kW (for one electrode).

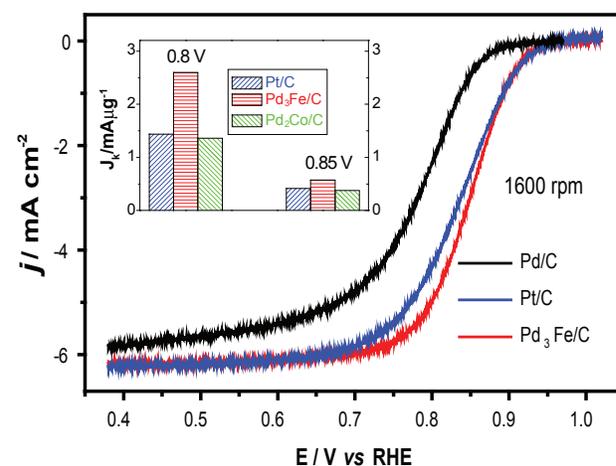


FIGURE 4. The ORR on Pd₃Fe/C and on commercial Pd/C and Pt/C nanoparticles in 0.1M HClO₄. Sweep rate 10 mV s⁻¹; room temperature. The Pd or Pt loading is 10 μg cm⁻². Insert: Comparison of mass activity for Pt/C, Pd₃Fe/C and Pd₂Co/C at 0.8 and 0.85 V.

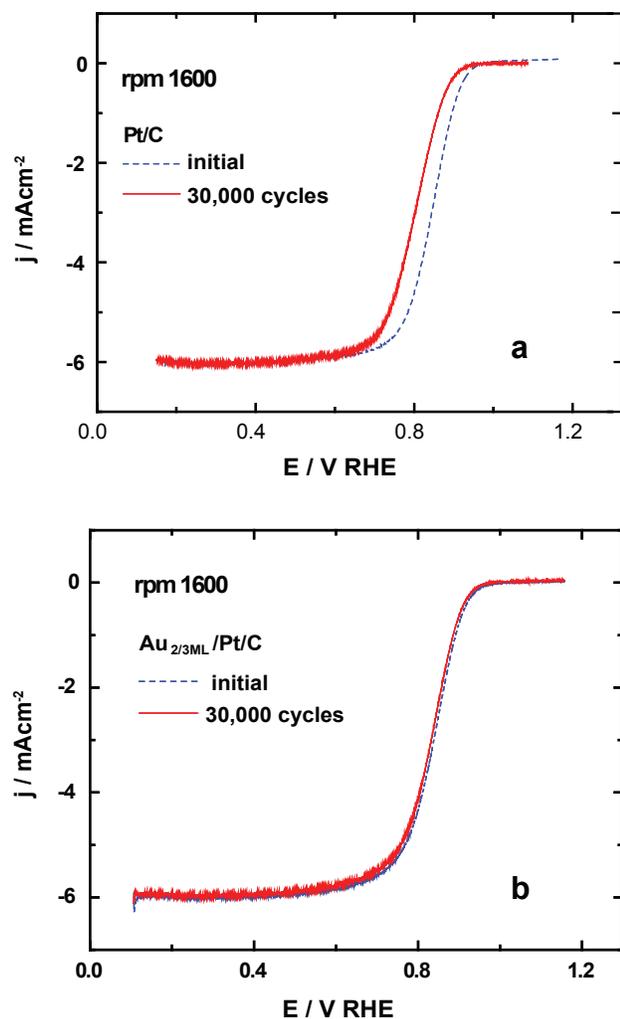


FIGURE 5 (a) The ORR on a Pt/C electrocatalyst before and after 30,000 cycles from 0.6 to 1.1 V. (b) The same experiment as in (a) except for Pt modification by Au clusters with the coverage equivalent to a 2/3 ML. Sweep rate 50 mV/s.

- Durability and CO tolerance of the PtRu₂₀ anode electrocatalyst were confirmed in a 2,400 h test at Plug Power. The performance of 0.063 g Pt/kW meets the 2010 target of 0.15 g/kW (Ru not counted).
- Scale-up of the synthesis of Pt ML electrocatalysts to 1 g/batch has been accomplished.
- A new class of electrocatalysts has been synthesized consisting of Pd-Fe alloys. Its activity is similar to that of Pt; methanol tolerance of Pd₂Co has been confirmed in a fuel cell test at LANL.
- NbO₂ is a promising support for Pt monolayer catalysts.

- A submonolayer of Au clusters has a pronounced stabilization effect on Pt under a potential cycling regime.

Future work will focus on fuel cell tests of several types of Pt monolayer electrocatalysts, post fuel cell tests, stability studies, the effects of Au clusters on stability of Pt in membrane electrode assemblies under potential cycling regimes, segregation of Pt and alloy supports, and further reduction of Pt content using core-shell nanoparticle and oxide supports. In addition, necessary basic *in situ* surface science and electrochemical studies will be conducted.

FY 2006 Publications/Presentations

- J. Zhang, M. B. Vukmirovic, Y. Xu, M. Mavrikakis, R. R. Adzic, Controlling the catalytic activity of platinum monolayer electrocatalysts for oxygen reduction with different substrates, *Angew. Chem. Int. Ed.* 117 (2005) 2170.
- J. Zhang, M. B. Vukmirovic, K. Sasaki, F. Uribe, R. R. Adzic, Platinum monolayer electrocatalysts for oxygen reduction: effect of substrates, and long-term stability, *J. Serb. Chem. Soc.*, 70 (2005) 513-525 (75th Anniversary issue).
- K. Sasaki, J. Zhang, J. Wang, F. Uribe, R. Adzic, Platinum submonolayer-monolayer electrocatalysts – an electrochemical and x-ray absorption spectroscopy study, *Res. Chem. Intermed.*, (special issue) in press.
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- M. H. Shao, R. R. Adzic, Spectroscopic identification of the reaction intermediates in oxygen reduction on gold in alkaline solutions, *J. Phys. Chem. B* 2005, 109(35): 16563-16566.
- J. Zhang, F. H. B. Lima, M. H. Shao, K. Sasaki, J. X. Wang, J. Hanson, R. R. Adzic, Platinum monolayer on non-noble metal - noble metal core-shell nanoparticles electrocatalysts for O₂ reduction, *J. Phys. Chem. B*, 109 (2005) 22701-22704.

Special Recognitions & Awards/Patents Issued

- In 2005 R. Adzic was inducted as a Fellow of The Electrochemical Society.
- Patents pending: Electrocatalyst for Oxygen Reduction Protected Against Oxidation and Dissolution.