

VII.C.4 Low Pt Loading Fuel Cell Electrocatalysts

Radoslav Adzic (Primary Contact), Junliang Zhang, Kotaro Sasaki, Tao Huang, Jia Wang, Miomir Vukmirovic

Brookhaven National Laboratory, Bldg. 555

Upton, NY 11973-5000

Phone: (631) 344-4522; Fax: (631) 344-5815; E-mail: adzic@bnl.gov

DOE Technology Development Manager: Nancy Garland

Phone: (202) 586-5673; Fax: (202) 586-9811; E-mail: Nancy.Garland@ee.doe.gov

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Projected End Date: Multi-year

Objectives

- Improve the activity of Pt monolayer electrocatalysts for O₂ reduction (Pt_{ML}/Pd/C).
- Demonstrate the stability of Pt monolayer electrocatalysts in fuel cell tests.
- Improve the syntheses of electrocatalysts with ultra-low or no Pt content (Pt/AuNi/C and Pd₂Co/C), and test the electrocatalysts in fuel cells.
- Explore a novel class of electrocatalysts for O₂ reduction consisting of mixed monolayers of Pt and late transition metals.

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:

- Q. Electrode Performance

Technical Targets

Performance Parameter	Units	2005 Target	BNL Electrocatalyst Status
Precious Metal Loading	g/kW	2.7	<ul style="list-style-type: none"> • 0.17~0.25 for Cathode Catalyst • 0.60 for Fuel Cell
Durability	hr	2000	<ul style="list-style-type: none"> • 3000 for Cathode Catalyst • 530 for Low-Pt Cell (Test in Progress)

Approach

- Develop low-Pt-loading electrocatalysts by placing Pt monolayers, or mixed Pt-late transition metal monolayers, on metal or alloy nanoparticles to obtain electrocatalysts with ultimately reduced Pt loading and enhanced activity.
- Further improve a method for Pt monolayer deposition on metal nanoparticles, and apply it for depositing mixed-metal monolayers.

Accomplishments

- The activity of a Pt monolayer on Pd/C cathode electrocatalyst (Pt_{ML}/Pd/C) was improved. The total noble metal mass-specific activity achieved was 4 times higher than that of a commercial Pt/C electrocatalyst.

- The first durability tests of the Pt_{ML}/Pd/C electrocatalyst for the oxygen reduction reaction (ORR) [F. Uribe and coworkers at Los Alamos National Laboratory (LANL)] showed a voltage loss of *ca* 140 mV after 3000 h at a constant current of 0.6 A/cm². The catalyst's performance ranged from 0.17 g Pt/kW to 0.25 g Pt/kW, which is below the DOE 2005 target of 1.35 g Pt/kW.
- A low-Pt-content fuel cell comprised of the PtRu₂₀ anode electrocatalyst (50 μg Pt/cm²) and the Pt/Pd/C cathode electrocatalyst (100 μg Pt/cm²) showed no loss of voltage after 530 h of the stability test (the test is still in progress). The catalysts' performance was 0.6 g Pt/kW, which is below the DOE 2005 target.
- A new class of the ORR electrocatalysts, *viz.*, mixed monolayers of Pt and late transition metals on Pd nanoparticles, was synthesized. The Pt mass-specific activity of a Pt_{0.8}Re_{0.2}/Pd/C electrocatalyst was about 20 times that of a commercial Pt/C catalyst. The lateral repulsion between Pt-OH and M-OH causes a decrease of Pt-OH formation, causing the catalytic effect.
- The Pt/AuNi/C electrocatalyst having a core-shell structure of the AuNi alloy nanoparticles (1-2 monolayers of Au around a Ni core) was further improved. Its Pt mass-specific activity was about 20 times that of Pt/C.
- A non-platinum Pd₂Co/C electrocatalyst achieved an ORR activity comparable to that of a commercial Pt/C electrocatalyst.

Future Directions

- Pt_{ML}/Pd/C electrocatalyst: i) Explore the Pd particle size effects and the surface segregation; ii) Post membrane electrode assembly (MEA) tests by Z-contrast transmission electron microscopy (TEM); iii) Perform fuel cell tests.
- Pd₂Co/C electrocatalyst: i) Continue synthetic studies; ii) Investigate the stability of Co; iii) Perform fuel cell tests.
- Mixed-metal Pt monolayer electrocatalysts: i) Continue basic studies of Pt-M/Pd/C; ii) Explore M-OH (MO)-Pt-OH interactions, activity, surface segregation; iii) Perform fuel cell tests.
- Pt/AuNi/C electrocatalyst: i) Investigate the segregation of Pt and Au, as well as the stability; ii) Perform fuel cell tests.
- Pt monolayers on other metal alloy nanoparticles: i) Conduct basic *in situ* surface and electrochemical studies; ii) Investigate new strategies to increase the stability of Pt under potential cycling conditions.

Introduction

Existing fuel cell technology still has two drawbacks: 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 at fuel cell cathodes. The large loss in potential of 0.3-0.4 V in the initial part of the polarization curves is mainly due to the inhibition of O₂ reduction caused by OH adsorption on Pt. To ameliorate the problem of slow kinetics, the cathode electrocatalysts require high Pt loadings.

Approach

Our approach to solving both problems is to design electrocatalysts having sub-monolayer or monolayer amounts of Pt on a surface of suitable

metal nanoparticles. This approach can facilitate modification of the catalytic properties of Pt in the right direction, and at the same time, achieve a considerable reduction in its loading. Enhanced activity of Pt can be a consequence of a low coordination of Pt atoms and tensile strain in Pt monolayer on a suitable substrate, which causes a shift of the d-band center of Pt, and of electronic (ligand) effects. A complete utilization of Pt atoms can be achieved. The electrodeposition of Pt monolayers on metal or alloy nanoparticles was accomplished using our method of galvanic displacement of a Cu monolayer.

Results

The study of Pt/Pd/C electrocatalysts with 5 nm particle size provided further verification of the promising features of the Pt monolayer

electrocatalysts for O_2 reduction by showing a higher activity than that obtained for 9 nm particles. The origin of the enhanced activity appears to be the larger surface area of the former electrocatalyst. Its total noble metal mass-specific activity (Pt + Pd) is 4 times that of a commercial Pt/C with 10% Pt.

The long-term fuel cell tests were conducted in a H_2 /air fuel cell at $80^\circ C$ with the anode containing 0.18 mg Pt/cm^2 (20% Pt-C, ETEK) and the cathode containing 0.077 mg Pt/cm^2 (20% Pd-4% Pt, Brookhaven National Laboratory) (F. Uribe and coworkers at LANL). Some losses in voltage (*ca* 140 mV) after 3000 h at a constant current of 0.6 A/cm^2 were observed (Figure 1). The catalyst's performance ranged from 0.17 g Pt/kW to 0.25 g Pt/kW , which is below the DOE 2005 target of 1.35 g Pt/kW .

In another test, the cell comprising the $PtRu_{20}$ anode electrocatalyst ($50 \mu\text{g Pt/cm}^2$) and the Pt/Pd/C cathode electrocatalyst ($100 \mu\text{g Pt/cm}^2$) showed no loss of voltage after 530 h of the stability test. The catalysts' performance was 0.6 g Pt/kW , which is also below the DOE 2005 target. These data demonstrated the long-term durability of the Pt_{ML} -Pd cathode electrocatalyst.

A new class of ORR electrocatalysts, *viz.*, mixed monolayers of Pt and late transition metals (M) on Pd nanoparticles, was synthesized (Figure 2). Measurements showed that the activity rose with increasing M coverage up to 0.2 (M is Ru or Ir in Figure 2). The Pt mass-specific activity of a $Pt_{0.8}Re_{0.2}/Pd/C$ electrocatalyst was about 20 times that of a commercial Pt/C catalyst (Figure 3). The lateral repulsion between Pt-OH and M-OH causes a decrease of Pt-OH formation, causing the catalytic effect. This conclusion is supported by x-ray absorption near edge spectroscopy measurements and density functional theory calculations that have been submitted for publication.

Further research on the metal alloy-supported Pt monolayer electrocatalysts involved the Pt/AuNi/C electrocatalyst, which has a core-shell structure of the AuNi alloy nanoparticles (1-2 monolayers of Au around a Ni core, *i.e.*, Pt: 1.44 wt%; Au: 2.92 wt%; Ni: 8.69 wt%). Surface segregation of Au was verified using x-ray powder diffraction technique. It

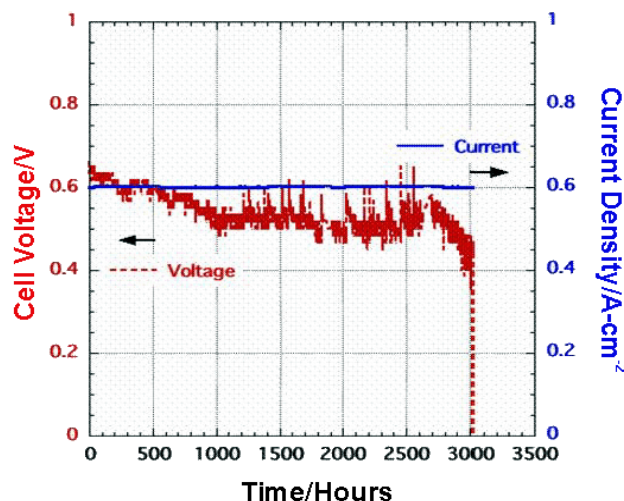


Figure 1. Fuel Cell Tests of $Pt_{ML}/Pd/C$ Electrocatalyst (50 cm^2 cell, $80^\circ C$, constant current of 0.6 A/cm^2 ; see text for other details)

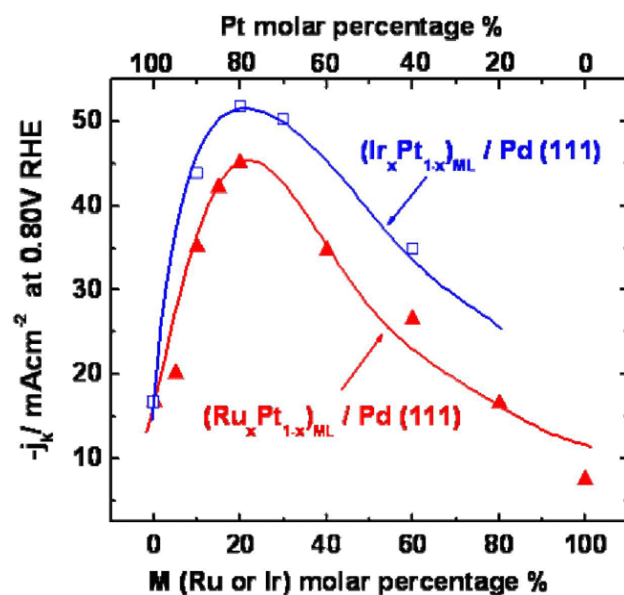


Figure 2. ORR Activity of Two Mixed Metal Monolayer Electrocatalysts Expressed as the Kinetic Current Density at 0.80 V as a Function of the M/Pt Ratio in the Monolayer (M = Ir or Ru)

was improved to reach a Pt mass-specific activity of about 20 times that of a commercial Pt/C (Figure 4) electrocatalyst. The fuel cell test at LANL was interrupted due to some technical problems, but the polarization curve in the MEA confirmed a high activity of this electrocatalyst.

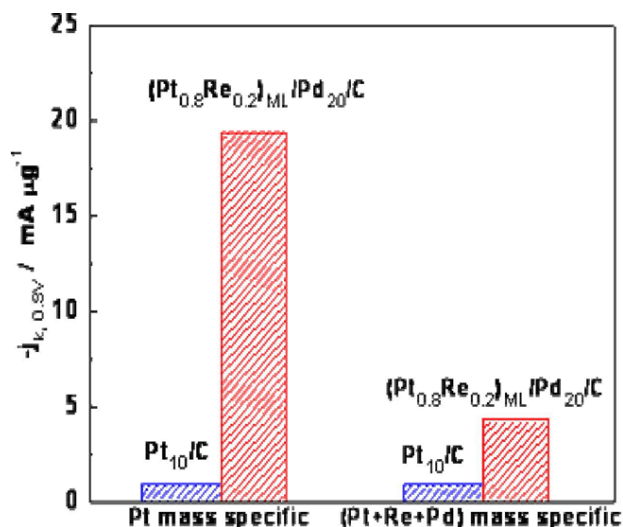


Figure 3. Pt and Total Noble Metal Mass-Specific Activities of $\text{Pt}_{0.8}\text{Re}_{0.2}/\text{Pd}/\text{C}$ and Commercial Pt/C Electro-catalysts at 0.80 V in 0.1M HClO_4

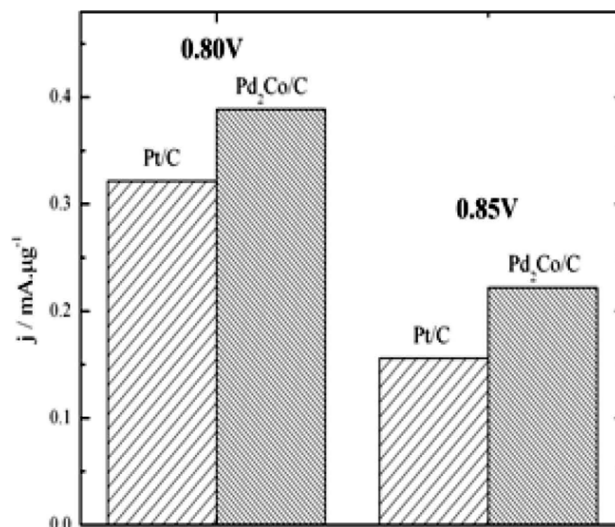


Figure 5. Pt and Pd Mass-Specific Activities for the ORR on Pd_2Co and Pt/C Electro-catalysts at 0.80 V and 0.85 V in 0.1M HClO_4 (Noble metal loadings: 11 mg/cm^2 of Pd vs. 12 mg/cm^2 of Pt.)

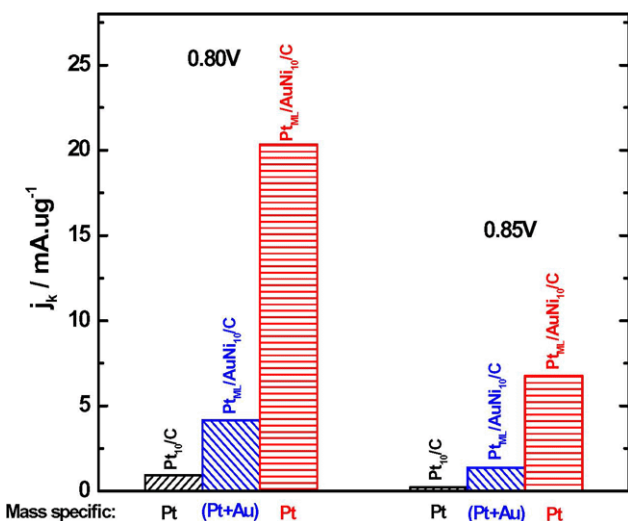


Figure 4. Pt and Total Noble Metal Mass-Specific Activities of Pt/AuNi/C and Commercial Pt/C Electro-catalysts at 0.80 V and 0.85 V in 0.1M HClO_4 (Noble metal loadings: 1.03 mg/cm^2 of Pt + 4 mg/cm^2 of Au vs. 12 mg/cm^2 of Pt)

The work on a non-platinum $\text{Pd}_2\text{Co}/\text{C}$ electrocatalyst involved further effort to synthesize it by reduction of metal salts in H_2 at elevated temperatures (900°C). The activity achieved is comparable to the ORR activity of a commercial Pt/C electrocatalyst (Figure 5). Further work will involve fuel cell and stability (surface segregation) tests.

Conclusions

- Further work on the Pt monolayer electrocatalysts for O_2 reduction was performed. The $\text{Pt}_{\text{ML}}/\text{Pd}/\text{C}$ with Pd nanoparticles of 5 nm diameter achieved total noble metal mass-specific activity 4 times higher than that of a commercial Pt/C electrocatalyst.
- A fuel cell test of the $\text{Pt}_{\text{ML}}/\text{Pd}/\text{C}$ electrocatalyst showed the long-term durability over 3000 h at a constant current of 0.6 A/cm^2 . The catalyst's performance ranged from 0.17 g Pt/kW to 0.25 g Pt/kW, which is below the DOE 2005 target of 1.35 g Pt/kW.
- Another stability test employing the PtRu_{20} anode electrocatalyst (50 $\mu\text{g Pt}/\text{cm}^2$) and the Pt/Pd/C cathode electrocatalyst (100 $\mu\text{g Pt}/\text{cm}^2$) showed no loss in voltage after 530 h (the test is still in progress). The catalyst's performance was 0.6 g Pt/kW, which is also below the DOE 2005 target.
- New ORR electrocatalysts consisting of mixed monolayers of Pt and late transition metals on Pd nanoparticles were synthesized. The Pt mass-specific activity of a $\text{Pt}_{0.8}\text{Re}_{0.2}/\text{Pd}/\text{C}$ electrocatalyst was about 20 times that of a commercial Pt/C catalyst.

- The Pt/AuNi/C electrocatalyst having a core-shell structure of the AuNi alloy nanoparticles (1-2 monolayers of Au around a Ni core) was further improved. Its Pt mass-specific activity was about 20 times that of Pt/C.
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Special Recognitions & Awards

1. R. Adzic was awarded Science and Technology Award, Brookhaven National Laboratory 2005.

Patents Pending

1. Palladium-cobalt particles as oxygen reduction electrocatalysts. Serial No. 11/054, 587
2. Platinum-coated palladium and palladium-alloy particles and uses thereof. Serial No. 11/019, 759
3. Electrocatalyst for oxygen reduction with reduced platinum oxidation and dissolution rates. Serial No. 11/132, 378

FY 2005 Publications/Presentations

1. J.X. Wang, N.M. Markovic, R.R. Adzic, "Kinetic Simulation of O₂ Reduction on Pt(111) in Acid Solutions: Intrinsic Kinetic Parameters and Anion Adsorption Effects", *J. Phys. Chem. B*, 108 (2004) 4127.

2. K. Sasaki, J.X. Wang, M. Balasubramanian, J. McBreen, F. Uribe, R.R. Adzic, "Ultra-low Platinum Content Fuel Cell Anode Electrocatalyst with a Long-term Performance Stability", *Electrochim. Acta*, 49 (2004) 3873.
3. J. Zhang, Y. Mo, M.B. Vukmirovic, R. Klie, K. Sasaki, R.R. Adzic, "Platinum Monolayer Electrocatalysts for O₂ Reduction: Pt Monolayer on Pd(111) and on Carbon-supported Pd Nanoparticles", *J. Phys. Chem. B*, 108 (2004) 10955.
4. 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.*, 44 (2005) 2132.
5. J. Zhang, M.B. Vukmirovic, K. Sasaki, F. Uribe, R.R. Adzic, "Platinum Monolayer Electrocatalysts for Oxygen Reduction: Substrates Effects and a Long-term Stability", *J. Serb. Chem. Soc.*, in press.
6. K. Sasaki, J. Zhang, J. Wang, F. Uribe, R.R. Adzic, "Platinum Submonolayer-Monolayer Electrocatalysts - An Electrochemical and X-ray Absorption Spectroscopy Study", *Research on Chemical Intermediates*, in press.