

# V.D.6 Contiguous Platinum Monolayer Oxygen Reduction Electrocatalysts on High-Stability Low-Cost Supports

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content of Pt-group metal (PGM) and more simple membrane electrode assemblies (MEAs) formation.

**TABLE 1.** Progress toward Meeting DOE Fuel Cell Electrocatalysts Technical Targets

Characteristic	Units	Target	Achieved
		2015	2011
PGM Total Loading	mg PGM/cm <sup>2</sup> electrode area	0.2	0.12
Mass Activity	A/mg Pt @ 900 mV iR-free	0.44	2.8 (Pd nanowires)
Specific Activity	μA/cm <sup>2</sup> @ 900 mV iR-free	720	1,100( Pd rods)
PGM Mass Activity		0.44	0.57 (hollow PdAu alloy)
Durability			Some loss in activity in 20,000 cycles to 1.4 V Pt/Pd(Au)

iR – internal resistance

## Fiscal Year (FY) 2012 Objectives

Developing high-performance fuel cell electrocatalysts for the oxygen reduction reaction (ORR) comprising contiguous Pt monolayer (ML) on stable, inexpensive metal or alloy:

- Nanoparticles
- Nanowires
- Hollow nanostructures
- Carbon nanotubes

## 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) Performance
- (B) Cost
- (C) Durability

## Technical Targets

We are focusing on simplifying synthetic processes to obtain better catalysts' activity, higher Pt utilization, lower

## FY 2012 Accomplishments

- Demonstrated the stability of Pt<sub>ML</sub>/Pd<sub>9</sub>Au/C and Pt<sub>ML</sub>/Pd/C electrocatalysts under potential cycling to 1.4 V is high. Self-healing-mechanism confirmed in this test.
- Four patents on their technology have been licensed to N.E. ChemCat Co. by BNL.
- Demonstrated synthesis of Pd alloys with refractory metals to provide stable and inexpensive cores, reduced PGM content.
- Developed an electrochemical method for Pt<sub>ML</sub> electrocatalysts syntheses involving electrochemical deposition on gas diffusion layers (GDLs). High-activity, high-stability electrocatalysts are obtained, Pt utilization close to 100%; scale up is simple.
- Synthesis of ultra-thin Pd alloy nanowires using simple surfactant has been developed to provide an excellent support for a Pt<sub>ML</sub>.
- An efficient method for Pt<sub>ML</sub> deposition on Pd nanoparticles using ethanol as a medium and reactant has been developed.
- Further development of synthesis of hollow Pd nanoparticle catalysts with hollow-induced lattice contraction enhancing the ORR activity of a Pt ML.



## Introduction

Further developments of oxygen reduction electrocatalysts to lessen the remaining technological difficulties that used to hamper the automotive applications of fuel cells still have to focus on reducing Pt, or PGM contents, increasing their stability and activity. The understanding of the properties of Pt ML electrocatalysts, and of a broader class of core-shell electrocatalysts, has grown up considerably. Thus, the complex influence of the nanoparticle core's composition, size and shape on the catalyst's activity make it possible to optimize the properties of certain classes making them ready for application.

## Approach

Based on our understanding of the role of  $\text{OH}_{\text{ads}}$  on Pt on the ORR our recent finding of significant weakening of binding energy of oxygen (BE-O) on the (111) facet compared to the extended surface due to nanoscale induced in-plane lattice contraction, our approach focuses on having surfaces with the high coordination (111) facets. These surfaces are most conducive to the ORR on nanoparticles. In addition, they are less prone to dissolution than low-coordinated edges, defects, and less close-packed facets. Thus, we will study the electrocatalysts comprising Pt monolayer deposited on selected shapes of nanoparticles (hollow cores), nanorods and nanowires. These nano-shapes have surface structures and the average atom coordination close to surfaces on bulk materials. Several synthetic approaches, including the electrodeposition to make Pd nanorods or nanowires on C nanoparticles and carbon fibers in GDL ( $5 \text{ cm}^2$  and  $25 \text{ cm}^2$ ), using simple surfactants to form ultra-thin bimetallic nanowires, using ethanol as a dispersion medium and reducing agent to make a Pt ML on Pd and hollow Pd nanoparticles.

## Results

Decreasing the content of Pd in cores: Ru, and PdW and NiW alloys as cores

A highly useful feature of PtML core-shell catalysts is a possibility of a simple and efficient tuning the ML shell-core interaction and consequently the catalytic activity. This feature also allows decreasing the catalysts' PGM contents. We showed that Ru nanoparticles can serve as a convenient, inexpensive cores if two Pt MLs are deposited, which is an optimal thickness positioned at the top of volcano plot of activity vs. Pt thickness. Pt mass activity is  $0.81 \text{ A/mg}$ ; specific activity =  $0.58 \text{ mA/cm}^2$  and PGM activity is  $0.50 \text{ A/mg}$ .

In order to make inexpensive and stable cores, Pd can be alloyed with suitable refractory metal, which, if exposed to

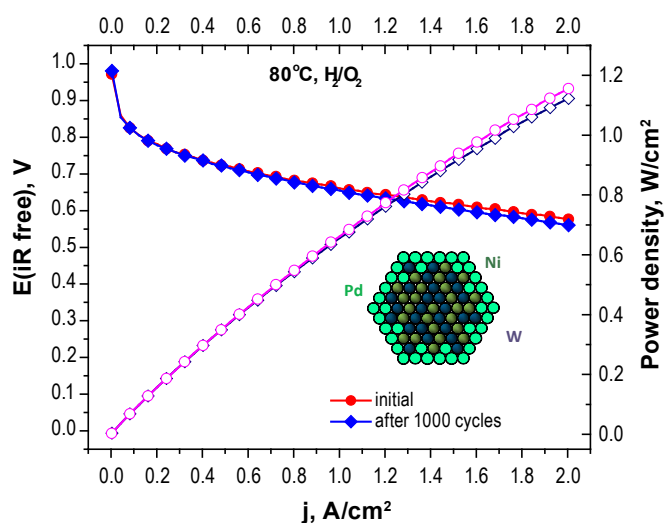
electrolyte, will passivate. A 1:1 PdW alloy was obtained in  $\text{H}_2$   $600^\circ\text{C}$ . Pt mass activity is  $0.81 \text{ A/mg}$ ; specific activity =  $0.58 \text{ mA/cm}^2$  and PGM activity is  $0.22 \text{ A/mg}$ .

Another very promising approach to decrease PGM content that we developed involves electrochemical co-deposition of W and Ni (deposition of W alone is not possible in aqueous solutions) to make W-Ni alloy cores. The 50:50 NiW alloy was deposited at carbon constituting a GDL, confirmed using energy dispersive X-ray spectroscopy (EDS). Two features of these nanoparticles are important: 1<sup>st</sup> they have no PGM content, their costs are negligible. Dissolution of Ni from these nanoparticles can take place from the top 1-2 layers and then it stops because W atoms dominating now in the surface layer will not dissolve. They will passivate above certain potential. We displace Ni in the surface layer by about 2 monolayers of Pd and then place a Pt monolayer on such nanoparticles. Figure 1 shows polarization curve for the ORR on the electrode having only  $40 \mu\text{g PGM/cm}^2$ .

Electrochemical deposition for a 100% Pt utilization

### Electrodeposition of $\text{Pd}_{0.9}\text{Au}_{0.1}$ alloy core for the $\text{Pt}_{\text{ML}}/\text{Pd}_{0.9}\text{Au}_{0.1}/\text{GDL}$ catalyst

Electrochemical deposition of Pt monolayer electrocatalysts has a great potential for syntheses of the low-Pt content electrocatalysts since it facilitates 100% utilization of Pt. The first step involves the electrodeposition of core nanoparticles on GDL. Subsequent deposition of a Pt monolayer, using the Cu underpotential deposition displacement method, will take place only on the nanocores surface that is in contact with electrolyte. This surface, upon



**FIGURE 1.** Pt ML on a NiW core obtained by codeposition. The ORR kinetics on  $\text{PtML}/\text{Pd}/\text{W}/\text{C}$ . Pt content is less than  $40 \mu\text{g/cm}^2$ . Insert: Model of NiW core with a partially displaced Ni by Pd.

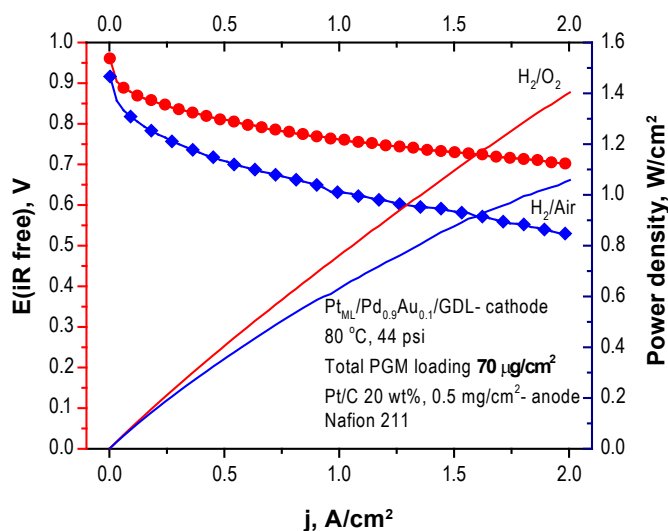
formation of the MEA, will be accessible to  $O_2$  and will be in contact with the membrane. None of Pt atoms will be blocked by contact with carbon or occluded by Nafion<sup>®</sup> having no contact with the current collecting carbon as commonly occurs with the catalyst ink or spraying used in MEAs preparation. Figure 2 shows polarization curves of Pt ML catalyst on electrodeposited PdAu alloy core.

### Stability of Pt ML electrocatalysts under potential cycling to 1.4 V

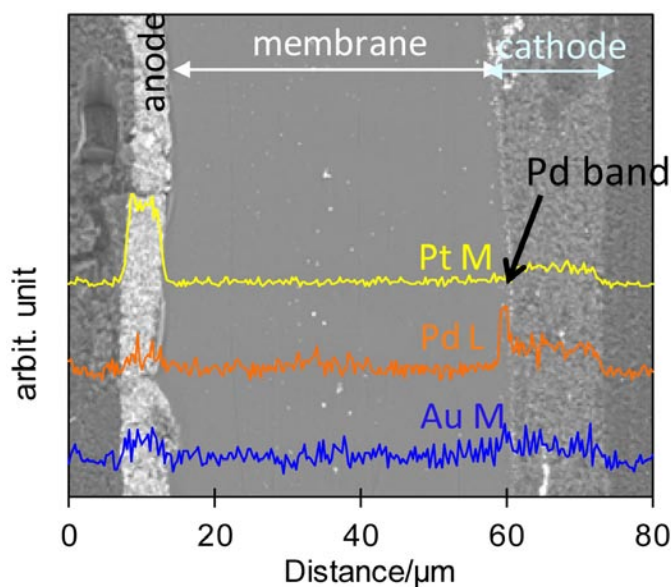
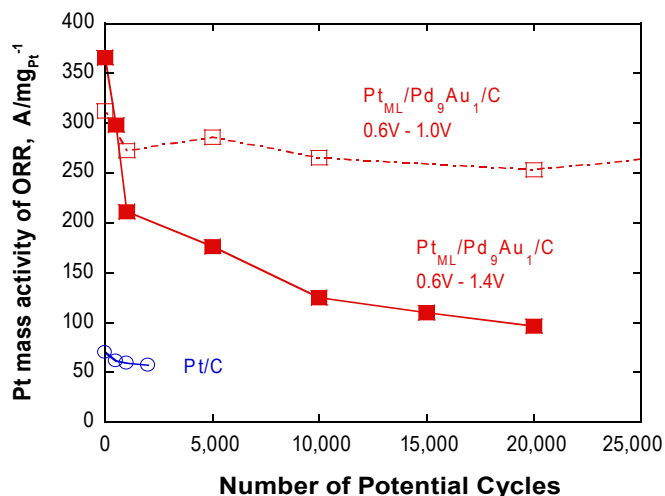
To verify stability of Pt ML catalysts at extreme potential excursions the test with potential cycling to 1.4 V has been carried out. Figure 3 shows a decrease in activity after 20,000 potential cycles and formation of a Pd band in the membrane, but no Pt or Au loss.

### Pt Monolayer on Hollow Pd Nanoparticles Electrocatalysts

We fabricated Pt monolayer catalysts on Pd and Pd-Au hollow cores that were made using Ni nanoparticles as sacrificial templates. The hollow architecture of the Pd-Au particles achieved is stemmed from the synergistic action of both galvanic replacement and Kirkendall effect in controlling reaction kinetics. The electrocatalyst has total-metal mass activities for the ORR up to  $0.57 \text{ A mg}^{-1}$ , which is 2.2 times that of  $0.25 \text{ A mg}^{-1}$  for a Pt monolayer on solid Pd cores, and 3.5 times that of  $0.16 \text{ A mg}^{-1}$  for solid Pt nanoparticles made by pulse electrodeposition. The cores' hollow structures enhance catalyst's properties and thus are promising for fuel cell applications.



**FIGURE 2.** Polarization curve for electrodeposited PtML on Pd<sub>0.9</sub>Au<sub>0.1</sub> alloy. Comparison of performance with oxygen and air. The PGM content is approximately  $70 \mu\text{g}/\text{cm}^2$ .



**FIGURE 3.** Stability of PtML/PdAu/C catalysts under potential cycling to 1.4 V. Top panel: polarization curves after 20,000 potential cycles from 0.6 to 1.4 V. For comparison, data for commercial Pt/C electrocatalyst are given and the cycling test 0.6-1. Bottom panel: scanning electron microscope image of the MEA cross-section and EDS distribution of catalyst constituents. A Pd band is formed from dissolved Pd; no dissolution of Pt and Au is observed. (With H. Naohara, Toyota Motor Co.).

### Conclusions and Future Directions

- Pt<sub>ML</sub>/Pd<sub>9</sub>Au/C and Pt<sub>ML</sub>/Pd/C are practical electrocatalysts. Stability under potential cycling to 1.4 V.
- Four patents on their technology have been licensed to N.E. ChemCat Co. by BNL.
- Pd alloys with refractory metals provide stable and inexpensive cores, reduced PGM content.
- An efficient method for Pt<sub>ML</sub> electrocatalysts synthesis involving electrochemical deposition on GDLs has been

developed. High activity, high stability electrocatalysts are obtained, Pt utilization close to 100%; scale up is simple.

- Synthesis of ultra-thin Pd alloy nanowires using simple surfactant has been developed to provide an excellent support for a Pt<sub>ML</sub>.
- The mechanism of stability of core-shell electrocatalysts, in which shell is protected by the core, and the self-healing mechanism have been verified in tests involving potential cycling to 1.4 V.

Future studies will focus on:

1. Scale up synthesis of Pd alloy nanowires by electrodeposition electrodes of 25 and 300 cm<sup>2</sup>.
2. Scale up of synthesis to produce 20 grams of ultra-thin nanowires using weak surfactants.
3. Developing the microemulsion method to synthesize hollow Pd nanoparticles.
4. Further work on the Pd-refractory metal alloy cores.
5. MEA fabrication and tests.

## Special Recognitions & Awards/Patents Issued

1. R. Adzic was named 2012 Inventor of the Year by the New York Intellectual Property Law Association (NYIPLA).
2. R. Adzic received The 2012 DOE Hydrogen and Fuel Cells Program Annual Award.
3. R. Adzic, J. Wang, M. Vukmirovic, K. Sasaki received an R&D100 Award.

## Patents

Electrocatalyst for oxygen reduction with reduced platinum oxidation and dissolution rates Radoslav Adzic, Junliang Zhang, Miomir Vukmirovic. U.S. Patent No. 8,062,552, issued November 22, 2011.

Three patent applications have been submitted.

Four patents on Pt monolayer electrocatalysts have been licensed by BNL to N.E. ChemCat Corp., Japan.

## FY 2012 Publications/Presentations

1. Carbon-supported IrNi core-shell nanoparticles: synthesis, characterization, and catalytic activity / Kotaro Sasaki, Kurian A. Kuttiyiel, Laura Barrio, Dong Su, Anatoly I. Frenkel, Nebojsa Marinkovic, Devinder Mahajan, Radoslav R. Adzic // *Journal of Physical Chemistry C*. 20 (2011) 9894-9902.
2. Electrodeposition of metals in catalyst synthesis: the case of platinum monolayer electrocatalysts / Miomir B. Vukmirovic, Stoyan T. Bliznakov, Kotaro Sasaki, Jia X. Wang, Radoslav R. Adzic // *Electrochemical Society Interface*. 2 (2011) 33-40.
3. Electrodeposition of Pd nanowires and nanorods on carbon nanoparticles / Stoyan Bliznakov, Miomir Vukmirovic, Eli Sutter, Radoslav Adzic // *Macedonian Journal of Chemistry and Chemical Engineering*. ISSN 1857-5552. 30 : 1 (2011) 19-27.
4. Enhanced electrocatalytic performance of processed, ultrathin, supported Pd-Pt core-shell nanowire catalysts for the oxygen reduction reaction / Christopher Koenigsmann, Alexander C. Santulli, Kuanping Gong, Miomir B. Vukmirovic, Wei-ping Zhou, Eli Sutter, Stanislaus S. Wong, Radoslav R. Adzic // *Journal of the American Chemical Society*. 25 (2011) 9783-9795.
5. Kirkendall effect and lattice contraction in nanocatalysts : a new strategy to enhance sustainable activity / Jia X. Wang, Chao Ma, YongMan Choi, Dong Su, Yimei Zhu, Ping Liu, Rui Si, Miomir B. Vukmirovic, Yu Zhang, Radoslav R. Adzic // *Journal of the American Chemical Society*. 34 (2011) 13551-13557.
6. Low-coordination sites in oxygen-reduction electrocatalysis: their roles and methods for removal / Yun Cai, Chao Ma, Yimei Zhu, Jia X. Wang, Radoslav R. Adzic // *Langmuir*. 13 (2011) 8540-8547.
7. Platinum monolayer electrocatalysts for the oxygen reduction reaction: improvements induced by surface and subsurface modifications of cores : [review article] / Yun Cai, Radoslav R. Adzic // *Advances in Physical Chemistry*. (2011) Special issue: *Advances in Electrocatalysis*; article ID 530397 (16 p.).
8. Platinum monolayer on IrFe core-shell nanoparticle electrocatalysts for the oxygen reduction reaction / Kotaro Sasaki, Kurian A. Kuttiyiel, Dong Su, Radoslav R. Adzic // *Electrocatalysis*. 2 (2011) 134-140.
9. Hollow core supported Pt monolayer catalysts for oxygen reduction/ Zhang, Y., Ma, C., Zhu, Y., Si, R., Cai, Y., Wang, J.X., Adzic, R.R., *Catalysis today*, in press.