

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

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- ² Johnson Matthey Fuel Cells (JMFC), London, England

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Project End Date: September 30, 2013

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

Technical Targets

Progress toward meeting DOE fuel cell electrocatalysts technical targets is shown in Table 1.

FY 2011 Accomplishments

- Demonstrated the stabilization mechanism of core-shell NPs by which a Pt ML shell is being protected by the cores.
- Demonstrated synthesis of hollow Pd NP with hollow-induced lattice contraction enhancing the ORR activity on a Pt ML.
- Demonstrated electrodeposition of Pd nanorods and nanowires on functionalized carbons as a support for high activity and durability of Pt ML catalysts. The performance of a 5 cm² MEA shows an excellent activity/stability.
- Demonstrated synthesis of one-dimensional interconnected Pt NPs on amine-functionalized multi-wall carbon nanotubes (MWCNTs).
- Demonstrated synthesis of tetrahedral Pd NPs – an excellent low-Pd content support for a Pt monolayer.
- Developed high performance Pt monolayer on non-noble metal core-noble metal shell NP –Pt/Ir/Ni/C-electrocatalyst. 1 ML Pt and 2MLs Ir around Ni core.
- Fuel cell stability tests of Pt/Pd₉Au₁/C electrocatalysts show no dissolution or loss in activity during 100,000 and 200,000 potential cycles. This electrocatalyst is ready for applications.



Fiscal Year (FY) 2011 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 (NP)
- Nanorods; Nanowires
- Carbon nanotubes (CNT)

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:

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

Characteristic	Units	Target	Target	Achieved
		2010	2015	2010
Platinum Group Metal (PGM) Total Loading	mg PGM/cm ² electrode area	0.3	0.2	0.11
Mass Activity	A/mg Pt @ 900 mV _{iR-free}	0.44	0.44	2.8 (Pt on Pd nanowires)
Specific Activity	μA/cm ² @ 900 mV _{iR-free}	720	720	1,100 (Pt on Pd rods)
PGM Mass Activity				0.58 (Pt on hollow Pd)
Durability				No loss in activity in 200,000 cycles Pt/Pd(Au) in fuel cell test

iR-free – internal resistance-free

Introduction

Building on the advances made in the last decade in fuel cell electrocatalysis yielding improved electrocatalysts, and increasing our understanding of the kinetics of the ORR, further developments during the last two years lessened some technological difficulties that used to hamper the automotive applications of fuel cells. The understanding of the properties of Pt ML electrocatalysts, and of a broader class of core-shell electrocatalysts, Pt alloys, dealloying approach, and of complex influence of the NP size and shape on the catalyst's activity made it possible to optimize the properties of certain classes.

Approach

Following our position on the role of OHads on Pt on the ORR from the late eighties, and 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 NPs. In addition, they are less prone to dissolution than low-coordinated edges, defects, and less close-packed facets. Because the ORR rate on Pt is OH-, or O-desorption limited, lowering BE-O enhances the ORR activity. Therefore, smooth, lattice contracted (111) like surface structures are needed to achieve durable high-ORR activity.

Therefore, we synthesized the supporting NPs having predominantly highly coordinated atoms that exist on nanorods, nanowires, smooth NPs, hollow Pd spheres, single crystalline NPs with predominantly (111) facets. We used the electrodeposition to make Pd nanorods on C NPs, Toray paper (5 cm²), and gas diffusion layer (GDL).

Results

Pt Monolayer on Electrodeposited Pd Nanorods, Nanowires Electrocatalysts

The nanorods and nanowires having smooth surfaces are attractive supports for Pt monolayer. Electrodeposition facilitates a better Pd utilization and a direct formation at the carbon surfaces that provides electrolyte access to a major part of the catalysts' surface and thus its best utilization. Figure 1 shows the polarization curve of 5 cm² electrode obtained electrochemically on Toray paper. Total PGM loading is 0.11 mg/cm².

Bimetallic IrNi Core Platinum Monolayer Shell Electrocatalysts

To further decrease the PGM content we synthesized the electrocatalyst consisting of a Pt monolayer placed on carbon-supported thermally treated IrNi core-shell NPs.

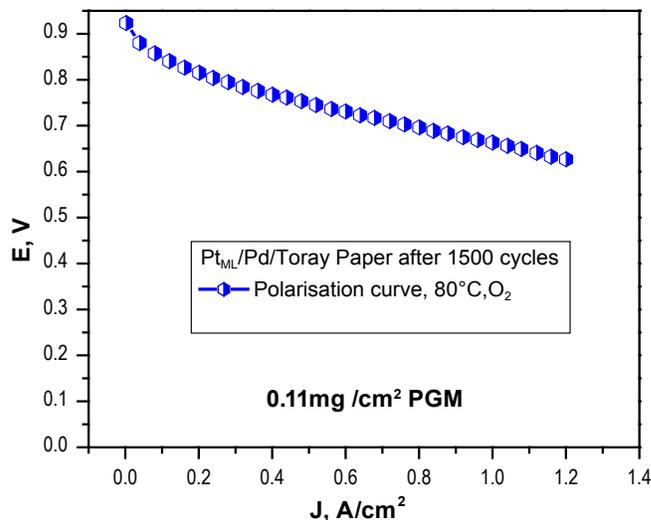


FIGURE 1. Polarization curve for the cell with 5 cm² cathode. The catalyst Pt_{ML}/Pd obtained electrochemically on Toray paper. Total PGM loading is 0.11 mg/cm².

The Pt mass activity of the Pt_{ML}/IrNi/C electrocatalyst obtained in a scale up synthesis is approximately three times higher than that of the commercial Pt/C electrocatalyst. The electronic and geometrical effects of the IrNi substrate on the Pt monolayer result in its higher catalytic activity than that of Pt NPs. The structure and composition of the core-shell NPs were verified using transmission electron microscopy and in situ X-ray absorption spectroscopy, while potential cycling test was employed to confirm the stability of the electrocatalyst (Figure 2).

Pt Monolayer on Hollow Pd NPs Electrocatalysts

Based on promising results obtained with hollow Pt NPs, we explored possibility to form hollow Pd nanoparticle support for a Pt monolayer. It is interesting to see whether hollow can induce a needed lattice contraction in an overlayer. Using Ni NPs as dissolvable template, we produced compact Pd hollow nanospheres. Excellent activity was found after deposition of a Pt monolayer: Pt+Pd+Au mass activity is 0.57 A mg⁻¹; Pt mass activity = 1.62 A mg⁻¹, specific activity = 0.85 mAcm⁻².

One-Dimensional Interconnected Pt NPs on Amine-Functionalized MWCNTs

MWCNTs were functionalized by amine groups in a Polyol synthesis. Further treatment involved rinsing in 6 M HCl and thermal treatment at 220°C. Excellent specific and mass activities were obtained (Figure 3). PGM mass activity is 1.4 times that of 40% Tanaka Kikinokogyo, while specific activity is 0.9 mA/cm².

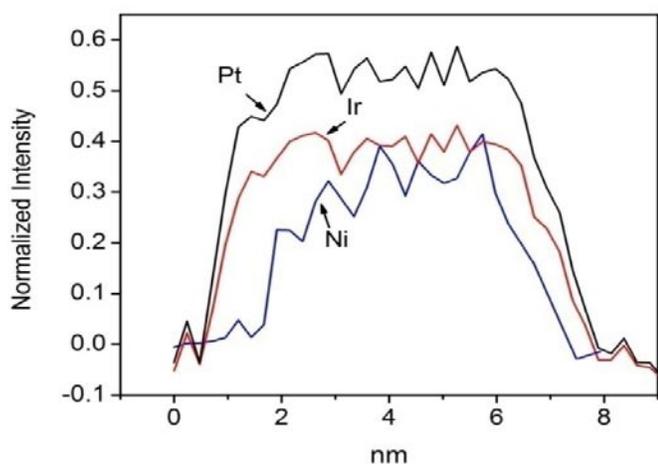
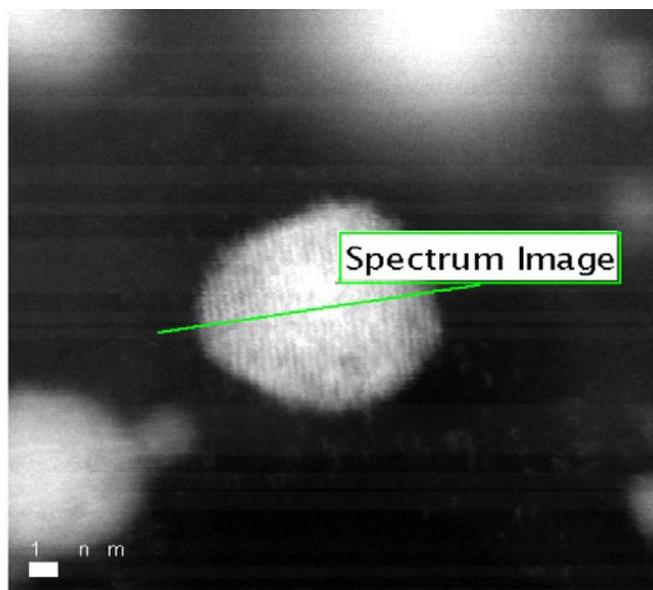


FIGURE 2. Bimetallic Ni-Ir Core Pt ML shell electrocatalysts after 50,000 potential cycles test. Upper panel: High angle annular dark field image of a single NP; Lower panel: Distribution of Pt and IrNi components in a single representative NP from M and L absorption edges. It is clearly shown that the core-shell structure of IrNi NP is maintained even after 50,000 cycles.

Fuel Cell Tests of the Pt_{ML}/Pd/C and Pt_{ML}/Pd₉Au/C at Toyota

Several stability tests of Pt/Pd/C and Pt/Pd₉Au/C catalysts involving potential cycling from 0.6 and 1.0 V; dwell time 10 sec; square-wave modulation; 80°C have been performed. High stability of Pt ML and a partial dissolution of Pd in some cases led to the mechanism of stability of core-shell electrocatalysts in which the shell is protected by the core. Pd dissolution precludes dissolution of Pt (cathodic protection effect) and more importantly, the contraction of Pt and Pd lattices, induced by loss of Pd, increases stability and activity of the catalyst – self-healing effect (Figure 4). Negligible loss in activity is observed in 100,000 cycles with Pt/Pd/C catalysts, while with the more stable Pt/Pd₉Au/C,

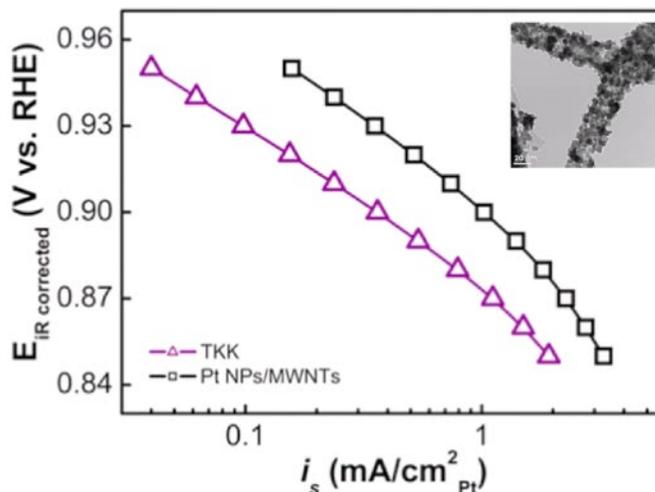


FIGURE 3. Polarization curve for the ORR on Pt interconnected NPs on MWCNTs compared with a commercial Pt/C catalyst. Insert: Scanning transmission electron microscopy image of the segment of CNT with the Pt deposit.

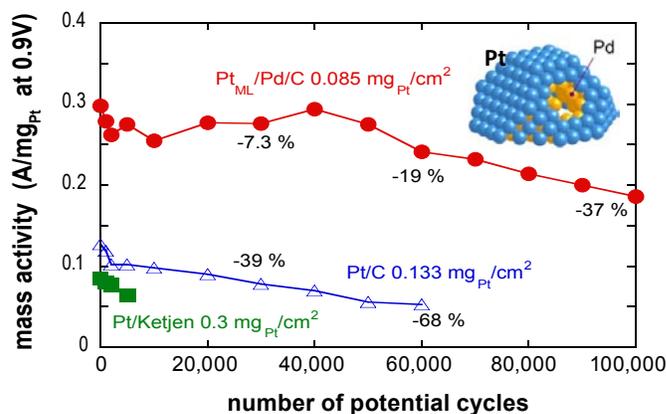


FIGURE 4. Accelerated stability fuel cell tests of the Pt/Pd/C and two commercial Pt/C cathode catalysts given for comparison. Potential cycling from 0.6 and 1.0 V; dwell time 10 sec; square-wave modulation; 80°C.

no loss is seen. Commercial Pt/C catalysts perish completely within 50,000 cycles. The Pt/Pd/C and Pt/Pd₉Au/C catalysts are ready for applications.

Conclusions and Future Directions

- Smooth surfaces, with highly-coordinated atoms, are suitable to support a Pt ML that yields very active catalysts.
- Pd nanowires were synthesized. Their thickness needs to be reduced and removal of surfactants simplified to obtain an excellent catalyst with a Pt ML.
- Electrodeposited NPs make excellent supports for Pt. Scale up of the cell for electrodeposition of Pd NPs

seems possible to the dimensions required for fuel cell stacks.

- Hollow Pd and Pt NPs are very attractive for further studies.
- Bimetallic IrNi core platinum monolayer shell electrocatalysts are highly promising for scale up syntheses and further reduction of PGM content (one ML of Pt and two MLs of Ir).
- The Pt/Pd₃Au₁/C electrocatalyst is ready for application in fuel cells for electric vehicles.

Future studies will focus on:

- Improve synthesis of Pd nanorods, nanowires, and Pd hollow NPs. (BNL, MIT, JMFC)
- Improve metallization and catalysation of CNTs, oxides, nitrides. (JMFC, MIT, BNL)
- Pd-Nb alloy NPs; start the work on Pd-W NPs and Pd-V. (BNL, MIT)
- Scale up of selected catalysts up to 20 grams. (JMFC, BNL)
- Scale up of electrodeposition on Toray paper and GDL to 50 and 500 cm² electrodes.
- MEA fabrication and tests.

Special Recognitions & Awards

1. Radoslav Adzic was named *Inventor of the Year* by Battelle Memorial Institute.

Patent Applications

1. "Hollow nanoparticles as active and durable catalysts and methods for manufacturing the same", Jia X. Wang, Radoslav R. Adzic, provisional application filed on July 14, 2010.
2. BSA 08-33 (2/18/2010) Platinum-Coated Non-Noble Metal-Noble Metal Core-Shell Electrocatalysts.
3. BSA 08-32 (8/26/2010) US2010/0216632 A1 High Stability, Self-Protecting Electrocatalyst Particles.
4. Patent BSA 10-03 entitled "Apparatus and method for the synthesis and treatment of metal monolayer electrocatalyst particles in batch or continuous fashion" BNL docket no. 1004305.034US.

Patents Issued

1. U.S. patent 7,691,780 B2 "Platinum- and Platinum Alloy-coated Palladium and Palladium Alloy Particles and uses thereof" (04/06/2010).
2. U.S. patent 7,704,918 B2 "Synthesis of Metal-Metal Oxide Catalysts and Electrocatalysts Using a metal cation Adsorption/Reduction and Adatom Replacement by More Noble Ones" (04/27/2010).

3. U.S. Patent No. 7,855,021 issued 12_21_2010- Electrocatalysts having Platinum Monolayers on Palladium, Palladium Alloy and Gold Alloy Core-Shell Nanoparticles and Uses Thereof.

FY 2011 Publications/Presentations

1. W-P. Zhou, K. Sasaki, D. Su, Y. Zhu, J.X. Wang, R.R. Adzic, "Structural and Electrocatalytic properties of Large-scale Synthesized Pt Monolayers on Pd₂Co Electrocatalysts for Oxygen Reduction Reaction", *Journal of Physical Chemistry C*, 114(19) (2010) 8950-8957.
2. Core-Protected Platinum Monolayer Shell High-Stability Electrocatalysts for Fuel-Cell Cathodes, Kotaro Sasaki, Hideo Naohara, Yun Cai, Yong Man Choi, Ping Liu, Miomir B. Vukmirovic, Jia X. Wang and Radoslav R. Adzic, *Angew. Chem. Int. Ed.*, 49 (2010) 8602.
3. Platinum Monolayer Electrocatalysts for O₂ Reduction: Pt Monolayer on Carbon-Supported PdIr Nanoparticles, Seth L. Knupp, Miomir B. Vukmirovic, Pradeep Haldar, Jeffrey A. Herron, Manos Mavrikakis, and Radoslav R. Adzic, *Electrocatal.*, 1 (2010) 213.
4. Enhancing Oxygen Reduction Reaction Activity via Pd-Au Alloy Sublayer Mediation of Pt Monolayer Electrocatalysts, Yangchuan Xing, Yun Cai, Miomir Vukmirovic, Wei-Ping Zhou, Jia Wang, Radoslav Adzic, Hiroko Karan, *J. Phys. Chem. Lett.*, 1 (2010) 3238.
5. K. Sasaki, J.X. Wang, H. Naohara, M. Marinkovic, K. More, H. Inada, R.R. Adzic, "Recent Advances in Platinum Monolayer Electrocatalysts for Oxygen Reduction Reaction: Scale-up Synthesis, Structure and Activity of Pt Shells on Pd Cores", *Electrochimica Acta*, 55(8) (2010) 2645-2652.
6. Intermetallics as Support for Pt Monolayer O₂ Reduction Electrocatalysts: Potential for Significantly Improving Properties, Tanushree Ghosh, Miomir B. Vukmirovic, Francis J. DiSalvo, Radoslav R. Adzic, *J. Am. Chem. Soc.*, 132 (2010) 906.

Book Chapter

- K. Sasaki, M. B. Vukmirovic, J.X. Wang, R.R. Adzic, "Platinum Monolayer Electrocatalysts: Improving Structure and Activity", *Fuel Cell Science: Theory, Fundamentals, and Bio-Catalysis*, J. Norskov, A. Wieckowski (eds), John Wiley & Sons, Inc. (New York), (2010) p. 215-236.

Presentations

1. R.R. Adzic, Electrocatalysis, Internat. Symp., Kloster Irsee, Germany, August 2010 (key-note lecture).
2. R.R. Adzic, 218th Electrochemical Society Meeting, Las Vegas, NV, October, 2010. (key-note lecture).
3. M.B. Vukmirovic, K. Sasaki, W-P. Zhou, Y. Cai, K. Gong, P. Liu, J.X. Wang, R.R. Adzic, Recent Advances in Developing Platinum Monolayer Electrocatalysts for the O₂ Reduction Reaction, Gordon Conference on Electrodeposition, Colby-Sawyer College in New London, New Hampshire, August 1-6, 2010, Invited Talk.

4. K. Sasaki, H. Naohara, Y. Cai, D. Su and R. Adzic, "Characterization of Platinum Monolayer Electrocatalysts in Long-Term Fuel Cell Cathode Tests", 217th ECS meeting, Vancouver, April 28, 2010.
5. K. Gong, K. Sasaki, M. Vukmirovic and R. Adzic, "In Situ Decomposing Prussian Blue Analogues to Form Multimetallic Aggregations with Various Surface Ensemble for Pt-Monolayer Electrocatalyst", 217th ECS meeting, Vancouver, April 28, 2010.
6. R. Adzic, K. Sasaki, H. Naohara, M. Vukmirovic, J.X. Wang, and Y. Cai, "Advances in Pt Monolayer Electrocatalysts for Oxygen Reduction Reaction and Prospects for Automotive Applications", 218th ECS meeting, Las Vegas, October 13, 2010.
7. A.T. Haug, R.T. Atanasoski, K. Sasaki, Y. Cai, and R. Adzic, "Stability of a Pt-Pd Core-Shell Catalyst: A Comparative Fuel Cell and RDE Study", 218th ECS meeting, Las Vegas, October 13, 2010.
8. K.A. Kuttiyiel, K. Sasaki, and R. Adzic, "Bimetallic Ni-Ir Core Platinum Monolayer Shell Electrocatalysts for the O₂ Reduction Reaction", 218th ECS meeting, Las Vegas, October 12, 2010.
9. Jia X. Wang, Chao Ma, YongMan Choi, Dong Su, Yimei Zhu, Ping Liu, Rui Si, and Radoslav R. Adzic, "Platinum hollow spheres as active and durable nanocatalysts for oxygen reduction in fuel cells", International conference of "Challenges in Inorganic and Material Chemistry", Hong Kong, July 22, 2010.
10. Jia X. Wang, Chao Ma, YongMan Choi, Dong Su, Yimei Zhu, Ping Liu, Rui Si, and Radoslav R. Adzic, "Platinum hollow spheres as active and durable nanocatalysts for oxygen reduction in fuel cells", 218th Electrochemical Society Meeting, Las Vegas, October 12, 2010.