

V.A.4 Contiguous Platinum Monolayer Oxygen Reduction Electrocatalysts on High-Stability Low-Cost Supports

Radoslav Adzic (Primary Contact), Jia Wang, Miomir Vukmirovic, Kotaro Sasaki, Yang Shao-Horn¹, Rachel O'Malley²
 Brookhaven National Laboratory (BNL), Bldg. 555
 Upton, NY 11973-5000
 Phone: (631) 344-4522
 Email: adzic@bnl.gov

DOE Manager

Nancy Garland
 Phone: (202) 586-5673
 Email: Nancy.Garland@ee.doe.gov

Subcontractors:

- Massachusetts Institute of Technology (MIT), Cambridge, MA
- Johnson Matthey Fuel Cells (JMFC), London, England

Project Start Date: July 1, 2009

Project End Date: September 30, 2013

Overall Objectives

- Synthesizing high-performance Pt monolayer (ML) on stable, inexpensive metal or alloy nanostructured fuel cell electrocatalysts for the oxygen reduction reaction (ORR).
- Increasing activity and stability of Pt ML shell and stability of supporting cores, while reducing noble metal contents.

Fiscal Year (FY) 2013 Objectives

Scale up of syntheses to produce multi-gram quantities of following three catalysts:

- Pt ML on Pd hollow nano-particles using a microemulsion or similar method
- Pt ML on ultra-thin Pd alloy nanowires (NWs)
- Pt ML on WNi and Pd₉Au₁ alloys obtained by electrodeposition
 - Delivering a 450-cm² membrane electrode assembly (MEA) for testing at United Technologies Corporation
 - Achieving a 100% utilization of Pt

Technical Barriers

This project addresses the following technical barriers from the Fuel Cells section of the Fuel Cell Technologies Office Multi-Year Research, Development, and Demonstration Plan:

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

Technical Targets

We are focusing on simplifying synthetic processes to obtain better catalysts' activity, higher Pt utilization, lower content of platinum-group metal (PGM) and more simple MEAs formation (Table 1).

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

Characteristic	Units	Target 2017	Achieved 2013
PGM total loading	mg PGM/cm ² electrode area	0.125	0.05 (Pt/PdAu, Pt/PdWNI/GDL)
Mass activity	A/mg Pt @ 900 mV _{IR-free}	0.44	1.7 (Pt/PdAu NWs)
Specific activity	mA/cm ² @ 900 mV _{IR-free}		1.4 (Pt/hollow Pd)
PGM mass activity			0.5 (Pt/hollow Pd)
Loss in initial catalytic activity	% mass activity loss	<48	No loss in activity in 200,000 cycles (Pt/PdAu)

GDL - gas diffusion layer

FY 2013 Accomplishments

- Demonstrated synthesis and high performance of hollow Pd nano-particles and Pt_{ML}/Pd_{hollow}/C catalyst. The synthesis methods are readily scalable to multi-gram quantities.
- Synthesis of ultra-thin bimetallic PdAu NWs has been developed to provide an excellent support for Pt_{ML}.
- Developed a method for electrochemical deposition of NW cores on GDLs.
- Developed a method for electrodeposition of metal, alloy and refractory metal alloy nano-particles on GDLs. Highly active and durable Pt_{ML}/Pd₉Au₁ NW/GDL and Pt_{ML}/Pd/WNi/GDL electrocatalysts have been obtained.
- Pt utilization close to 100% has also been demonstrated.

- Developed electrochemical cell for production of electrodes of 440 cm² (industrial size).



INTRODUCTION

Further developments of oxygen reduction electrocatalysts are inevitable to lessen the remaining technological difficulties that hamper automotive applications of fuel cells, and we thus have focused on reducing Pt, or PGM contents in our Pt ML electrocatalysts, while increasing their stability and activity. The understanding of the properties of Pt ML electrocatalysts, and of a broader class of core-shell electrocatalysts, has considerably grown up. Optimizing the properties of nanostructured cores such as the composition, size and shape makes it possible to facilitate the Pt ML catalysts ready for the applications.

APPROACH

The properties of Pt ML, particularly such as the ORR activity and stability, can be improved by core-shell interaction using appropriate cores, which reduces oxygen binding energy through the following measures [1]: (i) compression of Pt ML atoms induced by core, hollow core, subsurface ML, (ii) electronic effects of cores, (iii) decreasing the number of low-coordination atoms, and (iv) increasing stability of cores with specific structure, composition and shape. We have also performed electrodeposition of cores such as metal and alloy nanoparticles, nano-rods, and NWs to optimize their shapes and composition and maximize catalyst utilization. Refractory metal alloys electrodeposited by co-deposition of Ni and W, are also used as cores to further reduce the PGM content.

RESULTS

Synthesis and Performance of Hollow Pd Nano-Particles and Pt_{ML}/Pd_{hollow}/C Catalyst

Three different syntheses of hollow Pd nano-particles have been developed, i.e., (i) by microemulsion, (ii) reduction in water with citrate, and (iii) galvanic replacement of Cu as a sacrificial metal with no surfactant. These methods are scalable to multi-gram quantities. The formation of the hollow structure from these Pd nano-particles was verified by transmission electron microscopy. The activity and stability of the Pt_{ML}/Pd_{hollow}/C catalysts have been examined by rotating disk electrode and MEA tests. The catalyst synthesized by the method (iii) showed the most enhanced activity and stability for the ORR among these catalysts. The PGM loading in cathode was 70 μg/cm². In the MEA tests, the Pt and PGM mass activity was 1.2 A/mg and 0.53 A/mg (at 0.9 V), respectively (Figure 1), and the specific

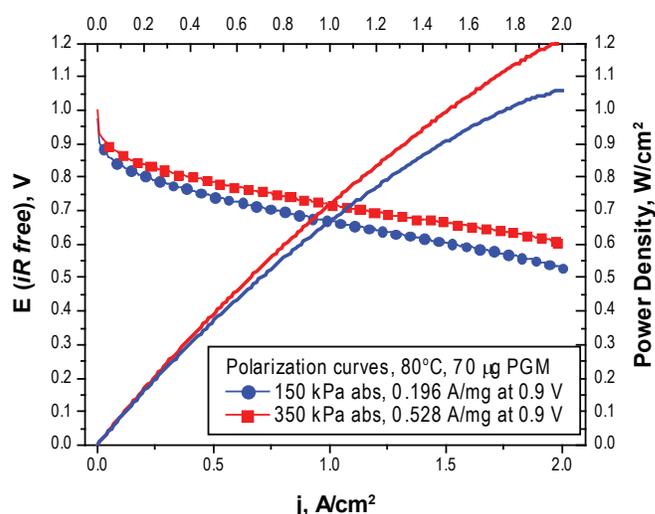


FIGURE 1. Polarization curves and power density curves of MEA tests from Pt_{ML}/Pd_{hollow}/C catalyst operating at 80°C. Cathode PGM loading: 70 μg/cm²; electrode area: 5 cm².

activity was 1.4 mA/cm² (at 0.9 V). There was no change in polarization curves with O₂ and air in 1,000 potential cycle stability tests.

We note that hollow Pt nano-particles were also prepared by the replacement of Cu. In rotating disk electrode tests, the PGM mass activity was 0.32 A/mg, and the specific activity was 2.06 mA/cm². No loss in ORR was observed after 10,000 potential cycles.

Pt_{ML}/Pd/C Catalyst Synthesized in Ethanol

We have developed a new Pt ML synthesis method on Pd nano-particles in ethanol. Galvanic displacement of Pd by Pt takes place, while Pd²⁺ ions are reduced by ethanol at elevated temperatures. High-angle annular dark field-scanning transmission electron microscope and electron energy loss spectroscopy measurements confirmed the core-shell structure. The PGM loading in the cathode was 150 μg/cm². The Pt and PGM mass activity in the MEA tests was 0.9 A/mg and 0.4 A/mg, respectively (Figure 2), and the activity with O₂ and air did not change after 2,000 potential cycle tests.

Pt_{ML} on Ultra-Thin Bimetallic PdAu NWs

The ultra-thin Pd_{1-x}Au_x NWs are prepared by a solution-based method wherein the chemical composition can be readily and predictably controlled. The composition and size-dependent performance in hierarchical Pd_{1-x}Au_x NWs encapsulated with a Pt_{ML} shell (Pt/Pd_{1-x}Au_x) was observed. After the deposition of a Pt_{ML}, a volcano-type composition dependence is observed in the ORR activity of the Pt/Pd_{1-x}Au_x NWs as the Au content is increased from 0 to 30% with the highest activity of the Pt/Pd₉Au₁ NWs, representing the optimum performance. In the MEA tests,

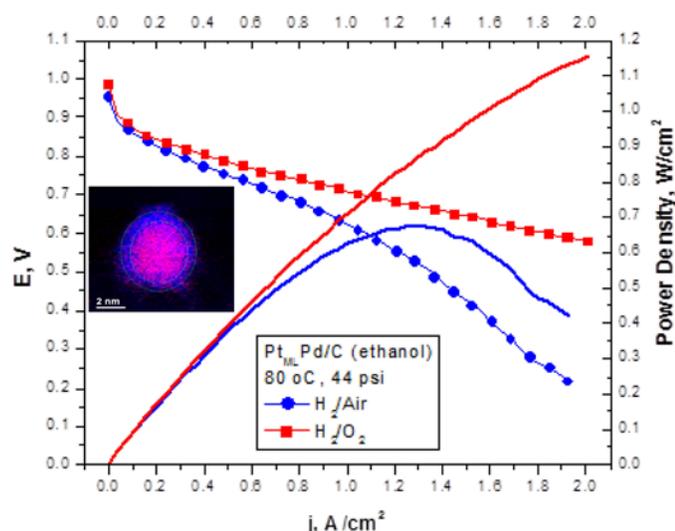


FIGURE 2. Polarization curves and power density curves of MEA tests from $Pt_{ML}/Pd/C$ catalyst synthesized in ethanol, operating at 80°C. The inset shows a two-dimensional image of Pd (red) and Pt (blue) electron energy loss spectroscopy signals from a $Pt_{ML}/Pd/C$ nano-particle. Cathode PGM loading: 150 $\mu\text{g}/\text{cm}^2$ (70 $\mu\text{g}/\text{cm}^2$ Pt); electrode area: 5 cm^2 .

the Pt and PGM mass activity was 1.7 A/mg and 0.72 A/mg at 0.9 V (Figure 3), respectively. The specific activity was 0.72 mA/cm^2 .

Electrochemical Deposition of NW Cores, Refractory Metal Alloys and 100% Pt Utilization

We have developed the scale up in electrodeposition of catalysts directly on GDLs, with three electrochemical cells of electrode areas of 5, 25, and 450 cm^2 . Potential pulse deposition protocol was tailored to optimize the deposition processes on GDLs. The unique feature of the electrodeposited PtML catalysts on electrodeposited cores on GDLs is that all Pt atoms are accessible to both electrons and protons and thus, they have a 100% utilization. In comparison with 15-20% Pt utilization in a conventional Pt/C catalyst (4-5 nm diameter) and about 50% in PtML catalysts obtained in conventional preparation of the MEA.

Pt_{ML}/Pd_9Au_1 NW/GDL

Similar ORR activity in MEA tests was obtained for 5- and 25- cm^2 electrode cells; the Pt and PGM mass activity was 1.2 A/mg and 0.5 A/mg, respectively, and the specific activity was 0.4 mA/cm^2 . Lower activity for 450 cm^2 may be caused by the ambient pressure applied and low open circuit potential indicating inadequate state of the surface.

$Pt_{ML}/Pd/WNi/GDL$

We demonstrated the electrodeposition of refractory metal alloy from aqueous solutions on GDLs. A co-deposition of W and Ni can take place, although W cannot

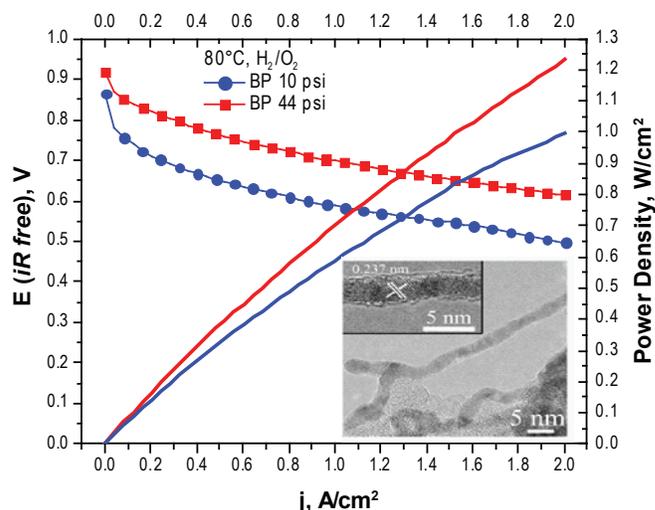


FIGURE 3. Polarization curves and power density curves of MEA tests from Pt_{ML} on ultra-thin PdAu NW catalyst operating at 80°C. The inset shows transmission electron microscope images of PdAu nanowires. Cathode PGM loading: 70 $\mu\text{g}/\text{cm}^2$; electrode area: 5 cm^2 .

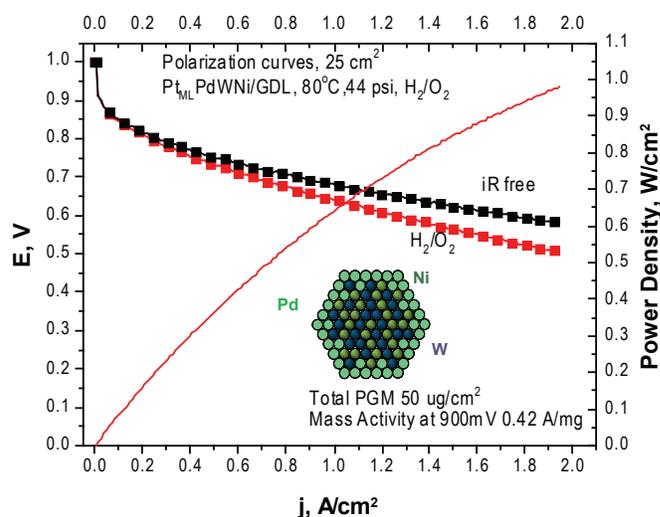


FIGURE 4. Polarization curves and power density curves of MEA tests from Pt_{ML} on Pd/NiW/GDL operating at 80°C. The inset shows a schematic model of NiW nano-particle core with a partially displaced by Pd. Cathode PGM loading: 50 $\mu\text{g}/\text{cm}^2$; electrode area: 25 cm^2 .

separately be deposited from aqueous solutions. These particles provide a stable and inexpensive support as cores. We then deposited Pd on NiW cores through the galvanic displacement of Ni, followed by Pt ML deposition by the Cu underpotentially deposited method. The PGM loading in cathode was 50 $\mu\text{g}/\text{cm}^2$. The Pt and PGM mass activity was 1.1 A/mg and 0.42 A/mg, respectively (Figure 4). We note that the performance even increased after 5,000 (5 cm^2) and 15,000 (25 cm^2) potential tests.

MEA Tests of Pt_{ML}/Pd/C at 3M

The MEA test under potential cycles between 0.6 V and 1.2 V at 70°C at 100% relative humidity demonstrated that the mass activity almost doubled and the specific activity increased ~3-4 times with an increase in the number of potential cycles, supporting the self-healing mechanism, in which we have proposed.

CONCLUSIONS AND FUTURE DIRECTIONS

- Further improvements of Pt ML catalyst aimed at reducing the cost of the Pd core, increasing stability and improving syntheses efficiency have been achieved.
- These include several syntheses of hollow Pd cores, Pd alloys with refractory metals, Pd₉Au₁ alloy, Pt ML on ultra-thin Pd NWs and electrodeposited Pd nanostructures, verified in scale up syntheses and the MEA tests.
- The unique features of Pt ML catalysts with electrodeposited cores including Pt utilization of 100% have been demonstrated. Technology based on electrodeposition of catalysts on GDLs appears promising.
- The mechanism of stability of core-shell electrocatalysts, including the self-healing mechanism, has been verified in tests involving potential cycling to 1.2 V at 3M.

Future work will focus on:

- Syntheses of hollow Pd and Pt to maximize the hollow and to optimize the particle size in relation to the degree of atom's contraction and activity.
- Tuning the effect of core on a Pt ML shell by hetero-layered core structure. Graphene oxide as support.
- Electrodeposition of selected alloys as stable, inexpensive cores with known segregation properties. Optimization of the cores shapes.
- Using non-aqueous solvents for electrodeposition of reactive metal cores, underpotentially deposited of various MLs for Pt ML deposition on reactive metals and alloys.

SPECIAL RECOGNITIONS & AWARDS/ PATENTS ISSUED

1. A special issue of the journal "*Electrocatalysis*" published to tribute R. Adzic's outstanding achievements in the areas of electrochemistry and electrocatalysis (volume 3, 2012).
2. R. Adzic, J. Wang, M. Vukmirovic, K. Sasaki received an R&D Award.
3. Four patent applications have been submitted in 2012-2013.

FY 2013 PUBLICATIONS/PRESENTATIONS

1. K.A. Kuttiyiel, K. Sasaki, D. Su, M.B. Vukmirovic, N.S. Marinkovic, R.R. Adzic, "Pt Monolayer on Au-Stabilized PdNi Core-Shell Nanoparticles for Oxygen Reduction Reaction", *Electrochimica Acta*, in press.
2. L. Yang, M.B. Vukmirovic, D. Su, K. Sasaki, J. Herron, M. Mavrikakis, S. Liao, R.R. Adzic, "Tuning the Catalytic Activity of Ru@Pt Core-Shell Nanoparticles for the Oxygen Reduction Reaction by Varying the Shell Thickness", *Journal of Physical Chemistry C*, in press.
3. K. Sasaki, H. Naohara, Y-M. Choi, J. X. Wang, M.B. Vukmirovic, P. Liu, R.R. Adzic, "Recent Advances in Platinum Monolayer Fuel Cell Electrocatalysts for the Oxygen Reduction Reaction", *The Journal of Fuel Cell Technology*, 12(3) (2013) 58-64.
4. Y. Zhang, C. Ma, Y. Zhu, R. Si, Yun Cai, J.X. Wang, R.R. Adzic, "Hollow Core Supported Pt Monolayer Catalysts for Oxygen Reduction", *Catalysis Today*, 202 (2013) 50-54.
5. K.A. Kuttiyiel, K. Sasaki, Y. Choi, D. Su, P. Liu, R.R. Adzic, "Nitride Stabilized PtNi Core-Shell Nanocatalyst for High Oxygen Reduction Activity", *Nano Letters*, 12(12) (2012) 6266-6271.
6. K. Sasaki, H. Naohara, Y.M. Choi, Y. Cai, W.-F. Chen, P. Liu, R.R. Adzic, "Highly Stable Pt Monolayer on PdAu Nanoparticle Electrocatalysts for the Oxygen Reduction Reaction", *Nature Communications*, (2012) DOI:10.1038/ncomms2124.
7. R.R. Adzic, "Platinum Monolayer Electrocatalysts: Tunable Activity, Stability, and Self-Healing Properties", *Electrocatalysis*, 3(3-4) (2012) 163-169.
8. H.I. Karan, K. Sasaki, K.A. Kuttiyiel, C.A. Farberow, M. Mavrikakis, R.R. Adzic, "Catalytic Activity of Platinum Monolayer on Iridium and Rhenium Alloy Nanoparticles for the Oxygen Reduction Reaction", *ACS Catalysis*, 2(5) (2012) 817-824.
9. K.A. Kuttiyiel, K. Sasaki, Y-M. Choi, D. Su, P. Liu, R.R. Adzic, "Bimetallic IrNi Core Platinum Monolayer Shell Electrocatalysts for the Oxygen Reduction Reaction", *Energy & Environmental Science*, 5(1) (2012) 5297-5304.
10. M.B. Vukmirovic, Y. Cai, S.T. Bliznakov, K. Sasaki, J.X. Wang and R.R. Adzic, "Platinum Monolayer Electrocatalysts for the Oxygen Reduction Reaction", *ECS Transaction*, doi: 10.1149/1.3701965 *ECS Trans.* 2012 volume 45, issue 2, 15-23.
11. C. Koenigsmann, E. Sutter, T.A. Chiesa, R.R. Adzic, S.S. Wong, "Highly Enhanced Electrocatalytic Oxygen Reduction Performance Observed in Bimetallic Palladium-Based Nanowires Prepared under Ambient, Surfactantless Conditions", *Nano Letters*, 12(4) (2012) 2013-2020.
12. K.P. Gong, Y. Cho, M.B. Vukmirovic, P. Liu, C. Ma, D. Su, R.R. Adzic, "Tetrahedral Palladium Nanocrystals: A New Support for Platinum Monolayer Electrocatalysts with High Activity and Stability in the Oxygen Reduction Reaction", *Zeitschrift für Physikalische Chemie*, 226(9-10) (2012) 1025-1038.
13. S.T. Bliznakov, M.B. Vukmirovic, L. Yang, E.A. Sutter, R.R. Adzic, "Pt Monolayer on Electrodeposited Pd Nanostructures: Advanced Cathode Catalysts for PEM Fuel Cells", *Journal of the Electrochemical Society*, 159(9) (2012) F501-F506.

REFERENCES

1. R.R. Adzic, “Platinum Monolayer Electrocatalysts: Tunable Activity, Stability, and Self-Healing Properties”, *Electrocatalysis*, 3(3-4) (2012) 163-169.