

V.A.3 Contiguous Platinum Monolayer Oxygen Reduction Electrocatalysts on High-Stability, Low-Cost Supports

Radoslav Adzic (Primary Contact), Jia Wang,
Miomir Vukmirovic, Kotaro Sasaki
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

Project Start Date: July 1, 2009
Project End Date: Project continuation and
direction determined annually by DOE

Overall Objectives

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

Fiscal Year (FY) 2015 Objectives

- To increase activity and stability of Pt monolayer catalysts to meet the DOE technical targets for 2020 through the following:
 - Electrodeposition of inexpensive refractory metal alloy nanoparticles on gas diffusion layers (GDLs) to fabricate the electrodes of 5 cm², 25 cm², and 50 cm² and perform membrane electrode assembly (MEA) tests at BNL and General Motors (GM)
 - Further developing the nitriding method of core (PdNi) stabilization; the stabilization method involving the addition of Au to nanoparticle cores will also be developed
 - Demonstrating suitability of graphene as support for Pt ML catalysts

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:

- Durability
- Cost
- Performance

Technical Targets

We are focusing on simplifying the synthetic processes to obtain better catalyst activity, higher Pt utilization, lower content of precious group metals (PGMs), and simpler MEA fabrication (see Table 1).

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

	DOE 2020 Targets	Pt _{ML} /Pd/WNi/GDL 80°C, H ₂ /O ₂ , 150 kPa	Pt _{ML} /Pd/WNi/GDL 80°C, H ₂ /O ₂ , 300 kPa
PGM total loading, mg _{PGM} /cm ²	<0.125	0.07 mg _{PGM} /cm ² at the cathode	0.07 mg _{PGM} /cm ² at the cathode
Loss in performance at 0.8 A/cm ²	<30 mV	19 mV after 34,000 AST	7 mV after 34,000 AST
Loss in performance at 1.5 A/cm ²	<30 mV	22 mV after 34,000 AST	19 mV after 34,000 AST
Mass activity at 900 mV _{IRfree} , A/mg _{PGM}	>0.44	0.37	0.46

AST – accelerated stress test

FY 2015 Accomplishments

- The stabilization method involving nitride-stabilized non-noble core components was developed. Pt_{ML} on nitride-stabilized PdNi core catalysts exhibited excellent properties.
- Electrodeposition of dendritic nanostructured cores was demonstrated to be a promising strategy for improving the MEA's performance under H₂/air feed at low or no back pressure and at high current densities.
- Using Au to stabilize various cores: Pt_{ML} on Au-modified W compounds showed no change of activity in the accelerated stability test of 30,000 potential cycles.
- Pt ML on Pd core on reduced graphene oxide (rGO) proved to be an excellent catalyst.
- Atomic level control of metal deposition using cation adsorption/reduction/atom displacement was shown to be possible with rGO.

- MEA with rGO was found to have promising properties: Pd content is reduced by 50% in comparison with the Pt/Pd/C catalyst, while stability and activity are enhanced.
- A very small increase in the ORR kinetics was demonstrated for adsorbed fluorinated short-chain molecules at small coverages likely as a consequence of surface hydrophobization and easier O₂ adsorption.



INTRODUCTION

Further improvements of oxygen reduction electrocatalysts are necessary to overcome the remaining technological difficulties that hinder automotive applications of fuel cells. Our research was focused on reducing Pt or PGM contents in our electrocatalysts while increasing their stability and activity. Optimizing the properties of supporting cores such as the composition, size and shape makes possible further improvements of the Pt monolayer catalysts.

APPROACH

We are improving Pt ML catalysts using novel core compositions and new synthetic methods including:

- Nitriding non-noble metal core components for increased stability.
- Electrodeposition of cores (refractory metal alloys) to optimize their composition and maximize catalyst utilization.
- Synthesis of ordered intermetallic compounds with high activity without Pt.
- Reactive spray deposition method of the synthesis of novel low cost cores.
- Pulse—potential deposition of cores on GDL carbon used to obtain nanoparticles with narrow size distribution and 100% Pt utilizations.
- Using graphene and reduced graphene oxide as supports.

RESULTS

We describe four results illustrating the new methods developed in FY 2015 for improving Pt ML catalysts for the ORR.

Electrodeposition of WNi and MEA Tests of Pt/Pd/WNi/C

Further studies of electrodeposition of PtML/Pd/WNi/C cores were focused on MEA stability tests. Polarization curves from a 5 cm² MEA with loading of 0.07 mg_{PGM}/cm²

were determined. After co-deposition of W and Ni, replacing the top layers of Ni by Pd, and placing a Pt ML by galvanic exchange of a Cu ML, we achieved low PGM loading and high Pt utilization. The data surpassed the DOE targets for mass activity and loss in performance at higher back pressure. The performance in air needs to be further improved (Table 1, Figure 1).

We used the electrodeposition method to make dendritic nanostructured cores, which is a promising strategy for improving the MEA performance at low or no back pressure and at high current density in H₂/air feed. The results illustrating these possibilities are shown in Figure 2.

Nitride-Stabilized Pt-M Core-Shell Catalysts in Acid Media

We developed highly active and stable oxygen reduction catalysts by depositing Pt monolayers on a nitrated PdNi alloy core (Figure 3). The prepared Pt_{ML}/PdNiN/C catalyst retains 89% of the initial electrochemical surface area after 50,000 cycles between potentials of 0.6 V and 1.0 V. Nanoparticles consisting of Pd₅₀Ni₅₀/C were calcinated in N₂ at 250°C for 1 h and in NH₃ at 510°C for 2 h. Scanning transmission electron microscopy/electron energy loss spectroscopy (STEM/EELS) show that Pd atoms segregate on the surface. X-ray absorption spectroscopy shows a decrease in Ni bonding due to the formation of Ni nitride. The experimental data and the density functional theory (DFT) calculations indicate that the nitride cores improve the

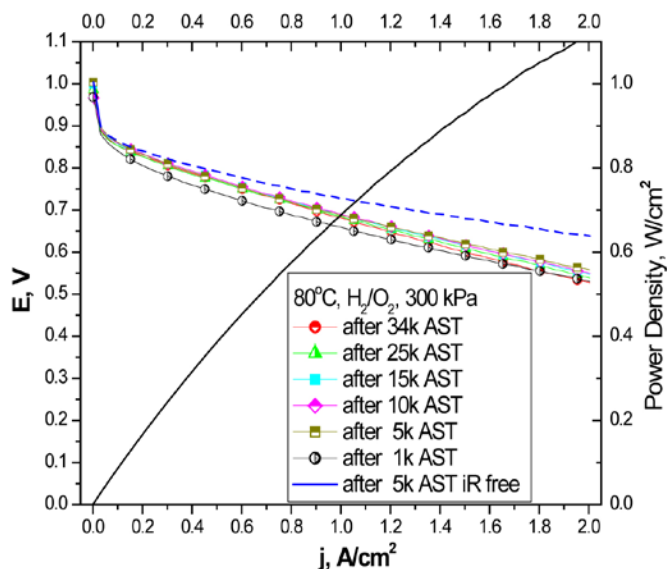


FIGURE 1. Polarization curves from a 5 cm² MEA with loading of 0.07 mg_{PGM}/cm² Pt_{ML}/Pd/WNi/GDL catalyst on the cathode obtained by co-deposition of WNi, replacing top layers of Ni by Pd and placing a Pt ML by galvanic exchange of a Cu ML. TKK Pt catalysts (0.05 mg_{Pt}/cm²) on anode and Nafion® HP membrane are used. A negligible loss in activity occurs after 34,000 potential cycles.

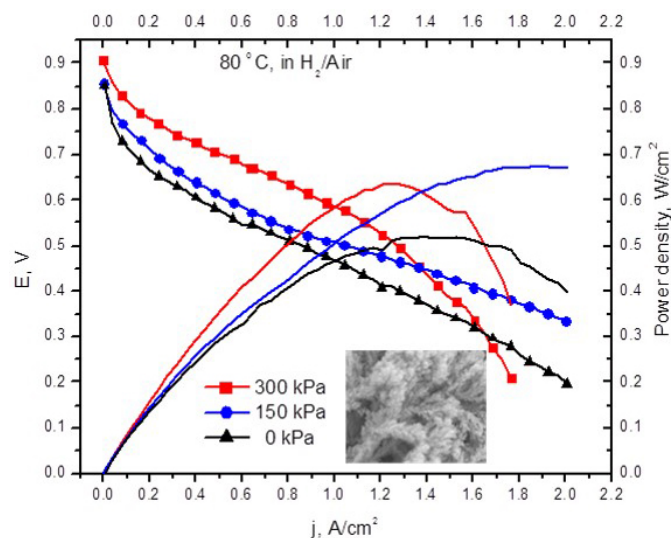


FIGURE 2. MEA polarization curve with H_2 /air feed at three different back pressures in the cathode obtained by electrodeposition of Pd dendrites to increase a three-dimensional (3D) porosity and mass transfer at low gas pressure; insert shows Pd dendritic deposit.

performance of the Pt shell by inducing both the geometric and electronic effects. Pd content is reduced by 50% in comparison with the Pt/Pd/C catalyst, while stability and activity are enhanced.

Graphene as Support for Pt Monolayer Catalysts

We synthesized Pt ML on Au core on rGO catalysts that verifies the possibility of using graphene as a support. Au nanoparticles were deposited on reduced graphene oxide using the Pb^{2+} cation adsorption/reduction/ Pb^0 atom displacement method. Highly crystalline Au nanoparticles having a narrow size distribution have been obtained. The activity and stability of this catalyst is excellent which demonstrates that graphene can be an excellent support for Pt ML catalysts (Figure 4).

CONCLUSIONS AND FUTURE DIRECTIONS

Further improvements of Pt ML catalysts have been achieved by the development of four methodologies (three discussed in some detail here) that reduced the Pd content in cores by 50%, increased catalyst stability, and improved syntheses efficiency. Electrodeposition methodology was improved and its use was expanded to dendritic growth of cores to form 3D porosity that facilitates a better performance with air, lower pressure, and operation at high current density ranges. The other two successful methodologies for improving activity and stability of these catalysts include nitriding of non-noble metal cores constituents and using Au as a Pt ML support on graphene and promoting the formation of ordered intermetallic compounds. The latter can act as catalyst without Pt or serve as high stability core for a Pt ML.

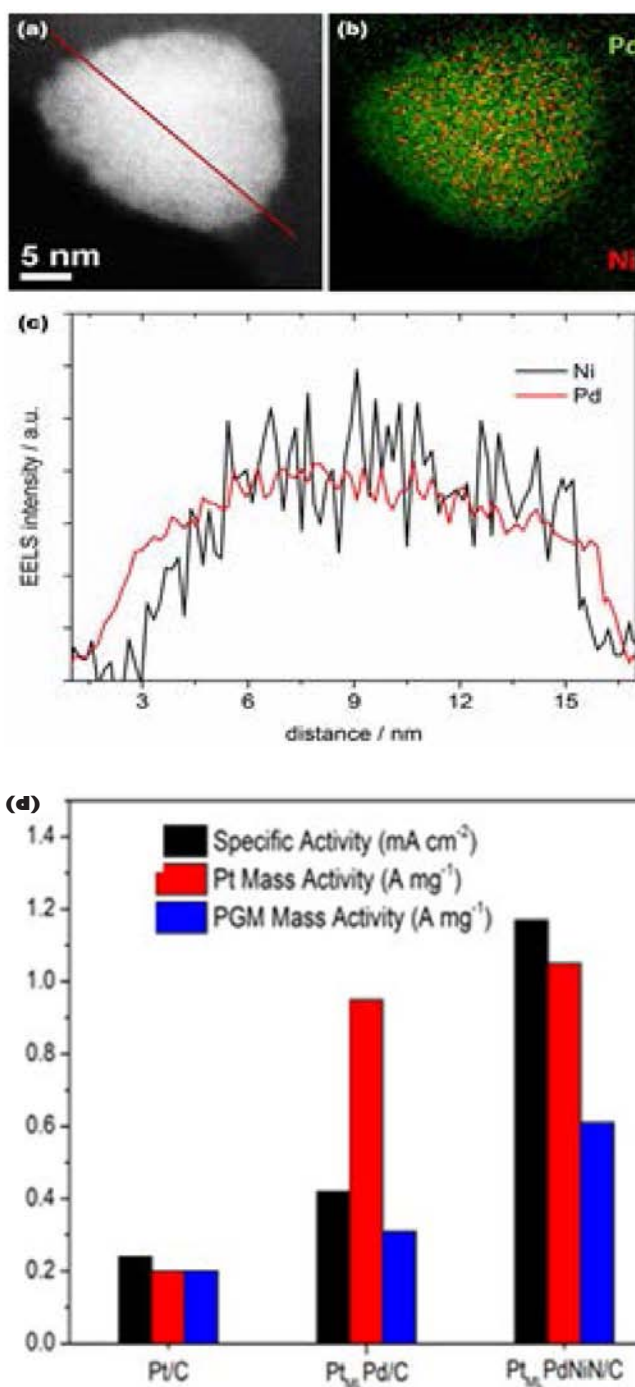


FIGURE 3. Nitride-stabilized Pt/PdNi/C core-shell catalyst; (a) high-angle annular dark-field-STEM image of PdNiN core-shell nanoparticle; (b) two dimensional EELS mapping of Ni L signal (red) and Pd M signal (green); (c) EELS line scan profile for Pd M-edge and Ni L-edge along the scanned line indicated in (a); (d) specific and mass activities for the commercial Pt/C, $Pt_{ML}Pd/C$ and $Pt_{ML}PdNiN/C$ catalysts at 0.9 V (RHE).

Future work will focus on:

- MEA and stack tests in 50 cm^2 electrodes will be performed at BNL and GM with Pt ML on graphene-

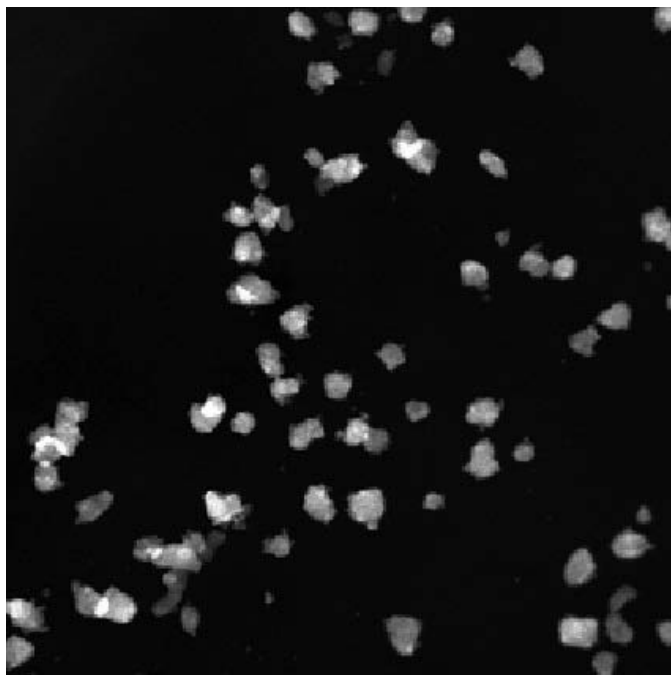


FIGURE 4. Pt deposited on Au nanoparticles on graphene using Cu UPD technique

supported cores and on nitride- and Au-stabilized noble and refractory metal alloy cores.

Novel strategies to synthesize high performance Pt monolayer electrocatalysts include:

- Electrodeposition from non-aqueous solvents to obtain new classes of cores.
- High pressure nitridation performed in a new tube reactor at temperatures up to 1,100°C in a NH₃ gas at pressures up to 10 MPa to generate various types of nitride nanoparticles with refractory metals such as Ti, V, Nb, Ta, and W to enhance the stability and activity of Pt shells.
- Reactive spray deposition technology as another method to obtain cores unattainable thus far with conventional syntheses.
- Onion-structured nanoparticles with new cores of multiple metal layers to tune Pt monolayer properties and shift E° closer to 1.23 V. Supporting DFT calculations have been completed.
- Searching for new ordered intermetallic compounds for Pt-free catalysts and supporting cores for Pt monolayers.
- Using a layer of Au to modify refractory metals and alloys. Some refractory metals and alloys could serve as highly corrosion-resistant cores but we found they need an Au interlayer to preclude too large negative shifting of

the *d*-band center of surface Pt atoms. A Pt ML on Au-W compounds (patent pending) already shows enhanced ORR performance with no degradation in 30,000 cycles.

SPECIAL RECOGNITIONS & AWARDS/ PATENTS ISSUED

1. R. Adzic, S. Bliznakov, and M. Vukmirovic, U.S. Patent: Core-Shell Fuel Cell Electrodes, US2015/0017565 A1, Jan. 15, 2015.
2. Jia X. Wang, Radoslav R. Adzic, “Underpotential deposition-mediated layer-by-layer growth of thin films,” U.S. Patent 9034165 B2, May 19, 2015.
3. R.R. Adzic, J. Zhang, K. Sasaki, “Method and Electrochemical Cell for Synthesis and Treatment of Metal Monolayer Electrocatalysts, Metal, Carbon, and Oxide,” U.S. Patent No. 9,017,530.
4. K. Sasaki, W.F. Chen, J.T. Muckerman, R.R. Adzic, “Molybdenum and Tungsten Nanostructures and Methods for Making and Using Same,” U.S. Patent No. 8,927,453.
5. Kurian Kuttiyiel, Kotaro Sasaki, Radoslav Adzic, “Nitride Stabilized Core-Shell Nanoparticles,” U.S. Patent -20150147682, 05/28/2015.

FY 2015 PUBLICATIONS/PRESENTATIONS

1. Kurian A Kuttiyiel, YongMan Choi, Sun-Mi Hwang, Gu-Gon Park, Tae-Hyun Yang, Dong Su, Kotaro Sasaki, Ping Liu, Radoslav R. Adzic, “Enhancement of the oxygen reduction on nitride stabilized Pt-M (M= Fe, Co, and Ni) core-shell nanoparticle electrocatalysts,” *Nano Energy*, 2015, 13, 442–449.
2. Jue Hu, Kurian A Kuttiyiel, Kotaro Sasaki, Dong Su, Tae-Hyun Yang, Gu-Gon Park, Chengxu Zhang, Guangyu Chen, Radoslav R. Adzic, “Pt Monolayer Shell on Nitrided Alloy Core—A Path to Highly Stable Oxygen Reduction Catalyst,” *Catalysts*, 2015, 5, 1321–1332.
3. Y. Li, K.A. Kuttiyiel, L. Wu, Y. Zhu, E. Fujita, K. Sasaki, R.R. Adzic, “Cobalt Manganese Oxynitride Nanocatalysts on Graphene as Oxygen Reduction and Evolution Bifunctional Catalysts,” *Journal of American Chemical Society*, submitted.
4. J. Hu, K.A. Kuttiyiel, K. Sasaki, D. Su, G.-G. Park, C. Zhang, G. Chen, R.R. Adzic, “Pt Monolayer Shell on Nitride Alloy Core—A Path to Highly Stable Oxygen Reduction Catalyst,” *Catalysts*, accepted.
5. H. Liu, W. An, Y. Li, A. Frenkel, K. Sasaki, C. Koenigsmann, D. Su, R. Anderson, R.M. Crooks, R.R. Adzic, P. Liu, S.S. Wong, “Combining Theory and Experiment to Deduce the Active Structure Geometry of Ultrathin Nanowires Analyzed In Situ for the Oxygen Reduction Reaction,” *Journal of American Chemical Society*, submitted.
6. K.A. Kuttiyiel, Y.M. Choi, S.-M. Hwang, G.-G. Park, T.-H. Yang, D. Su, K. Sasaki, P. Liu, R.R. Adzic, “Enhancement of the oxygen reduction on nitride stabilized Pt-M (M=Fe, Co, and Ni) core-shell nanoparticle electrocatalysts,” *Nano Energy* (2015) 13, 442–449.

7. S. Bliznakov, M. Vukmirovic, R. Adzic, in “Atomically-Precise Methods for Synthesis of Solid Catalysts,” S. Hermans and T. Visart de Bocarme, Editors, p. 144, The Royal Society of Chemistry Book Chapter, *RCS Catalysis Series No. 22*, (2015).

8. K. Sasaki, N. Marinkovic, “X-ray Absorption Spectroscopic Characterization of Nanomaterial Catalysts in Electrochemistry and Fuel Cells,” submitted to the 5th volume of SPRINGER book series on “Characterization Tools for Nanoscience & Nanotechnology,” submitted.

PRESENTATIONS

1. X. Wang, P. He, Y. Zhang, and S. Ye, “Can CO-tolerant Anodes be Economically Viable for PEMFC Applications with Reformates?” J Electrochemical Society Meeting, Cancun, Mexico, October 8, 2014.

2. Kurian Kuttiyiel, “Enhancement of the ORR on Nitride Stabilized Pt-M (M = Fe, Co & Ni) Core-Shell Electrocatalysts,” 227th Electrochemical Society Meeting, Chicago, IL, USA (May 2015).