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

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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) 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) 2014 Objectives

Scale-up of syntheses of three catalysts including:

- Pt ML on Pd hollow nanoparticles; Pt ML on WNi nanoparticles, and Pt ML on Pd_9Au_1 nanoparticles
- Obtaining perfect Pt ML deposition and achieving 100% utilization of Pt
- New methods for increasing stability of core-shell nanoparticles, while reducing the Pt-group metal (PGM) contents
- Delivering a 300-cm^2 membrane electrode assembly (MEA) for testing at General Motors

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 catalyst activity, higher Pt utilization, lower content of PGM and more simple MEA formation (see Table 1).

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

Characteristic	Units	Target 2017	Achieved 2014
PGM total loading	mg PGM/cm^2 electrode area	0.125	0.05 (Pt/PdAu, Pt/PdWNi/gas diffusion layer)
Mass activity	A/mg Pt @ 900 $mV_{iR\text{-free}}$	0.44	1.7 (Pt/PdAu nanowires)
Specific activity	mA/cm^2 @ 900 $mV_{iR\text{-free}}$	0.72	1.4 (Pt/hollow Pd)
PGM mass activity	A/mg PGM @ 900 $mV_{iR\text{-free}}$	0.44	0.5 (Pt/hollow Pd)
Loss in initial catalytic activity	% mass activity loss over 30,000 cycles	<48	No significant loss in activity in 200,000 cycles (Pt/PdAu)

FY 2014 Accomplishments

New methodologies for improving activity and stability of Pt ML catalysts:

- Synthesis of monodisperse cores
- Forming atomically ordered, sharp core-shell interfaces
- Gold promoting the formation of ordered intermetallic compounds (The AuPdCo compound is a Pt-free catalyst with activity approaching that of Pt. It can serve as an excellent core supporting Pt ML.)
- Nitrating non–noble metal cores constituents (Both ordered intermetallic compounds and nitrated.)

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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 nano-structured cores by varying their composition, size and shape can improve Pt ML catalysts to make them ready for applications.

APPROACH

Improving Pt ML using novel core compositions and new synthetic methods including:

- Depositing nearly perfect Pt MLs on various cores
- Ordering core-ML shell interface structure
- Synthetizing monodisperse, smooth cores, or hollow cores
- Nitrating non-noble metal core components for increased stability
- Electrodeposition and underpotential deposition of cores (refractory metal alloys) to optimize their composition and maximize catalyst utilization
- Ordered intermetallic compounds with high activity without Pt
- Reactive spray deposition method to synthesize novel low cost cores

RESULTS

We describe four results illustrating the new methods developed in FY 2014 for improving Pt ML catalysts for the ORR.

Synthesis of Atomically Perfect Ru(core)-Pt(shell) Nanoparticles

We developed a new method to produce an atomically sharp, ordered core-shell interface by avoiding partial alloying of Ru-rich cores and Pt-rich shells. We verified the interface structure using high-resolution scanning transmission electron microscopy techniques. For Ru(core)-Pt(bilayer) particles, we show, by overlapping the Ru-specific electron energy loss signal with the high-angle annular dark field image (Figure 1b), that the Ru core was completely encapsulated by uniformly thin Pt shells. More importantly, an atomically-resolved scanning transmission electron microscopy image (Figure 1c) shows that the measured lattice structure (white dots) matches well with the theoretically calculated structure for an perfectly ordered phase-transition between the hexagonal close packed (hcp) Ru core and a face-centered cubic (fcc) Pt shell. Attaining such a level of structural perfection is unprecedented. Thus, Ballard Power Systems evaluates its application as the anode catalysts for hydrogen and reformate polymer electrolyte membrane fuel cells (PEMFCs). A similar method also produced a uniform coating of a Pt ML or bilayer on Pd cores, as is evident in Figure 1d, and 1e.

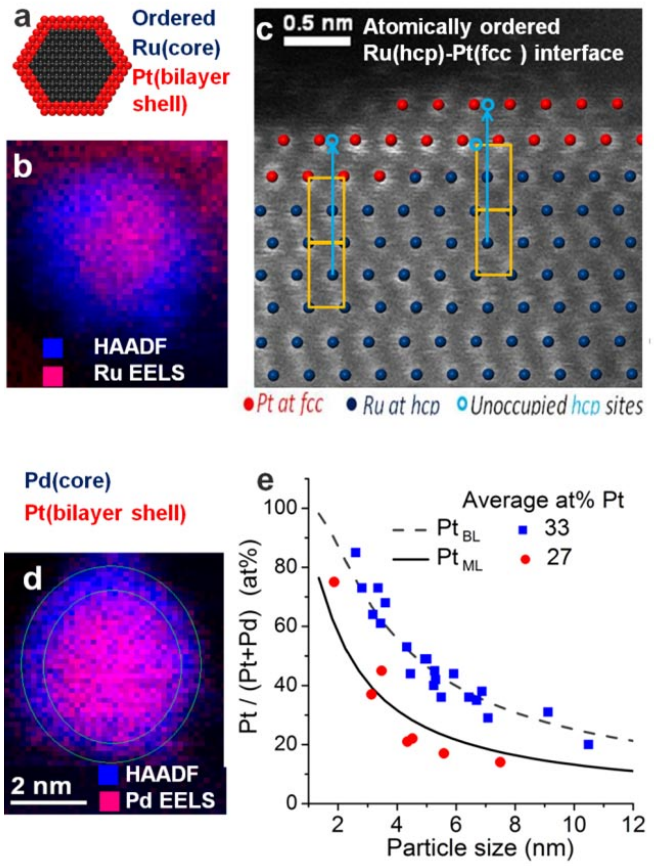

FIGURE 1. Structural schematics (a) and scanning transmission electron microcopy data for atomically perfect Ru(core)-Pt(bilayer shell) nanoparticles (b,c), and for Pd(core)-Pt(shell) nanoparticles (d,e).

Ru(core)-Pt(bilayer) Particles as the Anode Catalysts for PEMFCs

Currently, the anode Pt loading is targeted at 0.05 mg cm^{-2} for hydrogen PEMFCs using Pt nanoparticle catalysts based on the state-of-the-art technologies. With ordered Ru-Pt core-shell particles, the amount of Pt can be further reduced by half because the Pt specific surface area nearly doubles for a Pt bilayer catalyst compared to the commonly used Pt nanoparticles. In addition, the ordered Ru-Pt core-shell catalysts are highly uniform, stable, and resistant to airborne contamination. For applications in PEMFCs, we, in collaboration with Ballard Power Systems, further tested the catalysts' stability against potential cycles up to 0.95 V. Figure 2a shows the polarization curves measured before and after 2,500 startup/shutdown cycles (~65 hrs) that alternated the anode's potential between 0.02 and 0.95 V. The performance was unaffected with a loading as low as 0.025 mg cm^{-2} Pt and 10 mg cm^{-2} Ru.

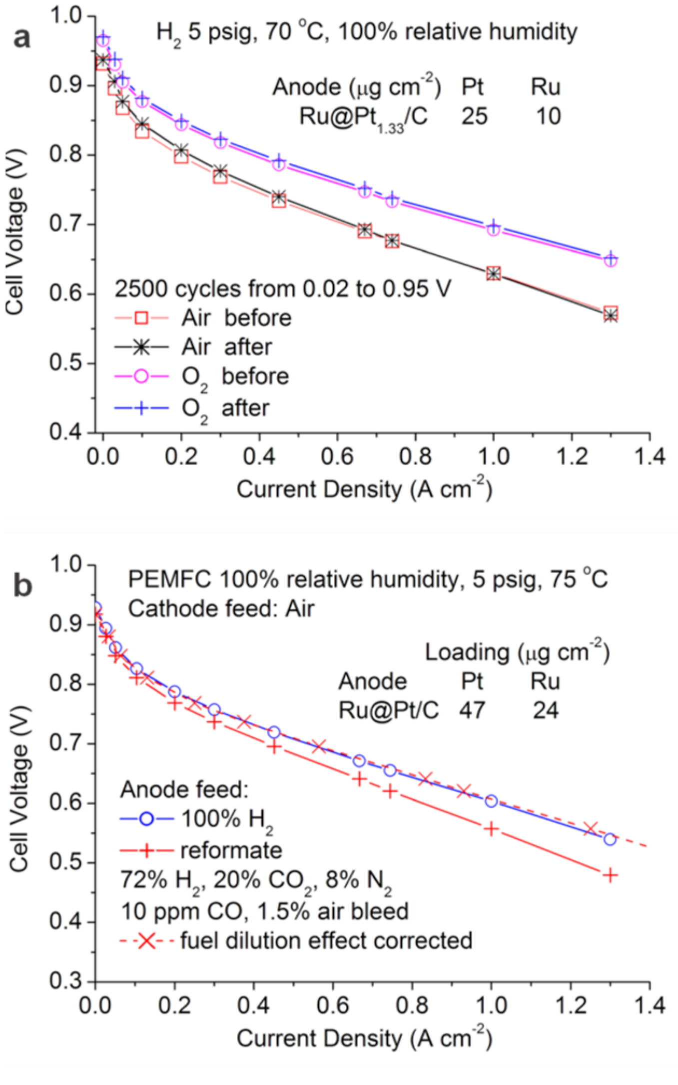

FIGURE 2. Results on anode durability (a), and CO tolerance (b) test for atomically perfect Ru(core)-Pt(shell) nanocatalysts.

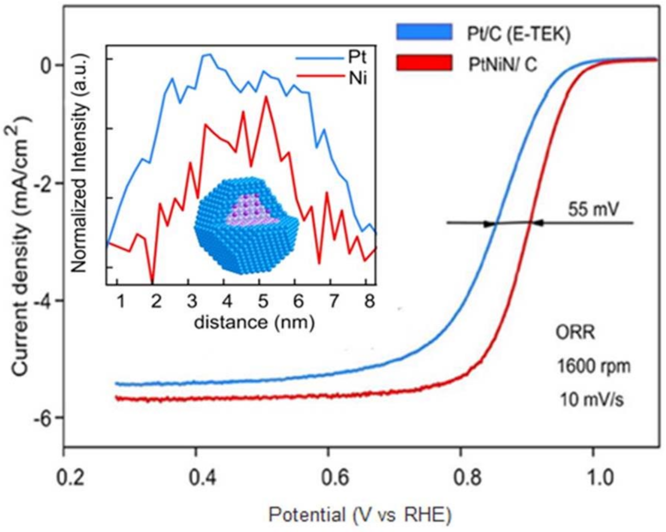

FIGURE 3. ORR polarization curves of PtNiN/C and Pt/C catalysts on a rotating disk electrode in 0.1 M $HClO_4$. Also shown is electron energy loss signal line-scan profiles of Pt and Ni in a single PtNiN nanoparticle (blue, Pt; gray, Ni; purple, N).

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

We developed novel nitride-stabilized PtM core−shell catalysts (M = Fe, Co, and Ni) with low-Pt-content shells and inexpensive metal-nitride cores having high activity and stability for the ORR. The synthesis involves nitriding metal nanoparticles (e.g., Ni_4N) and simultaneously encapsulating it by 2−4 ML-thick Pt shell (the inset of Figure 3). The PtM nitride catalysts showed 3 to 4 times higher mass activity and 3 to 7 times higher specific activity than that of Pt/C (Figure 3). The Pt mass and specific activity of PtNiN in the rotating disk electrode tests was 0.84 A/mg and 1.64 mA/cm^2, respectively. The order of both the activity is PtNiN/C > PtFeN/C > PtCoN/C > Pt/C. The accelerated stability tests for PtMN/C catalysts showed little loss in its electrochemical surface area and half-wave potential after 35,000 cycling tests, demonstrating that all the nitride cores improved the stability of the catalysts, and in particular the PtCoN catalyst showed the best durability among the catalysts. The experimental data and the density functional theory calculations indicated that nitride has the bifunctional effect that facilitates formation of the core−shell structures and improves the performance of the Pt shell by inducing both geometric and electronic effects.

Au–Promoted Formation of Structurally Ordered Intermetallic PdCo Nanoparticles

We established an innovative but simple methodology for synthesizing structurally ordered AuPdCo that exhibits comparable activity to Pt/C in both acid and alkaline media. Electron microscopic techniques demonstrate that by addition of Au atoms PdCo nanoparticles undergo at elevated temperatures an atomic structural transition from core-shell to a rare intermetallic ordered structure with twin boundaries forming stable {111}, {110} and {100} facets (the inset of Figure 4). The AuPdCo nanoparticles are a promising Pt-free catalyst that shows comparable ORR activity with commercial Pt/C but much better long-term stability in alkaline medium (Figure 4). The superior stability over Pt/C in potential cycling tests in alkaline media is specially attributed to the atomic structural order of PdCo nanoparticles along with protective effect of clusters of Au atoms on the surface. Since we use a simple and cost-effective strategy to make structurally ordered intermetallic PdCo nanoparticles, it is believed that this approach offers numerous possibilities in tailoring other transition metal intermetallic nanocatalysts.

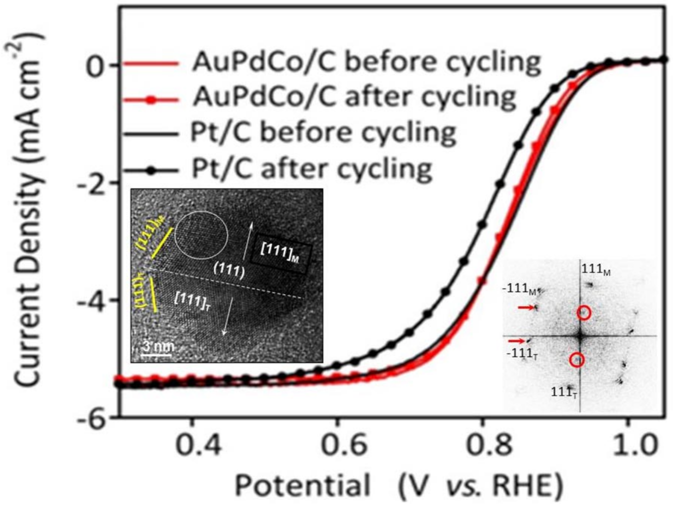

FIGURE 4. ORR polarization curves of AuPdCo/C-intermetallic and Pt/C catalysts before and after 10,000 cycle test between 0.6 and 1.0 V in 0.1 M KOH. Also shown is a high-resolution transmission electron microscope image and its diffractogram of a single AuPdCo intermetallic particle. Superlattice spots are visible in the diffractogram as indicated by the red circles.

CONCLUSIONS AND FUTURE DIRECTIONS

Further improvements of Pt ML catalysts aimed at reducing the cost of the Pd core, increasing stability and improving syntheses efficiency have been achieved. Further testing of Pt ML electrocatalysts demonstrated their attractive features, their application readiness, and the versatility of the core shell approach. New methodologies for improving activity and stability of these catalysts include:

- Synthesis of monodisperse cores.
- Forming atomically ordered, sharp core-shell interfaces.
- Gold promoting the formation of ordered intermetallic compounds.
- Nitrating non–noble metal cores constituents that demonstrate their attractive features, their application readiness, and the versatility of the core shell approach for designing catalysts are discussed in this report.

FUTURE DIRECTIONS

Future work will focus on:

- MEA and stack tests of selected catalysts.
- Electrodeposition from non-aqueous solvents to obtain new cores.
- Reactive spray deposition technology is another method to obtain cores unattainable so far with conventional syntheses.
- Modifying Pt-water interactions and enhance the ORR efficiency.
- Developing new non-noble-metal nitride and/or carbide (e.g., WN, WC, etc.) cores for Pt ML/shell to enhance the activity and stability for the ORR.
- Searching new ordered intermetallic compounds for Pt-free catalysts and supporting cores for Pt ML.

SPECIAL RECOGNITIONS AND AWARDS/ PATENTS ISSUED

1. R. Adzic, Member, Editorial Board, Scientific Reports; Nature.com.

2. R. Adzic, Member, International Academy of Electrochemical Energy Science, 2014,

3. R. Adzic, Distinguished Lecture, Hong Kong University of Science and Engineering, April 2014.

4. R. Adzic, Distinguished Lecture Xiamen University, April 2014.

5. R. Adzic, Invited talk, ECS-ECS meeting, Shanghai, China., April 2014.

6. R. Adzic, Plenary talk at International Symposium on Clean Energy from Ethanol, Rzeszow, Poland, 2014.

Patents

1. Two patent applications have been submitted in 2013-2014.

FY 2014 PUBLICATIONS/PRESENTATIONS

1. Tuning the Catalytic Activity of Ru@Pt Core-Shell Nanoparticles for the Oxygen Reduction Reaction by Varying the Shell Thickness, L. Yang, M. Vukmirovic, D. Su, K. Sasaki, J.A. Herron, M. Mavrikakis, S. Liao, R.R. Adzic, *J. Phys. Chem.,* 117, 1748-1753, 2013.

2. Ordered bilayer ruthenium-platinum core-shell nanoparticles. Y. Hsieh, Y. Zhang, D. Su, V. Volkov, R. Si, L. Wu, Y. Zhu, W. An, P. Liu, P. He, S. Ye, R.R. Adzic, J. Wang, Nat. Commun. 4:2466, 2013.

3. Hollow core supported Pt monolayer catalysts for oxygen reduction, Yu Zhang, Chao Ma, Zhu, Y., Rui Si, Yun Cai, Jia X. Wang, J.X., Adzic, R.R., Catalysis Today, 202, 50–54, 2013.

4. Au-Promoted Structurally Ordered Intermetallic PdCo Nanoparticles for the Oxygen Reduction Reaction, K.A. Kuttiyiel, K. Sasaki, D. Su, L. Wu, Y. Zhu, R.R. Adzic, Nat. Commun., in press.

5. Pt monolayer shell on hollow Pd core electrocatalysts: scale up synthesis, structure, and activity for the oxygen reduction reaction, Miomir B. Vukmirovic, Yu Zhang, Jia X. Wang, David Buceta, Lijun Wu and Radoslav R. Adzic, J. Serb. Chem. Soc. 18, 1983-1992, 2013.

6. Pt Monolayer on Au-Stabilized PdNi Core-Shell Nanoparticles for Oxygen Reduction Reaction, K.A. Kuttiyiel, K. Sasaki, D. Su, M.B. Vukmirovic, N.S. Marinkovic, R.R. Adzic, Electrochimica Acta, 110, 267-272, 2013.

7. Flame Based Synthesis of Core-Shell Structures using Pd-Ru and Pd Cores Prepared from the Vapor Phase with Reactive Spray Deposition Technology, Justin M. Roller, Haoran Yu, Dr. Miomir B. Vukmirovic, Dr. C.B. Carter, Dr. Radoslav R. Adzic, and Dr. Radenka Maric, presented at the 224nd ECS Meeting, San Francisco, California, October 27 – November 1, 2013.

8. Investigation of structural features in Pd nanoparticle cores comprising a shell layer of Pt , Justin Roller, M.J. Arellano-Jimenez, Miomir Vukmirovic, Radoslav Adzic, Paul Kotula, Radenka Maric and C. Barry Carter, 2013 MRS Fall Meeting & Exhibit, December 1–6, 2013, Boston, MA.

9. Core-Shell, Hollow-Structured Iridium-Nickel NitrideNanoparticles for the Hydrogen Evolution Reaction, K.A. Kuttiyiel,K. Sasaki, W.-F. Chen, R.R. Adzic, Journal of Materials Chemistry A, 3, 593-594,2014