V.E.9 Contiguous Platinum Monolayer Oxygen Reduction Electrocatalysts on High-Stability Low-Cost Supports

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Subcontractors:

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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:

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

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

		Target	Target	Achieved
Characteristic	**Units**	**2010**	**2015**	**2010**
Platinum Group Metal (PGM) Total Loading	mg PGM/cm^2 electrode area	0.3	0.2	-
Mass Activity	A/mg Pt @ 900 mViR-free	0.44	0.44	2.3 (Pd rods)
Specific Activity	μA/cm2 @ 900 mViR-free	720	720	1,100 (Pd rods)
PGM Mass Activity				0.58 (hollow Pt)
Durability				No loss in activity in 10,000 cycles Pt/Pd(Br-) and Pt hollow

Accomplishments

- Demonstrated a method of sub-surface modification of cores to tune the interaction of top layer of cores with a Pt ML.
- Demonstrated synthesis of hollow Pt nanoparticle catalysts with hollow-induced lattice contraction enhancing the ORR activity.
- Demonstrated a bromide adsorption/desorption method for removing low-coordination Pd atoms.
- Demonstrated syntheses of Pd nanorods and nanowires as an excellent support for a Pt ML.
- Demonstrated specific activity increases during cycling to 1.2 V.
- Demonstrated in situ NPs synthesis using square-wave pulse potential.

Introduction

The last decade has seen considerable advances made in fuel cell electrocatalysis yielding improved electrocatalysts, and increasing our understanding of the kinetics of the ORR along with affording significant advances in theoretical treatments. However, some technological difficulties that hamper the automotive applications of fuel cells have not been removed. It is generally accepted that there is an optimal size for the

ORR where the balance between the effects of increasing the surface area and the adverse effect of small particles oxidation are met.

Approach

The awareness of a complex influence of the nanoparticle size and shape on the catalyst's activity has been growing, but a clear description was not available. We examined the effects the thickness of the Pt shell, lattice mismatch, and particle size on specific and mass activities from the changes in effective surface area and activity for oxygen reduction induced by stepwise Pt ML depositions on Pd and Pd_3Co nanoparticle. We find 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. Because the ORR rate on Pt is desorption limited, lowering BE-O enhances the ORR activity. Thus, the high coordination (111) facets 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.

Therefore, smooth, lattice contracted (111) like surface structures are needed to achieve durable high ORR activity. Based on our understanding of the effect of shape, size and composition of nanoparticles on the kinetics of the ORR, we have studied Pt monolayers on surfaces having predominantly highly coordinated atoms that exist on nanorods, nanowires, smooth nanoparticles, hollow Pd spheres, single crystalline nanoparticles with predominantly (111) facets. We have studied hollow Pt electrocatalyst to optimize the nature and size of templates, deposition process and the size of hollow with respect to activity and stability. We will also study design and synthesis of, what we call, the second generation core-shell catalysts particularly using a sub-surface core modification.

Results

Pd Nanorods, Nanowires as Supports

The structural sensitivity of the ORR on Pt is now established for nanoparticles catalysts. The activity decreases in the sequence for the (111)> (100)> (110) oriented facets. The nanorods and nanowires with smooth surfaces present attractive option because they can be tailored to increase surface fraction of atoms of the most ORR active facets and decrease low coordination sites. Syntheses of nanorods and nanorwires were carried out using chemical and electrochemical deposition. In both cases enhanced reaction kinetics was observed. This is the first report on electrochemical deposition of nanowires. The results will be reported soon. They are quite promising; given the 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 the best utilization. Figure 1 shows the scanning transmission electron microscope (STEM) image of carbon supported Pd nanowires synthesized using a chemical procedure and polarization curves for a $Pt_{ML}/Pd/C$ catalysts. Their specific and mass activities for Pt monolayers on Pd nanorods are given in Table 1, while for nanowires are 641 $\mu A/cm^2$ and 1.01 A/cm^2, respectively. The results are preliminary, and indicate broad possibilities for improvements.

Smooth, or Smooth and Hollow, Pd Nanoparticles

Smooth Pd nanoparticles can be obtained by removing the low coordination support atoms (at edge and kink sites), which are places where OH strongly adsorbs and the dissolution first occurs can increase the catalyst's stability and activity without particle size growth. Several cycles of bromide adsorption and subsequent reductive desorption removes the low-

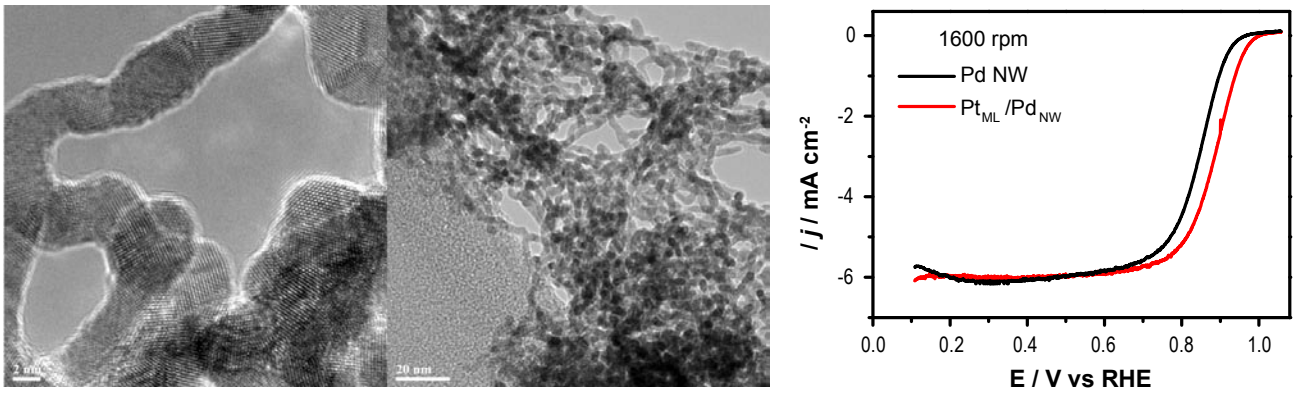

FIGURE 1. Pt ML on Pd nanowires: STEM images of Pd nanowires synthesized from $Pd(NO)_3$ octadecylamine, and dodecyltrimethylammonium bromide dispersed in toluene, reduced by $NaBH_4$ solution. Pd NWs collected by centrifugation and cleaned with ethanol. The ORR kinetics on Pd nanowires and $Pt_{ML}/Pd_{NW}/C$.

coordination atoms from Pd surfaces. The morphologies of the Pd nanoparticles before and after the bromide treatment show that the sharp edges appearing in most of the particles in the Pd/C can be hardly observed after the bromide treatment, resulting into a rounded-shape nanoparticles, much more uniform particle size distribution. The latter indicates a pronounced Ostwald ripening effect. The effect of the Br^- treatment of a Pd surface causes an increased activity and stability of a Pt/Pd/C catalyst having $i_m = 1.21$ A/mg Pt and $i_s = 0.78$ mA/cm^2 that surpasses commercial Pt/C catalysts by 5 times in mass activity. A negligible change in $E_{1/2}$ after 10,000 potential cycles indicates a high stability of a Pt monolayer on a smooth Pd surface.

Hollow Pt Nanoparticle Catalysts

We explored whether hollow can induce a needed lattice contraction as a no-cost, trouble-free core. Using Ni nanoparticles as dissoluble template, we produced compact Pt hollow nanospheres. Excellent durability was found: no loss after 10,000 potential sweep cycles between 0.65-1.05 V, and in severe pulse potential cycle test, 30 s alternatively at 0.65 and 1.05 V, sustainable Pt mass activity of 0.58 mA μg^{-1} was achieved, exceeding the DOE target of 0.44 mA μg^{-1} for platinum group metals. In another test, no further loss was confirmed after additional 7,000 potential cycles that last more than 200 hours. The enhancement over solid Pt nanoparticles (45% Pt/C, 3.2 nm) is six-fold after 100-hour durability test.

As shown in the STEM images (Figure 2), compact single grain nanospheres with 3-12 nm in diameter and 1-2 nm in shell thickness were found after durability test. Electron and X-ray diffraction measurements revealed up to 2% average lattice contraction compared to Pt lattice constant of 0.3923 nm. The density functional theory (DFT) calculation for solid and hollow Pt nanoparticles manifests a trend that the lattice contraction with a subsequent weakening of oxygen binding energies relative to that of Pt(111) is greater for hollow than for solid nanoparticles, independent of particle size. In addition to lattice contraction, we found significantly smoother surface on hollow particles. Both effects led to high sustainable ORR activity not achieved previously.

Conclusions and Future Directions

- Smooth surfaces, with highly-coordinated atoms, are suitable to support a Pt ML that yield 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.
- Sub-surface ML modification of cores is very promising; it opens up numerous possibilities for design of catalysts.
- Hollow Pd and Pt nanoparticles are very attractive for further studies.
- Initial difficulties with refractory metal alloys and metallization of CNTs are being resolved; the results are encouraging (not shown here).

Future studies will focus on:

1. Improve synthesis of Pd nanorods, nanowires, and Pd hollow NPs. (BNL, MIT, JMFC)
2. Improve metallization and catalysation of CNTs, oxides, nitrides. (JMFC, MIT, BNL)
3. Pd-Nb alloy NPs; start the work on Pd-W NPs and Pd-V. (BNL, MIT)
4. Scale-up of selected catalysts up to 20 grams. (JMFC, BNL)
5. MEA fabrication and tests.

Special Recognitions & Awards/Patents Issued

1. *Platinum monolayer electrocatalysts for oxygen reduction*, M.B. Vukmirovic, J. Zhang, K. Sasaki, F. Uribe, M. Mavrikakis, and R.R. Adzic, *Electrochim. Acta*, **52** (2007) 2257. **The most cited paper of 2007** in Electrochimica Acta.

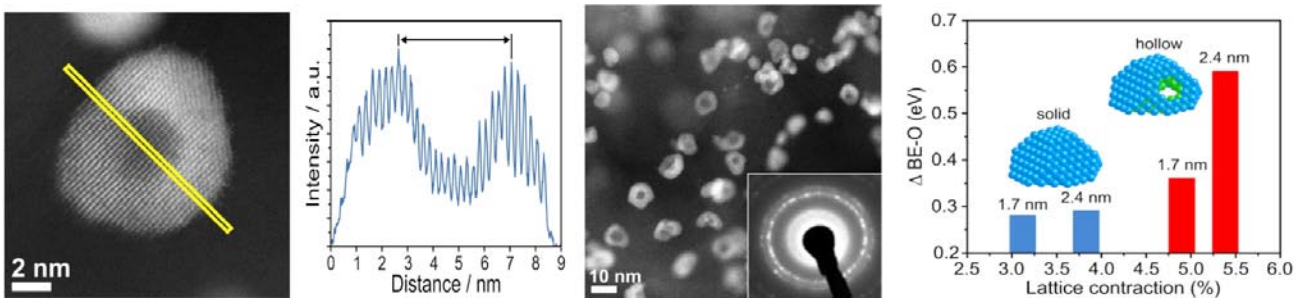

FIGURE 2. Hollow Pt nanoparticles: High resolution STEM images, line-scan intensity profile, and electron diffraction measurement of Pt hollow particles on carbon support after 100 hours stability test; DFT calculated weakening of binding energy for oxygen versus lattice contraction for solid and hollow Pt nanoparticles.

2. *Oxygen reduction on well-defined core-shell nanoparticles:Size, facet, and Pt shell thickness effects*, J.X. Wang, H. Inada, L. Wu, Y. Zhu, Y. Choi, P. Liu, W-P. Zhou, and R.R. Adzic, *J. Am. Chem. Soc.*, 131 (2009) 17298., **JACS Select 8**.

3. Three patents issued in 2010

- 7,704,919 Electrocatalysts having gold monolayers on platinum nanoparticle cores, and uses thereof
- 7,704,918 Synthesis of metal-metal oxide catalysts and electrocatalysts using a metal cation adsorption/reduction and adatom replacement by more noble ones
- 7,691,780 Platinum- and platinum alloy-coated palladium and palladium alloy particles and uses thereof

4. Three patent applications in 2010

- 20100177462 Platinum-Based Electrocatalysts Synthesized by Depositing Contiguous Adlayers on Carbon Nanostructures
- 20100099012 Electrocatalyst Synthesized by Depositing a Contiguous Metal Adlayer on Transition Metal Nanostructures
- 20100097742 Electrodes Synthesized from Carbon Nanostructures Coated with a Smooth and Conformal Metal Adlayer

FY 2010 Publications/Presentations

1. *Gram-Scale-Synthesized Pd_2Co-Supported Pt Monolayer Electrocatalysts for Oxygen Reduction Reaction*, Zhou, W.-P.; Sasaki, K.; Su, D.; Zhu, Y.; Wang, J.X.; Adzic, R.R., *J. Phys. Chem. C*, **114** (2010) 8950-8957.

2. *Recent advances in platinum monolayer electrocatalysts for oxygen reduction reaction: Scale-up synthesis, structure and activity of Pt shells on Pd cores*, K. Sasaki, J.X. Wang, H. Naohara, N. Marinkovic, K. More, H. Inada, R.R. Adzic, *Electrochimica Acta*, **55** (2010) 2645.

3. *Size-dependent enhancement of electrocatalytic performance in relatively defect-free, processed ultrathin platinum nanowires*, Koenigsmann, C.; Zhou, W.-P.; R.R. Adzic; Sutter, E.; Wong, S.S.,. *Nano. Lett.*, submitted.

4. *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, *Electrocatalysis*, submitted.

5. *Platinum Hollow Spheres as Active and Durable Nanocatalysts for Oxygen Reduction in Acid Fuel Cells*, Jia X. Wang, Chao Ma, YongMan Choi, Dong Su, Yimei Zhu, Ping Liu, Rui Si, and Radoslav R. Adzic, *J. Phys. Chem. Lett.*, submitted.