

V.A.5 Platinum Monolayer Electrocatalysts

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

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

Collaborator:
Piotr Zelenay, Los Alamos National Laboratory
Los Alamos, NM

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Overall Objectives

- Synthesizing high performance Pt monolayer (ML) electrocatalysts for the oxygen reduction reaction (ORR) consisting of a Pt ML shell on stable, inexpensive metal, alloy, metal oxide, nitride or carbide nanoparticle cores.
- Increasing activity and stability of Pt ML shells and stability of supporting cores while reducing noble metal contents.

Fiscal Year (FY) 2016 Objectives

- Exploring synthesis of new non-noble metal cores.
- Modifying core components by nitriding, alloying, doping.
- Syntheses of specific structures using reactive spray deposition technique without oxidation of core components.
- Electrodeposition of rare earths and refractory metal alloys from ionic liquids and non-aqueous solvents.
- Improving catalysts response at high current densities.

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

Technical Targets

We are focusing on simplifying the synthetic processes to obtain better catalyst activity, higher Pt utilization, lower content of platinum group metal (PGM), and simpler membrane electrode assembly (MEA) fabrication (See Table 1).

FY 2016 Accomplishments

- Developed nitrided refractory metal and non-noble metal cores for a Pt ML shell.
- Developed electrocatalysts based on cores modified by alloying with Mo.
- Developed a new class of core-shell catalysts with oxidized species segregated to edges and vertices of nanoparticles.
- Demonstrated the electrodeposition from ionic liquids and non-aqueous solvents of Y, Y alloys with Pt and Pd with high ORR activity.
- Achieved improved proton penetration into the catalyst layer by functionalizing carbon nanotubes.
- Improved gas diffusion electrodes as a method for fast screening of catalysts before MEA tests.



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 by varying their composition, size and shape makes possible further improvements of the Pt ML catalysts.

APPROACH

Our approach to improving Pt ML catalysts is based on developing new synthetic methods to obtain novel cores including:

- Nitriding non-noble metal core components for increased stability.
- Modifying cores by alloying for a better support for a Pt ML.
- A new class of core-shell catalysts having oxide segregated to edges and vertices of nanoparticles.

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

	DOE 2017 Targets	Pt _{ML} /Pd/Nb/ RDE	Pt _{ML} /Pd/Ni/N/GDL 80°C, H ₂ /Air, 300 kPa	PtAuTiOx	Pt _{ML} /AuNi _{alloy} Pt _{ML} /AuNi _{core-shell}
Pt loading mg/cm ²		0.0009	0.1		
PGM total loading, mg _{PGM} /cm ²	<0.125	0.0059 at the cathode	0.2 at the cathode		
Loss in performance @ 0.8 A/cm ² after 30,000 AST	<30 mV	No loss after 1,000 AST	7 mV after 34,000 AST	No loss after 10,000 AST	No loss 5,000 AST 25 mV
Mass activity @ 900 mV _{iR free} , A/mg _{Pt}		4.2	1.2	3	
Mass activity @ 900 mV _{iR free} , A/mg _{PGM}	>0.44	0.64	0.6	0.34 (Pt + Au)	1.52 1.18

RDE – Rotating disk electrode; AST – Accelerated stress test

- Electrodeposition from ionic liquids and non-aqueous solvents of metals inaccessible from aqueous solutions, and impractical by other methods.
- Achieve better proton penetration into the catalyst layer to increase the ORR kinetics.
- Gas diffusion electrodes improved as a method for fast screening of electrocatalysts.

RESULTS

We describe four results illustrating the new methods developed in FY 2016 for improving Pt ML catalysts for the ORR.

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

We further developed highly active and stable oxygen reduction catalysts by depositing Pt monolayers on a nitrated PdNi alloy core (Figure 1). Pd content is reduced by 50% in comparison with the Pt/Pd/C catalyst; RDE stability test with 50,000 potential cycles indicates a negligible change in activity.

MEA performance in H₂-air test shows a clear sensitivity to back pressures indicating mass transfer limitations with this catalyst. Further application of nitriding involved study of niobium nitride as a core. Commercial NbN nanoparticles had an initial size of 500 nm, which was reduced after ball milling to 50 nm. NbN has low resistance with resistivity of 150 μΩcm. Far from optimized, the Pt/NbN/C catalyst shows MA = 0.35 mA/mg_{Pt}, which is also the PGM activity and specific activity, SA = 0.49 mA/cm².

Nb and Nb Alloys as Cores

In addition to NbN as a core, we synthesized several catalysts with Nb without nitriding, but combined with other core constituents. A comparison of the activities of these

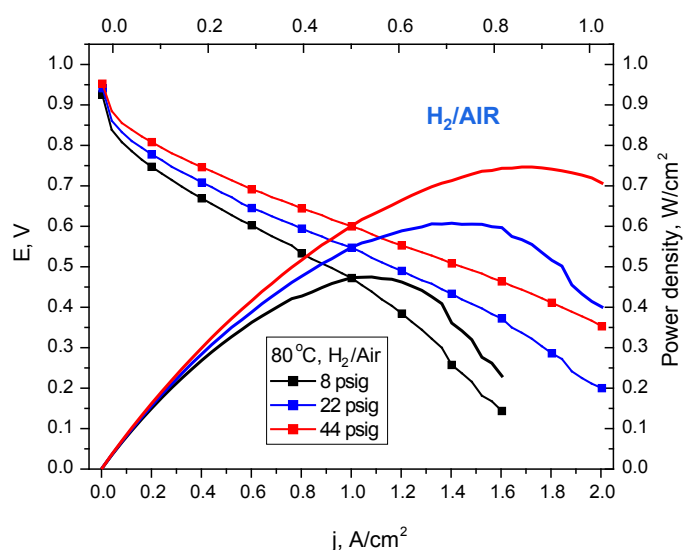


FIGURE 1. MEA polarization curve with H₂-air feed at three different back pressures in the cathode obtained: nitriding PdNi core. Anode Pt (TKK 46%), cathode PtPdNi/C, 17% Pt with loading of 0.1 mg/cm².

catalysts is given in Figure 2. Their PGM mass activities are high although the cores contained some noble metal. Optimization of Pt/Nb-containing catalysts is expected to produce further improvements.

Doping Cores with Mo

Along the same approach, modifications of cores were attempted by doping them by several metals. The effect of doping with Mo was quite pronounced. The Pt monolayer on Pd₃Mo has seven and eight times higher mass and specific activities than commercial catalysts, respectively. MEA tests showed the activity similar to the commercial Pt catalyst, which had about three times larger Pt loading than the Pt

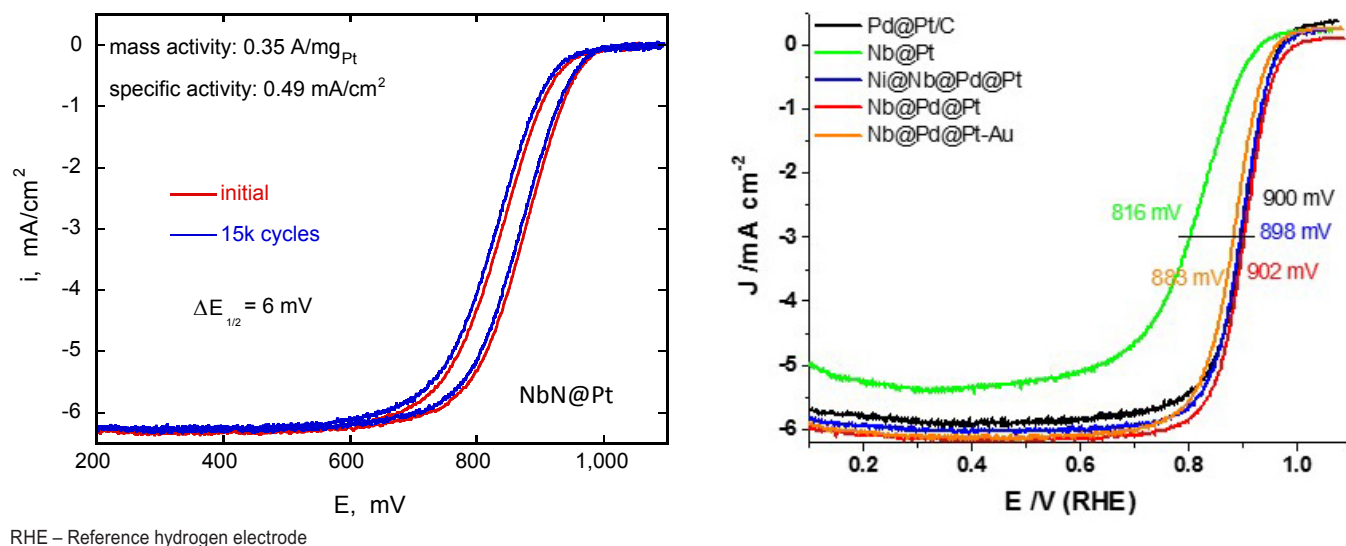


FIGURE 2. Polarization curves for a Pt nanocrystallites on NbN on a RDE (left panel). Polarization curves for several Nb-based nanoparticles on C with a Pt ML shell. Composition of the catalysts is indicated in the graph. 0.1 M HClO_4 ; 1,600 rpm; 10 mV/s.

monolayer catalyst. Further increase of PGM mass activity is possible.

Ordered Intermetallic $\text{AuPt}_4\text{Co}_5/\text{C}$

We have demonstrated that intermetallic compounds, and in particular, ordered intermetallics can be excellent core for a Pt monolayer shell and even catalysts on their own right. Here we show that a small addition of Au to PtCo alloy at appropriate temperature (800°C) can make an ordered compound. Figure 3 (left panel) shows electron energy loss spectroscopy mapping for Pt and Co, indicating a uniform distribution of both components, (middle panel) shows atomic resolution scanning transmission electron microscopy image that identifies Pt and Co atoms, and (right panel) displays

polarization curves. The catalyst has an excellent stability and high mass activity is $0.5 \text{ A}/\text{mg}_{\text{PGM}}$.

Core-shell Nanoparticle Catalysts Having Edges and Vertices Covered by Refractory Metal Oxide

We developed a new class of core-shell nanoparticle catalysts having edges and vertices covered by refractory metal oxide that preferentially segregates onto these catalyst sites. The monolayer shell is deposited on the oxide-free core atoms. The oxide on edges and vertices induces high catalyst stability and activity. This is exemplified by fabrication of Au nanoparticles doped by Ti atoms that segregate as oxide onto low-coordination sites of edges and vertices. Pt monolayer shell deposited on Au sites has the mass and specific

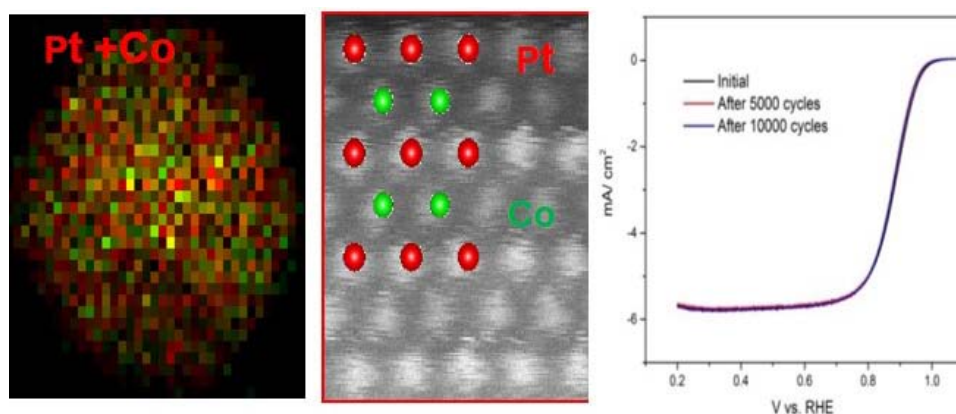


FIGURE 3. Two dimensional electron energy loss spectroscopy mapping of Pt and Co in $\text{Pt}_4\text{Co}_5\text{Au}$ (left panel); High resolution scanning transmission electron microscopy-high angle annular dark field image showing intermetallic structure of PtCo with Pt atoms (red) and Co (blue) (middle panel) and the ORR polarization curves the AuPtCo/C before and after 5,000 and 10,000 potential cycles. 0.1 M HClO_4 ; 1,600 rpm; 10 mV/s. (right panel).

activities for the ORR about 13 and five times higher than those of commercial Pt/C catalysts (Figure 4). The durability tests show no activity loss after 10,000 potential cycles from 0.6 V to 1.0 V. The superior activity and durability of the Ti-Au@Pt catalyst originate from protective titanium oxide located at the most dissolution-prone edge and vertex sites and Au supported active and stable Pt shell.

New Insights in Behavior of Core-Shell Catalysts

We demonstrated a very strong effect of the structure of bimetallic AuNi cores on the activity of Pt shell. Considerably higher activity of AuNi alloy as the core was found compared to a core-shell nanoparticle support. Electronic effects of the alloy change the O_2 and H_2O interaction with the Pt shell and facilitate increased ORR kinetics. This finding will be very useful in designing new core-shell catalysts.

Electrodeposition of Y and Y-Pt Alloys from Ionic Liquids and Non-Aqueous Solvents

High activity of Pt-Y alloys for the ORR has been predicted using density functional theory calculations and shown using sputter deposition catalyst's components [1]. Electrodeposition from ionic liquids offers a promising possibility for nanoparticle synthesis from metals such as yttrium that cannot be deposited from aqueous solutions and is not suitable for other synthetic methods. PtY was electrodeposited from ionic liquid 1-ethyl-3-methylimidazolium tetrafluoroborate (EMI), acetonitrile (AN) and dimethylformamide (DMF). The highest activity found for PtY-EMI catalyst, larger than for PtY-AN, PtY-DMF, or commercial Pt/C.

CONCLUSIONS AND FUTURE DIRECTIONS

New results show the possibility of developing high-performance, low cost Pt ML catalysts with non-noble metal cores. Nitriding core components can help achieve that. Non-precious metal NbN core is very promising.

New class of core-shell catalysts include oxidized component segregated to edges and vortexes causing stability and improved activity. Complex synthesis may be an obstacle.

Ordered intermetallic compounds can be cores with excellent properties. Y-Pt alloy deposition from ionic liquid and AN produced catalysts with high activity. This deposition opens new synthesis possibilities unachievable by conventional methods.

Improvements of the gas diffusion electrode response at the high current densities (CDs) have been obtained using functionalized carbon nanotubes and reducing the Nafion content in the catalyst ink.

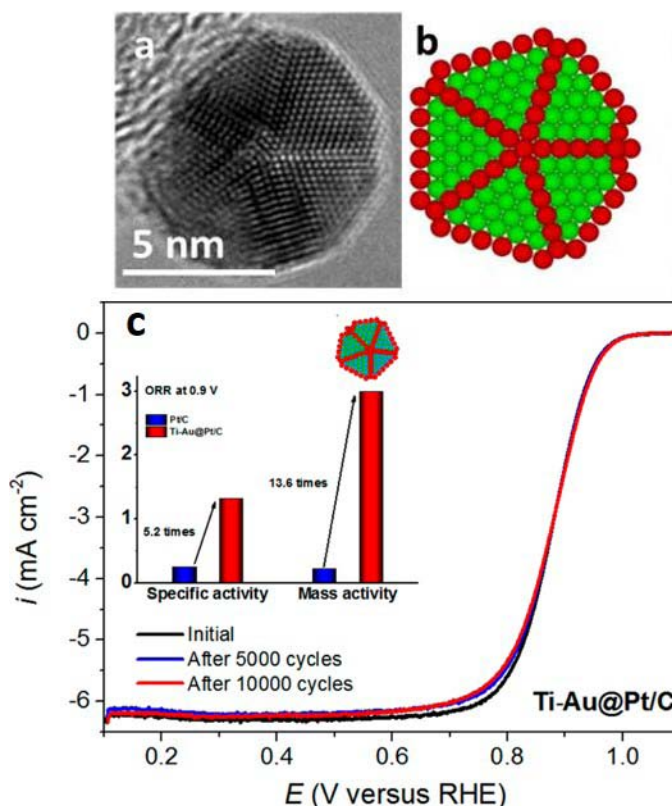


FIGURE 4. (a) High resolution transmission electron microscopy image of a Ti-Au nanoparticle viewed along five-fold axis ([110] direction in face-centered cubic lattice), showing five twins and truncated decahedral shape. (b) Schematic of a partially truncated decahedral Ti-Au multiply twinned nanoparticle with Au (green spheres) at core and Ti (red spheres) at the $\langle 110 \rangle$ edge of the facets. (c) ORR polarization curves (inset) of Ti-Au@Pt/C catalyst before and after 5,000 and 10,000 potential cycles between 0.6 V and 1.0 V. 1,600 rpm and a scan rate of 10 mV s⁻¹. Inset: Comparison of specific activities and mass activities at 0.9 V for Ti-Au@Pt/C and commercial Pt/C. Pt loadings for Ti-Au@Pt/C, Au@Pt/C and commercial Pt/C catalysts were 1.1 $\mu\text{g cm}^{-2}$, 1.3 $\mu\text{g cm}^{-2}$, and 9.7 $\mu\text{g cm}^{-2}$ respectively.

Future work will focus on:

- Nb-based non-noble metal cores synthesized using thermal routes and reactive spray deposition technique of non-noble metal alloys without oxidation of components.
- New synthesis of hollow Pd cores with a simple scale up will be completed.
- High pressure nitridation performed in a new tube reactor at temperatures up to 1,100°C in an NH_3 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.

- Electrodeposition of refractory metal alloys and earth metals using ionic liquids and/or non-aqueous solvents will be continued. This method will help obtaining the onion-structured nanoparticles with new cores of multiple metal layers. The goal is to tune Pt monolayer properties and shifts E° closer to 1.23 V. Supporting density functional theory calculations have been completed. Electrodeposited $Pt_{ML}/Pd/WNi$ will be improved for response at high CD. For these conditions, we will design nanoparticle cores to have porosity to provide a good response. Functionalized carbon nanotubes and reducing the Nafion content in the catalyst ink will be used to address that problem. Selected catalysts will be tested in MEAs and optimize for high CD response and durability.

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