V.A.5 Platinum Monolayer Electrocatalysts

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Project End Date: July 2018

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) 2017 Objectives

Further improvement of performance of Pt monolayer catalysts while reducing their platinum group metal (PGM) contents by the following studies and strategies:

- Membrane electrode assembly (MEA) testing of Pt ML catalysts with high rotating disk electrode (RDE) performance.
- Modifying non-noble metal core components by nitriding, alloying, doping.
- Modifying Pt ML shell by doping with a very small amount of Au.
- Metal aerogels as support.
- Doping carbon by NbO_2 oxide for stabilization.

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 the synthetic processes to obtain better catalyst activity, higher Pt utilization, lower content of PGM, and simpler MEA fabrication (see Table 1).

FY 2017 Accomplishments

- Developed catalysts with non-noble metal core components stabilized by nitriding.
- Developed catalysts with cores that have own core-shell structure with a refractory metal core (inner core) and thin noble metal shell (outer core).
- Nitriding at high pressure and high temperature of non-noble metal core components.
- Improved Pt ML shell by doping it by negligible amount of Au; improvements obtained also by doping core by small amount of Ir.

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

	DOE 2017 Targets	$Pt/NbO_2/C$	$Pt/Pd_4IrNi/C$	$Pd_{20}Au$ Aerogels
Pt loading mg/cm^2			C 71%, Pd 18%, Ni 3%, Ir 7%	30 ug/cm^2
PGM total loading, mg_{PGM}/cm^2	<0.125			
Loss in performance @ 0.8 A/cm^2 after 30,000 AST	<30 mV	No loss after 5,000 cycles to 1.5 V		
Mass activity @ 900 $mV_{iR\ free,}$ A/mg_{Pt}			1.59	5 A/mgPt
Mass activity @ 900 $mV_{iR\ free,}$ A/mg_{PGM}	>0.44	0.5 A/mg_{PGM} after 5,000 cycles to 1.5 V	0.155	0.75 A/mg_{PGM}

AST – accelerated stress test

- Improved stability of the Pt/C catalysts by doping C by NbO_2.
- Demonstrated that metal aerogels have properties of very promising supports.
- Improved catalyst response at high current densities.

INTRODUCTION

Further improvements of oxygen reduction electrocatalysts are necessary to overcome the remaining technological difficulties that cause slow automotive applications of fuel cells. To address these problems our research was focused on reducing Pt and PGM contents in our electrocatalysts while increasing their stability and activity. The improvements were obtained by optimizing the properties of supporting cores by varying their composition; size and shape for high activity and high stability of Pt monolayer shells have been studied.

APPROACH

Our approach to improving Pt ML catalysts is based on synthetic methods that facilitate stabilizing cores, controllable deposition of refractory metal core components from aqueous and ionic liquids solutions, doping cores and Pt monolayer shell for increased activity and stability. Cores in this approach have their own core-shell structure: a refractory metal inner core and noble metal thin outer cores.

Cores containing non-noble metals were stabilized by nitrating at high pressure, high temperature, or doping by negligible amounts of noble metals. Additional promising approaches for improving Pt monolayer catalysts include (i) doping Pt ML shells by negligible amount of Au, (ii) improving stability of the Pt/C catalysts by doping C by NbO_2, and (iii) use of metal aerogels as support to enhance stability activity and catalysts.

RESULTS

Improvement of MEA Performance of Nitride-Stabilized Pt/PdNiN/C

Nitride-stabilized Pt-M core-shell electrocatalysts (1 h, in NH_3 at 500°C) for the ORR in acid media showed high activity ($E_{1/2}$ = 0.9 V), and stability (30,000 potential cycles) in the RDE measurements. Pd content is reduced by 50% in comparison with the Pt/Pd/C catalyst. Figure 1a shows comparison of the results of the MEA tests having cathodes Pt/PdNiN/C, Pt/Pd/C, and reference Pt/C. Composition of catalysts is indicated in the graph. Hysteresis in polarization curves was observed at low voltage due to possible flooding. Decreased relative humidity (RH) from 100% to 60% caused a significant performance increase (Figure 1b). The current density at 0.3 V increased from 1 A/cm^2 to 1.4 A/cm^2. Optimization of the MEA structure, and of ionomer to catalyst ratio, is expected to further increase performance.

Preliminary results with high pressure nitriding showed formation of PtV_3N intermetallic compound which has a high activity and durability for the ORR (not shown). MA of

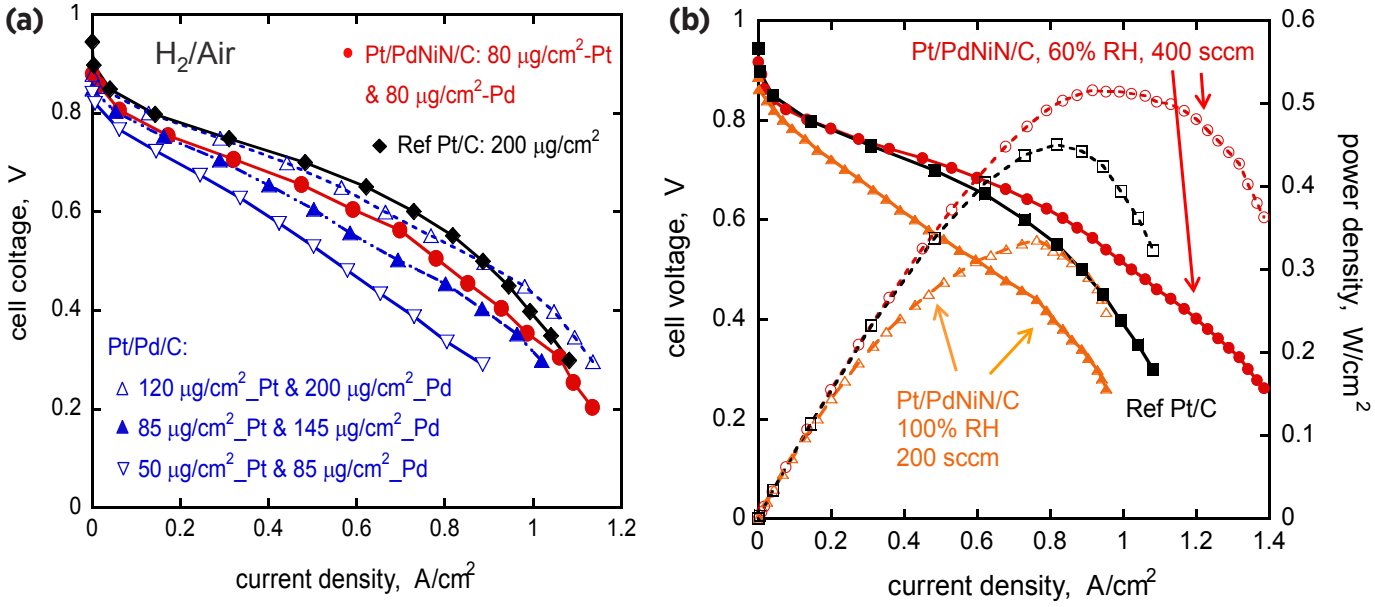


FIGURE 1. (a) MEA polarization curve with H_2–air feed at three different Pt/Pd/C loadings and nitrided Pt/Pd/NiN/C compared with the standard reference catalyst. (b) The effect of relative humidity on the MEA performance of the PtPdNiN/C catalyst. Cathode: Pt/PdNiN/C 120 $\mu g_{Pt} cm^{-2}$, 70 $\mu g_{Pd} cm^{-2}$, air, 1.0 bar air partial pressure.

PtV_3N is comparable to Pt/C; its SA is much higher, stability is significant.

Au-Doped Pt_{ML}/Pd/C and Au Outer Core on Metallic Tungsten Nanoparticle Inner Cores

Alloying or doping cores, or decorating Pt surface by Au can improve catalysts activity and stability for the ORR, as we demonstrated earlier [1]. Here we show that negligible amounts of Au ions can interact with Pd through pinholes in a Pt monolayer. Au replaces galvanically some Pd and "plugs" the holes. Au atoms in a Pt ML, by its size, can cause some contraction in the surrounding Pt atoms and increase activity and stability. A large increase of the response at high current density, 1.1–1.5 A/cm^2, is observed after placing a small amount of Au (it cannot be detected by energy dispersive X-ray spectroscopy) (Figure 2a). This simple procedure is a very efficient last step in improving core-shell catalysts.

Tungsten nanoparticles were prepared via decomposition of tungsten nitrides obtained from WCl_6 annealed in NH_3 at 600°C that decomposes at 800°C. Propylene carbonate as solvent was used to galvanically displace some W by Pd. Core-shell structure is indicated by a lack of W oxidation.

Interlayer of another metal to form a shell is necessary since the half-filled d-band has large electronic effect on adlayers. The best catalysts contained the following cores: Pd_6W_9 and Au_3Pd_2W. Pt/Pd_6W_9/C has mass activity 1.04 A/mg Pt or 0.1 A/mg PGM. Increasing activity, as a function of core composition, indicates a possibility for further improvements.

Pt on NbO_2: A Solution for ORR Performance Decay in Start-Stop Cycles to 1.5 V

The voltage transients of up to 1.5 V at the cathode accelerate the carbon degradation causing agglomeration of Pt particles and a loss of electrochemical surface area of Pt catalysts. This, and worsened transport properties of the porous catalyst layer, result in PEMFC performance decay. We developed a unique procedure to stabilize carbon support (Ketjen black) by oxide nanoparticles (NbO), which also stabilizes Pt against agglomeration. Niobium oxides are embedded into the porous surface of carbon blacks, by sonication and decomposing Nb(V) ethoxide and reducing dried Nb(V) precursor to small particles of NbO or NbO_2 or Nb_2O_5, controllable via hydrogen partial pressure, temperature, and time. Pt is deposited by galvanic reaction of NbO and $PtCl_4^{-2}$ giving Pt and NbO_2 with ethanol as solvent and additional reductant. Half-sphere Pt (bright dots) on NbOx (gray area on left) indicates that is confined in carbon. (Figure 3a). The Pt mass activity of Pt-NbO_2-C catalysts reaches 0.5 A/mg $_{Pt}$ having excellent durability against 0.6–1 V and 1–1.5 V potential cycles. (Figures 3b and 3c). The high degree dispersion and uniformity of NbO_x particles over the entire carbon surface achieved by utilizing the surface pores on carbon are unprecedented. Controlling particle size and distribution by size and density of surface pores allow a wide temperature range to be used in synthesis for fabricating small and well dispersed particles. The concept may be applied for making other metal, alloy, and oxide particles. All these unique and desirable features

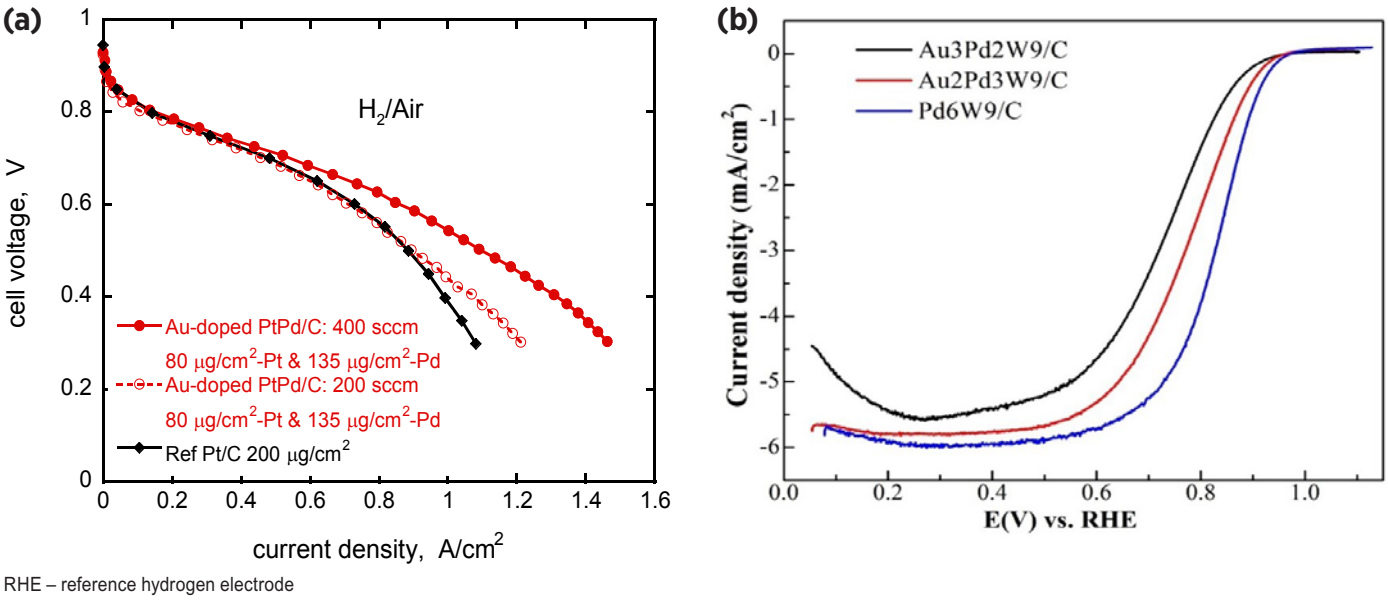
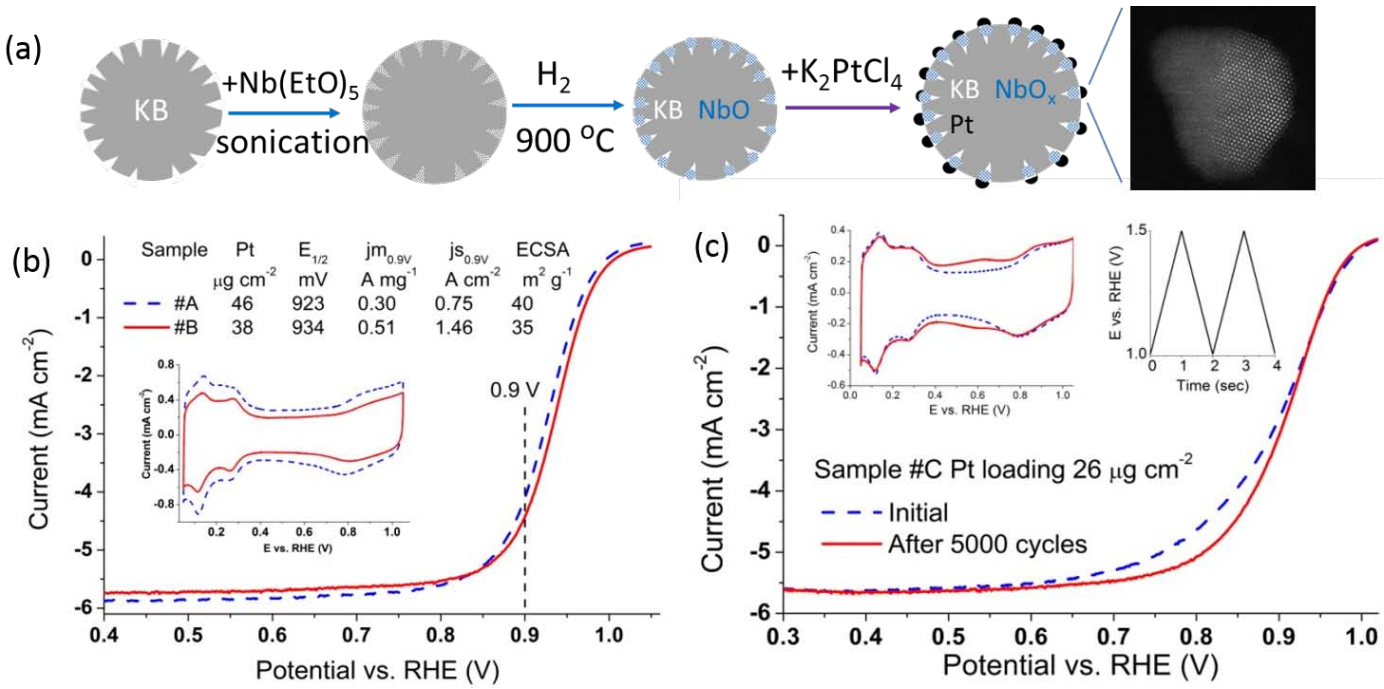


FIGURE 2. (a) MEA test of Au-doped Pt_{ML}/Pd/C. Cathode: BNL Au-doped Pt/Pd/C, air 200/400 sccm, 1.0 bar partial pressure 80 µg/cm^2-Pt, 135 µg/cm^2-Pd. The Au content is very small, difficult to measure. (b) Metallic tungsten nanoparticles as inner cores. Effect of interlayers on RDE polarization curves. Pt/Pd6W9/C Pt mass activity 1 A/mg; PGM mass activity 0.1 A/mg; 28% Pd, 72% W.



ECSA – electrochemical surface area

FIGURE 3. (a) Schematic illustration of ~4-nm pores on the surface of a ~30 nm carbon particle, filled by Nb ethoxide in ethanol, NbO-embedded carbon after thermal decomposition and reduction of Nb precursor, and semi-spherical Pt particles formed on top of NbO_x far right. Transmission electron microscopy image of Pt particle shows Pt atoms (bright dots) tightly bound with NbO_2 (gray area). The carbon surrounding NbO_2 is invisible due to its low electron density in the Z-contrast image. (b) ORR activities of two Pt-NbO_2-C samples prepared using different Pt precursors measured in O_2-saturated 0.1 M $HClO_4$ solutions. (c) Polarization curves of a Pt-NbO_2-C sample before and after 5,000 potential cycles between 1 V and 1.5 V. Voltammetry curves shown in the inserts were measured at 50 mV s^{-1}.

contributed to the high ORR activity and exceptional durability against potential cycles up to 1.5 V.

Aerogels PdAu as Cores

We demonstrate the use of metallic aerogels as cores in high activity core shell catalysts. The core-shell aerogel catalysts have several advantages: (i) rapid electron transfer, (ii) large surface area, high porosity (90%), (iii) accelerated mass transfer, (iii) no support corrosion. Core-shell aerogels amplify the enhancement factors of core-shell and aerogel structures, which integrate several catalysis enhancement factors. Here we demonstrate the synthesis of Pd_xAu-Pt core-shell aerogels comprised of an ultrathin Pt shell and a composition-tunable Pd_xAu alloyed core. Their activities for oxygen reduction exhibit a volcano-type relationship as a function of the lattice parameter of the core substrate. The maximum mass and specific activities are 5.25 A mg^{-1}_{Pt} and 2.53 mA cm^{-2}, which are 18.7 and 4.1 times higher than those of Pt/C, respectively, demonstrating the superiority of the core-shell metallic aerogels. Noble metal mass activity is 0.69 A/mg. Figure 4a shows the energy dispersive X-ray spectroscopy element maps for the $Pd_{10}Au$-Pt core-shell aerogel. Pt and noble-metal mass activities are given in Figure 4b. The proposed core-based activity descriptor provides a new possible strategy for the design of future core-shell electrocatalysts. This work highlights the great potential of pure metallic core-shell aerogels as highly efficient electrocatalysts through structural engineering.

CONCLUSIONS AND UPCOMING ACTIVITIES

New results show the possibility of developing high-performance, low cost Pt ML catalysts with non-noble metal cores. MEA tests were carried out with promising Pt ML catalysts including Pt/Pd/C, Au-doped Pt/Pd/C, aerogel Pt/PdAu, and nitride stabilized Pt/PdNiN/C. Pt/PdNiN/C has a similar performance as the control catalyst with higher Pt loading, but below expectations based on the RDE data. Decreased humidification improved its activity to better than that of the control. Au-doped Pt ML catalyst showed outstanding activity, with considerably better response in the high current density region (40%) than the control. Aerogel Pt/PdAu performed poorly in the first MEA test, possibly because a low Pt content of 30 μg/cm^2, or damaged structure in making MEA. The aerogel supports will have a strong impact on future electrocatalyst applications.

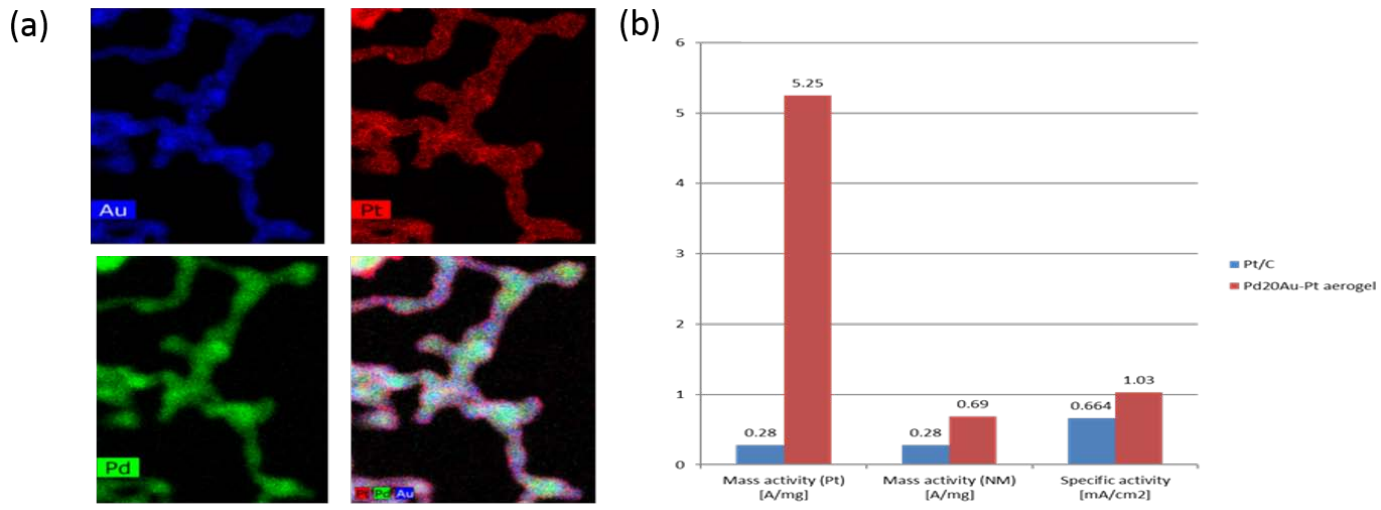


FIGURE 4. (a) Energy dispersive X-ray spectroscopy element maps for the $Pd_{10}Au$-Pt core-shell aerogel catalyst. (b) Pt mass, noble metal mass, and specific activity of $Pd_{10}Au$-Pt aerogel catalyst compared with commercial Pt/C catalyst.

Future work will focus on MEA studies of selected catalysts to optimize catalyst properties, MEA structure and composition, and to determine catalysts' stability in MEAs. These include:

- Pt/Pd/C with a Pt ML doped with small amount of Au atoms, $Pt/Pd_9Au_1/C$ catalysts, and Pt/PbW-Ni/C catalyst obtained by electrodeposition and by chemical route.
- W, WC, and WN nanoparticles of 4 nm particle size, will be used as an inner core with a Pd or PdAu thin layer outer core as a support for a Pt ML.
- High pressure nitridation (1,100°C in an NH_3 gas at 10 MPa) to generate various types of nitride nanoparticles with refractory metals to enhance the stability and activity of Pt shells.
- Further improvement of stabilizing carbon and Pt deposit to potential cycles of 1.5 V by NbO_2 in 4 nm pores.
- MEA tests of a new core-PdAu aerogel as support for a Pt ML.

SPECIAL RECOGNITIONS & AWARDS/ PATENTS ISSUED

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