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***Recent Advances in Developing Platinum Monolayer  
Electrocatalysts for the O<sub>2</sub> Reduction Reaction***

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## Recent Advances in Developing Platinum Monolayer Electrocatalysts for the O<sub>2</sub> Reduction Reaction

M. B. Vukmirovic, K. Sasaki, W-P. Zhou, M. Li, P. Liu, J.X. Wang, R. R. Adzic

For Pt, the best single-element catalyst for many reactions, the question of content and loading is exceedingly important because of its price and availability. Using platinum as a fuel-cell catalyst in automotive applications will cause an unquantifiable increase in the demand for this metal. This big obstacle for using fuel cells in electric cars must be solved by decreasing the content of Pt, which is a great challenge of electrocatalysis

Over the last several years we inaugurated a new class of electrocatalysts for the oxygen reduction reaction (ORR) based on a monolayer of Pt deposited on metal or alloy carbon-supported nanoparticles. The possibility of decreasing the Pt content in the ORR catalysts down to a monolayer level has a considerable importance because this reaction requires high loadings due to its slow kinetics. The Pt-monolayer approach has several unique features and some of them are: high Pt utilization, enhanced (or decreased) activity, enhanced stability, and direct activity correlations.

The synthesis of Pt monolayer (ML) electrocatalysts was facilitated by our new synthesis method which allowed us to deposit a monolayer of Pt on various metals, or alloy nanoparticles [1, 2] for the cathode electrocatalyst. In this synthesis approach Pt is laid down by the galvanically displacing a Cu monolayer, which was deposited at underpotentials in a monolayer-limited reaction on appropriate metal substrate, with Pt after immersing the electrode in a K<sub>2</sub>PtCl<sub>4</sub> solution.

The ORR is a complex multistep reaction involving the exchange of four electrons, whose detailed mechanism still defies formulation [3]. The overall four electron reduction of O<sub>2</sub> in acid aqueous solutions is



Irrespective of the microscopic mechanism, a four-electron process must involve the breaking of an O–O bond and the formation of O–H bonds [3]. Surfaces that strongly bind an adsorbate tend to enhance the kinetics of bond-breaking steps. On the other hand, surfaces that bind species weakly tend to facilitate the kinetics of bond-making steps.

In order to increase the activity of Pt monolayer for ORR, we synthesized three types of Pt monolayer electrocatalysts for the ORR: (i) Pt on carbon-supported Pd nanoparticles [2], (ii) mixed-metal Pt monolayers on Pd nanoparticles [4], and (iii) Pt monolayers on noble/nonnoble core–shell nanoparticles [1].

A monolayer of Pt on Pd substrate had higher activity than the bulk Pt surface [2]. This increased activity is partly due to the decreased Pt–OH coverage in comparison with bulk Pt (Pt–OH, derived from H<sub>2</sub>O oxidation on Pt, is a species blocking the ORR). In addition, the small compression of a Pt deposit on a Pd substrate, causes a downshift of the d-band center, thereby leading to the decreased reactivity of Pt (i.e. decline in the interaction strength between Pt and ORR surface intermediates). Both effects enhance the ORR rates.

A further enhancement in the ORR activity is expected to be achieved by replacing some of the Pt atoms with metal atoms that oxidize at lower potentials than Pt does. This idea was tested by depositing mixed Pt–M monolayers on Pd(111) and carbon-supported Pd nanoparticles [4]. These catalysts were prepared with Au, Pd, Rh, Ir, Os, or Re as the alternative M component in the  $(M_{0.2}Pt_{0.8})/Pd/C$ . The Pt mass activity of the Re–Pt catalyst is 20 times greater than that of the Pt/C catalyst (Fig. 1). On the Re–Pt monolayer, the Pt–OH coverage is decreased by the repulsion between Re–O and Pt–OH, as Re is covered with O rather than OH [4]. Evidence of the influence of the surface M metal atom on Pt–OH coverage was obtained using in situ XANES and voltammetry techniques. Both techniques show that oxidation of Pt is shifted towards more positive potentials, thus strongly supports our hypothesis on the repulsion between OH on M and OH on Pt.

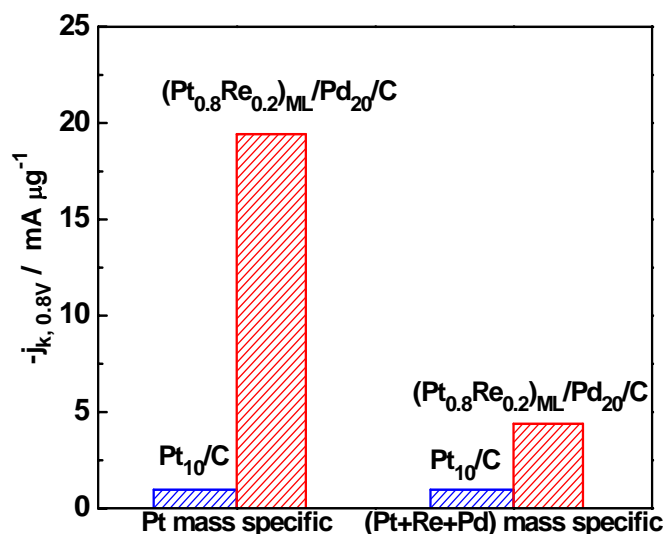


Figure 1. The Pt and total noble metal mass-specific activities of  $(Pt_{80}Re_{20})_{ML}/Pd/C$  and Pt/C commercial electrocatalyst for the ORR at 0.8 V (vs. RHE) in 0.1 M  $HClO_4$ .

The third type of the ORR Pt monolayer electrocatalysts that we synthesized comprised of Pt monolayers deposited on the surfaces of carbon-supported nanoparticles with non-noble metal core and noble metal shell [1]. The activity of a Pt monolayer can be enhanced through electronic and/or geometric effects by properly selecting the noble-metal shell. The choice of the metals constituting the shell and the core was based upon considering the segregation properties of the two metals, and their electronic—and strain-inducing effects on a Pt overlayer. The Pt-mass activity of  $Pt_{ML}/Au/Ni$  electrocatalysts was ca. 20 times higher than that of commercial Pt/C samples, Fig. 2. The very high activity of Pt monolayer on Au/Ni appear to be the consequence of a mismatch in the lattice constants between the Pt monolayer and substrate thus changing the d-band properties of the Pt monolayer itself, caused by its interaction with them, and the lesser Pt–OH coverage.

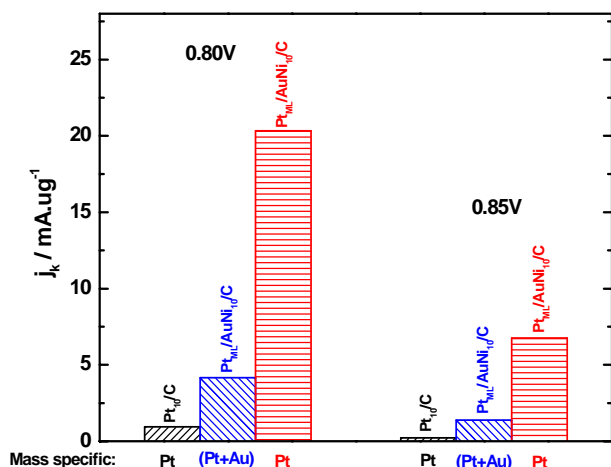


Figure 2. The Pt and total noble metal mass-specific activities of Pt<sub>ML</sub>/AuNi/C and Pt/C commercial electrocatalyst for the ORR at 0.8 V and 0.85 V (vs. RHE) in 0.1 M HClO<sub>4</sub>.

These catalysts showed good durability demonstrated by long-term fuel cell tests. Figure 3 illustrates the trace of the cell voltage with time at a constant current of 0.417 A/cm<sup>2</sup> at 80 °C. The cathode catalyst was Pt/Pd/C, with Pt loading of 99 μg/cm<sup>2</sup>, and Pd loading of 270 μg/cm<sup>2</sup> and the anode catalyst was Pt/Ru/C, previously developed by our group [5, 6], with Pt loading of 50 μg/cm<sup>2</sup>. By keeping the cell current density at 0.417 A/cm<sup>2</sup>, the cell completed 450 hr (terminated due to membrane failure) with an average voltage of 0.602 V, and catalyst performance of 0.47 gPt/kW achieved. This is a very good performance compared with 0.30 gPt/kW of the DOE target for 2010.

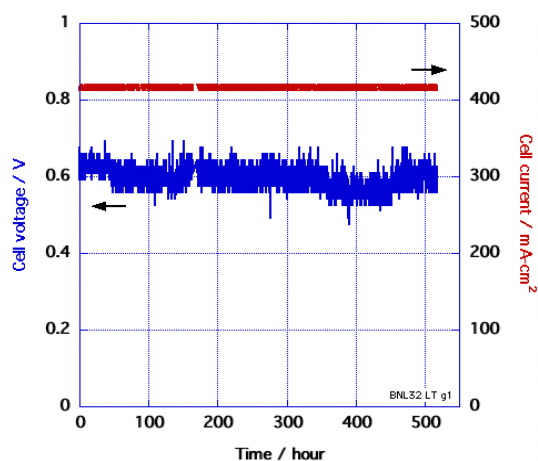


Figure 3. The long-term stability test of the fuel cell consisting of Pt/Pd cathode and Pt/Ru/C anode electrocatalysts at 80 °C.

One of the major problems with proton exchange membrane fuel cells is the loss of Pt surface area caused by Pt dissolution under electrode potential-cycling in the stop-and-go driving conditions. We demonstrated that platinum can be stabilized under potential cycling regimes, by modifying Pt nanoparticles with Au clusters [7]. The stabilizing effect of Au clusters on Pt was determined in an accelerated stability test by cycling the potential between 0.6 and 1.1 V (vs. RHE) for 30,000 cycles. Voltammetry showed that there was only 5 mV degradation in the half-wave potential for Au/Pt/C and no recordable loss of Pt surface area after such cycling.

The results obtained so far are very encouraging. They may significantly impact science of electrocatalysis and fuel-cell technology, as they have demonstrated an exceptionally effective way of using Pt that can resolve problems of other approaches, including electrocatalysts' inadequate activity and high Pt content.

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