Pt submonolayer electrocatalysts for H_2 oxidation and O_2 reduction

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Increasing the activity of electrocatalysts and reducing the noble metal loading, in addition to achieving the long term stability, remain the goals of the ongoing research in the fuel cell electrocatalysis. A new approach in this research involves a nanoengineering of electrocatalysts by depositing submonolayer amounts of Pt in the form of two-dimensional islands on the surface of metal nanoparticles[1,2]. Two new methods of catalysts preparation have been used, *viz.*, spontaneous deposition of Pt on Ru[1], and a deposition of Pt on Au or Pd by redox displacement of a Cu monolayer[2]. Spontaneous deposition of Pt on Ru is a new phenomenon of noble metal on noble metal (NMNM) deposition that we have recently reported[1] and used for the preparation of Pt/Ru bimetallic electrocatalysts[3,4] A redox replacement of UPD adlayers by more noble metals has been shown to produce uniform monolayer to multilayer deposits[2]. Pt can be deposited on Ru surfaces that are reduced in H_2 or prepared in UHV, followed by immersion in H_2PtCl_6 or K_2PtCl_4 solutions. Pt deposition on Au and Pd was carried out by immersion of these surfaces covered by a Cu UPD monolayer in K_2PtCl_4 solutions.

The basic idea of this approach is to take advantage of the possibility of having all the Pt atoms at the surface of Ru nanoparticles so that they can be actively involved in hydrogen oxidation and adjusting Pt coverage relative to the Ru surface to achieve high CO tolerance. In addition, some favorable electronic and bifunctional effects are expected for small-sized Pt clusters spread on a Ru nanoparticle surface compared to PtRu bulk alloys. New results for H_2/CO oxidation on $PtRu_{20}$, Pt/Ru(0001) and Pt/Ru(10-10), and the first results for O_2 reduction on Pt, or a mixed Pt and Pd submonolayer on Au(111), Pd(111) and Au and Pd nanoparticles, will be reported.

The mass-specific activity for H_2 oxidation of the $PtRu_{20}$ electrocatalyst was found to be 3-4 times higher than that of commercial PtRu alloy catalysts. Its CO tolerance appears also higher under the condition of the rotating disk experiments despite its three times smaller Pt loading (Fig. 1). Fuel cell tests at 80°C have shown practically the same activity of the $PtRu_{20}$ electrocatalyst for H_2 oxidation as that of the commercial catalyst containing a 10 times larger Pt loading. EXAFS measurements showed that Pt is coordinated with 4 Ru atoms in the $PtRu_{20}$ electrocatalyst, and a bond length of 2.68Å between Pt and Ru as in PtRu alloys has been determined.

Gold is a poor electrocatalyst for O_2 reduction and the rational behind its selection as a support for Pt is its stability and a possibility to affect the electronic properties of Pt in the right direction. An enhancement of the activity of Pt overlayer on Au(111) has been reported for CO adsorption in gas phase[5]. A $Pt_{0.75}Pd_{0.25}$ monolayer on Au/C, prepared by displacement of a Cu monolayer, is a very active electrocatalyst for O_2 reduction, which equals the activity of the Pt/C catalyst with a 2.5 larger Pt loading (Fig. 2). The activity of a Pt monolayer on Au(111) is also considerable. A single Tafel slope for the $Pt_{0.75}Pd_{0.25}$/Au/C catalyst, and a -120mV for Au(111), may indicate a smaller adsorption of OH on Pt on Au in comparison with bulk or nano Pt. Avoiding PtOH formation, which is a major inhibiting species in the O_2 reduction on Pt, may lead to a considerable improvement of these electrocatalysts. Pt monolayers on Pd(111) and on Pd nanoparticles cause a considerable increase of O_2 reduction kinetics in comparison with those on the substrate surfaces.

Further work utilizing the Pt monolayer on metal nanoparticles approach seems quite promising for both reduction of noble metal loading and designing electrocatalysts with improved properties.

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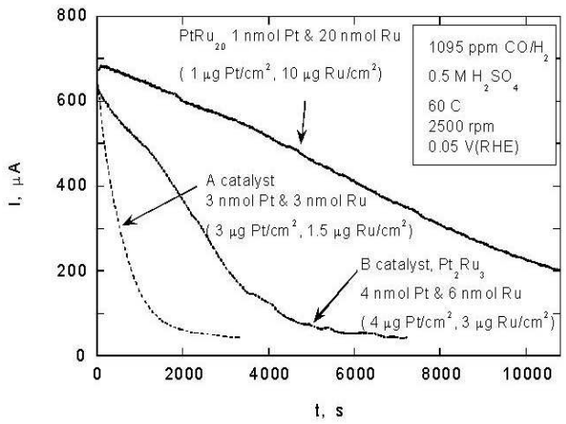

Fig. 1 CO tolerance of the $PtRu_{20}$ electrocatalyst compared with those of two commercial samples. Other data are given in the graph.

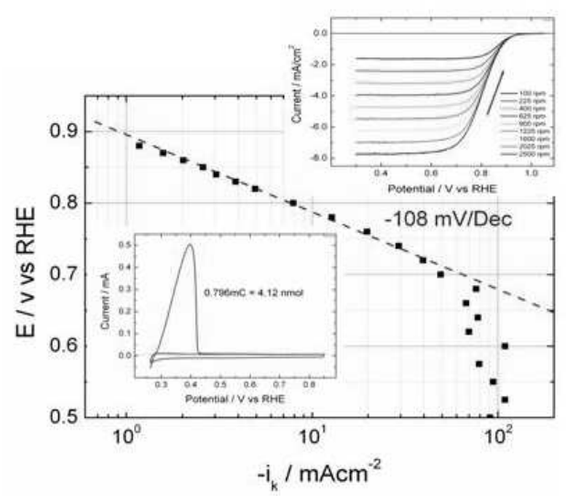

Fig. 2 Polarization curves, Tafel plot and Cu stripping from Au for O_2 reduction on $Pt_{0.75}$ $Pd_{0.25}$/Au in 0.1M $HClO_4$. Sweep rate 10 mV/s; temperature 25°C.