Pt submonolayer electrocatalysts for H₂ oxidation and O₂ 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. Two new methods of catalysts preparation have been used, viz., spontaneous deposition of Pt on Ru¹, and a deposition of Pt on Au or Pd by redox displacement of a Cu monolayer². Spontaneous deposition of Pt on Ru is a new phenomenon of noble metal on noble metal (NMNM) deposition that we have recently reported¹ and used for the preparation of Pt/Ru bimetallic electrocatalysts³. A redox replacement of UPD adlayers by more noble metals has been shown to produce uniform monolayer to multilayer deposits². Pt can be deposited on Ru surfaces that are reduced in H₂ or prepared in UHV, followed by immersion in H₂PtCl₆ or K₂PtCl₄ solutions. Pt deposition on Au and Pd was carried out by immersion of these surfaces covered by a Cu UPD monolayer in K₂PtCl₄ 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 properties of Pt on Ru is a new phenomenon of noble metal on noble metal (NMNM) deposition that we have recently reported¹ and used for the preparation of Pt/Ru bimetallic electrocatalysts³. A redox replacement of UPD adlayers by more noble metals has been shown to produce uniform monolayer to multilayer deposits². Pt can be deposited on Ru surfaces that are reduced in H₂ or prepared in UHV, followed by immersion in H₂PtCl₆ or K₂PtCl₄ solutions. Pt deposition on Au and Pd was carried out by immersion of these surfaces covered by a Cu UPD monolayer in K₂PtCl₄ solutions. The new results for H₂/CO oxidation on PtRu₃₀, PtRu(0001) and Pt/Ru(10-10), and the first results for O₂ 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 H₂ oxidation of the PtRu₃₀ 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. Pt monolayers on Pd(111) and Au(111) and Au and Pd nanoparticles, will be reported.

Fig. 1 CO tolerance of the PtRu₃₀ electrocatalyst compared with those of two commercial samples. Other data are given in the graph.

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.