

PLATINUM MONOLAYER ELECTROCATALYSTS FOR OXYGEN REDUCTION

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Oxygen reduction kinetics is presently the major problem of electrocatalysis because the slow O_2 reduction rates, even on Pt, are the source of a major decline in the fuel cell's efficiency. Any improvement critically depends on accelerating the kinetics of this reaction. The high Pt loading in fuel-cell cathodes is another drawback of existing technology. Placing atoms of a catalytically active metal on nanoparticles of suitable metal substrate facilitates its full utilization and an ultimate reduction of its loading. Most such atoms have low coordination that can maximize their activity. This is the basis of our *monolayer catalyst* concept that produced $PtRu_{20}$, a real electrocatalyst for H_2/CO oxidation (1). This concept was applied to design novel electrocatalysts for O_2 reduction that may alleviate some problems of existing fuel cell technology.

The kinetics of O_2 reduction was determined by rotating disk-ring method on a Pt monolayers on Au(111), Pd(111), Rh(111), Ir(111) and Ru(0001) surfaces and on Au and Pd nanoparticles. A new method of metal deposition involving a galvanic displacement of non-noble metal monolayer deposited at underpotential by a more noble metal monolayer, for example Cu on Pd displaced by Pt, was used to deposit Pt monolayers. STM and XANES were used to characterize Pt monolayers on single crystal and nanoparticles, respectively. The plot of the Pt monolayer catalytic activity vs. the d -band partial filling of the substrate has a maximum for the Pt/Pd(111) couple (Fig. 1) (2). This may represent a volcano plot if the data for Pt/Au are not affected by very strong surface anti-segregation. It can cause some Pt atoms to diffuse into the Au substrate, which would decrease the activity of that surface. Alternatively, the bonding of O_2 to this Pt monolayer may be too strong, which may be caused by its increased activity caused by a large expansion of Pt lattice. That would also cause lowering of the activity for O_2 reduction. This plot, however, indicates that the metals with low d -band filling may not be good support for Pt. The kinetics of O_2 reduction is significantly enhanced at Pt monolayers on Pd(111) and Pd nanoparticle surfaces in comparison with the reaction on Pt(111) and Pt nanoparticles, respectively (Fig.2). The observed increase in the catalytic activity of Pt monolayer surfaces compared with Pt bulk and nanoparticle electrodes appears to be caused partly by decreased formation of PtOH. A delayed oxidation of a Pt monolayer on Pd is indicated by voltammetry and XANES data. For Pt monolayer on carbon-supported Pd nanoparticles, the Pt mass-specific activity is 5-8 times higher than that of the Pt nanoparticle electrocatalyst. The total noble metal (Pt + Pd) mass-specific activity shows a twofold increase.

Further analysis of these results and those obtained using DFT methods will be presented.

References

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2. J. Zhang, Y. Mo, M.B. Vukmirovic, R. Klie, K. Sasaki, R. R. Adzic, *J. Phys. Chem. B*, in press.

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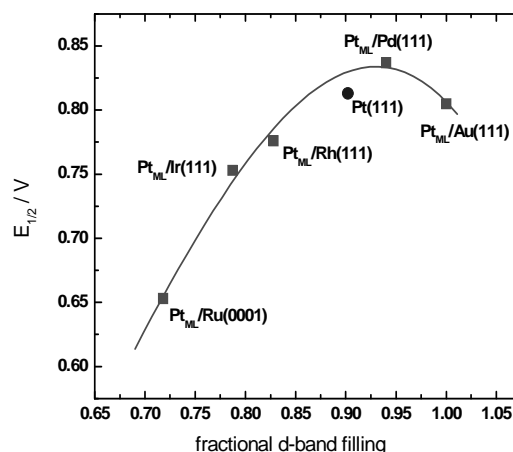


Fig. 1 $E_{1/2}$ for O_2 reduction on Pt monolayers as a function of the d -band filling of the substrates.

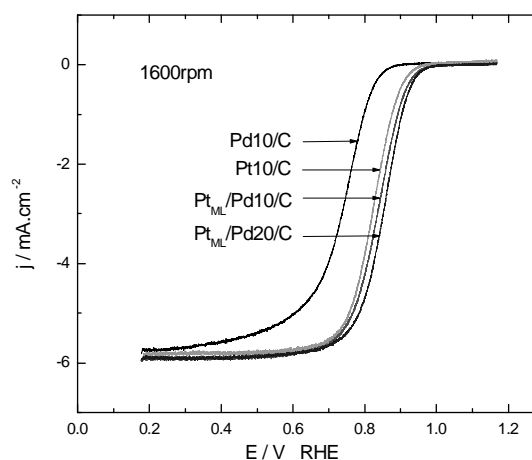


Fig. 2 A comparison of the activity of a Pt monolayer on Pd(10%) and Pd(20%) on carbon with that of Pt(10%) and Pd(10%) on carbon in 0.1 M $HClO_4$ at 25°C; sweep rate 20 mV/s.