

Oxidation of CO Monolayer on Nanosized Pt Particles Supported on Glassy Carbon

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Nanometer sized supported metal particles are of great interest as catalysts for various electrochemical reactions. The present paper continues efforts pursued in our group to establish a link between particle size, structure and reaction rates and mechanisms (see also [1,2,3]). In this work the properties of Pt nanoparticles are tested in CO monolayer oxidation, an electrode reaction, which is of considerable importance in relation to low temperature fuel cells.

One of the serious problems in studying electrochemical properties of metal nanoparticles is distribution in their size and structure. Thus, special effort has been drawn to obtain "ideal" model electrode nanoparticles, which (i) are monodispersed in size and structure, (ii) stable towards the potential variation, (iii) do not contain ligands strongly adsorbed on their surface, and (iv) are attached to a non-porous support (to avoid mass-transfer limitations).

Glassy carbon (GC) activated via mild anodic oxidation has proved to be a suitable support, meeting the above requirements. Pt/GC electrodes were obtained via deposition of Pt from  $H_2PtCl_4$  solutions with following reduction in a hydrogen flow. This allowed preparing very good model electrodes with nearly monodispersed Pt nanoparticles distributed uniformly over the GC surface, stable vs. potential cycling (figure 1).

CO oxidation appeared to be extremely sensitive to the Pt particle size. It has been found that CO stripping peak at 1.3 nm Pt nanoparticles on GC is extremely wide and shifted to positive potentials in comparison with that at Pt foil. Tailing size distribution towards large values results in a negative shift of the onset of CO stripping. When Pt particles coalesce to form large aggregates, CO stripping shows up as a narrow peak at the potential range of Pt foil oxidation. We assume that a considerable increase of the overvoltage of CO monolayer oxidation is due to the strengthening of the oxygen bonding to Pt nanoparticles. Indeed, oxygen desorption peak for Pt nanoparticles is considerably wider and shifted towards negative potentials.

The kinetics of CO monolayer oxidation at Pt nanoparticle electrodes has been studied via stepping the electrode potential from the potential of CO adsorption (0.53 V *rhe*) to more positive values where CO monolayer is oxidized. Remarkable differences have been observed between the current transients at smooth and nanosized Pt electrodes (figure 2) and will be discussed in terms of the particle size effect on the reaction mechanism.

Acknowledgements

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References:

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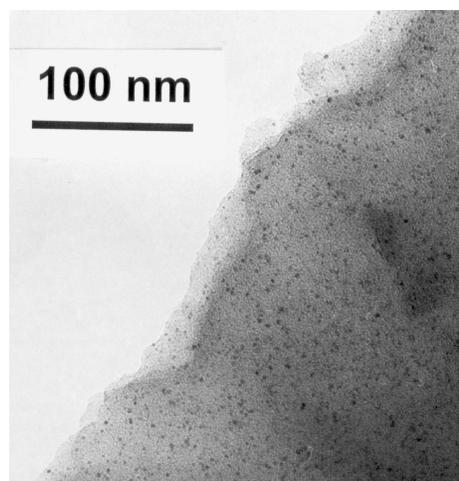


Figure 1. A transmission electron micrograph of Pt nanoparticles supported on GC anodically activated at 0.77 V.  $3.8 \mu gPt/cm^2$ ,  $\bar{d}_s = 1.5 \text{ nm}$ .

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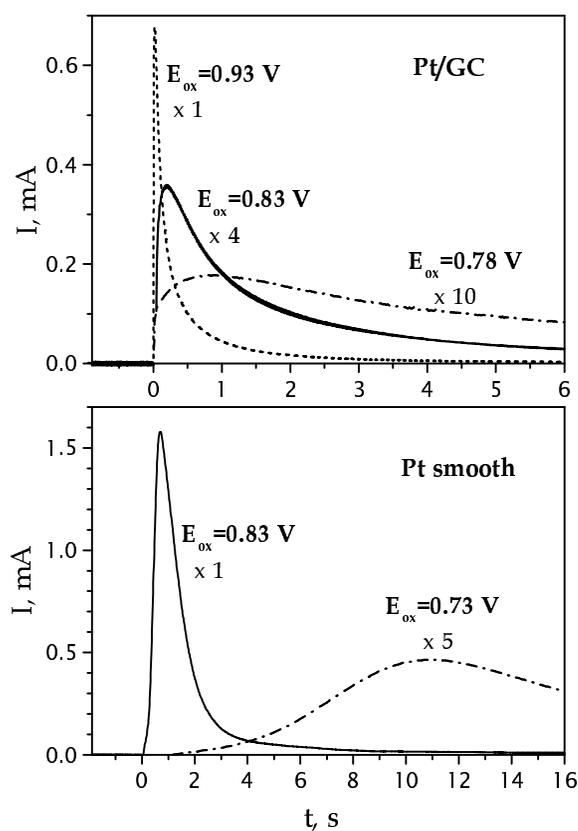


Figure 2. CO monolayer oxidation transients for Pt nanoparticles supported on GC (top) and smooth Pt (bottom) at  $20.0 \pm 0.05^\circ C$  in  $H_2SO_4$  0.1 M at 0.53 V *rhe* admission potential and different oxidation potentials  $E_{ox}$ . The transients were corrected to the charging current by subtracting the transients in supporting electrolyte.