

Effect of Surface Species on the Rate of Hydrogen Sorption into Nanostructured Palladium

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Mesoporous metals with regular nanoarchitectures can be prepared using chemical or electrochemical reduction of a metal salt dissolved in the aqueous domains of a lyotropic liquid crystalline phase[1]. In this approach the metal is formed from the lyotropic liquid crystalline phase of a non-ionic surfactant (typically between 30 and 60 wt%) and an aqueous solution of the appropriate metal salt. The resulting H₁-e metals are “casts” of the particular lyotropic phase used so that it is possible to produce mesoporous metals with different pore topologies and with different pore and wall thicknesses depending on the choice of surfactant and template solution composition[1]. H₁-e metal films have very high surface area (in excess of 10⁶ cm²/cm³) and were found to be useful as catalysts in chemical sensors[2], batteries[3] etc. Following the original work on the electrochemical deposition of mesoporous platinum films[1], this approach has been extended in our studies to the deposition of rhodium[4, 5] and palladium[6].

The electrochemistry of Pd differs significantly from that of Pt because Pd is able to absorb large quantities of hydrogen forming Pd α - β hydride phases. In previous studies[6] we were therefore particularly interested in the effects of the nanostructure of Pd on this process. In Pd films deposited from the H₁ hexagonal lyotropic liquid crystalline phase of C₁₆EO₈ or Brij56[®] the Pd walls between the pores are only a few nanometres thick. Consequently the diffusion of hydrogen atoms into Pd bulk is not the rate-limiting step. Studies of the hydrogen region of the resulting H₁-e Pd films in 1 M sulphuric acid reveal well resolved peaks associated to the hydrogen adsorption and absorption process which can be readily distinguished due to the thin walls of the nanostructure and the high surface area. Cyclic voltammetric measurements of H₁-e Pd films indicate that the absorption process takes place without passing through the adsorbed state so that hydrogen diffuses directly into Pd bulk. This process speeds up when the formation of adsorbed hydrogen is suppressed by the coverage of crystal violet or Pt. The permeation of hydrogen into the Pd metal lattice then occurs with fast kinetics. We suggest that strongly adsorbed hydrogen on the Pd surface acts as a blocking layer for the absorption of hydrogen into the Pd lattice. To demonstrate this behaviour we show in figure 1 a set of cyclic voltammograms of H₁-e Pd without a) and in the presence of 0.5 mM b) and 1 mM c) crystal violet, and we note from the results obtained in the voltammograms from a) to c) significantly enhanced kinetics of the hydrogen absorption process whilst the rate of the hydrogen evolution is unchanged[7].

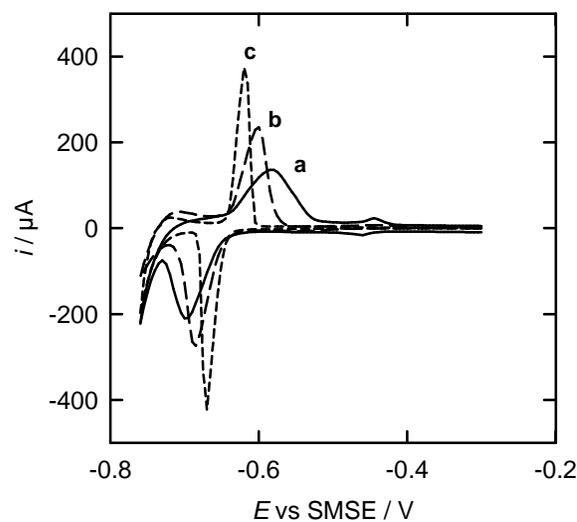


Figure 1

Set of cyclic voltammograms of H₁-e Pd (200nm thick, deposition charge 3.5 mC, deposited from the Brij[®]56 plating bath) deposited on a gold disc electrode (area 0.0079 cm²) recorded at 10 mV/s in 1 M H₂SO₄ a) without crystal violet, b) in the presence of 0.5 mM, and c) 1 mM crystal violet.

References

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