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Effect of the electrolyte composition on the electroreduction of palladium oxide films

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Abstract

The voltammetric electroreduction of Pd oxide layers grown at 2.00 V (RHE) was studied in H₂SO₄ and HClO₄ solutions containing different concentrations of LiClO₄, Na₂SO₄ and KHSO₄. The voltammetric electroreduction profiles show two main regions; the first is in the range 1.2–1.6 V and is related to the electroreduction of a fast redox system; the second region extends through the range 1.1–0.40 V, where the electroreduction of the thick oxide matrix takes place. This latter process is strongly affected by the solution composition, including the pH, in a manner contrasting to the effect on Pd oxide growth. The thick oxide layer electroreduction charge increases as the solution pH is decreased. These results are discussed in terms of specific interaction between sulphate ions and the oxide layer, so that the electroreduction process is favoured owing to the likely formation of sulphate-containing complex species.

INTRODUCTION

The growth of noble metal hydrous oxide layers produced by applying periodic potential cycles to metal electrodes immersed in aqueous solutions is relevant for the preparation of metal oxide electrodes which are promising in organic electro-oxidation reactions [1] and as starting materials for the preparation of rough metal electrodes of electrocatalytic interest [2–5].

The formation of Pt, Au and Pd oxide layers by applying fast periodic potential routines follows, in principle, a common reaction pathway [3,5]. The electrochemical behaviour of these oxide layers depends on the solution pH [6] but the dependence on the global composition of the electrolyte solution is far from

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proven. The composition of the Pd hydrous oxide anodic layers, as derived from X-ray photoelectron spectroscopy (XPS) data, would involve an oxide, such as PdO₃ [7]. Otherwise, from electrochemical measurements at different pH values, the formation of complex-ion-like species of the type [Pd(OH)₆]²⁻ has been postulated [5].

The present paper examines the effect of the solution composition on the growth of relatively thick Pd hydrous oxide layers and their electroreduction in acid solutions. Working acid solutions containing either ClO₄⁻ as a weakly adsorbable anion or SO₄²⁻/HSO₄⁻ as strongly adsorbable anions, covering a wide solution composition range, were employed.

EXPERIMENTAL

A three-electrode conical Pyrex glass cell was used. The working electrode (WE) consisted of a Pd wire (J. Matthey Chem. Co., Specpure) with a geometric area of about 0.14 cm². Prior to the electrochemical experiment, the WE was electropolished following the procedure already described in the literature [8], then rinsed thoroughly with Milli-Q water, washed with the electrolyte solution and finally placed into the cell filled with the air-free aqueous electrolyte solution. The WE potential was measured against a reversible hydrogen electrode in the same solution. The following aqueous solutions were used: 1 M H₂SO₄, 1 M HClO₄, 0.01 M H₂SO₄ + 1 M LiClO₄, 0.01 M H₂SO₄ + 1 M KHSO₄, 0.01 M HClO₄ + 1 M LiClO₄ and *x* M HClO₄ + *y* M Na₂SO₄ (0.01 ≤ *x* ≤ 3.7; 0 ≤ *y* ≤ 1). The solutions were prepared from Merck (p.a.) chemicals and Milli-Q water.

The potential routines applied to the WE were adjusted to minimize the interference of both oxygen evolution and hydrogen absorption into the Pd. Basically, each experiment consisted of the following steps: (i) the WE potential was stepped from 0.50 V to $E_{\tau} = 2.00$ V and held at E_{τ} for $\tau = 300$ s to produce a fixed amount of Pd oxide on the electrode; (ii) subsequently, the Pd oxide layer was electroreduced by sweeping the potential from E_{τ} to $E_{s,c}$, i.e. the cathodic switching potential (0.25 ≤ $E_{s,c}$ ≤ 0.30 V) at 5 mV s⁻¹. Runs were carried out under purified N₂ at 25°C.

RESULTS

The electroreduction voltammograms of the Pd oxide layers formed during the 300 s at $E_{\tau} = 2.00$ V on Pd, in a solution containing either 0.01 M H₂SO₄ or 0.01 M HClO₄, depend on the solution composition (Fig. 1). The voltammogram recorded in solutions containing ClO₄⁻ ions as the main constituent shows a first electroreduction potential region located between 0.8 and 1.6 V, comprising a broad peak (Ic) which increases with the ClO₄⁻ ion concentration, the height/width ratio of peak Ic being much smaller than unity. A second electroreduction potential region, involving two sharp peaks (IVc and Vc) appears from 0.8 V downwards. Peak IVc has been assigned to the electroreduction of the inner Pd

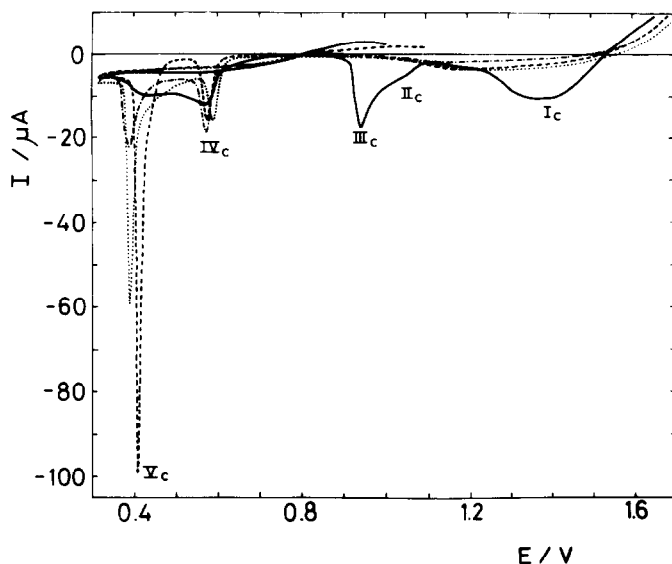


Fig. 1. Voltammetric electroreduction profiles of Pd oxide layers anodically formed during 300 s at $E_{\tau} = 2.00$ V in different aqueous electrolytes: —, 0.01 M $\text{H}_2\text{SO}_4 + 1$ M KHSO_4 ; $\cdots\cdots$, 0.01 M $\text{H}_2\text{SO}_4 + 1$ M LiClO_4 ; ---, 0.01 M $\text{HClO}_4 + 1$ M LiClO_4 ; $\cdot\cdot\cdot\cdot$, 0.01 M HClO_4 . $v = 5$ mV s^{-1} ; 25°C .

thin oxide layer [5,9], whereas peak Vc apparently involves the electroreduction of the outer thick hydrous oxide layer formed at E_{τ} . The height of peak Vc increases and shifts slightly to more positive potentials as the ClO_4^- ion concentration is increased.

A different behaviour is found in 0.01 M $\text{H}_2\text{SO}_4 + 1$ M KHSO_4 solution (Fig. 1, full curve). In this case, peak Ic becomes sharper and is shifted positively as compared with peak Ic obtained in ClO_4^- -ion-containing solutions. At the same time, peak IIIc and hump IIc appear at about 0.95 V and 1.05 V respectively. To establish the origin of peak IIIc, a set of experiments was carried out in 1 M $\text{HClO}_4 + x$ M Na_2SO_4 ($0 \leq x \leq 1$) (Fig. 2). Under these circumstances, in contrast to peak Ic, as x is increased, peak IIIc moves positively.

The effect of the ionic strength on both the Pd oxide layer formation and electroreduction was considered by performing comparative runs at constant ionic strength. For this purpose, the Pd electrode was anodized and later electroreduced in 1 M $\text{HClO}_4 + 0.5$ M Na_2SO_4 and 1 M $\text{HClO}_4 + 1.5$ M NaClO_4 (Fig. 3). The resulting voltammograms reveal that the changes observed in Fig. 2 can hardly be assigned to a change in the ionic strength.

The effect of the solution pH on the Pd oxide electroreduction was examined in 0.5 M $\text{Na}_2\text{SO}_4 + x$ M HClO_4 ($0.5 \leq x \leq 3.7$) (Fig. 4). As x is increased, peak IIIc moves positively, whereas peak Ic becomes sharper and, at the same time, shoulder IIc is progressively enhanced. These changes resemble those found in the range 0.1–7 M H_2SO_4 [10]. It should be noted that peak IIIc is not seen at any acid

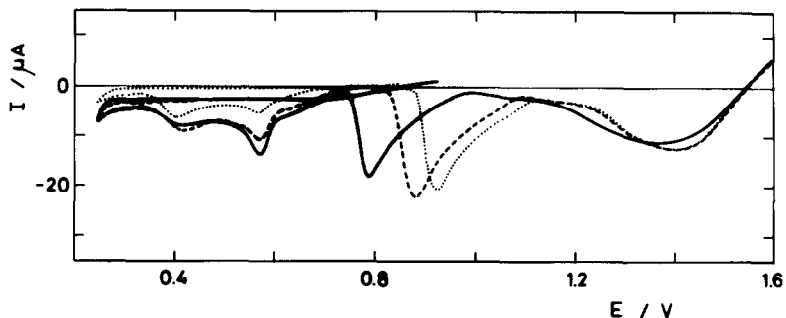


Fig. 2. Voltammetric electroreduction profiles of Pd oxide layers anodically formed in 1 M HClO₄ + 0.05 M Na₂SO₄ (—), 1 M HClO₄ + 0.25 M Na₂SO₄, (---), 1 M HClO₄ + 1 M Na₂SO₄ (·····). $\nu = 5 \text{ mV s}^{-1}$; 25°C.

concentration in the absence of Na₂SO₄. This means that peak IIIc should be related to specific sulphate ion–Pd oxide layer interactions.

Furthermore, as the pH is decreased, the charge Q_{Ic} of peak Ic decreases and the charge Q_{IIIc} related to peak IIIc increases (Fig. 5). However, the global electroreduction charge increases as the pH is decreased, in agreement with data already reported in the literature [6]. In addition, linear relationships between the potential of peak IIIc vs. pH at constant Na₂SO₄ concentration and between the potential of peak IIIc vs. the logarithm of the Na₂SO₄ concentration at constant

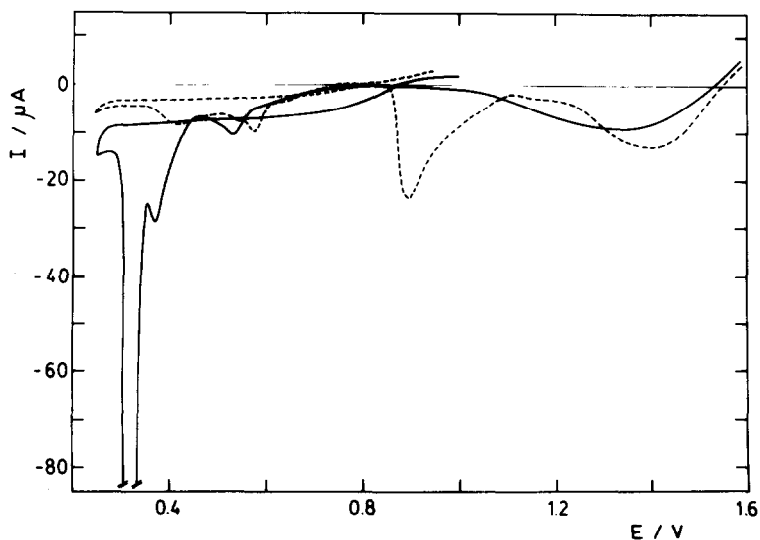


Fig. 3. Voltammetric electroreduction profiles of Pd oxide layers anodically formed at constant ionic strength: ---, 1 M HClO₄ + 0.5 M Na₂SO₄; —, 1 M HClO₄ + 1.5 M NaClO₄. $\nu = 5 \text{ mV s}^{-1}$; 25°C.

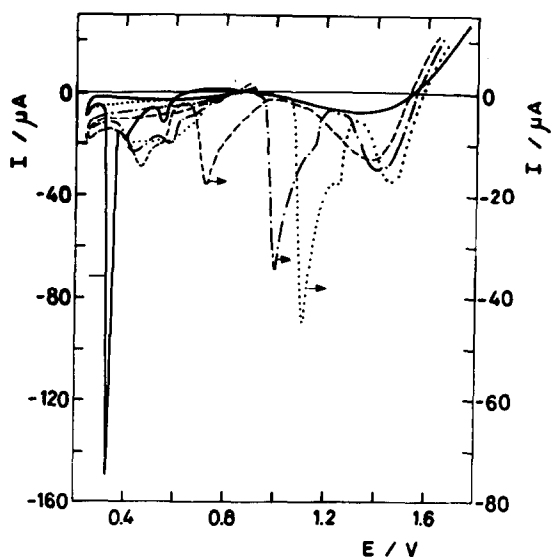


Fig. 4. Voltammetric electroreduction profiles of Pd oxide layers anodically formed in x M HClO_4 + 0.5 M Na_2SO_4 solutions: —, $x = 0.1$; ---, $x = 0.5$; ·-·-·, $x = 2$; ·····, $x = 3.7$. $\nu = 5 \text{ mV s}^{-1}$; 25°C .

pH have been obtained, the corresponding slopes being about $0.090 \text{ V decade}^{-1}$ and $0.110 \text{ V decade}^{-1}$ respectively (Fig. 6).

To determine whether the changes observed in the electroreduction voltammograms are due to specific characteristics of the oxide layers produced in the

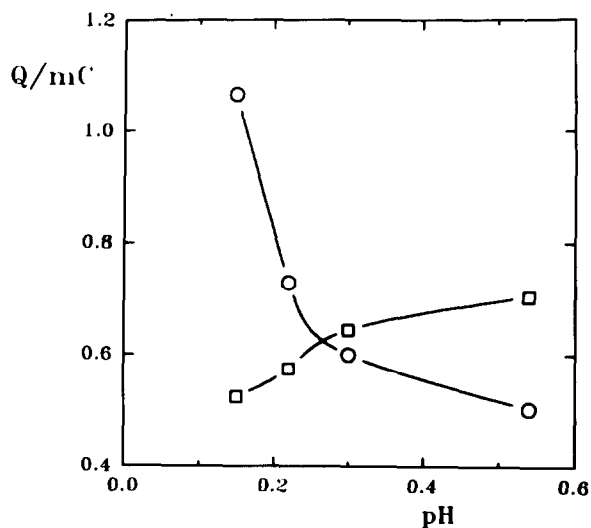


Fig. 5. Dependence of Q_{IIc} (□) and Q_{Ic} (○) on HClO_4 concentration.

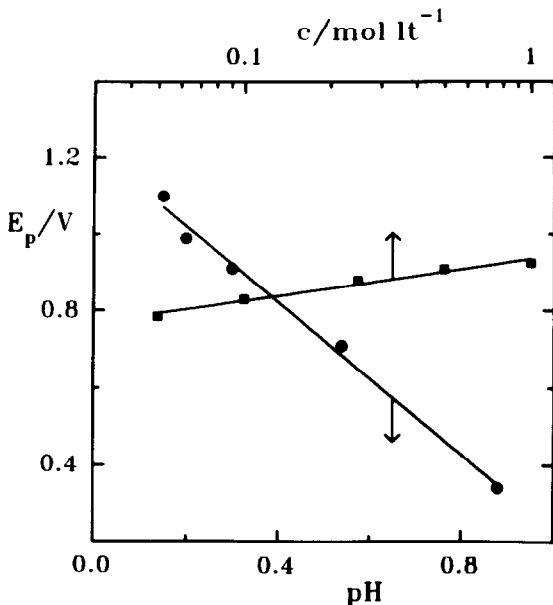


Fig. 6. Dependence of peak IIIc potential on solution pH in 0.5 M Na₂SO₄ (●); dependence of peak IIIc on Na₂SO₄ concentration in 1 M HClO₄ (■). $E_\tau = 2.00$ V; $\tau = 300$ s; $v = 5$ mV s⁻¹.

different solutions or to the effect of the solution composition on the oxide layer electroreduction, the following procedures were carried out. In one experiment, the Pd oxide layer was grown in 1 M H₂SO₄, the oxide-coated WE was transferred to water for 300 s, replaced in the cell containing 1 M HClO₄ and eventually voltammetrically electroreduced in this solution. The same type of experiment was performed, growing the Pd oxide layer in 1 M HClO₄ and eventually electroreducing it in 1 M H₂SO₄. Blanks were run to confirm the absence of artifacts in the voltammograms produced by the transfer and washing operations.

The Pd oxide layers formed in 1 M H₂SO₄ and electroreduced in 1 M HClO₄ exhibit electroreduction voltammograms in which peak IIIc is absent. In addition, peak Ic becomes broader and negatively shifted, and a new sharp peak appears at about 0.40 V (Fig. 7). This behaviour resembles the electroreduction of Pd oxide films grown and electroreduced in 1 M HClO₄ (Fig. 8, dotted curve). However, when the Pd oxide layer was formed in 1 M HClO₄ and finally electroreduced in 1 M H₂SO₄ (Fig. 8), the voltammograms show peak Ic as a positively shifted sharp peak with a shoulder on the ascending branch. Furthermore, a sharp peak at about 1.07 V is observed. The electroreduction of the remaining oxide film takes place at potentials lower than 0.7 V, displaying a double peak at about 0.45 V and 0.6 V, resembling the behaviour which was observed in 1 M H₂SO₄ (Fig. 7, dotted curve). From these runs, one can conclude that the main effect of the solution composition appears in the electroreduction process, whereas the growth of the anodic Pd oxide layers seems to be fairly insensitive to the solution composition.

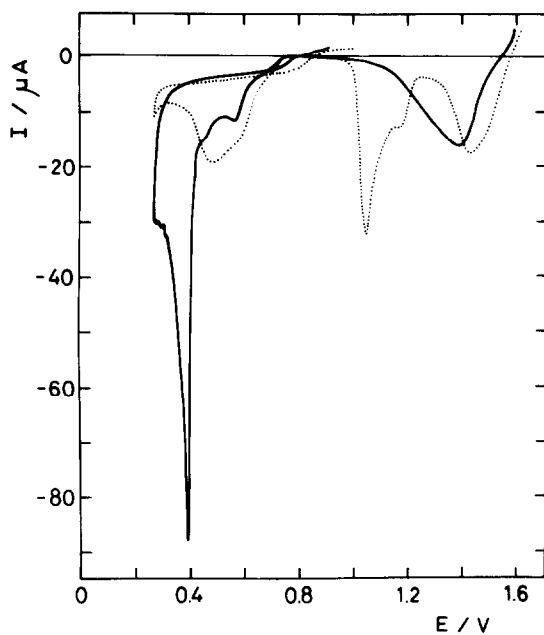


Fig. 7. Voltammetric electroreduction profiles of Pd oxide layers built up anodically during 300 s at $E_r = 2.00$ V in 1 M H_2SO_4 and electroreduced in 1 M H_2SO_4 (·····) and in 1 M HClO_4 (—). $\nu = 5 \text{ mV s}^{-1}$; 25°C .

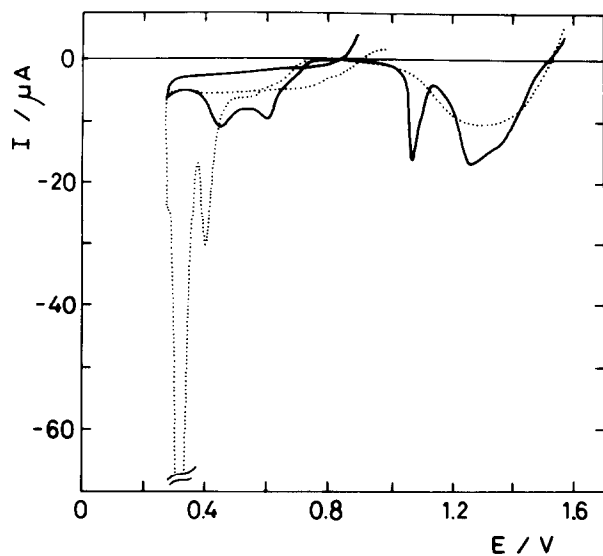


Fig. 8. Voltammetric electroreduction profiles of Pd oxide layers built up anodically during 300 s at $E_r = 2.00$ V in 1 M HClO_4 and electroreduced in 1 M HClO_4 (·····) and in 1 M H_2SO_4 (—). $\nu = 5 \text{ mV s}^{-1}$; 25°C .

DISCUSSION

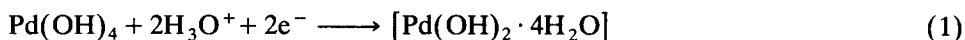
For discussing the voltammetric electroreduction of Pd oxide layers formed at 2.00 V in acid solutions, it is convenient to consider first the likely structure of these layers. According to the electrochemical data already reported [10], these films can be described as a duplex structure with an inner thin Pd oxide layer, in contact with the Pd substrate, and a much thicker outer Pd oxide layer. When $E_r > 1.90$ V, the outer layer constitutes a matrix where a redox system involving different oxidation states of Pd can be accumulated.

However, on the basis of the thermodynamic [11] and electrochemical [10] data of the Pd/Pd oxide/water system, peak Ic has been assigned to a simultaneous electron-proton transfer reaction which occurs in the anodic Pd oxide layer [10]. This reaction appears to be insensitive to the solution composition. Nevertheless, the peak Ic height-to-width ratio decreases and the corresponding voltammetric charge decreases as the acid concentration is increased (Figs. 4 and 5).

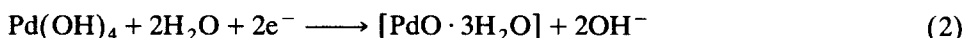
The subsequent thick Pd oxide layer electroreduction depends on the solution composition. It appears that the water content and the complexing characteristics of anions in solution determine the potential range where the electroreduction of the oxide matrix takes place yielding soluble Pd(II) species [10]. Peak IIIc and hump IIc are related to the electroreduction of the oxide matrix (Figs. 1 and 2) [5,10], which behaves as an irreversible process, involving a phase change and the formation of soluble Pd²⁺ species [10]. Peak IIIc appears only when the sulphate ion concentration in the solution exceeds 0.01 M; however, when it is observed, its characteristics depend on the solution pH (Fig. 4). It appears that the presence of SO₄²⁻/HSO₄⁻ favours the electroreduction as well as the electrodisolution of thick Pd oxide layers, probably through the formation of soluble surface complexes.

The formation of PdO(HSO₄) species as a precursor of highly soluble PdSO₄ in Pd electrodisolution in aqueous H₂SO₄ solutions has already been considered [12]. XPS and IR data, coupled with molecular orbital calculations, indicate that, whereas bisulphate ions promote a shift to high binding energies of the surface Pd atoms through the formation of complex-like bonding, ClO₄⁻ ions can interact only electrostatically with the Pd surface. This explanation can probably be extended to the interaction between Pd oxide layers and anions in solution [12].

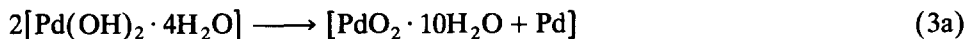
A reasonable approach for the Pd oxide layer electroreduction reactions can be advanced for the processes occurring in the range 0.8–1.60 V at $v = 5$ mV s⁻¹, as follows. For non-complexing anion-containing solutions, i.e. ClO₄⁻-ion-containing aqueous solutions, the electroreduction reaction can be represented as follows [10]:



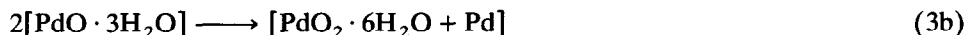
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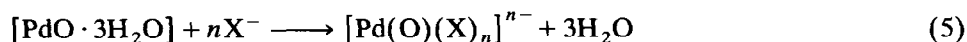
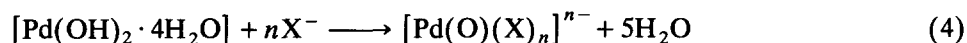
Reactions (1) and (2) are likely followed by reactions in the Pd oxide layer, coupled with a phase change, such as [10]



or



In contrast, for complexing anion-containing solutions, i.e. $\text{HSO}_4^-/\text{SO}_4^{2-}$ -ion-containing solutions, reactions (3a) and (3b) should imply the formation of a surface complex. In general, these complexing reactions can be represented as follows:



where X^- denotes a single-charged complexing anion. The value of n in reactions (4) and (5) should depend on the anion complexing characteristics.

Now, let us consider the processes taking place in the potential ranges of peaks IVc and Vc. The contributions of peaks IVc and Vc depend on the solution composition. Thus, in KHSO_4^- and Na_2SO_4^- -containing solutions the charge in these peaks is fairly similar. Peak IVc has been associated with the electroreduction of the PdO monolayer [5,9], whereas peak Vc has been related tentatively to the electroreduction of the partially aged oxide portion remaining after the phase change reaction (Peak IIIc) has taken place. Practically no effect of the solution composition on peak IVc is observed, as would be expected for the electroreduction of the compact oxide inner layer. A detailed analysis of the processes referred to the electroreduction of the innermost oxide layer under ageing effects has been given in previous publications [9]. However, in those solutions involving either a low acid (Fig. 4 (full curve) and Fig. 1 (dotted curve)) or sulphate concentration (Fig. 2), the height of peak Vc becomes greater than that of peak IVc. This effect is enhanced by using plain HClO_4 solutions. These facts suggest that the contribution of peak Vc could be related to some reaction involving ClO_4^- ions, which occurs simultaneously with the electroreduction of the partially aged PdO monolayer. This behaviour (peak Vc in Fig. 1) is very similar to the unusual voltammetry exhibited by Rh electrodes in HClO_4 [13]. For Rh, an analogous peak was found to be related to ClO_4^- anion electroreduction to Cl^- ion.

The diffusional limiting current, recorded after switching the potential scan from $E_{s,c}$ upwards, contains two contributions: one is due to the electrodeposition of soluble Pd^{2+} species produced during the electroreduction scan [10]; the other contribution is related to the electroreduction of traces of O_2 remaining at the interphase after anodization.

Finally, those results involving different solutions for growing and reducing the anodic films indicate that the growth of Pd oxide layers at high positive potentials remains fairly insensitive to the nature of the anions in the solution (Figs. 7 and 8).

Therefore, the structure of the Pd oxide layers becomes nearly independent of the solution composition [5,10], although the amount of Pd oxide layers accumulated during anodization increases with the acid concentration. This is due to the propensity of the base metal towards electrodisolution at low pH, assisting the formation of the anodic film. In fact, it is known that the oxide growth rate decreases rapidly as the solution pH is increased [5,6]. Then, the effect of the Na_2SO_4 in the solution is no longer observed in 1 M NaOH.

CONCLUSIONS

(1) The voltammetric electroreduction of Pd oxide layers produced at high positive potentials in acid solutions are affected considerably by the electrolyte composition.

(2) At low potential sweep rate, i.e. 5 mV s^{-1} , two main voltammetric peaks related to the electroreduction of Pd oxide layers are observed. The first peak at about 1.45 V is associated with the presence of a fast redox process involving different oxidation states of Pd which is accumulated in the Pd oxide matrix. This reaction becomes fairly insensitive to the solution composition. In contrast, the Pd oxide matrix electroreduction is strongly affected by the solution pH and the nature and concentration of anions in the solution. In the presence of weakly adsorbable anions, such as ClO_4^- ions, the reaction takes place at potentials lower than 0.6 V, whereas, in the presence of strongly adsorbable anions, such as SO_4^{2-} and HSO_4^- ions, the reaction occurs more positively, according to the concentration of the solution. In addition, the Pd oxide layer becomes thicker as the solution pH is decreased.

(3) The structure and composition of the oxide layer formed at high positive potentials appears to be hardly modified by the nature of the acid electrolyte.

(4) As the solution pH is decreased, the voltammetric charge related to the Pd oxide matrix increases, whereas that corresponding to the fast redox process decreases. However, the global amount of Pd oxide formed at 2.00 V increases as the solution pH is decreased.

(5) In $\text{SO}_4^{2-}/\text{HSO}_4^-$ -ion-containing solutions, the peak potential related to the electroreduction of the Pd oxide matrix varies linearly with either the solution pH or the logarithm of the $\text{SO}_4^{2-}/\text{HSO}_4^-$ ion concentration, this being the major effect produced by decreasing the solution pH.

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REFERENCES

- 1 L.D. Burke and M.E.G. Lyons, in R.E. White, J.O'M. Bockris and B.E. Conway (Eds.), *Modern Aspects of Electrochemistry*, Vol. 18, Plenum, New York, 1986, Ch. 4.
- 2 A.C. Chialvo, W.E. Triaca and A.J. Arvia, *J. Electroanal. Chem.*, 146 (1983) 96.
- 3 L.D. Burke and M.B.C. Roche, *J. Electroanal. Chem.*, 164 (1984) 315.
- 4 A.J. Arvia, R.C. Salvarezza and W.E. Triaca, *Electrochim. Acta*, 34 (1989) 1057.
- 5 L.D. Burke and M.B.C. Roche, *J. Electroanal. Chem.*, 186 (1985) 139.
- 6 L.D. Burke, M.M. McCarthy and M.B.C. Roche, *J. Electroanal. Chem.*, 167 (1984) 291.
- 7 V. Chausse, P. Regull and L. Victorí, *J. Electroanal. Chem.*, 238 (1987) 115.
- 8 T. Schober, V. Sorajic and A. Meisenberg, *Metallography*, 8 (1975) 359.
- 9 A.E. Bolzán, M.E. Martins and A.J. Arvia, *J. Electroanal. Chem.*, 157 (1983) 339.
- 10 A.E. Bolzán and A.J. Arvia, *J. Electroanal. Chem.*, 322 (1992) 247.
- 11 A.J. Bard, R. Parsons and J. Jordan (Eds.), *Standard Potentials in Aqueous Solutions*, Marcel Dekker, New York, 1985.
- 12 T. Solomun, *J. Electroanal. Chem.*, 302 (1991) 31.
- 13 C.K. Rhee, M. Wasberg, P. Zelenay and A. Wieckowski, *Catalysis Lett.*, 10 (1991) 149.