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# The role of anions in the electrochemical behaviour of thick palladium oxide layers—Effect of chloride ions

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The influence of chloride ions on the electrochemical behaviour of palladium oxide films grown at 2:00 V in 1 M H<sub>2</sub>SO<sub>4</sub> + x M HCl (0 < x < 10<sup>-5</sup>) is investigated by means of voltammetry, rotating ring-disk and potential step techniques. Both voltammetric and current transients electroreduction data show that the presence of CF ions accelerate the electroreduction of palladium oxide films. The potential of the electroreduction voltammetric peak increases with the chloride concentration. Cathodic current transients show current maxima related to the presence of a nucleation and growth process. The mechanism of palladium oxide layer electroreduction can be interpreted through the formation of chloride-containing complex species which favours the electroreduction by decreasing the time needed to start the nucleation and growth of the new electroreduced phase. This effect is achieved by the breakdown of the anodic layer. The results are discussed within the frame of data previously obtained for perchlorate, phosphate and sulphate ion-containing solutions.

The growth of thick palladium oxide films at high positive potentials can be achieved by applying fast repetitive either triangular<sup>1-4</sup> or square<sup>5</sup> wave potential routines. They can also be obtained under potentiostatic conditions<sup>6</sup> though the thicknesses attained under such are usually lower than those obtained by potentiodynamic routines. The structure of the palladium oxide films formed at high positive potentials has been described as an outer hydrous oxide layer, usually denoted as  $\beta$ -layer, which grows above an inner more compact anhydrous layer, usually denoted as  $\alpha$ -layer<sup>1-7</sup>. The growth of the  $\beta$ -layer is accompanied by the electroformation of a reversible electrochemical system which is embedded in the oxide matrix<sup>6</sup>.

Some attempts have been made using *ex-situ* methods, like XPS and UPS, to investigate the nature, primarily the composition, of thin<sup>8.9</sup> and thick<sup>10</sup> electrochemically formed Pd oxide films. TEM views of  $\beta$ -palladium oxide films<sup>11</sup> indicated that this type of film exhibits a porous structure. Otherwise, AFM imaging showed the formation of a columnar-like structure of the palladium surface resulting from the electroreduction of the hydrous oxide layer<sup>5</sup>. The appearance of 3D structures correlates with electrochemical data derived from current transients, which indicate that the electroreduction of the  $\beta$ -oxide layer formed at relatively high potentials can

be described in terms of an instantaneous nucleation and 3D growth process with nuclei death12. One point which is still not clear is how the electrolyte composition influences the electroformation of the palladium oxide layer or its electroreduction. In alkaline solutions the voltammetric electroreduction of the B-layer takes place at potentials lower than that corresponding to the  $\alpha$ -layer'. On the other hand, in acid solutions the electroreduction potential for the  $\beta$ -layer depends on the solution pH, the potential sweep rate and the nature of the anions present at the oxide/solution interphase<sup>6,13</sup>. In HClO<sub>4</sub> or H<sub>3</sub>PO<sub>4</sub> solutions the palladium oxide film layers are electroreduced at remarkable less positive potentials than in  $H_2SO_4$  solutions. Furthermore, at low pH the electroreduction threshold potential for the outer thick oxide film moves positively as the SO42 /HSO4 concentration is increased, while at high pH the presence of SO422 ions do not exert a major effect on the voltammetric electroreduction of the palladium oxide film<sup>6.13</sup>. Electrolyte composition and pH also play an important role in the dissolution of the oxide layer, which increases as pH decreases and anion adsorbability increases<sup>6</sup>. Thus, it is apparent that the electroreduction of relatively thick palladium oxide films is a complex process which might be strongly influenced by the nature of the anions present in the solution.

This work examines the effect of C1 ions on the electrochemical behaviour of palladium oxide films

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formed at relatively high positive potentials. It is well known that CF ions are strongly adsorbable on metal electrodes, and posses the capacity of forming aqueous metal, in the present case palladium<sup>14</sup>, complex species. Both features make Cl ions suitable for examining the role played by the oxide-anion interactions during both the electroreduction and the electroformation of palladium oxide films. As base electrolyte, 1 M H<sub>2</sub>SO<sub>4</sub> solution has been chosen as it allows a facile growth of the thick oxide film, and the voltammetric profiles and the electroreduction current transients exhibit a clear distinction of the different electrochemical processes involved during the electroreduction. Results are discussed in relation to those obtained for sulphate, phosphate and perchlorate ion-containing solutions.

# Materials and Methods

The working electrode was a palladium wire (J. Matthey Chem. Co., Specpure) with a geometric area of about 0.14 cm<sup>2</sup>. The electrode was electropolished before each experiment using a LiCl/methanol solution<sup>15</sup>. After the electropolishing the electrode was thoroughly rinsed with Milli-Q water and placed in the electrochemical cell. The working solutions 1 M H<sub>2</sub>SO<sub>4</sub> + x M HCl ( $0 \le x \le 10^{-4}$ ) were prepared from Merck (p.a.) chemicals and Milli-Q water.

The experimental routine consisted of introducing the electrode at E = 0.5 V to avoid interferences from either H absorption or oxide electroformation. Then, the potential was stepped to 2.0 V in order to grow a relatively thick palladium oxide film during a preset time  $\tau$ = 300 s. Afterwards, either a potentiostatic or a potentiodynamic routine were performed to electroreduced anodic oxide the film. Voltammograms were obtained with a slow potential scan at  $v = 0.005 \text{ V s}^{-1}$  run between 2.00 V and 0.3 V. This v value was selected as it allowed to separate the current peaks related to the different stages of the electroreduction of the palladium oxide film". Current transients were recorded by stepping the potential from 2.00 V to 0.7 V, i.e. a potential where only the electroreduction of the B-oxide layer takes place. It should be pointed out that each potentiostatic measurement was repeated five times and the average value was taken for the calculations.

A rotating palladium-disc/gold-ring electrode, mechanically polished with  $0.3\mu$  m alumina, was occasionally employed to detect the formation of soluble species during the voltammetric electroreduction of the palladium oxide layer. The electrochemical setup comprises a conventional potentiostat and waveform generator. The electroreduction voltammograms and the current transients were recorded on a Houston Omnigraphic recorder and on a model 140L LeCroy oscilloscope, respectively, RRDE experiments were performed using a type BI-PAD Tacussel bipotentiostat.

All the potentials in the text are referred to the reversible hydrogen electrode in the same solution. Runs were carried out under purified  $N_2$  at 25°C.

### Results

# Voltammetric scans

The voltammetric electroreduction scan at v = $0.005 \text{ V s}^{-1}$  from 2.0 V to 0.3 V of a palladium oxide film formed at 2.00 V during 300 s in 1 M H<sub>2</sub>SO<sub>4</sub> exhibits five current peaks (Fig. 1a). At ca. 1.4 V peak I appears which has been related to a fast electrochemical system embedded in the thick oxide matrix<sup>6</sup>. In the 1.3 V to 0.9 V range the voltammogram exhibits an asymmetric current peak (III) with a hump (II) on the ascending branch, both related to the electroreduction of the outer oxide film taking place through a nucleation and growth process<sup>6</sup>. At potentials lower than 0.8 V, peaks IV and V appear overlapping a background diffusional current contribution. This diffusional current is due to the electroreduction of traces of O- and Pd2+ soluble species formed during the anodisation of the palladium electrode<sup>5,16,17</sup>. Peaks IV and V are mainly related to the electroreduction of the innermost, or  $\alpha$ -, oxide layer<sup>6.7</sup>. The electroreduction voltammetric profile changes as x, the concentration of CI ions in the base electrolyte, is increased. Thus, for x increasing from  $6.8 \times 10^{-4} M$  to  $3.7 \times 10^{-3} M$ , peak III shifts positively and at the same time hump II disappears, seemingly overlapped by peak III (Figs 1b-d). Incidentally, peaks I, IV and V exhibit no significant influence of the increasing Cl concentration.

It should be noted that the diffusional current contribution formerly recorded at potentials lower than 0.8 V (Fig. 1a) slightly decreases with the addition of CI ions. Whilst a net limiting current is observed in the 0.7 V-0.8 V range during the subsequent positive potential scan in the absence of CI ions, such current contribution does not appear in the presence of them. Instead, an increasing positive current shows up from ca, 0.7 V upwards.

The potential of peak III fulfill a linear relationship with log  $c_{HCD}$  with a slope of ea. 0.245 ± 0.015 V



Fig. 1—Electroreduction voltammograms of palladium oxide films grown at 2.00 V during 300 s in 1 M H<sub>2</sub>SO<sub>4</sub> + x M HCl, v = 0.005 V s<sup>-1</sup>

decade<sup>-1</sup>, a value appreciably higher than that reported for the case of 1 *M* HClO<sub>4</sub> + *x M* Na<sub>2</sub>SO<sub>4</sub> (0.110 V decade<sup>-1</sup>), where a linear dependence of  $E_p^{10}$  with log  $c_{SO4}^{2-}$  was also found<sup>13</sup>.

The cathodic charge recorded between 1.0 V and 1.55 V, i.e. that related to the electroreduction of the outer thick oxide layer (involving peaks I, II and III), decreases abruptly when the Cl<sup>-</sup> ion concentration exceeds  $1 \times 10^{-3}$  *M*, apparently due to the dissolution of the anodic film (Fig. 2). The apparent changes observed can be due to an effect of chloride ions on either the electroreduction process or the formation of the anodic oxide film. In the first case, it means that there exists an interaction between the oxide surface and the anion specifically adsorbed, which affects the kinetics of the electroreduction process. In the second case, a change in the nature of the oxide film is produced by the presence of Cl<sup>-</sup> ions during its formation at 2.00 V.

To elucidate this point the following experiments were performed. In a first set of experiments (Fig. 3), the palladium electrode was immersed in 1 M H<sub>2</sub>SO<sub>4</sub> and anodised at 2.00 V during 300 s in order to grow the oxide layer, and afterwards the anodic film was voltammetrically electroreduced through a potential scan from 2.00 V to 0.3 V at v = 0.005 V s<sup>-1</sup> (Fig. 3,



Fig. 2—Dependence of the electroreduction charge recorded between 1.6 V and 1.0 V (peaks I and III) with HCI concentration in 1 M H<sub>2</sub>SO<sub>4</sub> + x M HCI.



Fig. 3—Electroreduction voltammograms of palladium oxide films grown at 2.00 V during 300 s under the following conditions: electroformed and electroreduced in 1 M H<sub>2</sub>SO<sub>4</sub> ( ): electroformed in 1 M H<sub>2</sub>SO<sub>4</sub>, washed with water and then electroreduced in the same electrolyte (- --): electroformed in 1 MH<sub>2</sub>SO<sub>4</sub>, washed with water and then electroreduced in 1 M H<sub>2</sub>SO<sub>4</sub> + 1.23×10<sup>-3</sup> M HC1 (—).

dotted trace). This was considered as the blank experiment. In a second run, the electrode was subjected to the same procedure but before reducing the oxide film, the electrode was taken out of the cell at constant potential (E = 2.00 V), washed and immersed for 300 s in Milli-Q water in order to remove as far as possible, traces of sulphate ions from the oxide layer. Afterwards, the electrode was immersed at  $E_i = 2.00$  V in the cell containing 1 M H<sub>2</sub>SO<sub>4</sub>+1.23×10<sup>-3</sup> M HCl, and an electroreduction scan was immediately started from the immersion potential Ei downwards. The resulting voltammogram (Fig. 3, full trace) shows that in the presence of Cl ions, peak III is no longer observed and instead a double peak is recorded in the range 1.3 V-1.4 V in good agreement with the results depicted in Fig. 1. At the same time the voltammogram shows that the potential region related to peaks IV and V exhibits no major changes, just a decrease in the base diffusional cathodic current. To disregard any influence of the washing procedure on the resulting voltammograms, a third experiment consisting of introducing the electrode in plain 1 M H<sub>2</sub>SO<sub>4</sub> after the washing stage, was performed. The voltammogram (Fig. 3, dashed trace) shows that the effect of washing the oxide film with Milli-Q water exerts a very little influence on peak III and rather promotes a small potential shift of peak I to less positive values, increasing, at the same time, its height-to-width ratio. In a second set of experiments, the procedure was inverted (Fig. 4). The palladium oxide film was first grown and reduced in 1  $M H_{2}SO_{4} + 1.23 \times 10^{-3} M HCl$  (Fig. 4, dotted trace). Afterwards, the palladium oxide film was first built up in this solution, washed in Milli-Q water as before, and finally electroreduced in plain 1 M H<sub>2</sub>SO<sub>4</sub> (Fig. 4, full trace). As blank experiment once again the oxide film grown in the Cl<sup>-</sup> ion-containing H<sub>2</sub>SO<sub>4</sub> solution was electroreduced in the same electrolyte after the washing procedure formerly described (Fig. 4, dashed trace). These results clearly show that peaks II and III are originated from a specific effect of HSO<sub>4</sub>/SO<sub>4</sub><sup>22</sup> ions, as reported elsewhere13

Therefore, from the above sets of experiments it can be concluded that the main influence of chloride ions appears during the electroreduction process and not during the growth of the oxide layer.

# RRDE data

The voltammogram of a palladium RRDE recorded at  $\omega = 2000$  rpm and v = 0.005 V s<sup>-1</sup> for the electroreduction of an oxide film grown at 2.00 V



Fig. 4—Electroreduction voltammograms of palladium oxide films grown at 2.00 V during 300 s under the following conditions: electroformed and electroreduced in 1 M H<sub>2</sub>SO<sub>4</sub> +  $1.23 \times 10^{-1}$  M HCl (<sup>-</sup>); electroformed in 1 M H<sub>2</sub>SO<sub>4</sub> +  $1.23 \times 10^{-1}$  M HCl, washed with water and then electroreduced in the same electrolyte (- - -): electroformed in 1 M H<sub>2</sub>SO<sub>4</sub> +  $1.23 \times 10^{-1}$  M HCl, washed in water and then electroreduced in 1 M H<sub>2</sub>SO<sub>4</sub> (-)

during 300 s in 1 M H<sub>2</sub>SO<sub>4</sub> + 3 × 10<sup>-3</sup> M HCl, shows a net anodic current which decreases as the negative potential scan goes from 2.00 V to 1.6 V. Then, the current increases exhibiting an anodic peak at ca. 1.55 V, and afterwards decreases steadily to reach a cathodic peak at ca. 1.37 V. From 1.25 V to 0.8 V a practically null current is recorded, which is followed by the appearance of two cathodic peaks at ca. 0.65 V and 0.35 V. During the subsequent positive potential scan the current remains cathodic up to 0.7 V, where an abrupt anodic current increase is observed (Fig. 5). By setting  $E_R = 0.4$  V, the ring current response closely follows that of the disk (Fig. 5, full trace), i.e. firstly there is a progressive cathodic current decrease for  $2.0 \le E_D \le 1.7$  V followed by the appearance of a cathodic peak at ca. 1.45 V concomitantly with the anodic peak at the disk. Afterwards, a shoulder at cu 1.35 V, concomitantly with the appearance of the eathodic peak at 1.37 V at the disk, is recorded. Subsequently, the cathodic ring current tends to a limiting value that decreases to zero for  $E_D < 0.5$  V. During the following positive potential scan the current at the ring remains at zero but increases from  $E_D = 0.7 V$  upwards.

 $E_{e} = 1.15 V$ 04V 1.0 1.5 0.5 V Potential 5 RRDE voltainmogram corresponding Fig 10 the electroreduction of a palladium oxide film grown at 2.00 V during 300 s in 1 M H<sub>2</sub>SO<sub>4</sub> + 3 ×10<sup>-1</sup> M HCL  $\omega$  = 2000 rpm:

By setting  $E_R = 1.15$  V (Fig. 5, dotted trace) the current profile at the ring shows a plateau from 2.00 V to 1.6 V and a cathodic peak at ca. 1.5 V which is much lower than that previously recorded for  $E_R = 0.4$ V. It should be noted that in this case no shoulder is observed at ca. 1.35 V and no current increase is observed in the range 0.3 to 0.9 V during the subsequent positive potential scan.

#### Potentiostatic current transients

 $v = 0.005 V s^{-1}$ 

As Cl ions produce dramatic changes in the voltammetric response for the electroreduction of thick palladium oxide films compared to that observed for plain sulphuric acid solution, it is worth to know whether they reflect a change in the electroreduction mechanism previously found for sulphuric acid solutions in the absence of chloride ions12

For this purpose, potentiostatic current transients at E = 0.7 V for the electroreduction of the palladium oxide film grown at 2.00 V in 1 M  $H_2SO_4 + x M HCl$  $(0 \le x \le 10^{-2})$  were recorded.

For plain 1 M H<sub>2</sub>SO<sub>4</sub>, the current transient exhibits an initial current decay followed by two current peaks (Fig. 6, full trace) that are characteristic of an electrochemical reaction undergoing under a phase

Fig. 6-Potentiostatic current transients at E = 0.7 V for the electroreduction of a palladium oxide film grown at 2.00 V during 300 s.

change process<sup>18</sup>. On the other hand, for  $1 M H_2SO_1 +$  $3.7 \times 10^{-3}$  M HCl also the current transient shows two maxima, but the time (t<sub>m</sub>) for reaching the maximum is appreciably shorter and the current at the maximum (Im) higher than that recorded in the absence of Cl ions (Fig. 6, dotted trace).

As the chloride concentration is increased in the range  $1 \times 10^{-5}$   $M \le c_{\rm HCI} \le 5 \times 10^{-3}$  M, t<sub>m</sub> decreases linearly with the logarithm of cutci while Im increases linearly with cuci.

#### Discussion

The growth of thick palladium oxide films at high involves three positive potentials main electrochemical process<sup>1,6,1</sup>. At the very beginning the oxidation of the palladium surface produces the formation of a thin, compact, anhydrous film, usually denoted as  $\alpha$ -layer, which is built up through a place exchange mechanism<sup>1,11</sup>. The further oxidation of the surface results in the growth of an outer, thick, hydrous oxide layer, usually denoted as  $\beta$ -layer<sup>1/2</sup>, accompanied by the formation of the following reversible electrochemical system<sup>6</sup>

$$[(xPd^{4+}/yPd^{2+})(OH)_{(4x+2y)},nH_2O] + 2H_3O^{-} + 2e^{-} = [\{(x-1)Pd^{4+}/(y+1)Pd^{2+})\}(OH^{-})_{(4x+\frac{1}{2})-\frac{1}{2}} - (n+4)H_3O]$$
(1)





This reaction involves changes in the oxidation state of Pd as well as changes in the amount of bounded OH species and water molecules in the oxide layer. A similar redox system has also been found during the formation of thick oxide films on Pt<sup>19</sup>.

This reversible electrochemical system, which is related to presence of peak I<sup>6</sup>, is not influenced by the presence of Cl<sup>-</sup> ions (Fig. 1). The lack of any significant effect of the anions of the electrochemical behaviour of peak I supports the former assumption that this reversible electrochemical system is embedded in the oxide matrix.

The comparative voltammograms run in different acid solutions (Figs 5 and 6) clearly show that the electroreduction of the oxide film and not its anodic formation, is influenced by the adsorption of Cl<sup>-</sup> ions. This effect agrees with data previously reported for 1 M H<sub>2</sub>SO<sub>4</sub> and 1 M HClO<sub>4</sub> solutions<sup>13</sup>. By washing the anodic film a redistribution of the cathodic charge takes place, but does not alter the oxide film in such a way to modify the potential windows where the different electroreduction processes take place. The comparatively minor changes observed in the electroreduction voltammograms can be assigned, in principle, to local changes of pH and anion content in the oxide film.

The electroreduction of the oxide films is accompanied by the formation of soluble species as shown by the RRDE experiments. When  $E_R$  is set at 0.4 V, the current at the ring exhibits an exponential decay while for  $E_R = 1.15$  the ring current is rather constant. This difference arises from the fact that at 0.4 V the oxygen formed at the palladium electrode during the anodisation process can be electroreduced, while for  $E_R = 1.15$  V this reaction is precluded.

At first sight, it should be expected that for  $E_R = 1.15$  V the electrochemical reaction

$$Cl_2 + 2e \rightarrow 2Cl$$
 ... (2)

should be observed as it has a standard potential  $E^0 = 1.395 V^{20}$ , and if  $CI_2$  evolves at the potentials where the palladium electrode is anodised, the formation of CI ions at the ring electrode should be detected. However, though the contribution of this reaction cannot be disregarded, the simultaneous appearance of current peaks at both the disk and the ring electrodes, and the fact that the appearance of the ring current peak depends on  $E_D$ , indicates that the ring collects mainly products coming from the electroreduction of the oxide film produced at the disk. Thus, the appearance of an anodic peak at *ca*. 1.6 V at the disk can be assigned to the formation of soluble palladium chloride-complex species such as  $PdCl_6^{2-}$ . For  $E_R = 1.15$  V, these ions are reduced according to

$$PdCl_6^{2^-} + 2e^- \rightarrow PdCl_4^{2^-} + 2Cl^- \qquad \dots (3)$$

This reaction has a standard potential  $E^0 = 1.47 V^{20}$ . On the other hand, for  $E_R = 0.4 V$ , the electroreduction of the  $PdCl_4^{2-}$  species can proceed further to Pd(0) according to

$$PdCl_4^{2^-} + 2e^- \rightarrow Pd + 4Cl^- \qquad \dots (4)$$

the corresponding standard potential being  $E^0 = 0.62$  V<sup>20</sup>.

Therefore, the increase in the height of the peak recorded at the ring at *ca*. 1.5 V when  $E_R$  is changed from 1.15 V to 0.4 V can be explained by an increase in the base current due to the electroreduction of  $O_2$ , and probably  $Cl_2$  species also, and the electroreduction of soluble Pd(IV) and Pd(II) chloride-complexes.

The electroreduction process of the thick palladium oxide layer can then be schematically express as:

$$Pd_xPdO_{2*}xH_2O_{(s)} + nX^{-}(aq) \rightarrow [Pd_xPd(O)(X)_n]^{n-}_{(s)} + xH_2O \qquad \dots (5)$$

$$[\operatorname{Pd}_{x}\operatorname{Pd}(O)(X)_{n}]^{n}_{(s)} + 2 \operatorname{H}^{+} + 2e \rightarrow [\operatorname{Pd}(X)_{n}]_{aq} + \operatorname{Pd}_{x} + \operatorname{H}_{2}O \dots, (6)$$

The value of n depends on the type of anion considered. For the case of  $Cl^-$  ions, it can take the values of 4 or 6 depending on the electrode potential. Conversely, for non-complexing or weak adsorbable anions, the electroreduction reaction operates schematically as:

$$Pd_xPdO_2.xH_2O+4H^++4e^- \rightarrow Pd_xPd+(4+x)H_2O^-$$
...(7)

The PdO<sub>2</sub> 'x H<sub>2</sub>O species here represents in a lax way the  $\beta$  or outer palladium oxide layer, the electroreduction of which takes place under peak III.

According to the presence of strong interactions between anions and the palladium oxide layer, the electroreduction potential should be affected by the concentration of anions and move in the direction of the standard potential of the complex formation, as experimentally observed. This potential shift tends to a limiting value related to the standard potential for the redox couple  $[Pd(CI)_6]^{2-}/[Pd(CI)_4]^{2-}$ , and peak III eventually overlaps the potential related to peak 1 (Fig. 1).

Therefore, it seems that the decrease of the threshold potential for the electroreduction of the palladium oxide layer is assisted by the specific adsorption of Cl<sup>-</sup> ions which favours the formation of Cl<sup>-</sup>-containing complexes. This effect can be correlated with data reported for HSO<sub>4</sub><sup>-</sup>-containing solutions<sup>6,13</sup>, where the electroreduction potential shifted positively as the HSO<sub>4</sub><sup>-</sup> concentration was increased, supporting the possible formation of a surface complex of the type Pd(O)(HSO<sub>4</sub>)<sup>21,22</sup>.

The potentiostatic current transients recorded in the presence and in the absence of Cl<sup>-</sup> ions show that, though Cl<sup>-</sup> ions accelerate the electroreduction process, they do not change the electroreduction mechanism. From potentiostatic current transients and voltammetric measurements, it has been shown that the electroreduction of relatively thick palladium oxide layers proceeds through an instantaneous nucleation and 3D growth process with nuclei death due to the depletion of the reacting species<sup>5,12</sup>.

For this type of mechanism, the time dependence of the transient current can be written as<sup>6,12</sup>:

$$J(t) = P_1 [1 - exp(-P_2(t-P_3)_2]exp(-P_2(t-P_3)_2) \qquad \dots (8)$$

where  $P_1 = zFk_1$ ,  $P_2 = \pi M^2 k_2^2 N_0/\rho^2$ , being  $k_1$  and  $k_2$ the rate constants perpendicular and parallel to the reacting surface, respectively,  $N_0$  the number of active sites per cm<sup>2</sup>. M and  $\rho$  the molecular weight and the density of the new phase. The second exponential in the rhs term accounts for the depletion of reactants in the palladium oxide layer<sup>23</sup> and  $P_3$  represents and induction time for beginning the growth of the new phase<sup>12</sup>.

This equation fits very well the transients obtained in Cl-ion-containing solutions (Fig. 7), suggesting that the electroreduction mechanism in acid media is independent on the solution composition. The parameters  $P_1$  and  $P_2$  in Eq. (7) are related to the current density maximum ( $j_m$ ) and the time to reach the maximum ( $t_m$ ) in the potentiostatic transients, according to:

$$\mathbf{P}_1 = 4\tilde{j}_m \qquad \dots, (9)$$

$$P_2 = \ln 2t^{-2}_m$$
 ... (10)



Fig. 7—Selected numerical fits (full trace) of the cathodic transients recorded at  $E_c = 0.7$  V in 1 *M* H<sub>2</sub>SO<sub>4</sub> + x m*M* HCl, according to equation (9) using the following set of parameters: (•) P<sub>1</sub> = 11.14 mA cm<sup>-2</sup>, P<sub>2</sub> = 0.16 s<sup>2</sup>, P<sub>3</sub> = 0.1 s; (o) P<sub>1</sub> = 4.85 mA cm<sup>-2</sup>, P<sub>2</sub> = 0.012 s<sup>2</sup>, P<sub>3</sub> = 1.37 s.

As  $c_{HC1}$  is increased,  $t_m$  decreases and  $P_2$  increases, i.e. the product  $k_2^2 \times N_0$  increases. On the other hand  $j_m$ , i.e.  $P_1$  increases linearly with  $c_{HC1}$ . The different dependencies of  $P_1$  and  $P_2$  on  $c_{HC1}$  should be assigned to the fact that in the former case the influence shows up through the value of  $k_1$  while in the latter, the increase in  $c_{HC1}$  is reflected in N<sub>0</sub>. Assuming that  $k_1$ obeys a Butler-Volmer type relationship, then  $k_1$ should be proportional to exp(-K E), and E being  $\propto \log_{HC1}$ ,  $k_1$  should be proportional to  $c_{HC1}$  as found experimentally.

Comparing the present results with previously reported data<sup>°</sup>, it can be observed that the time needed to reach the current peak decreases in the order HCl <  $H_2SO_4 < H_3PO_4 < HCIO_4$ . The threshold potential for the electroreduction process also shifts negatively as the adsorbability of the anion decreases<sup>12</sup>. Therefore, it can be concluded that strong adsorbable anions promotes the electroreduction of the thick outer oxide layer by breaking this layer through the formation of a surface complex. Transient current peaks at potentials as high as 1.2 V or 1.4 V have been recorded for H<sub>2</sub>SO<sub>4</sub> solutions<sup>12</sup>. At these high potentials transient current peaks can hardly be related to the growth of an electroreduced palladium phase. Seemingly, as dissolution of the oxide phase takes place through the formation of a palladium complex species, negative

nucleation, i.e. nucleation of holes could also take place. From a phenomenological point of view this type of process cannot be differentiated from a proper nucleation and growth of a new phase. The dependence of  $N_0$  with  $c_{HCI}$  probably indicates that at the surface of the oxide layer the adsorption of anions produce the nucleation of pits which grow in the perpendicular direction to the base metal.

Peaks IV and V do not exhibit an appreciable influence of the anions, neither for Cl<sup>-</sup> nor for SO<sub>4</sub><sup>-</sup> or ClO<sub>4</sub><sup>-</sup> ions-containing solutions<sup>13</sup>. The absence of a significant effect of the solution composition in the electroreduction current peaks appearing at lower potentials, i.e. below 0.8 V in the present work, is consistent with the two-layer model<sup>1,11</sup> which assumes that they are related to the electroreduction of the innermost part of the oxide film grown on the palladium surface. There is some decrease in the base limiting diffusion current onto which the proper oxide electroreduction currents are surmounted. This change is probably due to a change in the current efficiency for the electroformation of O<sub>2</sub> due to the evolution of chlorine as the Cl<sup>-</sup> ion concentration is increased.

Finally, it is apparent that the formation of the surface oxide film is independent of the Cl ion concentration in the Cl<sub>2</sub> evolution potential region. This suggests that both, CI adsorption and OH and O electrosorption, follow a potential-dependent adsorption isotherm with the same argument of the exponent in VF/RT, that their relative 50 (competitive) adsorption almost potential is independent<sup>24</sup>. The Cl<sub>2</sub> evolution reaction proceeds with a low yield in the case of very diluted Cl<sup>-</sup> ioncontaining solutions<sup>25</sup>, allowing the evolution of O<sub>2</sub> during the oxide film formation at high potentials.

#### Conclusions

The voltammetric and potentiostatic results obtained in low CI<sup>-</sup>-containing 1 M H<sub>2</sub>SO<sub>4</sub> solutions, indicate that the adsorption of CI<sup>-</sup> ions produce a breakdown of the outer oxide layer. This produces a time decrease and a positive shift of the threshold potential for the electroreduction of the outer thick oxide layer. Both time and electroreduction potential decrease linearly with the logarithm of CI<sup>-</sup> concentration. The structure and nature of the thick palladium oxide film formed at high potentials appears independent of the nature of the anions present in the solution. Furthermore, the mechanism of electroreduction is apparently independent of the solution composition. The voltammetric and potentiostatic results support the model of an outer hydrous oxide layer, embedding a fast electrochemical system, located above a compact anhydrous oxide film.

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#### References

- Burke I, D & Lyon M E G (1986) In Modern aspects of electrochemistry (R E White, J O M Bockris, and B E Conway, eds.), vol. 18 (Plenum Press, New York), 169–248
- Burke L D & Roche M B C, J electroanal Chem, 186 (1985) 139
- 3 Burke L D & Casey J K. J electrochem Soc. 140 (1993) 1284
- 4 Burke L D & Casey J K, J electrochem Soc, 140 (1993) 1292
- 5 Kessler T, Visintín A, Bolzán A E, Andreasen G, Salvarezza R C, Triaca W E, & Arvia A J, Langmuir, 12 (1996) 6587
- 6 Bolzán A E & Arvia A J, J electroanal Chem, 322 (1992) 247
- 7 Zhang A J, Gaur M & Birss VI. J electroanal Chem, 389 (1995)
- 8 Kim K S, Gossmann A F & Winograd N, Anal Chem, 46 (1980) 197
- 9 Peuckert M, J phys Chem, 89 (1985) 2481
- Chausse V, Regull P&Victori L, J electroanal Chem. 238 ((1987) 115
- 11 Birss V I, Thomas S C & Zhang A J, Electrochim Acta, 40 (1995) 1551
- 12 Bolzán A E, J electroanal Chem, 437 (1997) 199
- 13 Bolzán A E & Arvia A J, J electroanal Chem. 354 (1993) 243
- 14 Cohen A J and Davidson N, J Am chem Soc, 73 (1955) 1955
- 15 Schober T. Sorajic V & Meisenberg A. Metallography, 8 (1975) 359
- 16 Cadle S H, J electrochem Soc. 121 (1974) 645
- 17 Bolzán A E, Martins M E & Arvia A J, J electroanal Chem. 172 (1984) 221
- 18 Fleischmann M & Thirsk H R (1963) In Advances in electrochemistry and electrochemical engineering (P Delahay, ed.), vol. 3 (Wiley, New York)
- 19 Bolzán A E & Arvia A J. J electroanal Chem, 341 (1992) 93
- 20 Bard A J, Parsons R, & Jordan J (1985) Standard potentials in aqueous solutions (Marcel Dekker, Inc., New York)
- 21 Solomun T. J electroanal Chem, 217 (1987) 435
- 22 Solomun T, J electroanal Chem, 255 (1988) 163
- 23 Armstrong R D, Fleischmann M & Thirsk H R, J electroanal Chem, 11 (1966) 208
- 24 Conway B E & Novak D M, J chem Soc Faraday Trans 1, 75 (1979) 2454
- 25 Trassati S & Lodi G (1980) In Electrodes of conductive metallic oxides (S Trasatti, ed.), vol. Part B, chap. 11 (Elsevier, Amsterdam)