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The behaviour of platinized platinum electrodes in acid solutions: correlation between voltammetric data and electrode structure

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The electrochemical behaviour of platinized platinum electrodes prepared by different methods was studied in the H-adatoms and O-adatoms electroadsorption–electrodesorption potential range in 1 M $HClO_4$ at 30° C. Porous platinized platinum electrodes of different degrees of platinization prepared at a constant potential show an anomalous voltammetric behaviour. The magnitude of the anomalous effect depends on the electroplating conditions and it becomes more remarkable at the lowest voltammetric sweep rate. The anomalous behaviour is explained on the basis of absorption of hydrogen into the porous structure and its influence on the different stages of the hydrogen electrode reaction. The absorption of hydrogen occurs either during electroplating and/or during the potentiodynamic stabilization of the porous electrode.

1. Introduction

The structural characteristics of platinum electrocatalysts have a considerable influence on the kinetics and mechanism of different electrochemical reactions [1–4]. Thus, freshly platinized platinum has a specific activity for methanol electro-oxidation lower than that of smooth platinum due to the effects of a disordered surface structure on the reaction rate [5]. It has also been demonstrated that the potential of platinizing significantly affects the structure and, consequently, the adsorptive and electrocatalytic properties of platinized platinum electrodes [1, 5–9]. In this respect platinum electrodeposits obtained potentiostatically in the neighbourhood of the reversible hydrogen electrode potential absorb large quantities of hydrogen and exhibit an anomalous voltammetric behaviour. The anomalous behaviour has been the subject of different interpretations which are at present still a matter of discussion [5, 6, 8].

The present work refers to the electrochemical behaviour of platinized platinum electrodes prepared by different methods in acid solutions. The correlation between the voltammetric behaviour and the corresponding electrode structure is presented.

2. Experimental details

Platinum wire electrodes of area ~0.12 cm^2 previously electropolished [10] were platinized at a controlled potential, E_d, in 2% chloroplatinic acid in 1 M HCl, using a separate compartment electrolysis cell. The value of E_d given in the text is referred to the reference hydrogen electrode (RHE) in 1 M HCl. Each freshly platinized platinum electrode was repeatedly rinsed with triply distilled water and stored in such water for 24 h before use. Afterwards, the electrode was stabilized by means of triangular potential cycling at a potential sweep rate, v, of 0.4 V s^{-1} between 0.04 and 1.50 V in 1 M $HClO_4$ at 30° C, using a conventional three-electrode compartment Pyrex glass cell. The working electrode potential was measured against a RHE in the same electrolyte solution.

The surfaces of the platinum electrodeposits were examined by both conventional and scanning electron microscopy.

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3. Results

3.1. *Degree of platinization*

The degree of platinization, w, is defined as

$$w = m/A \qquad (1)$$

where m is the mass of electrodeposited platinum and A the initial true electrode area. The latter was evaluated through the H-adatom monolayer charge resulting from conventional voltammograms run at $0.4\,\mathrm{V\,s^{-1}}$ between 0.04 and 1.40 V [11, 12]. The degree of platinization was determined by coulometry assuming a faradaic efficiency of 95% for $E_d > 0.05\,\mathrm{V}$ and 80–90% for $E_d < 0.05\,\mathrm{V}$ [7, 13, 14]. The values of w were confirmed, within 5%, through the direct measurement of the thickness of electrodeposited platinum for micrographs of electrode cross-sections.

3.2. *Influence of E_d on the voltammetric characteristics of stabilized platinized platinum electrodes*

The voltammograms run at $4 \times 10^{-3}\,\mathrm{V\,s^{-1}}$ between 0.04 and 1.5 V with stabilized platinized platinum electrodes, obtained for a constant w, in 1 M $HClO_4$ depend markedly on E_d (Fig. 1). These voltammograms are usually denoted as either normal or anomalous depending whether the ratio between the voltammetric electroreduction charge of the O-containing monolayer, Q_O, and the saturation H-electroadsorption voltammetric charge, Q_H^S, is equal to or lower than 2, respectively. The charge corresponding to the saturation hydrogen coverage is evaluated by integrating the charge passed to 0.05 V and dividing this integral by the fractional hydrogen coverage at 0.05 V, i.e. 0.88 [3, 11, 12]. For conventional smooth platinum electrodes the Q_O/Q_H^S ratio is 2 when the anodic scan extends up to 1.4 V, whereas for platinized platinum the anodic switching potential which corresponds to $Q_O/Q_H^S = 2$ lies between 1.4 V and 1.5 V [3, 15]. In the present case, this potential limit was set at 1.5 V.

The voltammograms depicted in Fig. 1, and especially in Fig. 1b and c, show a remarkable change as compared to the conventional voltammograms for low platinized platinum electrodes (Fig. 2a), particularly in the potential range of the reactions related to the hydrogen electrode. Thus, the Q_O/Q_H^S ratio derived from the voltammograms of Fig. 1 is lower than 2. Furthermore, the voltammogram run with a platinized platinum electrode prepared at $E_d = -0.02\,\mathrm{V}$ (Fig. 1c) exhibits a large base anodic current which shifts the voltammogram over the line of zero current. At a constant w, the Q_O/Q_H^S ratio derived from voltammograms run at $4 \times 10^{-3}\,\mathrm{V\,s^{-1}}$ decreases as E_d decreases (Fig. 3).

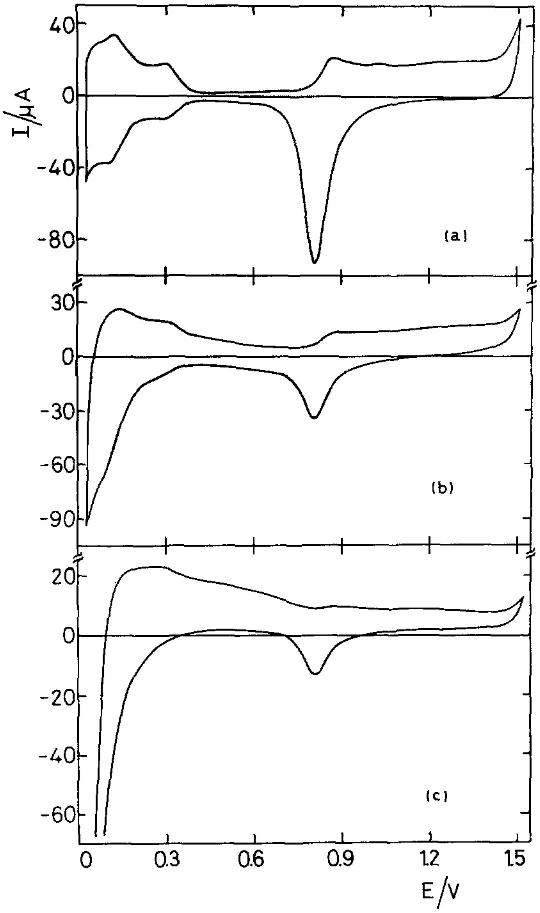

Fig. 1. Voltammograms at $4 \times 10^{-3}\,\mathrm{V\,s^{-1}}$ in 1 M $HClO_4$, 30° C, for stabilized platinized platinum electrodes prepared with $w = 10\,\mathrm{mg\,cm^{-2}}$ at different E_d. (a) $E_d = 0.20\,\mathrm{V}$; (b) $E_d = 0.06\,\mathrm{V}$; (c) $E_d = -0.02\,\mathrm{V}$.

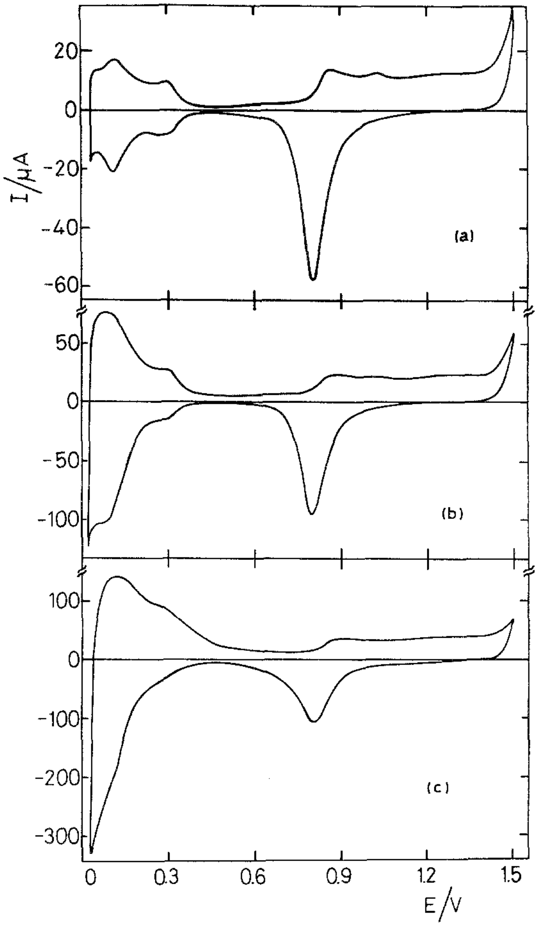

Fig. 2. Voltammograms at 4×10^{-3} V s^{-1} in 1 M HClO$_4$, 30° C, for stabilized platinized platinum electrodes prepared at $E_d = 0.08$ V with different w. (a) $w = 0.20$ mg cm^{-2}; (b) $w = 4.6$ mg cm^{-2}; (c) $w = 12$ mg cm^{-2}.

3.3. *Influence of w and v on the voltammetric characteristics of stabilized platinized platinum electrodes*

Platinized platinum electrodes obtained at a constant $E_d = 0.08$ V exhibit an anomalous voltammetric behaviour at low v which increases accordingly to w, particularly when the latter is greater than 0.5 mg cm^{-2}. Thus, the voltammograms depicted in Fig. 2b and c show a considerable departure of the normal Q_O/Q_H^S ratio (Fig. 2a). The E_d range related to the net transition from normal to anomalous behaviour becomes more positive on increasing w (Fig. 3).

At constant E_d and w, the anomalous effect

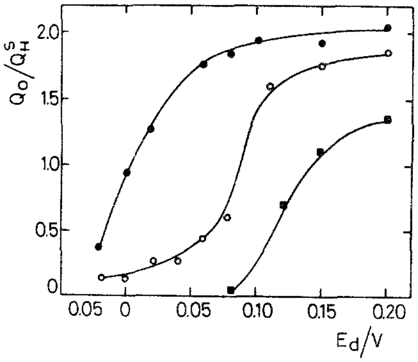

Fig. 3. Dependence of the Q_O/Q_H^S ratio on E_d derived from voltammograms at 4×10^{-3} V s^{-1} in 1 M HClO$_4$, 30° C, for stabilized platinized platinum electrodes prepared with different w. ●, $w = 0.5$ mg cm^{-2}; ○, $w = 10$ mg cm^{-2}; ■, $w = 30$ mg cm^{-2}.

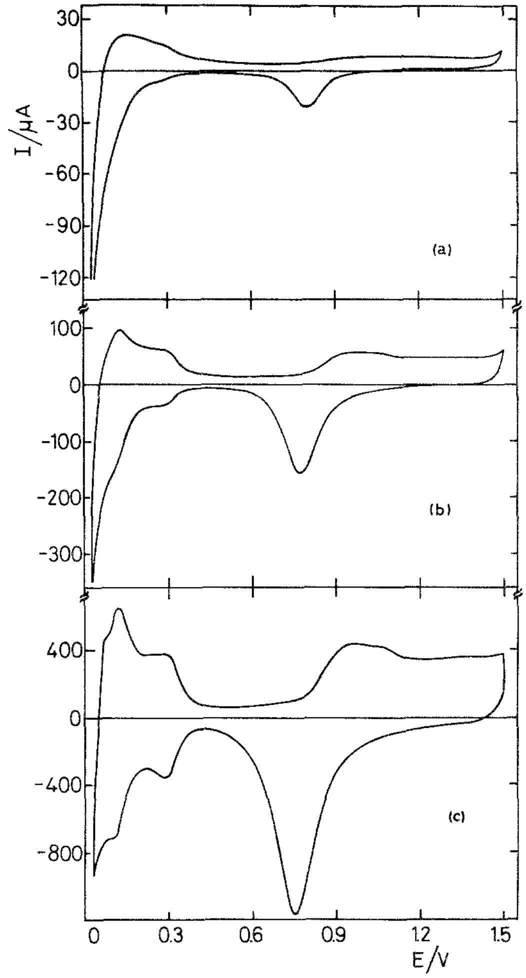

Fig. 4. Voltammograms at different v in 1 M HClO$_4$, 30° C, for stabilized platinized platinum electrodes prepared at $E_d = -0.02$ V with $w = 8$ mg cm^{-2}. (a) $v = 4 \times 10^{-3}$ V s^{-1}; (b) $v = 4 \times 10^{-2}$ V s^{-1}; (c) $v = 4 \times 10^{-1}$ V s^{-1}.

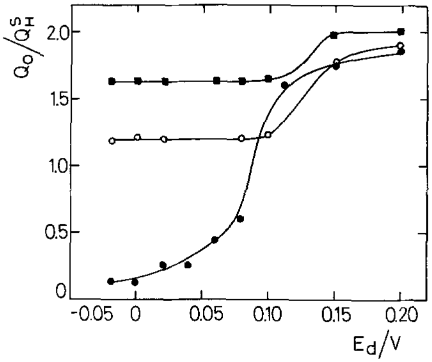

Fig. 5. Dependence of the Q_O/Q_H^S ratio on E_d derived from voltammograms at different v, in 1 M $HClO_4$, 30° C, for stabilized platinized platinum electrodes prepared with $w = 10\,mg\,cm^{-2}$. ●, $v = 4 \times 10^{-3}\,V\,s^{-1}$; ○, $v = 4 \times 10^{-2}\,V\,s^{-1}$; ■, $v = 4 \times 10^{-1}\,V\,s^{-1}$.

decreases as v increases. This result is also valid even at $E_d < 0\,V$, that is, at potential values where platinum and hydrogen are co-deposited (Figs 4 and 5).

3.4. *Changes in the voltammetric characteristics of platinized platinum electrodes during the potentiodynamic stabilization*

The initial voltammogram run at $4 \times 10^{-3}\,V\,s^{-1}$ with a relatively thin ($w = 0.5\,mg\,cm^{-2}$), freshly platinized platinum electrode prepared at $E_d = -0.02\,V$, shows clearly the H-adatoms and O-adatoms electroadsorption–electrodesorption current peaks, although the O-electrodesorption current peak appears sharper and located at a potential lower than that usually found in conventional voltammograms (Fig. 6). The voltammograms recorded at $4 \times 10^{-3}\,V\,s^{-1}$ after 45 min and 4 h, respectively, of repetitive potential cycling at $0.4\,V\,s^{-1}$ between 0.04 and 1.50 V show a progressive decrease in current, indicating a decrease in the real electrode area by sintering and recrystallization and an appreciable distortion of the overall voltammogram, particularly in the H-adatom potential region.

For freshly platinized platinum electrodes obtained at $E_d = 0.08\,V$ with different w, the Q_O/Q_H^S ratio derived from voltammograms run at $4 \times 10^{-3}\,V\,s^{-1}$ decreases as the time of potentiodynamic stabilization (t) at $0.4\,V\,s^{-1}$ increases (Fig. 7). Qualitatively similar dependences are found for electrodes platinized at different E_d and constant w (Fig. 8). In both cases the Q_O/Q_H^S ratio attains a constant value after a time ranging between 2 and 4 h, depending on E_d and w.

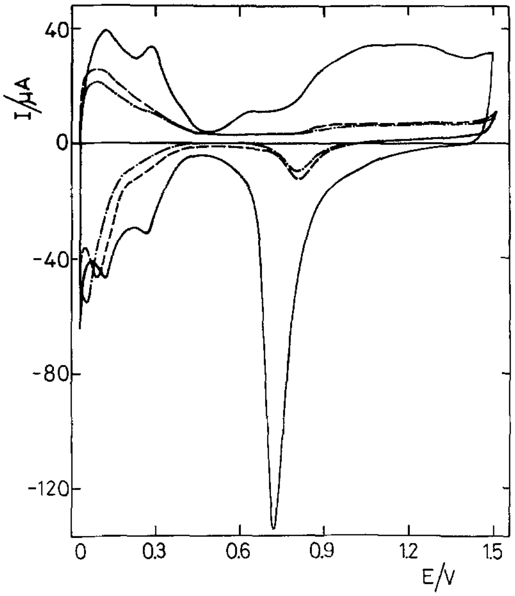

Fig. 6. Voltammograms at $4 \times 10^{-3}\,V\,s^{-1}$ in 1 M $HClO_4$, 30° C, for a freshly platinized platinum electrode prepared at $E_d = -0.02\,V$ with $w = 0.5\,mg\,cm^{-2}$ at different times, t, of potentiodynamic stabilization. ——, $t = 0$; - - -, $t = 45\,min$; -·-·-, $t = 4\,h$.

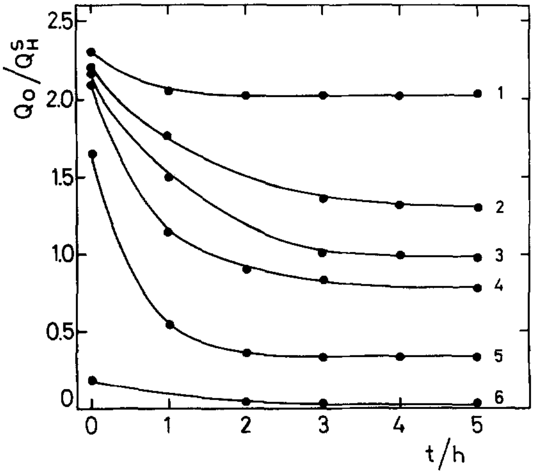

Fig. 7. Dependence of the Q_O/Q_H^S ratio on t derived from voltammograms at $4 \times 10^{-3}\,V\,s^{-1}$ in 1 M $HClO_4$, 30° C, for freshly platinized platinum electrodes prepared at $E_d = 0.08\,V$ with different w. 1, $w = 0.14\,mg\,cm^{-2}$; 2, $w = 0.70\,mg\,cm^{-2}$; 3, $w = 2.3\,mg\,cm^{-2}$; 4, $w = 6\,mg\,cm^{-2}$; 5, $w = 15\,mg\,cm^{-2}$; 6, $w = 40\,mg\,cm^{-2}$.

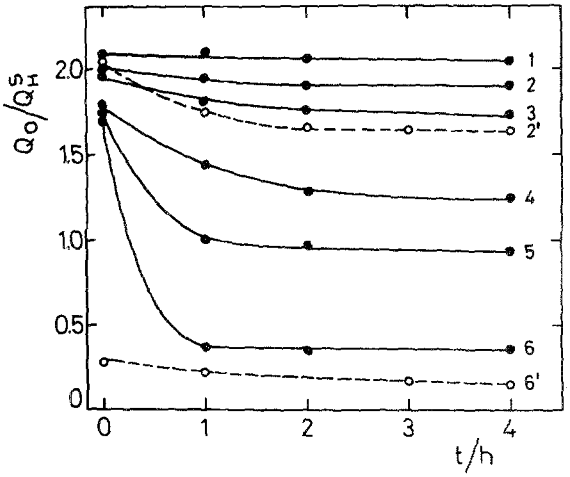

Fig. 8. Dependence of the Q_O/Q_H^S ratio on t derived from voltammograms at 4×10^{-3} V s^{-1} in 1 M HClO$_4$, 30° C, for freshly platinized platinum electrodes prepared at different E_d with w = 0.5 mg cm^{-2} (●) and w = 12 mg cm^{-2} (○). 1, E_d = 0.20 V; 2 and 2′, E_d = 0.15 V; 3, E_d = 0.06 V; 4, E_d = 0.02 V; 5, E_d = 0 V; 6 and 6′, E_d = −0.02 V.

3.5. *Kinetic relationships derived from potentiodynamic and stationary current–potential measurements*

For platinized platinum electrodes which exhibit anomalous voltammetric behaviour, E/log i plots can be made with data taken from the cathodic portion of stabilized voltammograms run at different v by extending the lower switching potential down to −0.05 V (Fig. 9). In the 0.30 to 0.05 V range, reasonably straight lines with slopes decreasing from 0.145 V per decade to 0.115 V per decade are found as v changes from 4×10^{-2} V s^{-1} to 1×10^{-3} V s^{-1} respectively. At 0.4 V s^{-1} no definite Tafel line is observed. On the other hand, the stationary current–potential measurements yield linear Tafel relationships with a common slope equal to the 2.3 (RT/2F) ratio in the 0.05 V to −0.10 V range (Fig. 9). Furthermore, this is consistent with the fact that at potentials lower than 0 V the E/log i plots derived from the potentiodynamic runs at the lowest v tend to attain the slope corresponding to the stationary Tafel line.

3.6. *Correlation between voltammetric behaviour and structure of stabilized platinized platinum electrodes*

The observation by conventional microscopy of the surface of a platinized platinum electrode prepared at E_d = 0.08 V with a low w, e.g. 0.2 mg cm^{-2}, shows an uneven distribution of the electrodeposit and uncovered base metal zones (Fig. 10a). In this case the electrode exhibits a normal voltammetric behaviour (Fig. 2a). As w increases, the electrode surface becomes totally covered with a porous electrodeposit (Fig. 10b) and, correspondingly, an anomalous voltammetric response is observed (Fig. 2b). Furthermore, for large values of w, the porous electrodeposit presents cracks and fissures (Fig. 10c). In these cases, the anomalous voltammetric behaviour is appreciably enhanced (Fig. 2c).

SEM photographs of platinized platinum electrodes prepared at E_d > 0.10 V and w = 10 mg cm^{-2} show a fine grained structure (Fig. 11). After the potentiodynamic stabilization these electrodes exhibit sealing of cracks and fissures and a more uniform surface (Fig. 11b),

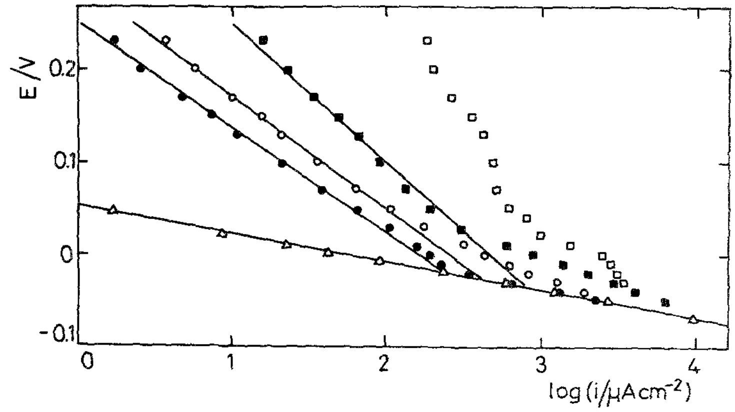

Fig. 9. E/log i plots derived from stationary and potentiodynamic measurements; platinized platinum electrode (E_d = −0.02 V; w = 10 mg cm^{-2}); 1 M HClO$_4$; 30° C. △, stationary data; ●, 1×10^{-3} V s^{-1}; ○, 4×10^{-3} V s^{-1}; ■, 4×10^{-2} V s^{-1}; □, 4×10^{-1} V s^{-1}.

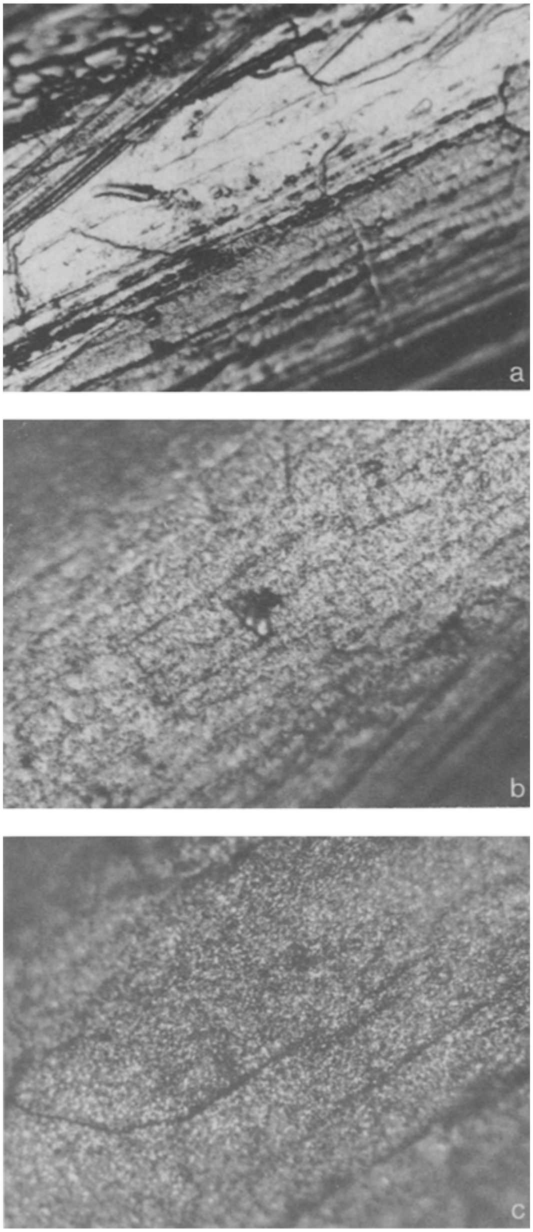

Fig. 10. Photographs of surfaces of stabilized platinized platinum electrodes prepared at $E_d = 0.08\,V$ with different w. (a) $w = 0.20\,mg\,cm^{-2}$; (b) $w = 4.6\,mg\,cm^{-2}$; (c) $w = 12\,mg\,cm^{-2}$. × 130.

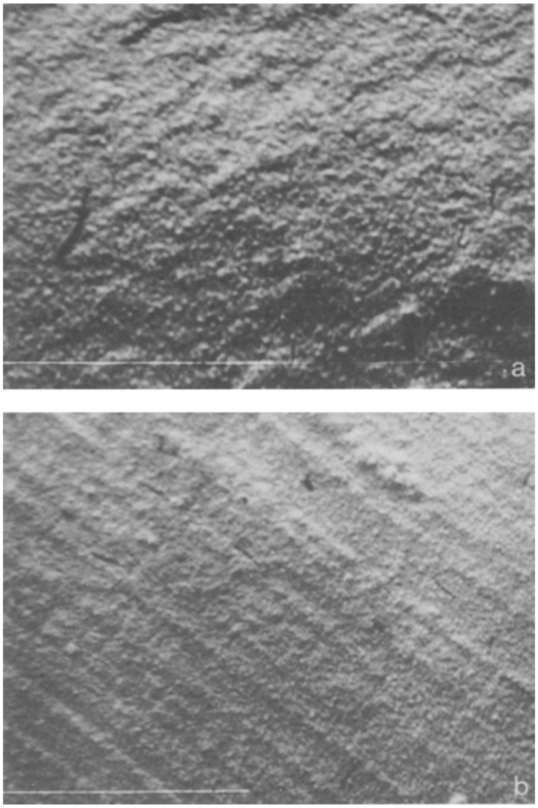

Fig. 11. SEM patterns of the surface of a platinized platinum electrode prepared at $E_d = 0.15\,V$ with $w = 10\,mg\,cm^{-2}$ before (a) and after (b) the potentiodynamic stabilization. (a) × 1300; (b) × 650.

and correspondingly, a normal voltammetric behaviour is approached (Fig. 1a). On the other hand, freshly platinized platinum electrodes prepared at $E_d < 0\,V$ with a relatively large w, have a globular deposit with cracks and fissures apparently produced by internal stresses (Fig. 12a). In this case a smoother surface results after the potentiodynamic stabilization (Fig. 12b). In all cases these highly porous structures exhibit a clear anomalous voltammetric response (Fig. 1c). A SEM pattern of a cross-section of a platinized platinum electrode prepared at $E_d = -0.02\,V$ and $w = 30\,mg\,cm^{-2}$ reveals a sponge-like structure (Fig. 13).

4. Discussion

4.1. *General remarks*

In earlier papers [5, 7–9], the anomalous voltammetric behaviour of platinized platinum electrodes at low potential sweep rates was explained principally by taking into account the dependence of their hydrogen and oxygen adsorptive properties either on the deposition potential or

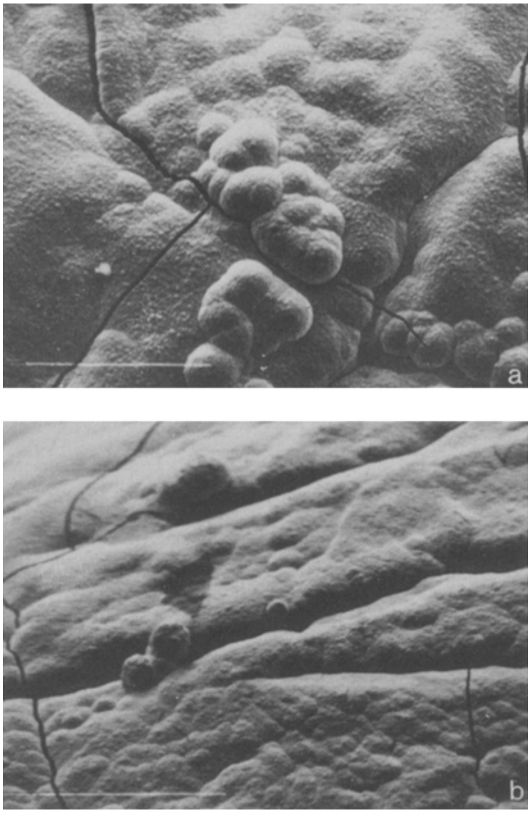

Fig. 12. SEM patterns of the surface of a platinized platinum electrode prepared at $E_d = -0.02\,V$ with $w = 10\,mg\,cm^{-2}$ before (a) and after (b) the potentiodynamic stabilization. × 325.

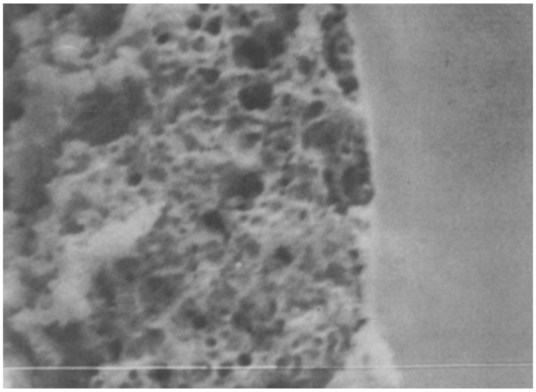

Fig. 13. SEM patterns of the cross-section of a freshly platinized platinum electrode prepared at $E_d = -0.02\,V$ with $w = 30\,mg\,cm^{-2}$. × 1300.

on the electrodeposit thickness. The present results suggest that the anomalous voltammetric behaviour of platinized platinum is mainly determined by the formation of porous structured electrodeposits and their properties for absorption of hydrogen. This explains why the potential sweep rate used in the voltammetric runs, or the value of current density in galvanostatic charging curves, plays a fundamental role in the appearance of anomalous behaviour.

Platinum absorbs hydrogen from the gaseous phase to a very low level [3, 16]. Experiments on hydrogen permeation through a platinum (1 0 0) single crystal have shown that the solubility at 1 atm and 25° C is in the order of one hydrogen atom for every 10^{11} platinum atoms [16]. However, a greater hydrogen absorption from the gas phase into the ordered stepped surface of platinum was detected [17]. Recently it was found that hydrogen could be trapped in micro- and macro-defects and open surfaces of platinum leading to effective values of solubility significantly higher (e.g. 200 times higher) than those of the 'true' solubility [18].

On the other hand, reported results on hydrogen absorption on bright platinum electrodes from the solution phase in the H-adatom region, e.g. in the 0–0.4 V range, are not coincident although it is accepted that, in this case, the absorption of hydrogen on bright platinum requires a high hydrogen overpotential which is not normally reached in the H-adatom adsorption–desorption region [3]. Otherwise, platinized platinum electrodes can absorb anomalously large quantities of hydrogen depending on the electrodeposition potential. Thus, the electrodes prepared by electrodeposition at negative potentials with respect to the RHE exhibit a Q_O/Q_H^S ratio comprised between 0.3 and 0.6 [7, 8]. In this case, mass spectral analysis confirms that such deposits absorb an amount of hydrogen which considerably exceeds a monolayer of H-adatoms [19]. Furthermore, platinum electrodeposited at negative potentials also yields anomalous hydrogen adsorption isotherms [5]. These effects were attributed to the presence of a defect structure produced by the occlusion and removal of hydrogen co-deposited during platinizing [5, 8].

The present results demonstrate that even in the absence of hydrogen co-deposition during platinizing, e.g. carrying out the electrodeposition at $E_d > 0$ V, providing that a porous structure is formed, the potentiodynamic cycling of freshly platinized platinum electrodes in the H- and O-adatoms electroadsorption–electrodesorption region, particularly at low v, promotes a gradual penetration of hydrogen into the metal lattice, probably through H-adatom. Furthermore, the penetration of hydrogen is favoured in freshly prepared electrodes due to the presence of cracks and fissures. As these defects are gradually removed, either spontaneously because these electrodes are thermodynamically unstable or by the occurrence of the electrochemical reactions during the potentiodynamic stabilization, the electrode surface becomes smoother, the active area is progressively decreased and the processes with the participation of occluded hydrogen achieve the condition corresponding to that of the stationary anomalous voltammetric response. At smooth platinum electrodes where the hydrogen electrode equilibrium

$$H_2(\mathrm{sol}) = 2H(\mathrm{ads}) = 2H^+(\mathrm{sol}) + 2e \quad (2)$$

is established at the metal surface–solution interface, the surface properties of the metal catalyst become very important. However, in the case of porous platinized platinum electrodes their bulk properties are also relevant and different processes involving occluded hydrogen, either as H-adatom, hydrogen ion or molecular hydrogen, should perturb the equilibrium expressed by Equation 2. In this case the time-dependent characteristics of the different reactions involved in Equation 2, which are specific to platinized platinum electrodes, are shown through their electrochemical response when subjected to non-stationary electrical perturbations.

On the basis of these ideas the anomalous voltammetric behaviour of platinized platinum electrodes prepared either at $E_d < 0$ V or $E_d > 0$ V can be further discussed.

4.2. *The behavior of platinized platinum electrodes prepared at $E_d < 0$ V*

Platinized platinum electrodes prepared at $E_d < 0$ V contain a certain amount of hydrogen occluded in the metal lattice which was co-deposited during the platinizing procedure. During the potentiodynamic cycling in the positive potential direction at low v, as the occluded hydrogen is electro-oxidized the local concentration of hydrogen ions within the pores is increased and, accordingly, the reversible hydrogen electrode potential shifts towards values more positive than that of the standard hydrogen electrode. Therefore, during the potential scan in the negative potential direction the faradaic discharge of hydrogen takes place. The occurrence of these reactions is confirmed in the voltammogram depicted in Fig. 1c where the anodic oxidation of molecular hydrogen shifts the whole voltammogram over the base line corresponding to the zero current. On the other hand, a fraction of both H-adatoms and molecular hydrogen formed during the cathodic sweep may enter into the pores or cracks at the electrode surface feeding back the generation of hydrogen ions during the potentiodynamic cycling. The change of the local concentration of hydrogen ions with the pores during the potentiodynamic stabilization also produces a shift of the potential of the oxygen electroadsorption–electrodesorption peaks towards more positive values (Fig. 6). Furthermore, it was recently demonstrated through calibrated porosimetry that a large fraction of micropores smaller than 10 Å exist in relatively thick platinized platinum electrodes prepared by electrodeposition at $E_d = -0.05$ V, namely under conditions comparable to those employed in the present work [20]. As this pore size is comparable to the thickness of the electric double layer in moderate concentrated solutions, this stressed the possibility of changes in the properties of the solution in the small pores which may have a significant influence on the specific catalytic activity of the electrode material [20].

4.3. *The behaviour of platinized platinum electrodes prepared at $E_d > 0$ V*

In this case, no hydrogen is co-deposited during the platinizing procedure. However, for electrodeposits having a porous structure, as in the case of electrodeposits with a relatively large w, a fraction of the H-adatoms formed during the voltammetric cathodic half-cycle at low v between 0.4 and 0.04 V may enter and recombine into the porous structure without being oxidized in the subsequent anodic half-cycle. Furthermore, as a certain fraction of the occluded hydrogen is voltammetrically oxidized, the local concentration of hydrogen ions within the pores should increase and again during the cathodic half-cycle hydrogen is discharged at positive potentials feeding back the whole process. As a result of the electrochemical reactions, the different rates of diffusion of hydrogen ions, surface H-adatoms and molecular hydrogen within the porous structure, together with sintering and recrystallization effects, there is a net accumulation of hydrogen in the bulk porous structure which is directly related to the stationary anomalous effect, particularly at low v.

The formation of hydrogen at potentials more positive than the reversible hydrogen potential has also been reported for PTFE-bonded platinum black fuel cell electrode in 85% orthophosphoric acid under nitrogen at 150° C [21]. In this case the effect was attributed to the formation of hydrogen at very low partial pressure, due to the porous electrode structure permitting a very rapid diffusion of hydrogen away from the electrode surface. However, the discussion of the present results also applies to the porous structure of the PTFE-bonded platinum electrode.

4.4. *Influence of the potential sweep rate on the magnitude of the anomalous effect*

The dependence of the voltammetric response of platinized platinum electrodes on the potential sweep rate (Fig. 4), which had already been noted in a previous paper [5], can be also explained on the basis of the preceding discussion. Thus, at a relatively high v, e.g. $0.4\,\mathrm{V\,s^{-1}}$, the H-adatoms formed during the cathodic half-cycle are immediately consumed in the subsequent anodic half-cycle discarding any appreciable hydrogen penetration into the porous structure. Likewise, any contribution of occluded hydrogen co-deposited during platinizing is neglibible. Hence a normal voltammetric response is approached at high v which is mainly determined by the processes taking place in the external metal surface–solution interface. At low v, e.g. $4 \times 10^{-3}\,\mathrm{V\,s^{-1}}$, the quasi-equilibrium of the H-adatom electrodeposition reaction is perturbed by the penetration and recombination of H-adatoms and the absorbed hydrogen electrooxidation. In this case the anomalous voltammetric behaviour is then observed.

4.5. *The Tafel plots for the hydrogen electrode reactions*

The dependence of the voltammetric cathodic Tafel slopes on the potential sweep rate is consistent with the preceding discussion. Thus at high v, e.g. $0.4\,\mathrm{V\,s^{-1}}$, no single E–log i relationship is found at potentials more positive than the reversible hydrogen electrode potential as the current is mainly pseudocapacitive. At lower v, e.g. $4 \times 10^{-3}\,\mathrm{V\,s^{-1}}$ and at potentials more positive than ~0.05 V, the non-stationary Tafel slope approaches the 2.3 $(2RT/F)$ ratio. In this case the rate of diffusion of H-adatoms into the pores appears faster than that of the proper H-adatom electroadsorption reaction, so the H-adatom surface coverage becomes negligible. Thus, the H-adatom penetration process acts by depolarizing the hydrogen discharge reaction. On the other hand, as the negative potential-going scan attains potentials sufficiently negative, the rate of the proper electrochemical reaction exceeds that of the H-adatom diffusion into the pores. Hence, at the electrode surface the equilibrium concentration of H-adatom builds up and the overall hydrogen discharge reaction tends to follow preferentially the stationary reaction pathway, involving the H-adatom recombination reaction as rate determining step yielding molecular hydrogen as final reaction product.

This trend is clearly appreciated in the cathodic E–log i plot made from the voltammogram run at $1 \times 10^{-3}\,\mathrm{V\,s^{-1}}$, where at potential values more negative than the reversible hydrogen electrode potential a Tafel slope equal to the 2.3 $(RT/2F)$ ratio is approached. The same Tafel slope value arises from the stationary current–potential measurements since the overall hydrogen discharge reaction is interpreted through a slow H-adatom recombination step with a negligible participation of H-adatom diffusion [22].

5. Conclusions

These results demonstrate the influence of the porous structure of platinized platinum electrodes on the appearance of the anomalous voltammetric behaviour. The absorption of relatively large quantities of hydrogen into the porous metal structure either by co-deposition during platinizing or produced by voltammetric scanning changes the composition of the electrolyte solution in the small pores and also affects the local pH. These changes cause an apparent depolarization mainly associated with the initial stage of the hydrogen electrode reaction during the voltammetric measurements. This reaction is coupled to H-adatom diffusion, H-adatom recombination yielding molecular hydrogen, proton diffusion and molecular hydrogen diffusion in solution within the porous structure.

The present results must be taken into account in determining the real surface area of porous platinum electrodes either from the hydrogen electrosorption or the oxygen monolayer electroreduction charge [3], as the interface of the anomalous effect eventually may lead to misleading results.

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