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Overlap of the oxide and hydrogen regions of platinum electrodes in aqueous acid solution

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Abstract Two unusual features of noble metal electrode surfaces, active states of the metal and their anodic oxidation products (hydrous oxides), are of increasing interest at the present time owing to the important role of such species in electrocatalysis. The extent to which the hydrous oxide reduction process overlaps with the hydrogen adsorption region was investigated for platinum in acid solution. At least three distinct hydrous oxide reduction peaks (or regions) were observed and in some cases one of these peaks commenced at ca. 0.0 V, i.e. it was almost totally within the hydrogen gas evolution region. Following repeated hydrous oxide growth and reduction, which disrupted and thus activated the metal surface, a sequence of four low-level premonolayer oxidation peaks (each of which has been noted earlier by other authors) appeared in the positive sweep. As discussed earlier for copper in base, the transitions giving rise to such peaks are assumed to be mediator generation reactions, which strongly influence electrocatalytic processes occurring on platinum at low potentials.

Keywords Platinum · Hydrous oxide · Surface activation · Anomalous behaviour

Introduction

Two unusual aspects of the electrochemistry of the noble metals in aqueous media have received considerable attention in this laboratory. One of these is hydrous (or β) oxide electrochemistry [1]; characteristic features of the materials in question are that they are often amorphous and ill-defined from a structural and compositional

viewpoint, and both their formation and reduction, especially at the multilayer level, usually occurs under highly irreversible conditions [2], i.e. at quite high overpotentials. The second feature is the electrochemistry of the active state of metals; this was discussed recently for both platinum [3, 4] and gold [5, 6]. The active state is intrinsically unstable; it is well known in metallurgy, where it is usually attributed to the presence of extended defects [7] such as dislocations and grain boundaries, and is now a source of considerable interest in microelectronics where the new on-chip connector, electrodeposited copper, exists initially in the active state [8].

The active state of metals is assumed to be important for a number of reasons. For instance, it provides an explanation of the origin of two types of oxide (α and β) electrochemistry observed for metal surfaces [3]. The α (or monolayer) oxide is assumed to be formed on the oxidation of rather stable, well-embedded, low-energy surface metal atoms and the layer formed tends to be of a passivating character, e.g. its formation is usually accompanied by a severe drop in electrocatalytic activity. The β oxide is assumed to be formed on oxidation of protruding, low lattice coordination, high-energy surface metal atoms or minute clusters of the same. Owing to the high-energy state of such atoms the oxidation occurs at unusually low potentials, i.e. within the double layer region (this phenomenon is known as premonolayer oxidation [9]), and the extent of (and response for) this reaction is usually quite low as the surface coverage of the highly active state atoms is low. The difficulty in forming multilayer β oxide films on a conventional metal surface is attributed to the low-energy state of the metal atoms involved, while the high negative overpotential required to reduce such films is assumed to be due to the intervention, as the primary reduction product, of highly active states of the metal. The relevance of these ideas to electrocatalysis is based on the assumption, made initially by Taylor [10], that real metal surfaces contain low-coverage active sites, which act as a source of active metal atoms; the latter

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may be mobile and there may be sites of different energy values. The relationship between active metal atoms, hydrous oxides and electrocatalysis was discussed in a recent publication from this laboratory [11].

One of the main problems in platinum electrochemistry is that its basic electrochemical response is variable or dependent on electrode pretreatment. This was demonstrated recently both for polycrystalline [3, 4] and single-crystal [12] platinum surfaces. The limitations of the single-crystal approach from an electrocatalytic viewpoint were also highlighted recently; such idealized surfaces are extremely difficult to produce in a defect-free state [12], defects (or surface roughness) are an essential requirement for high catalytic activity [13] and there is a lack of agreement as to the interpretation of data obtained in this area [14]. The extent to which active surface states and β oxide behaviour cause complications in the responses for platinum in aqueous media is probably not widely appreciated at the present time. Hydrous oxide deposits (which may be formed at low potentials at surface active sites) are surprisingly resistant to reduction on platinum in base [15] even at $E < 0.0$ V (RHE). While such behaviour is less common in acid solution, an example will be shown here of a hydrous oxide peak, occurring at a quite slow sweep rate, at $E < 0.0$ V.

Experimental

The working and counter electrodes usually consisted of lengths of platinum wire (1.0 mm diameter, ca. 0.7 cm² exposed area, Johnson Matthey, Puratronic grade) sealed directly into soda glass. The working electrode was usually pretreated prior to use by mild abrasion with fine grade Emery paper followed by washing the surface with triply distilled water. The electrode was usually cycled ($0.05 \rightarrow 1.50$ V at 50 mV s⁻¹) in the acid electrolyte until the conventional cyclic voltammetric response for platinum was observed.

The potential of the working electrode was recorded and is reported with respect to a reversible hydrogen electrode (RHE scale) [$p(\text{H}_2) = 1.0$ atm] in the same solution; it was contained in a separate vessel which was connected to the working electrode compartment via a Luggin capillary. Solutions were made up using high-purity (Analar grade) chemicals and triply distilled water. The cell, including the reference electrode, was immersed in a water bath in which the temperature was controlled electronically. All solutions were purged with oxygen-free nitrogen before use. Cyclic voltammograms were obtained with the aid of a potentiostat (Wenking, model LT-78), a function generator (Metrohm, E612) and an X-Y recorder (Rikadenki, RW21). The plots were subsequently transferred, with the aid of a scanner, to a computer and are reproduced directly here.

Hydrous oxide deposits were produced on platinum in acid solution by repetitive potential cycling [1], typically 0.50 to 2.10 V at 40 V s⁻¹ for ca. 13 min. The reduction of such deposits in a single negative sweep, e.g. 1.0 to 0.0 V at 5 mV s⁻¹, is known, in some instances [2, 16], to yield three hydrous oxide reduction peaks, labelled in order of appearance of their reduction peaks as HO1, HO2 and HO3. Much of the emphasis in the present work was focused on HO3, whose reduction response overlaps not only with the hydrogen adsorption but in some cases also with the hydrogen gas evolution region for platinum in acid solution.

Results

Typical examples are shown in Fig. 1 of hydrous oxide reduction sweeps for deposits grown and reduced in 1.0 mol dm⁻³ H₂SO₄ at different cell temperatures. The sweep rate (5 mV s⁻¹) used for oxide film reduction in these experiments was quite slow; this had the advantages that all the hydrous oxide deposit was reduced in the first sweep (at a sweep rate of 20 mV s⁻¹ a significant residual oxide reduction response was observed in the second sweep) and the HO3 reduction peak was more clearly defined (it tended to overlap with the hydrogen evolution response). In all cases in Fig. 1 the monolayer response at ca. 0.6 V was relatively small and broad; in some instances there were indications of an overlapping

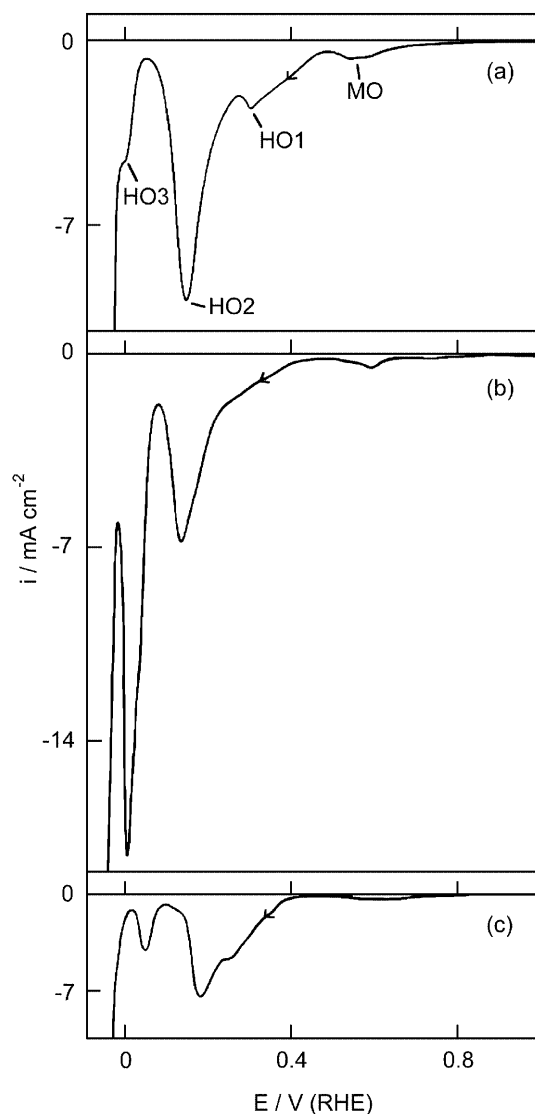


Fig. 1 Reduction profiles ($1.0 \rightarrow -0.05$ V, 5 mV s⁻¹) for hydrous oxide coated Pt electrodes in 1.0 mol dm⁻³ H₂SO₄ at **a** 25 °C, **b** 45 °C and **c** 65 °C; the oxide was grown in situ (1×10^4 cycles at 40 V s⁻¹) using the following limits: **a** $0.6 \rightarrow 2.1$ V, **b** $0.45 \rightarrow 2.1$ V and **c** $0.48 \rightarrow 2.1$ V

doublet in this region. There is no indication of a discrete HO1 reduction peak in some instances, e.g. in Fig. 1b, although such a feature is quite evident with films of low thickness in Fig. 6 below. Usually in the present case there was a significant increase in cathodic current commencing at 0.45 to 0.40 V, this increase continuing (in some instances passing through a maximum) until it overlapped with the HO2 reduction response. With hydrous oxide films of appreciable thickness the response for HO2 was quite distinctive. As shown in Fig. 1a, the peak for HO3 reduction at 25 °C overlaps quite appreciably with the response due to hydrogen gas evolution. However, the resolution of these two responses was significantly improved on raising the solution temperature and the approximate E_{\max} values for HO3 reduction in Fig. 1 are 0.0 V (25 °C), 0.01 V (45 °C) and 0.04 V (65 °C); these potential values are clearly of no thermodynamic significance.

An example of the type of complication that may arise in platinum electrochemistry owing to the involvement of hydrous oxide species is outlined in Fig. 2. In this case a hydrous oxide deposit was first grown on the electrode surface and the lower limit of the sweep used in subsequently recorded cyclic voltammograms was set at 0.02 V, i.e. at the early stage of the HO3 reduction process (Fig. 1a). A number of successive cyclic voltammograms were then recorded in the usual manner (Fig. 2), commencing at the lower limit. Large cathodic currents, associated with reduction of much of the hydrous oxide film, were observed at $E < \text{ca. } 0.1$ V in the first positive sweep. The cathodic current in this region decayed on repeated cycling, but it was still present in the tenth positive sweep at $E < 0.08$ V. Much of the

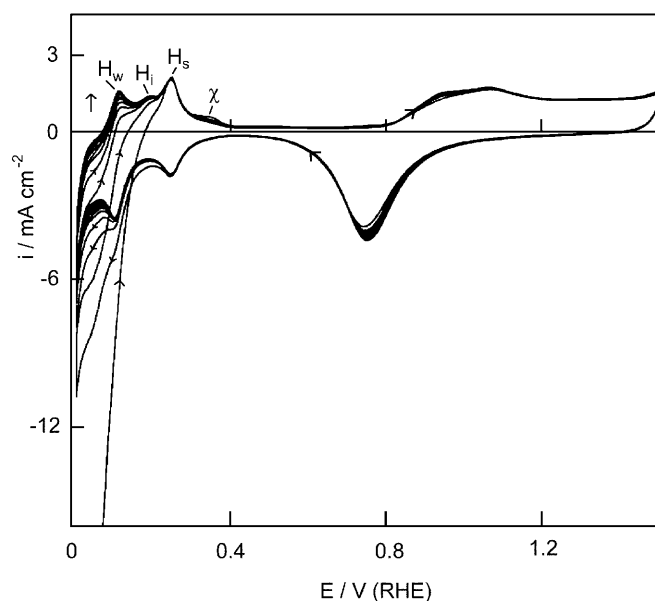


Fig. 2 Cyclic voltammograms (10 successive sweeps; 0.02→1.5 V, 50 mV s⁻¹) for a platinum electrode in 1.0 mol dm⁻³ H₂SO₄ at 25 °C; these were recorded following initial hydrous oxide growth (0.45→2.1 V, 40 V s⁻¹, 1×10⁴ cycles)

remainder of the response, e.g. peak H_S (due to the removal of strongly bound hydrogen) and its cathodic counterpart, scarcely altered on repeat scanning. Attention is drawn here to two features, viz.:

1. The shoulder (χ) in the positive sweep at ca. 0.36 V (this minor feature was most pronounced in the first sweep).
2. The cathodic currents at low potentials (< 0.08 V) are rather persistent. This distorts the response in the weakly bound hydrogen (H_W) region; there is an excess of negative charge below ca. 0.2 V as the oxide reduction response is superimposed on the usual H_W response. This has significant consequences as it means that when a superactive state of the metal, and in particular a HO3-type oxide, is present at the interface, the charge in the hydrogen region of the voltammogram may not be proportional to the surface area of the electrode, as is generally assumed for conventional platinum [17].

In some instances in cyclic voltammetry work the presence of a HO3 oxide deposit at the interface may not be obvious. An example is shown in Fig. 3a of the reduction response for a hydrous oxide deposit in 3.0 mol dm⁻³ H₂SO₄ at 45 °C. Under these conditions the peak maxima for HO2 and HO3 reduction are at ca. 0.1 V and -0.04 V, respectively. In much work with platinum in acid the lower limit of the sweep is set at 0.0 V; this avoids complications due to large currents associated with hydrogen gas evolution. However, it is clear from Fig. 3a that if there are HO3 species present at the interface, these may not be reduced, especially if the sweep rate is reasonably rapid, e.g. 50 mV s⁻¹.

A further illustration is outlined here in Fig. 3b and c, where a large fraction of the hydrous oxide deposit survives an excursion well into the hydrogen region (to -0.08 V). The acid-grown hydrous oxide deposit was subjected to a negative sweep in base and an oxide reduction peak (possibly due to reduction of HO1 species) was observed ($E_{\max} \approx 0.27$ V) prior to the commencement of hydrogen gas evolution; the latter was reasonably vigorous at $E < 0.0$ V. However, the presence of a significant residue of oxide at the interface, at the end of the sweep in base, was confirmed by transferring the electrode back into acid solution and repeating the negative sweep (Fig. 3c). Two cathodic peaks of appreciable magnitude were observed in the latter case, $E_{\max} = 0.14$ and 0.05 V, which are characteristic of HO2 and HO3 reduction in acid solution under the conditions in question.

The HO3 component in the hydrous oxide film is not particularly labile, despite the fact that it is clearly thermodynamically unstable at low potentials. In the case of the first negative sweep in Fig. 4 the lower limit was set at 0.10 V, with the result that the HO1 and the vast majority of the HO2 component were reduced. Then, as shown in Fig. 4b, the negative sweep was repeated, the lower limit being extended to -0.03 V; the peak for HO3 reduction clearly dominates the response

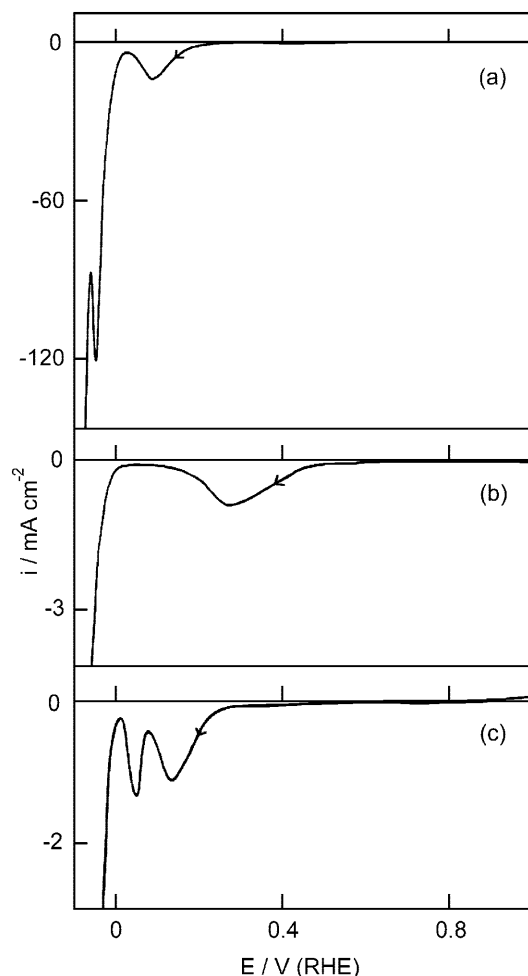


Fig. 3 Reduction profiles for a platinum electrode: **a** 1.0→−0.06 V, 5 mV s^{−1}, in 3.0 mol dm^{−3} H₂SO₄ at 45 °C, following hydrous oxide growth (0.5→2.1 V, 40 V s^{−1}, 1×10⁴ cycles) in the same solution; **b** 1.0→−0.08 V, 1 mV s^{−1} at 25 °C, in 1.0 mol dm^{−3} NaOH, following hydrous oxide growth (0.58→2.1 V, 40 V s^{−1}, 1×10⁴ cycles) in 1.0 mol dm^{−3} H₂SO₄; **c** second sweep, as in **b**, recorded after transferring the electrode back into 1.0 mol dm^{−3} H₂SO₄ at 25 °C

prior to hydrogen gas evolution in this case. The only features evident prior to gas evolution in the third negative sweep (Fig. 4c) are the hydrogen adsorption peaks, H_S and H_W.

With regard to the growth of the HO3 component in multilayer hydrous oxide films produced by potential cycling on platinum in acid solution, two of the more important variables are cell solution temperature and the lower limit used in the growth cycling process. The data are summarized here in Fig. 5. Comparing the data for HO3 reduction in Fig. 5a (for 25 °C) and in Fig. 5b (for 45 °C) shows that the amount of this oxide produced at the latter temperature is nearly an order of magnitude greater than at 25 °C. At both 25 °C and 65 °C the major product was the HO2 oxide; however, there are numerous variables in the system, e.g. number of cycles (or overall film thickness), upper limit, etc. At 45 °C (Fig. 5b) the yields of HO3 and HO2 in some

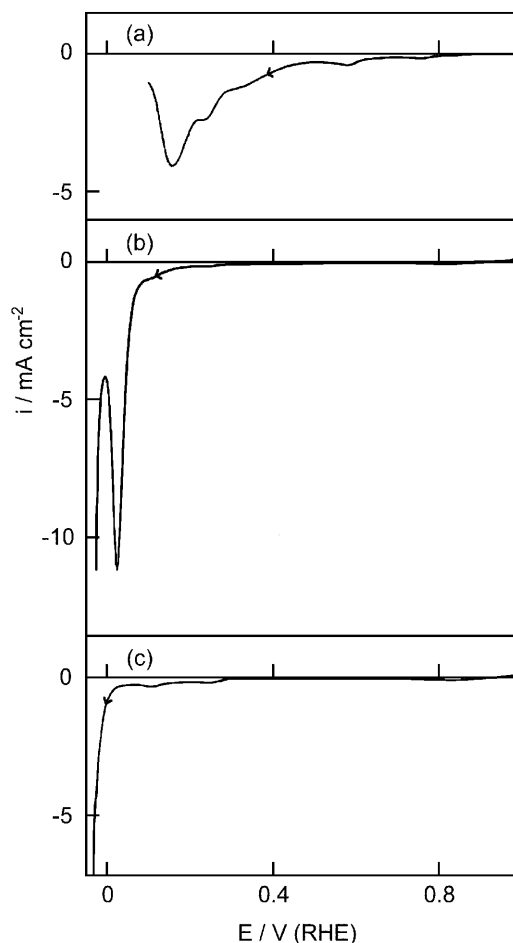


Fig. 4 Reduction profiles for a hydrous oxide coated platinum electrode in 1.0 mol dm^{−3} H₂SO₄ at 45 °C: **a** 1.0→0.1 V, **b** 1.0→−0.03 V and **c** 1.0→−0.03 V, 5 mV s^{−1}; the hydrous oxide was grown initially (0.45→2.1 V at 40 V s^{−1}, 1×10⁴ cycles) in the same solution; these were successive experiments without intermediate oxide growth

instances were approximately of equal magnitude. Decreasing the oxide growth sweep rate over the range 80 to 20 V s^{−1} increased the net yield of oxide (for 1×10⁴ cycles) without affecting the ratio of HO3 to HO2.

With regard to the appearance of the hydrous oxide reduction peaks on cycling, the response for HO1 was most obvious (or dominant), together with a trace of HO2, after a short number of oxide growth cycles (or with thinner β oxide deposits) (Fig. 6a). HO3 was observed after 3000 cycles (Fig. 6b); the latter diagram shows clearly the response for all three hydrous oxide components. With longer growth times and thicker films the responses for HO2 and HO3 were enhanced much more than that for HO1 (Fig. 6c). The growth and reduction of hydrous oxide deposits on platinum in the presence of other acids was not investigated in detail; however, limited work with a HClO₄ electrolyte showed that with thicker films there was a considerable overlap between the HO2 and HO3 reduction peaks (Fig. 6d). A curious feature evident in Fig. 6d for HClO₄ solution, and occasionally with H₂SO₄ solutions, e.g. in Fig. 4a,

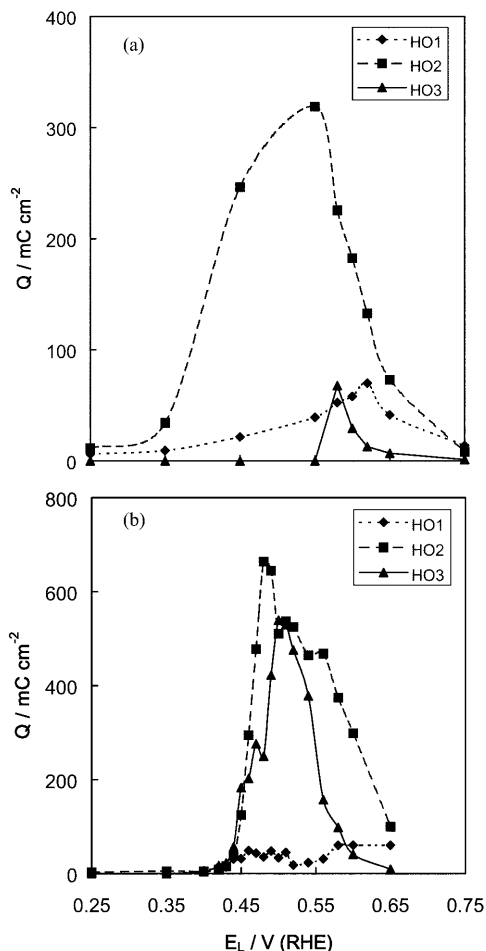


Fig. 5 Effect of the lower limit (E_L) used for oxide growth ($E_L \rightarrow 2.1$ V, 40 V s^{-1} , 1×10^4 cycles) on the charge associated with the HO1, HO2 and HO3 peaks observed for Pt in 1.0 mol dm^{-3} H_2SO_4 at **a** 25°C and **b** 45°C ; the films were reduced at 5 mV s^{-1} , $1.0 \rightarrow -0.05$ V

was the appearance of a small shoulder, or overlapping minor peak, on the positive side of the HO2 reduction peak.

It was demonstrated earlier that disturbing a metal surface by severe thermal [3, 4, 6] or cathodic [5] pretreatment, or by repeated growth and reduction of hydrous oxide films [18], activates the metal surface with regard to premonolayer oxidation, which in some instances may be quite dramatic. While producing the active state of the metal was not the major objective of the present work, it was noted that, after repeated growth and reduction of hydrous oxide films on an electrode, some unusual, low-level, anodic features appeared in the positive sweep with the evidently partially active, bare metal. These are labelled 1–4 in Fig. 7a; peak 1 is quite well known, even for conventional polycrystalline platinum, although its origin is a matter of debate [9]; the feature labelled 2 is less common but it was noted in an earlier review by Conway [19]; responses 3 and 4 were mentioned recently in work concerned with thermally pretreated platinum [3]. Some

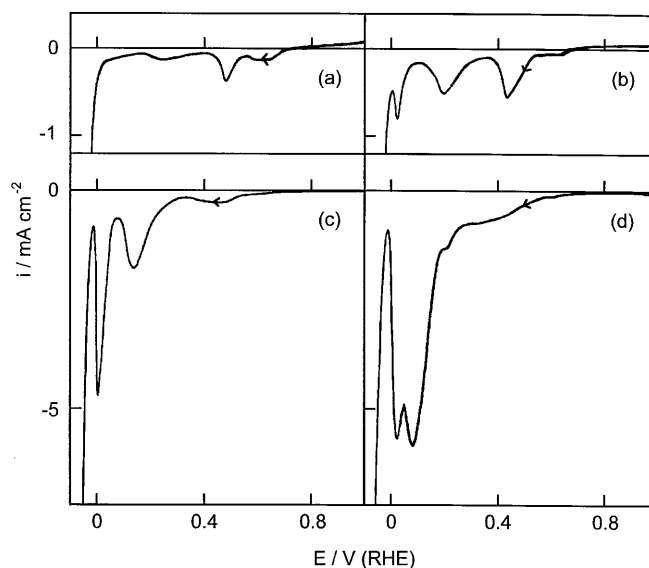


Fig. 6 Reduction profiles ($1.0 \rightarrow -0.08$ V, 1 mV s^{-1}), for hydrous oxide coated Pt in 1.0 mol dm^{-3} H_2SO_4 at 25°C : **a–c** the films were grown, $0.58\text{--}2.1$ V, 40 V s^{-1} , for **a** 1×10^3 , **b** 3×10^3 and **c** 1×10^4 cycles; **d** typical response (same reduction conditions) for a Pt oxide film grown ($0.45\text{--}2.1$ V, 40 V s^{-1} , 1×10^4 cycles) and reduced in 1.0 mol dm^{-3} HClO_4 at 25°C

of these minor responses are also evident in the first positive sweep in Fig. 7b; the magnitude of these peaks is significantly smaller in the second sweep (dashed line in Fig. 7b) while, at the same time, there was a significant increase in the height of the first conventional anodic peak (H_W).

The effect of sweep rate on the voltammetric response of these slightly activated electrodes is illustrated in Fig. 8. In both cases, at 5 mV s^{-1} (Fig. 8a) and 100 mV s^{-1} (Fig. 8b), the anomalous anodic features, peaks 1–4, were of low magnitude and, in the case of peaks 3 and 4, quite broad. At 5 mV s^{-1} , peak 1 appeared as a shoulder attached to peak H_W , whereas at 100 mV s^{-1} it appeared as a shoulder attached to H_S . This seemed to be partly due to the fact that the height of peak H_W , compared with H_S , is greater at 5 mV s^{-1} (evidently more of the adsorbed hydrogen was removed in the H_W region at the slower sweep rate). Also, the oxidation process associated with peak 1 was completed at a lower potential at 5 mV s^{-1} . Hence decreasing the sweep rate improved the resolution of peak 1 with respect to H_S but reduced it with respect to H_W . Altering the sweep rate did not affect the resolution of peak 2; it appeared in all cases as a shoulder attached to H_S . There was a marginal improvement in definition of peaks 3 and 4 at 5 mV s^{-1} , but even at the latter sweep rate the features in question were quite broad. The oxygen gas evolution response at $E > 1.40$ V (positive sweep) was much more evident at 5 mV s^{-1} (presumably the extent of oxidation of the metal surface is greater in this region at the slower sweep rate and this evidently favours the gas evolution reaction). Approximate values for the peak maximum potentials in the positive sweep in

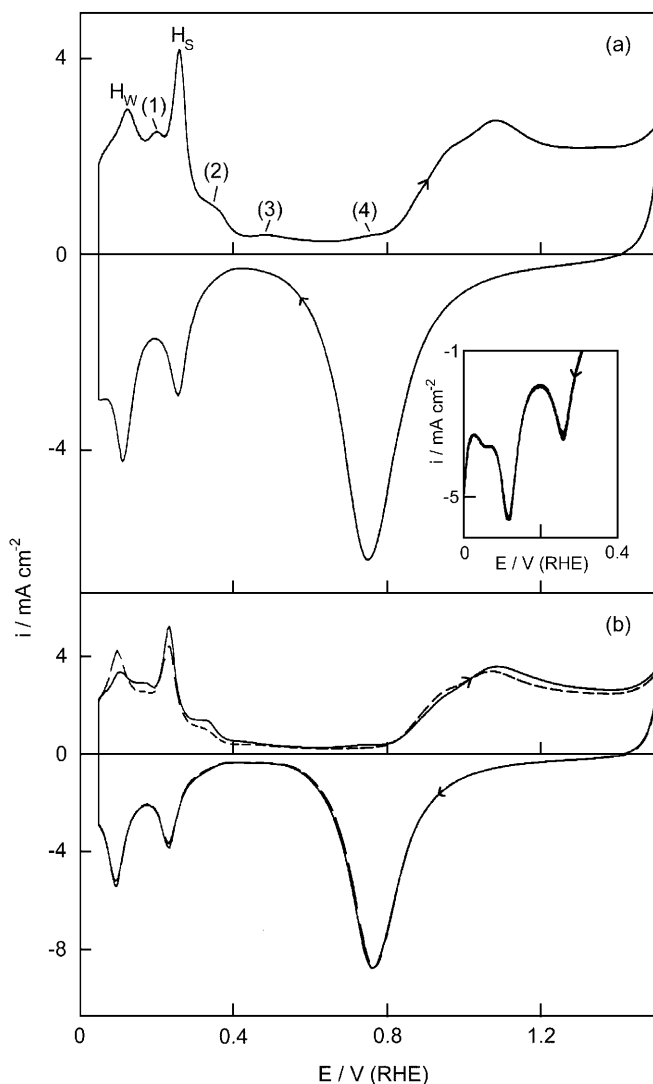


Fig. 7 Cyclic voltammograms ($0.05 \rightarrow 1.5$ V, 50 mV s^{-1}) recorded for oxide-free Pt in $1.0 \text{ mol dm}^{-3} \text{ H}_2\text{SO}_4$ at **a** 25°C and **b** 45°C ; the surfaces involved here are assumed to be somewhat active (these voltammograms were run after numerous hydrous oxide growth and reduction experiments with these electrodes; the nature of peaks 1–4 is discussed in the text). The inset in **a** shows the presence of a minor cathodic feature at ca. 0.05 V on extending the lower end of the sweep to 0.0 V; the dashed line in **b** represents a second sweep (note the increase in the H_W response)

Fig. 8a are as follows: 0.13 V (H_W), 0.20 V (1), 0.26 V (H_S), 0.35 V (2), 0.50 V (3), 0.72 V (4), and 1.06 V.

In the subsequent negative sweep the peak maximum potential for the monolayer oxide reduction process occurred at a more positive potential at the slower sweep rate (the maximum in question, at ca. 0.78 V at 5 mV s^{-1} , is not shown here in Fig. 8a). The only other unusual feature in the negative sweep is the presence of a minor cathodic maximum at ca. 0.06 V (after the response for removal of weakly bound hydrogen) in Fig. 8b. This feature was not observed in the sweep recorded at 5 mV s^{-1} (Fig. 8a); it is present in the inset in Fig. 7a, where the sweep rate involved was 50 mV s^{-1} .

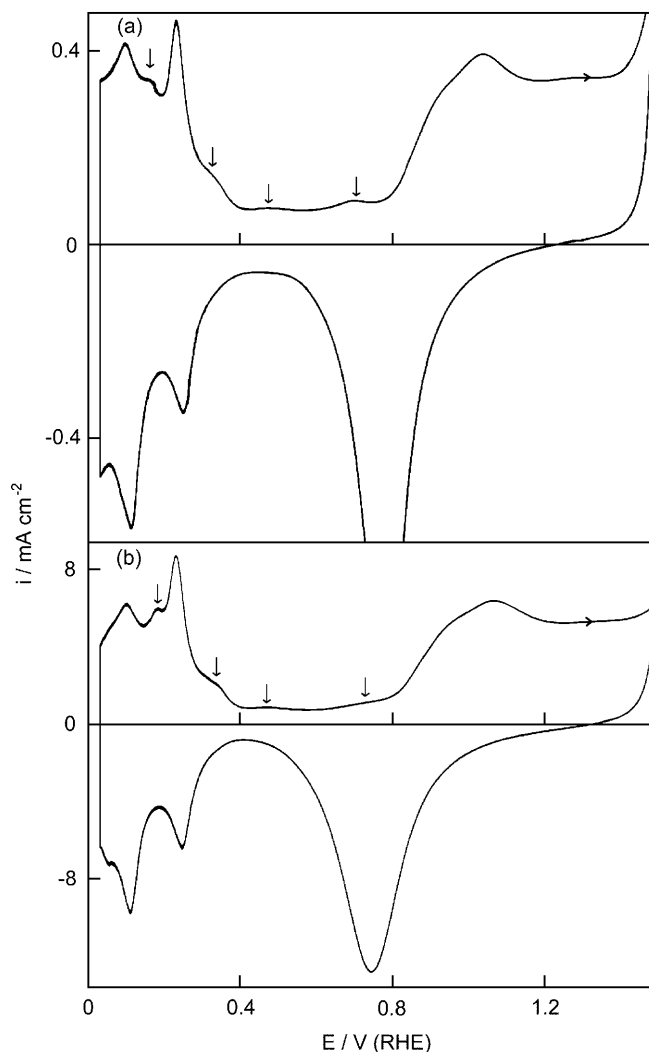


Fig. 8 Cyclic voltammograms ($0.05 \rightarrow 1.5$ V) recorded for Pt in $1.0 \text{ mol dm}^{-3} \text{ H}_2\text{SO}_4$ at 25°C at **a** 5 mV s^{-1} and **b** 100 mV s^{-1} ; in both cases these voltammograms were run after a hydrous oxide growth and reduction experiment (same conditions for oxide growth and reduction as in Fig. 6c); the arrows indicate the small anodic peaks which are numbered in Fig. 7a

Discussion

One of the main objectives of this work is to highlight the fact that the electrochemical behaviour of platinum in aqueous media beyond the traditional accounts [17, 19] of this electrode system. According to both Taylor [10] and Somorjai [13], roughness, disorder, metastable states or active sites are essential ingredients for high surface catalytic activity. From a fundamental (or research) viewpoint this is a problem. Modern surface science techniques, e.g. STM and AFM, work best with atomically flat or stepped surfaces (even step atoms, especially at kinks, are difficult to image [20]). These are low-energy surfaces; the inability to bridge the gap between these and high-energy surfaces was pointed out by Somorjai [13] (“much less information [is] available from

surface science studies on the bonding of adsorbed molecules at atomically rough surfaces”).

The involvement of unusual high-energy surface atoms explains: (1) premonolayer oxidation effects (minute particles of metal undergo oxidation in the double layer region, i.e. at potentials lower than that of the extended, low-energy, conventional surface layer of the same metal); (2) the fact that electrocatalytic processes quite often commence and terminate at potentials well within the double layer region (such reactions are often mediated [11] by the active state of the metal, or the oxidized state of the latter, present at active sites); (3) the reduction of hydrous oxide species (Fig. 1) at unusually low potentials (the primary product of such reactions being the highly active state of the metal).

The basic assumption involved in the present work, i.e. that increasing the disorder of the surface decreases the energy or potential required to remove electrons from the metal, is in agreement with earlier work function data [21]. However, to identify the nature of the active state is quite difficult. Such a state, generated by reduction of a hydrous oxide species, $\text{PtO}_2 \cdot n\text{H}_2\text{O}$, is intrinsically unstable; this is why multilayer hydrous oxide reduction reactions (Fig. 1) are usually one-shot, irreversible reactions, i.e. the metal surface returns rapidly to its conventional form. However, as a result of this process the surface roughness is usually increased [22] and there is often retention of a residue of the active state; this was demonstrated earlier for palladium [18] and is assumed to be the origin of the minor anodic peaks labelled 1–4 in Fig. 7.

A surprising feature of the multilayer hydrous oxide reduction reaction is the appearance of three, rather than one, cathodic peaks. These were ascribed earlier [3] to different states of metal atom activity; however, the nature of the oxide may also be of some significance. HO1 is assumed to be an uncharged oxyspecies, $\text{PtO}_2 \cdot n\text{H}_2\text{O}$ or $\text{Pt}(\text{OH})_4$, as it does not exhibit a super-Nernstian E/pH [15] shift. Since HO2, and apparently HO3, exhibit such a shift, the species involved are assumed to be of anionic character, e.g. $\text{Pt}(\text{OH})_6^{2-}$ (this is evidently why, as illustrated in Fig. 3b and c, these materials remained largely unreduced in base even in a sweep extending to -0.08 V; such behaviour was discussed earlier [15] for the HO2 deposit). Another factor of some importance may be that HO2 contains a significantly higher content of dissolved anions (HSO_4^- or SO_4^{2-}) than HO1 [1, 23]. The anion content of HO3 has not been investigated; it may be quite substantial. This would explain the quite low reduction potential of HO3 in $3.0 \text{ mol dm}^{-3} \text{ H}_2\text{SO}_4$ (Fig. 3a); the high activity of the anions in solution increases the stability of the complex with respect to reduction. The difference in the nature of the incorporated anion may also explain the change in resolution of the HO2 and HO3 reduction peaks on working with HClO_4 (Fig. 6d), compared with H_2SO_4 , electrolyte.

The type of unusual response at low potentials shown in Fig. 2 has been observed in previous work reported

from this laboratory [2, 24]. The cathodic currents at the early stages of the positive sweep are attributed to continuing partial reduction of the HO3 deposit, i.e. the lower limit was not sufficiently negative to yield total reduction of this material in a rapid manner. A surprising feature in this case was the rather invariant nature of the H_s , and to a large degree the α oxide, responses. The real area of the metal electrode evidently does not change dramatically after the initial period of oxide reduction below 0.2 V at the beginning of the first positive sweep.

The four minor anodic peaks labelled 1–4 in Fig. 7 are assumed to be premonolayer oxidation responses, i.e. they reflect the reaction of residues of the highly active states of the metal surface remaining after repeated disruption of the outer layers of the metal in earlier hydrous oxide growth and reduction work (such behaviour was described earlier for palladium [18]; the effect was even more dramatic for the latter metal). Irrespective of their interpretation, the appearance of these four features is not novel. Peaks 1 and 2 have been mentioned by Conway (they are labelled H_2 and H_0 in fig. 17 of [19]). Peak 1 is a very well-known feature in platinum electrochemistry and has been referred to as the “anomalous third peak” in the hydrogen region [19]. It lacks the typical characteristics of the other hydrogen peaks, e.g. (1) it rarely, if ever, has a cathodic counterpart and is usually absent in base, (2) the kinetic response for the peak 1 process is quite different in character [25] (it is of much more prolonged character) from that of the other hydrogen peaks, (3) a similar dramatic difference is evident in the entropy values quoted [19] for these peaks [the negative value for the peak 1 process is unusually large], (4) peak 1 appears consistently in repeated sweeps only when the upper limit of the cycle is at least within the early stages, e.g. 1.0 V, of the monolayer oxide formation/removal region [25], (5) the charge associated with peak 1 is also enhanced [25] on holding the potential of the electrode at more negative potentials, e.g. 0.06 or 0.02 V (this is probably due to hydrogen activation of the metal surface [5]).

Peak 1 appears to be associated with a disturbed or activated state of the platinum surface; to observe this peak in a consistent manner on cycling it is necessary to maintain the activity of the surface at a high level by place exchange of metal atoms in the outer layer [item (4) above]. Alternatively, one can enhance the peak 1 response [item (5) above] by hydrogen embrittlement pretreatment (as outlined recently for gold [5], this also enhances the anomalous, active state, response). In fact, peak 1 has far more of the characteristics of an active platinum/hydrous oxide than a $\text{H}_{\text{ads}}/\text{H}^+$ transition, e.g. the absence of this peak in base is the type of behaviour expected on the basis of the super-Nernstian E/pH shift described earlier [1] for hydrous oxide systems. Further support for an oxide involvement in the redox behaviour of platinum in acid at ca. 0.2 V is provided by the appearance of a major metal oxidation response in this

region with thermally activated platinum [3, 4] and the marked changes in electrocatalytic activity reported for this electrode system [26] at the same potential value. The unusual character of the peak 1 response was discussed earlier by Woodard and co-workers [25]. They assumed the involvement of active surface state phenomena and explained most of their observations in terms of anion adsorption effects. Participation of anions in anomalous behaviour is not excluded here; as pointed out earlier [1], these species are assumed to be involved in Pt (HO₂) formation and, according to Conway and co-workers [27], premonolayer oxidation of gold in acid generally occurs at an anion-coated surface. The objection to an interpretation based solely on anion adsorption effects is that it cannot explain the correlation between premonolayer oxidation and multilayer hydrous oxide responses, or the dramatic enhancement in electrocatalytic activity observed in the region of the anomalous peak (it is assumed for instance that strong anion adsorption should inhibit, rather than enhance, electrocatalytic oxidation processes; this is contrary to the observed behaviour for platinum in acid, where high activity with respect to oxidation is often observed above 0.2 V).

Peak 2 in Fig. 7 is also evident in earlier work by Arvia and co-workers [28, 29, 30], Nakamura and Kita [31], Woodard and co-workers [25] and Hoare [32]. This feature ($E_{\max} \approx 0.35$ V) overlaps with H_S , i.e. the peak associated with the oxidation of strongly bound hydrogen. Sometimes this feature has a cathodic counterpart in the negative sweep, i.e. the process involved behaves in a reversible manner. This is particularly evident in the work of Arvia and co-workers [28, 29, 30], who activated the metal surface by extensive cycling (the use of the latter again suggests that an active state of the surface is involved). The appearance of peak 2 in Arvia's case (see fig. 7 in [29]) was accompanied by a reduction in peak H_W and an increase in H_S . Similar changes were observed in the present work; in Fig. 7a, H_W is quite small, while in Fig. 7b the reduction in the height of peak 2 on going from the first to the second cycle is accompanied by an increase in H_W . Such behaviour was pointed out also by Woodard and co-workers [25], who attributed the effect to a combination of surface restructuring plus the involvement of a hard-to-reduce (or recalcitrant) oxide.

The presence of peaks 3 and 4 has been noted (and discussed in considerable detail) in earlier publications from this laboratory [3, 33]. These features, which are quite small here, may be greatly enhanced by thermal [3] pretreatment and the processes involved are assumed to be active metal/hydrous oxide transitions. Anomalous responses for platinum in aqueous media obviously do not agree with the accepted behaviour pattern for this electrode system and are often attributed to the involvement of impurities. Highly active, usually quite localized, surface states exhibit a number of the characteristics of impurity species, e.g. they display a different type of electrochemistry (they are assumed to be oxidized to β , rather than α , oxide species), they ap-

parently adsorb differently (it has been suggested [4] that superactive platinum is reluctant to adsorb hydrogen, the atoms involved being in an unusually electropositive state), their oxidation potentials are quite different from that of the surface of the conventional metal (this assumption is supported by work function data [21]) and, finally, the coverage of these active surface states may be gradually enhanced (rather like the accumulation of an impurity species) by prolonged cathodic polarization [5]. However, impurity effects cannot explain the correlation between anomalous responses for the active metal/hydrous oxide transition and electrocatalysis [11], while the kinetics of surface activation under cathodic pretreatment conditions in the case of platinum in acid solution [34, 35] are not characteristic of the behaviour of low-level impurities.

One of the problems of dealing with the active states of metal surfaces is the variety of such states: according to the present work there are four for platinum in acid, peaks 1–4 in Fig. 7a, corresponding to four states of decreasing surface metal atom activity (in fact the range of surface metal atom activity may be quite extensive, the number of peaks and their potential values being strongly influenced by the nature of the hydrous oxide species involved). Furthermore, the occupancy of the different states (or magnitude of their oxidation responses) is dependent on the electrode pretreatment conditions [3]. Optimizing a particular surface site or anomalous response, especially with regard to maximizing the rate of an electrocatalytic reaction associated with the same [11], may be a very challenging task.

Much of the uncertainty as to the interpretation of the electrochemical responses (whether these are due [14] to hydrogen, oxygen species or anions) at low potentials for Pt(111) surfaces in acid solution may be resolved by assuming the presence of residual surface defects which are not easily detected [3] and are evidently appreciably more common [12] than was generally assumed. With a partially active, thermally pretreated platinum surface one may assume the presence of a hydrogen region (up to ca. 0.35 V) of somewhat uncertain H_{ads} capacity (the more active, or more electropositive, surface metal atoms being less likely to function as hydrogen adsorption sites). The more active metal atoms are prone to undergo oxidation at low potentials, yielding hydrous oxide species. Since, as outlined here earlier, there is an anion involvement in the latter reaction, all the species mentioned by Lazarescu and Clavilier [14] (hydrogen, oxyspecies and anions) may be involved in the anomalous voltammetric features of thermally pretreated Pt(111) electrodes in acid solution. Certainly the anomalous response for such an electrode over the range 0.0–0.5 V (RHE) in fig. 2A of [12] seems to be split into two regions, probably involving H_{ads} below 0.3 V and an anomalous hydrous oxide (and anion) reaction above 0.3 V. The sharp butterfly peak in the response for these Pt single-crystal surfaces may not be quite unique to this type of electrode. Somewhat similar behaviour is evident (although the cathodic response is subject to some

inhibition) in responses recorded for polycrystalline platinum when the latter was also subjected to severe thermal pretreatment (see fig. 4a in [4]).

The hydrous oxide growth reaction (Fig. 5) was not investigated in detail in this project. It is interesting that raising the cell temperature from 25 °C in Fig. 5a to 45 °C in Fig. 5b dramatically increased the percentage yield of HO₃. A somewhat similar effect is observed with thermally activated Pt electrodes, where the anodic peak associated with premonolayer oxidation at ca. 0.25 V is also enhanced on raising the cell temperature [4]. Evidently elevating the cell temperature favours the promotion of surface metal atoms to high-energy states, thereby enhancing the premonolayer oxidation response at low potential, the net amount of hydrous oxide formed on repetitive cycling and the percentage of HO₃ in the product.

Conclusions

The main objective of the present work is to highlight the fact that, contrary to the conventional view of platinum electrochemistry which relates to rather stable, low-energy, surface states of the metal, the oxide and hydride responses of this electrode system in some instances may overlap; indeed, in extreme cases an oxide reduction process may occur (Fig. 3a) within the hydrogen evolution region. Such anomalous behaviour appears to be rather widespread; it is also evident, for instance, in the case of silver [36] and copper [37] electrodes in base (these were investigated using surface enhanced Raman spectroscopy).

Anomalous behaviour, which is assumed to be quite important in electrocatalysis [11], was considered here in terms of an interaction between active states of the metal surface and hydrous oxide species. However, there is a further entity, subsurface oxygen, which may also be of some significance with regard to such behaviour. The participation of this unusual species in the oxidation of gaseous CO on platinum was discussed recently by von Oertzen and co-workers [38].

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