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A survey of platinum hydrous oxide electrochemistry at elevated temperature: evidence for a new component in the β-deposit

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Hydrous (or β) oxide films produced on platinum in acid at room temperature usually give rise to two reduction peaks, in addition to the monolayer oxide response, on a negative sweep extending to about 0 V. This has been attributed to the presence of two hydrous oxide components (designated as HO1 and HO2) in the film. It was confirmed in the present work that under more severe conditions, 3.0 M H_2SO_4 at 60 °C, an additional, quite significant, peak – apparently due to the presence of a further hydrous oxide component (HO3) – may be observed. The approximate peak maximum potential values (RHE scale) were 0.4 V (HO1), 0.2 V (HO2) and 0.0 V (HO3); the E_p values are given here only as a guide: the processes involved occur under very irreversible conditions and the values vary with factors such as sweep rate, film thickness, temperature, etc. The differences in behaviour between these components is assumed to be due to factors such as the degree of aggregation and compactness in different regions of the gel-type, amorphous deposit. A brief account is given of the increasing evidence from different laboratories of unusual responses for platinum electrodes in aqueous acid solution.

1. Introduction

Platinum is frequently the electrode material of choice in both fundamental and applied work in electrochemistry. Its main advantages are high corrosion resistance and marked electrocatalytic activity. The conventional view of the behaviour of platinum in aqueous media [1], in terms of the hydrogen, double layer and monolayer oxide (or OH_{ads} and O_{ads}) phenomena, has received widespread acceptance. However, it was suggested recently [2, 3] that more attention should be devoted to an alternative anodic product of platinum, namely platinum hydrous oxides. These are not only interesting materials in their own right, but they may well have an important role in electrocatalysis. A review of the involvement of these hydrous oxide species in the electrocatalytic behaviour of gold in aqueous media was also published recently [4].

Accounts of platinum hydrous oxide electrochemistry, with references to recent work in other laboratories, were published recently [5, 6]. Both the formation and reduction of these materials (especially in multilayer form) at a platinum electrode surface occur in a very irreversible manner. The source of inhibition in both cases is assumed to be associated with the lattice coordination number (LCN) value, or lattice coordination energy, of surface metal atoms. This is rather high initially for most surface metal atoms in the case of the oxide-free electrode surface; the barrier to hydrous oxide formation is related to the need for most interfacial metal atoms to decrease their LCN value (and lattice energy) so that O, OH and OH_2 ligands can be coordinated to the metal ion formed on oxidation, usually the product is a Pt(IV) species [7, 8]. Conversely, in the reduction process the starting material is the rather low density hydrous oxide material. Reduction is assumed to yield, as an initial product, poorly lattice stabilized, low LCN value, high energy (or active) metal atoms, hence the high overpotential for reduction. A more detailed account of this approach is available [6].

Hydrous oxide deposits on the parent metal are usually produced by d.c. polarization [9, 10], potential cycling [11] or potential pulsing [12] techniques. Complications in this area include the fact that the initial deposit is usually duplex in character, with an inner, conventional (or α) monolayer oxide film (which may be selectively removed [13, 14]), and an outer, usually multilayer (β), deposit of hydrous oxide. The notation used here is from the work of Shibata [15], a brief synopsis of whose contribution to this area is given in a review of hydrous oxide electrochemistry [16]. Since the hydrous oxide tends to be a rather amorphous, low density, water swollen, gel-type material detailed information as to its structure and composition is generally lacking. Reduction of a hydrous β-oxide film on platinum in acid under potential sweep conditions usually gives rise to two main peaks [3, 17]; these occur at more negative potentials than the response for removal of the inner

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monolayer oxide. The current view is that the β-oxide deposit may contain two components, designated as HO1 and HO2 (with an appropriate choice of oxide growth conditions a β-layer composed of virtually pure HO1 may be produced [17] while it is possible, with a two-component β-layer, to selectively reduce the HO1 material [18], thus producing a virtually pure HO2 deposit). At a moderately slow negative sweep rate the HO1 oxide reduces in acid or base [5, 17] to yield a peak with a maximum at about 0.37 V. Oxide reduction potentials are of no thermodynamic significance in this area, they vary with sweep rate as the overall reaction involved is usually irreversible (especially with thick films). The HO2 oxide reduces in acid at about 0.2 V (E_{max} occurs at ~0.17 V). As discussed in detail recently [5], HO2 deposits are not readily reduced in base at room temperature, the material involved being additionally stabilized at high pH due to excess OH^- ion coordination. It was suggested recently [5] that the HO1 material is some type of uncharged hydrated oxide or hydroxide (possibly $PtO_2.xH_2O$ or $Pt(OH)_4.yH_2O$) species while HO2 is assumed to be an anionic species (e.g., $[Pt(OH)_6]^{2-}$ or $[PtO(OH)_22H_2O]^{2-}$) with counterions present in the intercalated water regions of the deposit. The oxide species quoted here are assumed to exist in an aggregated or polymerized form in the layer; the HO2 material usually also contains foreign (e.g., HSO_4^-) anions [8].

The present work arose initially in connection with methanol/air fuel cells [19]. Hence, the emphasis on the behaviour of platinum in relatively concentrated acid at elevated temperature. In some instances in this earlier work [3] minor reduction peaks (which at that stage were largely ignored) were observed with hydrous oxide coated electrodes at potentials more negative than that of the large HO2 reduction peak. In the present work it was found that at elevated temperature a further hydrous oxide component (which for consistency may be labelled HO3) may be distinguished that reduces on platinum in acid at 60 °C only at, or below, 0 V. The discovery of this new component may explain the discrepancy pointed out earlier by other authors [20] between charge values reported for platinum hydrous oxide reductions in acid as recorded under (i) single sweep, and (ii) a combination of constant potential plus sweep, conditions.

2. Experimental details

The conditions used in this work were similar to those outlined earlier [3, 6, 19]. The working and counter electrodes consisted of bright platinum wires (1.0 mm diameter, ~0.5 cm^2 exposed surface area, Johnson and Matthey PLC, Puratronic grade) sealed directly into glass. Solutions were made up using Analar grade chemicals and triply distilled water. Potential values were measured (and are reported) with respect to a hydrogen reference electrode in the same solution. The solution in the working compartment of the cell was usually purged of dissolved oxygen, prior to recording cyclic voltammograms or oxide reduction sweeps, using a flow of purified nitrogen gas.

The electrochemical equipment consisted of a potentiostat (Wenking, model LT-78), programmed with a function generator (Metrohm VA scanner, model E612). Responses were recorded using a Rikadenki (RW-21) XY recorder. A Luggin capillary was used to minimize errors due to iR_e drop across the electrolytic solution.

3. Results

3.1. *Basic cyclic voltammetry*

A typical cyclic voltammogram for platinum in 1.0 M H_2SO_4 at 60 °C is shown in Fig. 1(a). Two pairs of peaks (H_w/H_w' and H_s/H_s') for processes that behave reversibly are evident in the hydrogen desorption/adsorption region (0 to ~0.4 V) and after the double layer region, on the positive sweep, surface oxidation (or OH_{ads} and O_{ads} formation) commenced at ~0.8 V. On the subsequent negative sweep the oxide reduction process gave rise to a rather symmetrical cathodic peak with a maximum at ~0.78 V. A minor, but apparently quite significant, feature of the positive sweep is the small broad peak (labelled X in Fig. 1(a)) in the double layer region (extending from about 0.6 to 0.8 V, with a maximum at about 0.7 V) which, as pointed out earlier [3], and confirmed in the present investigation, Fig. 1(b), is even more pronounced at 80 °C.

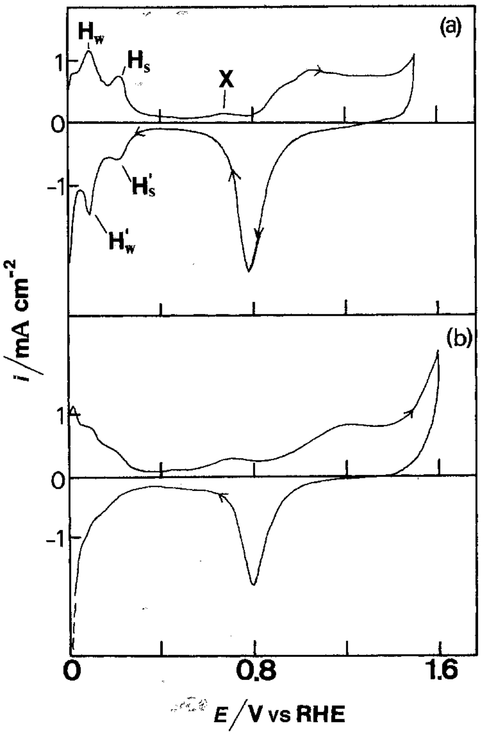

Fig. 1. Cyclic voltammogram (50 mV s^{-1}) for a bright platinum wire electrode in 3.0 M H_2SO_4: (a) 0 ⟶ 1.5 V at 60 °C, (b) 0 ⟶ 1.6 V at 80 °C.

3.2. *Thick hydrous oxide film reduction*

Examples of negative sweeps recorded for electrodes coated with hydrous oxide films grown by cycling for different periods of time (with a relatively low oxide-growth upper limit of 1.9 V) are shown in Fig. 2. The reduction of the film commenced at about 0.85 V and usually a series of about five cathodic peaks, see Fig. 2(c) were observed, although occasionally some of these were quite small. The peak potential values ranged (with increasing growth time or thickness) as follows: (A) 0.70 to 0.55 V, (B) 0.55 to 0.27 V, (C) 0.29 to 0.15 V, (D) 0.1 V, (E) 0.02 to −0.02 V. Peak A and (to an even greater extent) peak D were small: peaks B and C seemed to correspond to the reduction of the oxides HO1 and HO2, respectively, as described earlier [3]. Peak E at about 0.0 V was often quite significant, e.g. Fig. 2(d); it overlapped appreciably with (and at lower temperature is probably overshadowed by) the response due to hydrogen gas evolution.

Some further examples of hydrous oxide reduction behaviour for films grown using different oxide growth upper limits, are shown in Fig. 3. The magnitude of the peaks (especially C) varied initially (commencing with a fresh electrode), as pointed out elsewhere [21], for the same set of growth conditions, from one run to another. Apparently the ease of oxide growth or the amount produced was influenced by the metallurgical state of the outer layers which, in turn, is determined by factors such as electrode history.

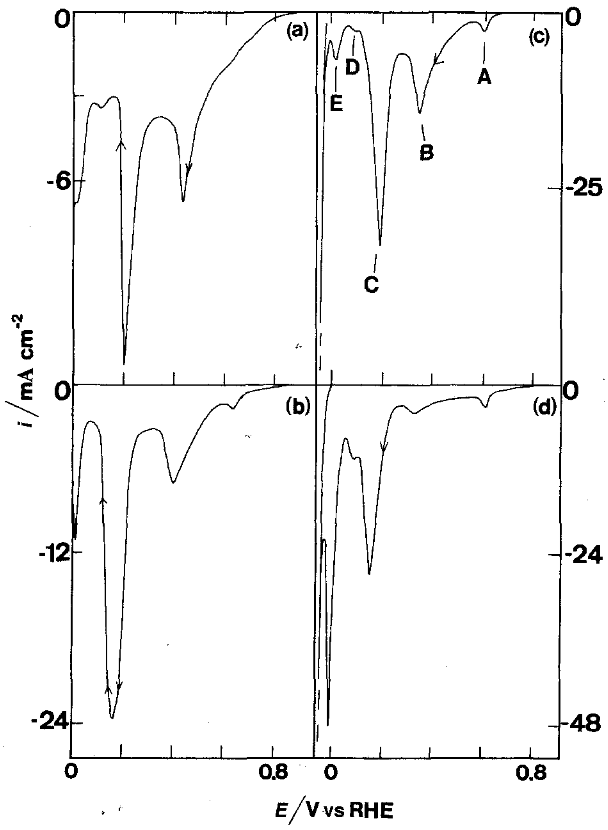

Fig. 2. Typical reduction profiles (1.0 ⟶ 0.0 V, 10 mV s^{-1}) for hydrous oxide coated platinum electrodes in 3.0 M H_2SO_4 at 60 °C. The oxides were grown by potential cycling (0.58 ⟶ 1.9 V, 80 V s^{-1}) for (a) 2, (b) 4, (c) 6 and (d) 10 min.

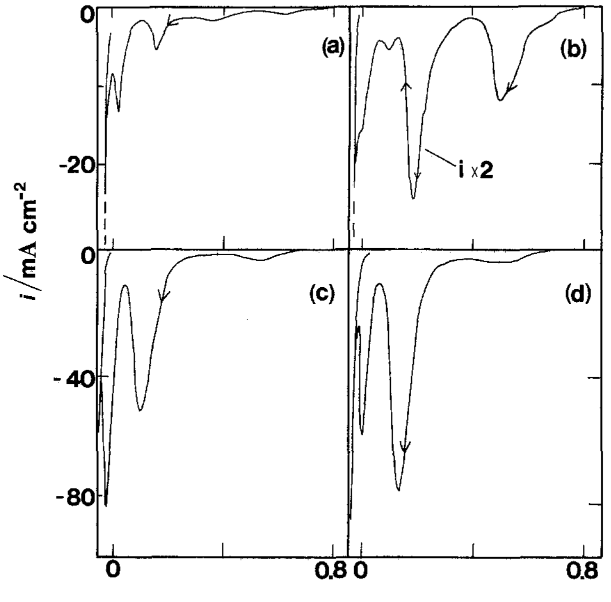

Fig. 3. The effect of the upper limit during oxide growth (in 3.0 M H_2SO_4 at 60 °C) on the subsequent reduction profile (1.0 ⟶ −0.05 V, 10 mV s^{-1}). Oxide growth conditions were: 0.58 ⟶ E_u, 80 V s^{-1} for 10 min, with $E_u = 1.8$ V (a), 2.1 V (b) 2.2 (c) and 2.3 V (d).

In the curve shown in Fig. 3(a), upper limit for oxide growth at 1.80 V, the extent of oxide growth was low and peak D (at ~0.1 V) was absent on the subsequent reduction sweep. With the upper limit for growth at 2.10 V, Fig. 3(b), peak D was present in the subsequent reduction sweep while peak B was quite broad. When this experiment was repeated, without withdrawing the electrode from the cell, peak C (for HO2 reduction) was enhanced; the peak remained sharp but the current density for the maximum was about three times greater. Two further examples, for higher oxide growth limits, are shown in Fig. 3(c) and (d). The predominant features in both cases were peaks C and E.

An interesting feature of this work was that in a repeat of the experiment shown in Fig. 3(c) it was possible to eliminate peak E. As outlined in Fig. 4, when the negative sweep was stopped at the early stages (or even just prior to the onset) of peak E for a short period (e.g., 2 min) the only faradaic response observed in the lower region on resuming the sweep was that associated with hydrogen gas evolution below 0.0 V (i.e., the oxide involved in peak E was reduced during the arrest period).

The effect of oxide growth cycling rate on the charge associated with the subsequent reduction (or the extent of oxide growth) is illustrated in Figs 5 and 6. It is clear that for a constant number of oxide growth cycles the net amount of oxide produced (or the mean amount produced per cycle) decreased (for oxide growth sweep rates ≥ 20 V s^{-1}) with increasing oxide growth sweep rate, Fig. 6. The effect of oxide reduction sweep rate is illustrated in Figs 7 and 8. In all cases reduction commenced at a significant rate at about 0.6 V. For the hydrous oxide reduction processes peak heights (i_p) were proportional to

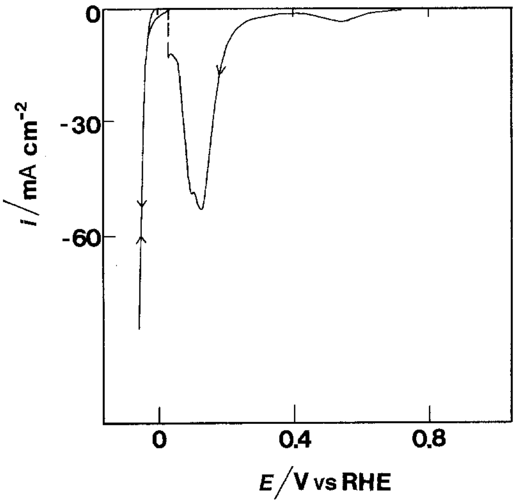

Fig. 4. Repeat of the experiment shown here in Fig. 3(c). The electrode was not even removed from the cell. In this case the electrode potential, during the negative sweep, was held constant for ~2 min at 0.03 V until the reduction current had decayed to zero. The sweep was then resumed: note the absence of peak E under such conditions.

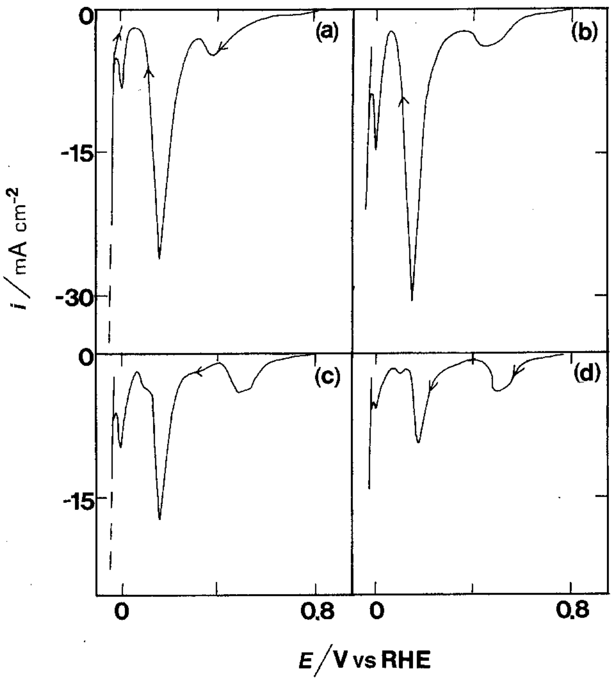

Fig. 5. Effect of oxygen growth sweep rate on the reduction profile (1.0 ⟶ 0.05, 10 mV s^{-1}) after growing the oxide by cycling the electrode potential 0.58 ⟶ 2.1 V, 3158 cycles at (a) 10, (b) 20, (c) 40 and (d) 80 V s^{-1}; 3.0 M H_2SO_4 at 60 °C.

sweep rate while peak maximum potential (E_p) decreased with increasing oxide reduction sweep rate. For the experiments shown in Fig. 7 the net charge for oxide reduction (in mC cm^{-2}) varied with reduction sweep rate in the following manner: 635.9 (5 mV s^{-1}); 577.3 (10 mV s^{-1}); 536.8 (20 mV s^{-1}); 581.2 (40 mV s^{-1}).

The general complexity of the hydrous oxide reduction response should not be underestimated. An example is given in Fig. 9(a) of a reduction sweep that shows seven maxima. The behaviour of the system at room temperature, Fig. 9(b), appeared a little simpler. There is, for instance, no indication of reduction peak E at 0 V. However, this may be deceptive: significant reduction currents were still present at, or below, 0.1 V. It is quite possible that some unreduced oxide was present at 0 V, even

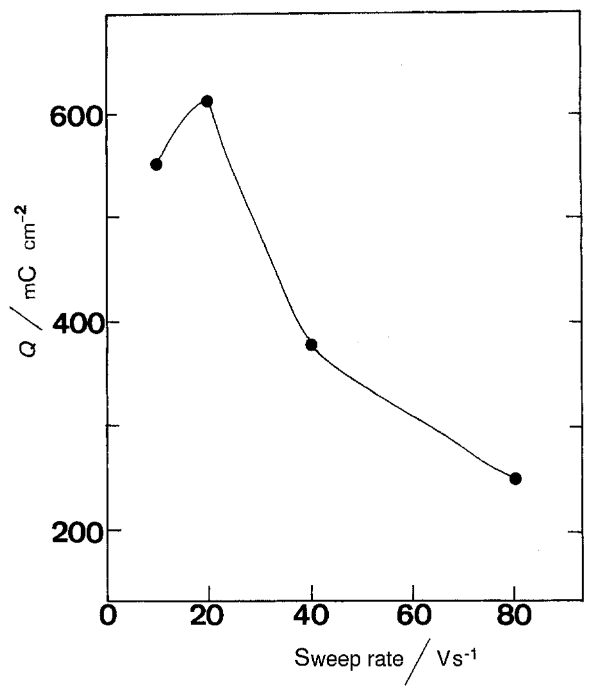

Fig. 6. Plot of the net cathode charge from 0.7 V to the onset of hydrogen gas evolution at −0.02 V, as a function of the oxide growth sweep rate. Data obtained from the experiments described in Fig. 5.

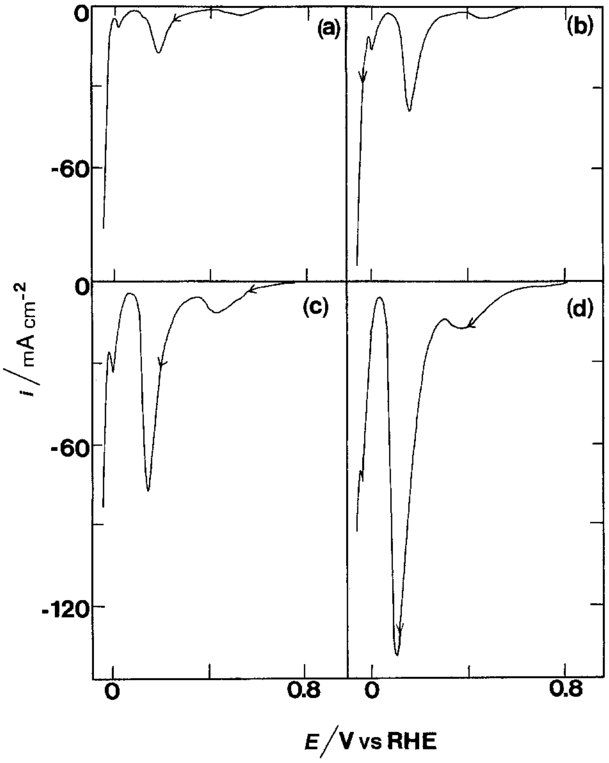

Fig. 7. Effect of the negative (analytical) scan sweep rate on the reduction profile. The oxide was grown in each case by cycling 0.58 ⟶ 2.1 V, 80 V s^{-1} for 8 min and then reduced (1.0 ⟶ −0.05 V) at (a) 5, (b) 10, (c) 20 and (d) 40 mV s^{-1} in 3.0 M H_2SO_4 at 60 °C.

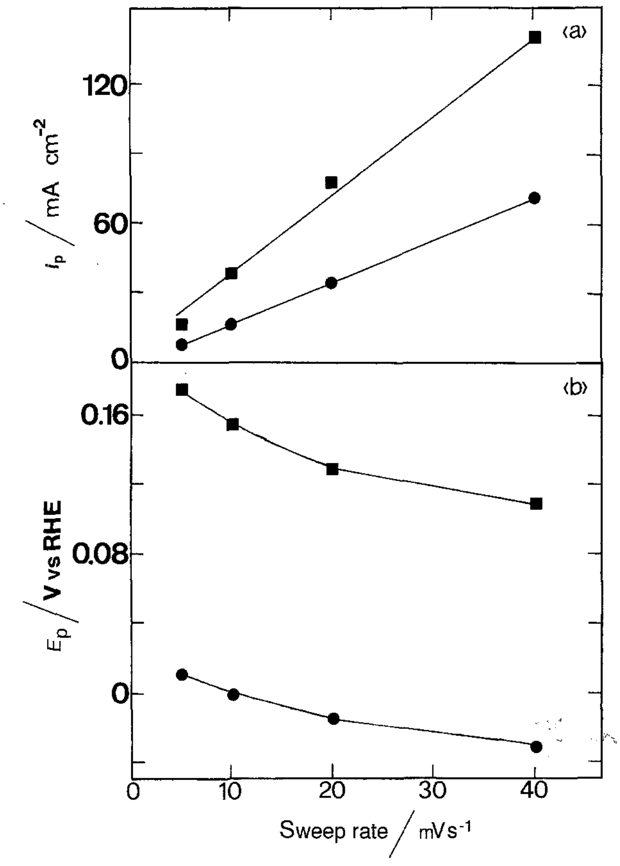

Fig. 8. Effect of the negative (analytical) scan sweep rate on (a) peak current (i_p) and (b) peak potential (E_p): data derived from Fig. 7: (■), peak C; (●) peak E.

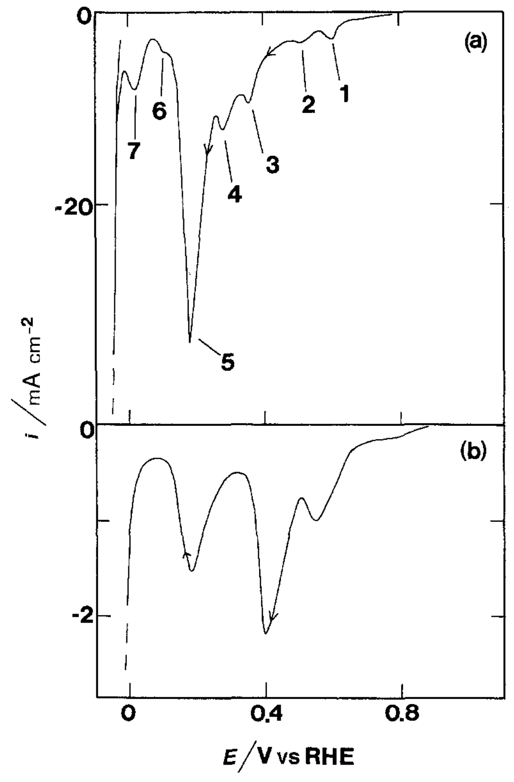

Fig. 9. Typical reduction profiles (1.0 ⟶ −0.05 V, 10 mV s^{-1}) for hydrous oxide-coated platinum electrodes in 1.0 M H_2SO_4 at (a) 60 and (b) 20 °C. The oxide growth conditions were as follows: (a) 0.58 ⟶ 1.9 V, 20 V s^{-1} for 20 min; (b) 0.58 ⟶ 2.1 V, 80 V s^{-1} for 2 min.

though at 20 °C there was no indication of an oxide reduction peak close to, or overlapping with, the hydrogen gas evolution reaction.

4. Discussion

The cyclic voltammogram shown for platinum in acid in Fig. 1(a) exhibits the usual behaviour for this system with, on the positive sweep, the three standard [1] processes, viz. (i) removal of adsorbed hydrogen (0 to ~0.35 V), (ii) double layer charging (0.35 to ~0.8 V) and (iii) monolayer oxide (or OH_{ads} and O_{ads}) formation (above 0.8 V). The processes responsible for the two pairs of peaks in the hydrogen region ($H_w/H_{w'}$ and $H_s/H_{s'}$) behave in a rather reversible manner while the monolayer oxide formation and removal process exhibits significant hysteresis. The unusual feature here is the appearance of peak X on the positive sweep: this feature (at ~0.7 V) is more pronounced at the higher temperature, Fig. 1(b). A peak in the same region, again for rather severe conditions (Pt in concentrated H_3PO_4 at $T \geqslant 150\,°C$), was reported earlier by both Vogel and Baris [22] and Clouser and coworkers [23]. Since the appearance of this peak appears to be independent of the nature of the acid, and is not apparently due to the presence of an impurity [22, 23], it may be attributed to the formation of a premonolayer oxide [3].

Although the concept of premonolayer oxidation, especially in the case of platinum, is controversial [2] its importance in electrocatalysis is borne out in the recent work of Iwasita and Pastor [24]. These authors investigated the electrooxidation of adsorbed ethanol on polycrystalline platinum in dilute H_2SO_4 using a combination of cyclic voltammetry and online mass spectrometry (DEMS). As is clear from Fig. 1 of their report, the oxidation of the organic adsorbate commenced during the positive sweep at about 0.5 V and the major peaks for both the anodic current due to oxidation of the adsorbed material (i/E) and the mass ($m/z = 44$, for $^{12}CO_2$) variation due to carbon dioxide release were virtually completed at 0.8 V, at which value the current increase associated with the onset of regular monolayer oxide film formation commenced. It is reasonable to assume that the oxygen transfer reaction involved in the production of CO_2 entails the intervention of a surface oxygen species. Since CO_2 production in the work in question [24] commenced at about 0.5 V, it is not unreasonable to assume that the premonolayer, rather than the monolayer, oxide was involved. It seems highly unlikely that the oxygen transfer process is mediated by other species (e.g., adsorbed anions). The distinction between these two types of oxide is clearly demonstrated by SERS data in the case of gold [25]. Unfortunately, there appears to be no application of a technique of comparable sensitivity, to date, to investigate premonolayer oxidation of platinum. However, there is a recent report [26] of an EXAFS spectroscopy study of the oxidation of carbon-supported platinum clusters in an acidic environment at 80 °C in which it was claimed that surface oxidation commenced at about 0.6 V, the premonolayer product (formed over the range 0.6 to 0.9 V) being structurally different from that involved at higher voltages, i.e. the regular α film. Clearly such data reinforces the premonolayer oxidation approach to noble metal electrochemistry.

The five peaks listed in Fig. 2(c) were reported earlier (see Fig. 2(b) in [3]). At that stage peaks D and E were considered as minor features, possibly related to hydrogen adsorption (in fact this may still be the origin of peak D). However, peak E (which in some experiments in the present work was quite large) is now assumed to be associated with the reduction of a distinct component (HO3) of the hydrous oxide deposit. It was considered initially that this new oxide, which reduced at about 0 V, was due to the presence of oxygen incorporated in some way into the metal lattice, for example, some HO1 or HO2 material trapped due to reduction of the outer regions of the initially quite thick oxide deposit. However, peak E was often quite sharp and reasonably symmetrical, which is not what is expected for reaction of a trapped species (the reaction of the latter should be inhibited by slow diffusion), hence the assumption of a new form of platinum hydrous oxide.

One of the problems in the hydrous oxide area is that the use of the term 'oxide' frequently conjures up an image of a highly ordered structure, for example, a spinel or perovskite. A much more realistic model in the case of hydrous oxides may well be found in the sol–gel area [27]. Extended regular structure is not found in gels: the material exists in some instances as linear chains, with occasional cross-linking (yielding a rather open structure) and in others as highly branched chains that form discrete clusters. The chains and/or clusters link to yield initially colloidal particles (or sols) and then gels. A characteristic feature of the latter is an interconnected pore network filled with solvent. Differences within a gel layer may arise for a variety of reasons, for example, variation in the degree of cross-linking or branching, pore size (and unusual species such as foreign anions trapped therein), extent of partial crystallization etc. The differences in reduction behaviour observed in the present work suggest that there are three main components in the platinum hydrous oxide deposit. However, the lack of thermodynamic significance of the peak potential values [4] should be borne in mind. The complexity of the films grown on platinum by potential cycling is demonstrated in the present work by the multitude of reduction peaks (superimposed on a large background current) in the sweep shown in Fig. 9(a). Diversity in oxide structure, for nominally the same material, is a well known phenomenon in certain areas, e.g. battery materials; a detailed account of such diversity in the case of manganese dioxide is given by Burns and Burns [28]. The results of an ellipsometric investigation of multilayer oxide growth on platinum in aqueous media were reported recently by Gottesfeld and coworkers [29]. It was concluded that the outer (β) deposit was hydrated and that a significant number of defect states were present within the bandgap of the oxide. This indicates that the material is not a perfect insulator. While no direct structural data was obtained from the ellipsometry data, it appears that the β oxide is not homogeneous – such a conclusion is supported by the multitude of oxide reduction peaks recorded in the present investigation.

The notion of oxygen species entering or becoming trapped in the outer layers of the platinum lattice can be found in the earlier works of Schuldiner [30, 31] and Hoare [32]. Recently ultrahigh vacuum spectroscopy investigations have indeed established the reality of such 'dermasorbed oxygen' formation in the case of both palladium [33] under potential cycling conditions in aqueous acid solution and platinum single crystals [34] on exposure to gaseous oxygen (the latter work involved the interaction of the gas with the metal in the absence of the liquid phase). The oxygen is probably trapped in lattice vacancies which are assumed to be present at a significant level in the disturbed outer layers of a cycled electrode or generated by place-exchange-type reactions in the case of the more ordered metal lattice. Subsurface oxygen, trapped in the metallic lattice is assumed to be an anionic species, the positive countercharge being distributed over the surrounding metal atoms. These charged species in the outer region of the metal lattice are assumed to play a significant role in binding low coverage active oxide species to the metal electrode surface.

It is clear from Fig. 3 that peak E (i.e., hydrous oxide component HO3) may be produced over a wide range of upper limit values (1.8 to 2.3 V). In some instances (e.g., Fig. 3(c)), the peak maximum potential for the reduction of HO3 was clearly more negative than 0 V, that is, the reduction of this oxide component clearly overlapped with currents due to hydrogen gas evolution. The absence of this peak (E) in Fig. 4 is interesting. All the hydrous oxide components of platinum are reduced electrochemically under thermodynamically irreversible conditions (i.e., the rate is strongly affected by kinetic factors [4]) as demonstrated earlier by the positive shift in peak potential with decrease in reduction sweep rate [11]. Stopping the sweep just prior to peak E enabled the HO3 material to reduce slowly so that on resuming the sweep, after the current during the arrest had dropped to a very low value, no indication of peak E was observed (Fig. 4).

There are two possible interpretations as to why HO3 reduced, during the arrest, prior to peak E. The first is that HO3 altered chemically, at a slow rate, to form a deposit of HO2 which is easily reduced at the arrest potential (0.03 V). However, the more likely explanation is that the peak potential during the uninterrupted sweep, Fig. 3(c), is determined by the activity of the initial reduction product, the active (poorly lattice-stabilized) metal atom, which is itself an unstable species. During the arrest the potential is such that a significant level of metal atom activity is maintained at the interface by virtue of the fact that the following type of equilibrium is maintained:

$$\mathrm{Pt(OH)_6^{2-} + 4e^- + 6H^+ = Pt^* + 6H_2O} \qquad (1)$$

However, since the active metal atoms (Pt*) decay (or become stabilized) by increasing their lattice coordination number, reduction of the HO3 oxide continues at 0.03 V until the deposit is totally reduced. Obviously when the negative sweep is then resumed there will be no HO3 oxide reduction peak.

Varying the oxide growth sweep rate did not greatly affect the appearance of the subsequent oxide reduction profile, Fig. 5. However, for a constant number of cycles the net amount of oxide produced was greater, Fig. 6, at the slower cycling rate. In practice this may not be an advantage as with very slow cycling the time for a given number of oxide growth cycles is clearly far longer. An interesting feature in Fig. 5 is the variation of the peak potential for HO1 reduction (these four reductions were carried out at the same sweep rate) for the different films. There was a systematic increase in peak maximum potential for this first hydrous oxide reduction peak with increasing hydrous oxide growth rate. This shift may be partly due to the lower overall oxide coverage involved in going from Fig. 5(a) to (d). However, perhaps what such behaviour indicates, and this is much more obvious from the type of response shown in Fig. 9(a), is the complexity in some instances of the oxide reduction response. These thick oxide films reduce over a wide range of potentials in a manner that is influenced by an interaction between thermodynamic and kinetic factors. The peaks probably reflect predominant forms of the oxidized or reduced states, for example, oxide components of different localized structure or composition (e.g., different types of aggregation, different water or foreign ion content, etc.), in addition to different nucleation and adatom decay processes in the reduced state. Similar complex behaviour has been demonstrated in the case of thick hydrous oxide film reduction on gold in base [35].

With films grown under similar conditions but reduced at different sweep rates, Figs 7 and 8, the peak current densities for peaks C and E (HO2 and HO3 oxide reduction, respectively) increased linearly with increasing reduction sweep rate, Fig. 8(a). As pointed out in earlier work carried out at 25 °C [11] this indicates a fast interfacial redox reaction. However, the peak maximum potential value decreased with increasing sweep rate, Fig. 8(b); as again outlined earlier [11] this is assumed to reflect the greater activity of the reduced form of the couple when the reduction is carried out at the faster sweep rates. In the normal case (involving rapid reaction of a couple with a stable oxidized and reduced state) i_p should be a linear function of sweep rate whereas E_p should be independent of sweep rate [36]. The variation of E_p with sweep rate in the present case is attributed to the more active state of the product, for a given degree (e.g. 50%) of film reduction at the faster sweep. In other words, the initial reduction step, Equation 1, is fast (and reversible) but the subsequent, post-electrochemical step ($\mathrm{Pt^*} \longrightarrow \mathrm{Pt}$) is relatively slow. This causes a drop in activity of the reduced form of the couple, and hence an increase in the reduction potential (or E_p value), that is more marked (as observed) at the slower reduction sweep rates.

In a recent account of hydrous oxide (or β) film reduction on platinum in acid at 22 °C Birss and Goledzinowski [20] pointed out that the charge for β film reduction on a single sweep was lower than the value observed when the reduction was carried out using a combination of sweep + hold (in the latter case some reduction was carried out at constant potential (e.g., 0.3 V); the remaining oxide was then reduced in a subsequent negative sweep, 0.3 to 0 V). The difference was attributed to either loss of oxide by dissolution during the single sweep reduction experiment or to electrodeposition of dissolved platinum species (produced during oxide growth cycling between 0.5 to 2.82 V) during the potential arrest period. It is not clear that in the work in question [20] all the β oxide deposit was reduced in the single negative sweep. For example, in Fig. 7 of [20] the cathodic current at the end of the negative sweep, i.e. at 0 V, was about 0.5 mA in the cyclic voltammogram for the oxide-free metal and about 1.25 mA in the β-oxide reduction experiment. It may be noted that in the same diagram the β and β' peaks are quite similar (apart from the magnitude); the same oxide seems to have been involved.

From the peak potential values shown in [20] the β oxide involved is evidently a HO2-type deposit. The larger charge values observed in the sweep + hold experiments may arise for the following reasons:

(i) Incomplete reduction of a HO2 deposit under single negative sweep conditions. Arresting the sweep increases the net time for reduction, giving rise to more complete reaction, and hence a greater reduction charge, when the potential is subsequently reduced to 0 V.

(ii) Although the β film in [20] appears to be predominantly a HO2 deposit there may have been some HO3 present or some HO2-type material that is reduced only with some difficulty at 0 V. There is normally no sign of a HO3 reduction peak for platinum at room temperature (see Fig. 9(b) here). This may be due to either an absence of HO3 or that reduction of HO3 occurs at such a low potential (<0) that it is totally overshadowed by hydrogen gas evolution. Holding the potential constant during the β oxide reduction process may have caused slow, partial, reduction of HO2 material which may, in turn, also permit slow reduction of either HO3 (as outlined here in Fig. 4) or some particularly stable HO2 component (the latter may be viewed as a type of precursor species, that is, the component that separates to form HO3 at 60 °C). The less reactive components may not reduce during a single sweep to 0 V.

(iii) Obviously if some of the β oxide dissolved during the reduction sweep, as suggested in [20], the oxide reduction charge should be low. A minor objection to this explanation is that there is obviously a longer time for dissolution during the sweep + arrest reduction procedure.

A most remarkable feature of the work of Birss and Goledzinowski [20] is the conditions used to record their β′ peak. This peak, which we assume is due to reduction of a HO2-type species, was observed only on the first negative sweep after reduction of the β deposit. Furthermore, the β deposit had to be reduced in a specific manner (by the sweep + arrest procedure which, as outlined earlier, gave the maximum reduction charge) and then the potential had to be cycled to a limit, on the positive sweep, of 0.7 to 1.8 V (the β′ peak was observed only on the subsequent negative sweep). The charge on the β′ peak increased with decreasing value of the holding potential (over the range 0.6 to 0.3 V), with increasing holding time and with increasing value for the upper limit of the subsequent positive/negative cycle. When the sweep was held at 0 V for 5 min (after β oxide reduction by the sweep + arrest procedure) the β′ peak was not observed on the subsequent cycle.

One possibility in the work in question [20] is that after the β oxide reduction by the sweep + arrest procedure the oxide-free metal surface was rather active: that is, it probably contained an unusually high defect density or coverage of surface metal atoms in a very reactive, low lattice coordination, state. Then on the subsequent positive sweep both monolayer oxide plus hydrous (β) oxide were produced, giving rise to both the monolayer oxide reduction and β′ reduction peaks on the next negative sweep. The active surface state, which is intrinsically unstable, was then lost (as it apparently was by polarizing at 0 V for 5 min after the β oxide reduction sweep) and thus the β′ peak is not observed in subsequent cycles. Some evidence to support this view can be seen in Fig. 12 of [20]. First, on the positive sweep the potential for the onset of surface oxidation (at the end of the double layer region) decreased in the same sequence as the experiments were carried out (this sequence is given by the full, dashed and dotted line in the original diagram). Second, again on the positive sweeps, there was a small increase in anodic charge in the hydrogen desorption region, possibly due to a small increase in roughness or surface area. However, there was a much larger increase in the charge in the surface oxidation region (~0.75 to 1.5 V); again this increase followed the sequence full, dashed and dotted line. Finally, in the case of the dotted line (the final experiment in Fig. 12 of [20]) the anodic current at the early stage (0 to 0.1 V) of the positive sweep was extremely small while the cathodic current at the lower end (0.2 to 0 V) of the negative sweep was unusually large. Such a response is not normal for hydrogen chemisorbed on platinum – but has been observed [6, 37] in an even more dramatic form for highly activated platinum where again hydrous oxide species were assumed to be involved.

It may be noted also that unusual behaviour, somewhat similar to that outlined above, has been described for platinum in highly concentrated H_2SO_4 by Conway and Novak [38]. They observed that oxidation (apparently of the electrode surface) commenced on the positive sweep at about 0.25 V vs RHE while on the negative sweep cathodic peaks were appeared at about 0.4 V (monolayer oxide or HO1 reduction), 0.14 V (HO2 reduction) and −0.2 V (the latter was a major feature; its irreversibility, and absence of an anodic counterpart, is not a characteristic of a H_{ads} species; it is tentatively attributed here to HO3 reduction). The authors explained these unusual responses in terms of the responses of products formed by reduction of the acid. However, since somewhat similar behaviour has been observed [37] for activated platinum in a variety of aqueous acid solutions (H_2SO_4, $HClO_4$ and H_3PO_4) it is assumed here that the anomalous responses are determined by an unusual state of the electrode surface, rather than by the breakdown of the electrolyte.

5. Conclusions

(i) It is now evident that the basic electrochemistry of platinum in aqueous media extends beyond the conventional surface hydride, monolayer oxide and double layer model. Hydrous oxide behaviour is complicated by the fact that both the formation and reduction of these materials, at least in multilayer form, occur under very irreversible conditions. This has been explained earlier [2] in terms of the important role of lattice coordination number and lattice energy of surface metal atoms in such reactions. It is interesting to note that both anomalous oxide stability and the interfacial cyclic redox mechanism of electrocatalysis, a rather controversial topic in the case of platinum [2], was postulated quite recently by Schiffrin and coworkers in the case of hydrogen peroxide [39] and oxygen [40] reduction on polycrystalline copper in aqueous media.

(ii) Because of their rather amorphous character hydrous oxide seem to have been regarded as somewhat nebulous, unimportant species, especially in the noble metal area. There is a need for further information as to the localized structure, composition and state of charge of these materials, especially at low coverages where they appear to play a role in electrocatalysis. A gel model was used to explain the present results in which three major hydrous oxide reduction peaks were observed with films prepared and reduced in aqueous acid solution at elevated temperature.

(iii) There are now several, reliable, independent reports [6, 20, 22, 23, 37, 38] of unusual responses for platinum in aqueous acid solution. An attempt was made in the present paper to rationalize such behaviour in terms of a hydrous oxide approach.

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