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The role of hydrous oxide in the electrochemical behaviour of platinum

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The role of hydrous oxide species in the behaviour of platinum electrodes in aqueous media has been largely ignored until recently. The material may be produced in thick film form by vigorous anodization or potential cycling techniques. The extent of its formation at low potentials in a single anodic unit sweep is quite limited as special, high energy, metal adatom sites are involved. The electrochemical behaviour of this material is complicated by the interaction between its acid–base and redox properties, plus the fact that the reduced form of the couple (the platinum adatom) is unstable at significant coverage. In electroorganic oxidation reactions the low coverage hydrous material functions as a weak but reactive oxidizing (or oxygen donating) agent – the high activity evidently being due largely to interaction of the organic with the reduced form of the couple. This view of electrocatalysis, which is an extension of earlier work with gold, is supported by the observation that, with precautions taken to minimize poisoning effects, many reactive organics commence oxidation on the anodic sweep at the same potential, i.e. in the region of the adatom/hydrous oxide transition. The influence of thick hydrous oxide layers on the oxygen gas evolution process, as well as the previously unexplained inhibition of certain redox reactions, are discussed. Complications associated with hydrous oxide growth, and reduction, in base are outlined.

1. Introduction

In an earlier publication [1] a study was reported of the growth of hydrous oxide films on platinum under potential cycling conditions. Most of the electrochemical oxidation work on the latter metal to date has been devoted to monolayer, i.e. compact, oxide growth. The two materials differ significantly in density, water content, thickness values attainable and, especially, potential/pH behaviour. An extensive account of hydrous oxide behaviour at both noble and non-noble metals has been published recently [2]. To elucidate the anodic behaviour of platinum in aqueous media both types of oxide need to be considered. For example, it was pointed out recently [3] that the initial product formed on oxidation of platinum displayed some of the characteristics of hydrous, rather than anhydrous, oxide. In addition, Kuhn and Randle [4] have suggested that conflicting data for certain reactions at oxidized platinum electrodes may be due to the presence of ill defined mixtures of the two different types of oxide. Furthermore, the electrocatalytic behaviour of gold for certain electroorganic oxidation reactions was interpreted recently [5] in terms of the mediation of the interfacial reaction by sub-monolayer levels of hydrous oxide species generated *in situ*; it will be demonstrated here that a similar mechanism operates for many electroorganic oxidation reactions on platinum. In view of the relative neglect of the hydrous oxide in the field of platinum electrochemistry to date a brief review of the nature of this material will be given here prior to presenting the results of the present investigation.

As pointed out in a recent review [2], two fundamentally different types of oxide layer can be grown on noble metals in general under anodic or potential cycling conditions. The first is a compact oxide, usually of monolayer character, whose composition in the case of platinum varies with potential and apparently spans the range from PtOH, PtO and $Pt(OH)_2$ to $Pt(OH)_4$ and $PtO(OH)_2$ [6, 7]; this type of material is not of primary interest here. The second type of material, which under appropriate conditions can be produced in thick film form, is a hydrated, hyper-extended (low density) material which, again in the case of platinum, has been formulated as $[PtO_2(OH)_2(H_2O)_2]^{2-}$ [1] or $[Pt(OH)_6]^{2-}$ [2] – the latter is now the preferred assignment. There is ample evidence from X-ray photoelectron spectroscopy (XPS) data [8, 9] for the existence of Pt(IV) species – as required by the above assignment for this type of material – in the case of the thick yellow anodic deposits produced on platinum at high potentials.

The conditions for growing the second type of oxide under d.c. conditions have been explored by Balej and Spalek [10]. According to these authors the optimum potential in acidic media in about 2.3 V(RHE); very little hydrous oxide is produced below about 2.1 V(RHE) while at (or above) 2.5 V(RHE) the hydrous material is not observed (apparently it is unstable at high potentials). Although Peuckert and coworkers mention hydrated platinum oxides in their recent publications [7, 11, 12] on the XPS investigation of anodically produced platinum oxide, it is important to note that the deposits examined by these authors were apparently not hydrated (or hydrous) oxides of the type under discussion here. Their films were produced in acid at about 3.0 V(SHE) – at low pH the SHE and RHE scales virtually coincide. Under such conditions the hydrous material (which under appropriate conditions can be grown to thicknesses of hundreds of monolayers) cannot be produced. This is borne out by the quite low thicknesses quoted on p. 1312 of [11]; for example the values (after 15 min anodization in acid) for film growth potentials of 3.0 or 4.0 V(SHE) are only about double that for a film formed at 1.5 V(SHE). The conditions used by Peuckert and coworkers to grow the film on platinum in base [7] were even more severe; 3.0 V(Ag/AgCl) – for 20 h – corresponds to 3.233 V(SHE) or about 4.0 V(RHE), pH $\approx$ 13.6 (this corresponds to an oxygen evolution overpotential of about 2.8 V). The obvious conclusion is that the platinum oxide films examined by Peuckert and coworkers were composed of a few monolayers of compact, largely anhydrous, oxide, oxyhydroxide or hydroxide; it should be noted also that the voltammetry data reported by this group for acid show no trace of a hydrous oxide reduction peak (which should appear in acid [1], at the sweep-rate involved, in the hydrogen adsorption region – in base this material (see later) is reduced only with considerable difficulty). It is clear that considerable attention must be devoted to the growth conditions when examining these hydrous oxides; the complexity of this field is also demonstrated by the report of James [13] of a splitting of the lower (hydrous oxide) reduction peak in the case of platinum, i.e. the hydrous material in these thick, acid-grown, films in certain cases may be heterogeneous.

The main reason for suggesting that the basic unit in the hydrous platinum oxide layer is the hexahydroxy platinic acid anion is that it is otherwise quite difficult to explain the inability to readily reduce such films in base; the latter is an independently established feature [1, 14] of this system. If the species involved is neutral, e.g. $Pt(OH)_4$, then the reversible reduction potential on the RHE scale should be pH-independent as the numbers of protons (or hydroxide ions) and electrons participating in the reaction, namely

$$Pt(OH)_4 + 4H^+ + 4e^- = Pt + 4H_2O \qquad (1)$$

are equal. Yet, while the hydrous oxide reduction process in acid is quasi-reversible (the peak height for the reduction process is proportional [1] to sweep-rate), the film reduces at about 0.2 V(RHE), at 0.1 V s^{-1}, in acid whereas it is virtually impossible to reduce in base. This behaviour can be rationalized by assuming that with regard to hydrous oxide redox activity platinum behaves like a whole range of other noble and non-noble metals [2] in so far as the reversible potential shifts cathodically by about $3/2(2.303\,RT/F)$ V per unit increase in solution pH. The factor 3/2 in this case is the ratio of hydrogen or hydroxide ions to electrons in the reduction step and this ratio follows automatically from the equation

$$[Pt(OH)_6]^{2-} + 6H^+ + 4e^- = Pt + 6H_2O\ (\text{acid}) \qquad (2)$$

or

$$[Pt(OH)_6]^{2-} + 4e^- = Pt + 6OH^-\ (\text{base}) \qquad (3)$$

The only other possibility likely to explain the pH shift, namely that the base grown film differs significantly in structure and composition from its acid equivalent, is improbable as the base grown deposit, on transfer to acid, reduces in an identical manner to the acid grown material. Some evidence for the anionic character of anodic films grown on platinum comes from Peuckert's observation [7] of the presence of sodium ions in the anodic deposit formed in the base.

It is worth noting also that platinic acid, $H_2Pt(OH)_6$, and its salts are established chemical species that have been characterized in the bulk state by X-ray techniques [15]. Essentially they are the insoluble hydroxy acid or salt analogues of the perhaps better known chloroplatinic acid, H_2PtCl_6, system which is readily produced in the hydrated form (the latter is known also for the lithium and sodium salts), namely $H_2PtCl_6 . 6H_2O$ [16]. While the X-ray data [15] confirm that platinic acid is a hydroxy compound, the thick film grown on platinum under vigorous anodic conditions has previously been regarded [7] as a hydrated oxide $PtO_2 . xH_2O$; if these two types of species are considered to coexist, even with the equilibrium, Equation 4, far to the left, it is

$$H_2Pt(OH)_6(s) \rightleftharpoons PtO_2.4H_2O(s)$$
$$\longrightarrow PtO_2.(4-x)H_2O(s) + xH_2O(g) \qquad (4)$$

easy to envisage loss of water under high vacuum conditions, e.g. in XPS experiments. One can, therefore, foresee problems in trying to establish the precise composition of the hydrated film using high vacuum, *ex situ*, techniques. It is also evident that the high charge on the central metal ion will induce hydrolysis of coordinated water molecules – thus creating the type of anionic hydroxy surface complex postulated here.

According to Greenwood and Earnshaw's recent account of the oxides of platinum [17] the Pt(IV) hydroxy species, i.e. $[Pt(OH)_6]^{2-}$, produced as a yellow precipitate by base hydrolysis of $PtCl_4$ (the hydrous deposit grown on platinum has the same colour), is more stable than its Pt(II) analogue – this is in agreement with the more cathodic potential [1] required for the reduction of hydrous, as compared with the monolayer, oxide deposits (these are assumed to be Pt(IV) and Pt(II) species, respectively). These authors also point out that $[Pt(OH)_6]^{2-}$ is amphoteric as it dissolves in acid. The general behaviour of the hydroxy complex may be rationalized in a Nernstian manner by assuming that Equation 2 can be sub-divided in two components, namely

$$[Pt(OH)_6]^{2-} + 6H^+ = Pt^{4+} + 6H_2O \quad (5)$$

$$Pt^{4+} + 4e^- = Pt \quad (6)$$

From Equation 6

$$E = E^0 - \frac{2.303RT}{4F} \log \frac{a_{Pt}}{a_{Pt^{4+}}} \quad (7)$$

On defining the dissociation constant of the hydroxy complex (represented here as C) by the expression

$$K_d = \frac{a_{Pt^{4+}} a_{H_2O}^6}{a_C a_{H^+}^6} \quad (8)$$

it is easily shown that

$$E = E^0 - \frac{2.303}{4F} \log a_{Pt} - \frac{2.303RT}{4F} \log \frac{a_{H_2O}^6}{K_d a_C} - \frac{3}{2}\left(\frac{2.303RT}{F}\right) pH \quad (9)$$

This simple treatment not only rationalizes the amphoteric behaviour of the material in question (in a strong acid the equilibrium represented by Equation 5 would lie far to the right while in a strong base it would lie far to the left), but also elaborates on the interpretation of the unusual pH dependence of the reduction potential. In terms of this treatment the lower reduction potential (or greater stability) of the hydroxy material in base is due to marked lowering of the activity of the Pt^{4+} species in the deposit on increasing the solution pH (according to Equation 8, $a_{Pt^{4+}}$ varies with the *sixth* power of a_{H^+}, rather than the fourth power of a_{H^+} if the complex is assumed to be $Pt(OH)_4$). In general terms it is well worth noting that the unusual shifts, i.e. departures from conventional ($2.303RT/F$ V/pH unit) E/pH behaviour for surface layers are not confined to hydrous oxides. They have also been observed recently with certain types of organic polymer coatings [18] and the behaviour has been interpreted, as in the present case, in terms of an interaction between the acid–base and redox properties of the materials in question. As in the case of the organic deposit, the $[Pt(OH)_6]^{2-}$ material is assumed to be present in a relatively open polymer aggregate, with solvent plus counterion species present in the reactive regions of the film; the density, degree of hydration and extent of hydrolysis in these films may well be a function of thickness (the degree of hydration being most marked at the oxide–solution interface).

Some further support for the view that the hexahydroxy platinate (IV) anion is involved in these materials can be found in the work of Kozawa [19]. According to the latter the reduction of $[Pt(OH)_6]^{2-}$ occurs at a dropping mercury electrode in 1–19 mol dm^{-3} NaOH at -1.0 to -1.25 V(Hg/HgO), i.e. -0.07 to -0.32 V(RHE). Evidently in base this compound, like the hydrous oxide material, cannot be reduced at a platinum cathode prior to the hydrogen gas evolution reaction (the reaction on mercury is assumed to be reversible). Assuming that the reduction potential for the hydrous oxide film drops with increasing pH by 0.5 ($2.303RT/F$) V/pH unit [2], the value of about 0.2 V (RHE) in acid [1] would correspond to about -0.17 V (RHE) in base (ΔpH = 12.5) – this is within the range quoted by Kozawa for the reduction of the anionic hydroxy complex in alkaline solution.

2. Experimental details

The working and counter electrodes consisted of short length of platinum wire (0.5 mm diameter, about 0.2 cm^2 exposed area) sealed directly into glass. The counter electrode was contained in a separate compartment connected to the main body of the cell via a sintered glass disc. In potential cycling experiments smooth platinum electrodes were cleaned before use by brief (30 s) immersion in warm aqua regia (this removed the finely divided layer of active platinum [1] formed in previous experiments) followed by washing with distilled water. In experiments involving anodic oxidation of dissolved material, e.g. hydrazine or methanol, the surface was activated by platinization – a platinum black layer was deposited by cathodizing at 20 mA cm^{-2} for 5 min in H_2PtCl_6 solution (1 g in 100 ml of 0.1 mol dm^{-3} HCl): typically this resulted in an increase in surface area (as measured in terms of adsorbed hydrogen capacity) by a factor of 150 as compared with smooth platinum. Solutions were made up using high purity (usually Analar grade) reagents and triply distilled water. Potentials were measured, and are quoted, with respect to a hydrogen reference in the same solution.

The electrochemical equipment consisted of a potentiostat (Wenking, Model LT-78) programmed with a function generator (typically a Metrohm VA Scanner, E612). Cyclic voltammograms were usually recorded using a Rikadenki (RW-21) XY recorder. In some experiments two potential sweep conditions were employed: the first was the hydrous oxide growth or activation scan (usually 100 V s^{-1} for acid or 4.52 V s^{-1} for base [1]) while the second, referred to later as the analytical scan, was that used to cathodically reduce the hydrous oxide material – and hence monitor the coverage of the latter (this single, analytical, reduction scan was run at a much lower rate – typically 40 mV s^{-1}).

In all experiments described here the effect of iR_e error was minimized with the aid of a Luggin capillary. In addition, in the oxygen gas evolution work, the measured potential was corrected for the residual, uncompensated iR_e component by subtracting the appropriate value from the measured potential. R_e values were determined beforehand by a current interruption technique, and were found to be essentially constant at about 0.3 Ω over the range 0 to 50 mA cm^{-2} (geom). The potential values quoted for this experiment, Fig. 5, were taken after a 10 min period of electrolysis – as in similar experiments reported earlier for iridium [20].

3. Results and discussion

3.1. *The role of hydrous oxides in electrocatalysis*

It was postulated recently [5, 21] that the electrocatalytic oxidation of organic materials at noble metal surfaces involves incipient hydrous oxide as the oxygen donating species. The initial work was carried out with gold and extended later to silver [22]. Basically it is assumed that while the organic reactant may be activated by chemisorption, the oxidation only commences in the region where significant quantities of hydrous oxide is formed on the metal surface. In the case of gold this occurs at about 1.0 V(RHE) in acid and about 0.65 V(RHE) in base. The hydrous oxide formation process on gold in acid may be represented as follows [2]

$$2Au^* + 9H_2O = Au_2(OH)_9^{3-} + 9H^+ + 6e^- \quad (10)$$

The peak for this reaction observed under cyclic voltammetry conditions is normally quite small (in many cases it is either not observed, ignored or attributed to the presence of impurities). However, the peak for the reverse reaction may be quite large if provision is made to grow a substantial thickness of hydrous oxide material on the surface prior to the reduction sweep [23]. After reduction the adatom (Au^*) species tend to relax, i.e. occupy regular surface metal lattice sites ($Au^* \rightarrow Au_l$) so that on the next anodic cycle the response for hydrous oxide formation is again low. Apart from this low level direct response in the absence of organics, the formation of hydrous oxide is also suggested in the case of platinum by the ability of this metal to oxidize compounds such as methanol under anodic conditions, namely

$$CH_3OH + H_2O = CO_2 + 6H^+ + 6e^- \quad (11)$$

This reaction involves an oxygen insertion step; however, this oxygen cannot by supplied directly from water (which is stable below about 1.23 V) or from compact monolayer oxide whose formation commences in acid only at about 0.8 V. Since methanol oxidation or platinum can be observed at potentials as low as 0.5 V [1], or even 0.2 V (see later), it is not unreasonable to assume that incipient hydrous oxide species are involved in such reactions.

While full details of the oxidation mechanisms, even in the case of gold, are unknown at present, an interfacial cyclic redox process is assumed to be involved in which Equation 10 is succeeded, in a repetitive manner, by the following

$$Au_2(OH)_9^{3-} + \text{organic} = 2Au^* + \text{products} \quad (12)$$

Three features of the reaction [5] support this view of electrocatalysis: (a) the onset (anodic sweep) and termination (cathodic sweep) potentials for organic oxidation coincide (at the adatom–hydrous oxide transition potential), (b) the onset–termination potential is independent of the nature of the organic compound, and (c) this potential decreases in the case of gold from about 1.0 to 0.65 V(RHE) on altering from acid to base, i.e. the organic oxidation process moves in the cathodic direction in the same manner as the hydrous oxide–metal transition.

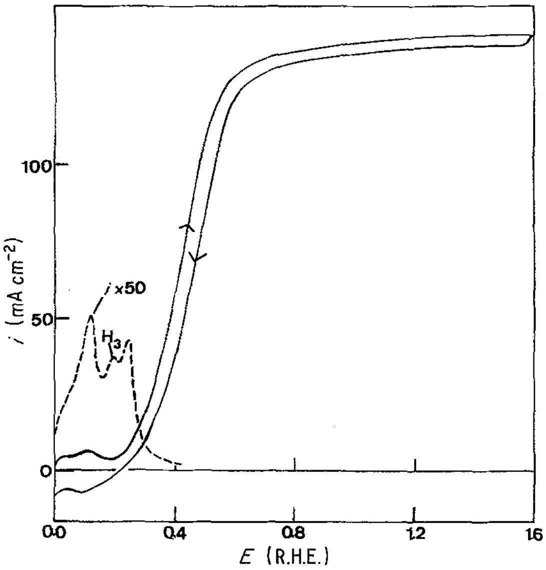

Fig. 1. Cyclic voltammogram (0–1.6 V, 50 mV s^{-1}) for a platinized platinum electrode in 1.0 mol dm^{-3} H_2SO_4 solution containing 0.1 mol dm^{-3} N_2H_4 (full line): the dashed line shows the anodic response in the hydrogen region for the same electrode and conditions – except in the absence of N_2H_4. The solution was nitrogen stirred, T = 25° C.

In the case of platinum in acid the hydrous oxide reduction at moderate sweep-rates (50 to 100 mV s^{-1}) occurs in the region just above 0.2 V(RHE). By analogy with the earlier gold work oxidation of organics should commence (and terminate) in this region. However, such reactions of carbonaceous species are difficult to investigate as they are generally complicated by the formation of CO-type poisoning species [24]. Other compounds, in particular hydrazine, are free of such complications and, as outlined in Fig. 1, reaction does indeed commence in the expected manner in the hydrous oxide film reduction region at about 0.2 V. The oxidation of hydrazine evidently occurs according to the following cyclic redox mechanism, namely

$$\begin{array}{l} Pt^* + 6H_2O = Pt(OH)_6^{2-} + 6H^+ + 4e^- \quad (13a) \\ \uparrow\!\underline{\qquad\qquad\qquad\qquad\qquad\qquad}\!\downarrow \\ Pt(OH)_6^{2-} + N_2H_4 + 2H^+ = Pt^* + N_2 + 6H_2O \quad (13b) \end{array}$$

Further evidence that this is a major route for electrooxidation at platinum electrodes was obtained from experiments carried out with a range of organics, e.g. methanol and isopropanol. In this case precautions were taken to minimize poisoning effects by using a stepping procedure. The electrode potential was stepped from the oxide layer region (where CO-type poisons are removed by oxidation) to a range of lower values and the currents at t = 0, i.e. when the lower limit was impressed, were obtained by extrapolation of the subsequent decay curves. As shown in Fig. 2 the organic oxidation currents generally commenced at

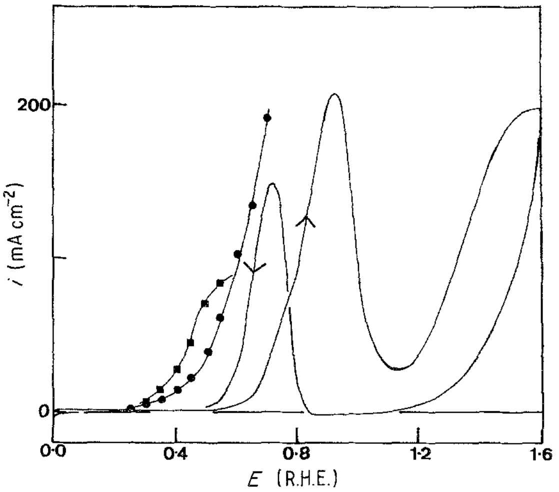

Fig. 2. Typical cyclic voltammogram (50 mV s^{-1}) showing the response for methanol oxidation at a platinized platinum electrode above 0.4 V in continuous sweep (0 to 1.60 V) experiments: nitrogen stirred 1.0 mol dm^{-3} H_2SO_4 + 0.5 mol dm^{-3} CH_3OH solution, T = 25° C. Also shown are t_0 currents recorded after anodizing the electrode (1.10 V for 30 s) and stepping the potential to specified lower values (see text for details) in the above methanol solution (●). The same type of experiment was carried out with 0.1 mol dm^{-3} $CH_3CHOHCH_3$ in acid (■), the electrode being preanodized for 30 s at 1.3 V.

about 0.2 V(RHE): a similar result for methanol has been obtained in earlier Russian work [25].

A more detailed account of these experiments will be published shortly. They clearly indicate a significant new factor in electrooxidation processes on platinum. The suggestion that hydrous oxide is produced (even at a low level) in the hydrogen region of platinum is likely to be controversial but evidence for unusual behaviour in this region already exists. Conway and coworkers [26, 27] have pointed out that one of the minor peaks (the so-called anomalous H_3 peak) has a totally different entropy value to that of any of the other peaks in this region. More interesting is the data obtained by Woodard and coworkers [28] who, using time resolved staircase voltammetry, were unable to detect any response for the main hydrogen peaks using this approach (the technique only gives a response for slow, inhibited, processes). However, quite a large response was observed for the H_3 peak – but only on the anodic sweep. The conclusion from this work was that there is a slow process in the H_3 peak region at about 0.2 V(RHE). Such behaviour is easily explained in terms of the following scheme

$$\mathrm{Pt^* + 6H_2O} \underset{\text{fast}}{\overset{\text{slow}}{\rightleftharpoons}} \mathrm{Pt(OH_2)_6}$$

$$\overset{\text{fast}}{\rightleftharpoons} \mathrm{Pt(OH)_6^{2-} + 6H^+ + 4e^-} \qquad (14)$$

i.e. in the H_3 region a low level of hydrous oxide formation takes place at metal adatom sites (as on gold); this reaction is inhibited by the need, prior or during the course of oxidation, for adspecies to acquire a total of six coordinated ligands – hence the slow anodic response. The absence of a response, using staircase voltammetry, in this region during the cathodic sweep is evidently due to the fact that the fast electrochemical step now preceeds loss (or, more likely, partial loss) of the hydration shell – the latter may in fact be quite rapid.

3.2. *The quasi-reversible character of the hydrous oxide–metal transition*

The hydrous oxide reduction process in the case of platinum simultaneously displays elements of reversibility and irreversibility. The reversible character has been commented on previously by James [13] and Shibata [29]; the latter work is particularly impressive (the outer layer was reduced with a periodically interrupted current and the potential fluctuations observed on repetitively switching off and on the current were quite small). Also, as mentioned here earlier, the height of the sharp reduction peak is directly proportional to sweep-rate [1]. On the other hand the hydrous oxide reduction reaction is clearly irreversible at a macroscopic level as the layer is quite difficult to regrow. In addition the peak potential (E_p) for the hydrous oxide reduction process is significantly dependent on sweep-rate [1] – especially at low values of the latter where, ideally, E_p variation with sweep-rate for a reversible process is expected to be minimal. Finally, close inspection reveals [1] that the hydrous oxide reduction peak is asymmetric; the current decays at an unusually rapid rate on the cathodic sweep as the applied potential drops below E_p.

These strongly contrasting features of the hydrous oxide reduction process may be rationalized by assuming that the overall reaction, Equation 2, is composed of two successive steps, namely

$$\mathrm{[Pt(OH)_6]^{2-} + 6H^+ + 4e^- = Pt^* + 6H_2O} \qquad (15)$$

$$\mathrm{Pt^* \rightarrow Pt_l} \qquad (16)$$

While the first step here is considered to be reversible, it is followed by an irreversible, post-electrochemical reaction in which adatoms (Pt*), generated according to Equation 15, move about and eventually occupy regular surface metal atom lattice sites. Such atoms (Pt_l) are far less reactive from an electrochemical viewpoint because of their much greater bulk metal lattice coordination number – their ability to react with, or coordinate, solution species is dramatically reduced – hence the overall irreversibility of the reduction process. If the adatom decay step, Equation 16, is not particularly rapid, a short interruption in the reduction current – as in Shibata's experiments [29] – leads to only a small loss in adatom activity and, hence, only a small variation in potential. The potential response is assumed here to be Nernstian and therefore described by Equation 7; the metal activity in the latter is now assumed to be the adatom activity and as the potential variation is proportional to the logarithm of the latter the short-term loss of adatom activity clearly will have minimal effect on potential under relatively high frequency current interruption conditions.

The process represented here in Equation 16 is basically an electrocrystallization process and the slow nature of this step is borne out by the fact that on reduction the hydrous oxide layer yields a platinum black rather than a smooth surface metal deposit [1]. The increase in potential [1] on reducing the sweep-rate, especially at low values of the latter, is also understandable as over the E_p range observed for platinum, 0.5 to 0.2 V, the time required to transverse this span increases from 3 s at a sweep-rate of $100\,\mathrm{mV\,s^{-1}}$ to 5 min at $1\,\mathrm{mV\,s^{-1}}$, i.e. the time for adatom decay is much greater at slow sweep-rates. According to Equation 7, with a_{Pt} taken as a^*_{Pt}, a drop in metal atom activity at the surface with decreasing sweep-rate should yield (as observed) an increase, or anodic drift, in potential. Finally, the sharp drop in current at the cathode side of the hydrous oxide reduction peak [1] may be explained in terms of the present scheme, Equations 15 and 16. At any point on the sweep the measured, or applied, potential may be considered in terms of two components: (a) a reversible Nernstian component (E_{rev}) relating to the equilibrium shown here in Equation 15; (b) an irreversible component (E_{irr}) associated with any uncompensated iR_e drop or other (apparently minor) source of inhibition at the interface. Just after the peak the current begins to decay (the supply of reactant becomes limited), both the iR_e and a_{Pt^*} values decrease (in the latter case the process represented by Equation 16 is assumed to be virtually potential independent but the rate of formation of Pt* – and hence its activity – drops, i.e. E_{rev} becomes more anodic). Thus the component in the applied potential available to overcome any electrochemical barrier is increased with the result, as observed, that the reduction process goes to completion at an unusually rapid rate. The interpretation outlined here for platinum is assumed to apply also to the same type of reaction involving other metals; certainly the behaviour of palladium, as outlined in [30], is remarkably similar.

It is virtually impossible to determine the standard potential for a reaction involving adatom species, e.g. the process represented by Equation 15. At significant coverage or activity such species apparently agglomerate – the reaction probably proceeding via metal atom clusters to form bulk metal (platinum black) crystallites. It is interesting that the current for oxidation in the case of a platinum electrode in the presence of oxidizable solution species, e.g. hydrazine (Fig. 1) or isopropanol, occurs (for both the anodic and cathode scans) over the range 0.2 to 0.6 V – virtually the same span as the increase in E_p for hydrous oxide reduction (Fig. 3 in [1]) with decreasing sweep-rate. This behaviour at low potentials outlined in Fig. 1 is attributed to a reversible increase in hydrous oxide, Pt(IV), coverage with increasing potential. Because of the cyclic nature of the oxidation, Equation 13, there is extensive interconversion between Pt* and Pt(IV), and to a lesser extent Pt* and $\mathrm{Pt_l}$, states. At low potential (0.2 V) the Pt* activity is high – see Equation 9 – and this will favour the $\mathrm{Pt_l}$ rather than Pt(IV) state, i.e. the following set of equilibria (Equation 17) will shift to the left

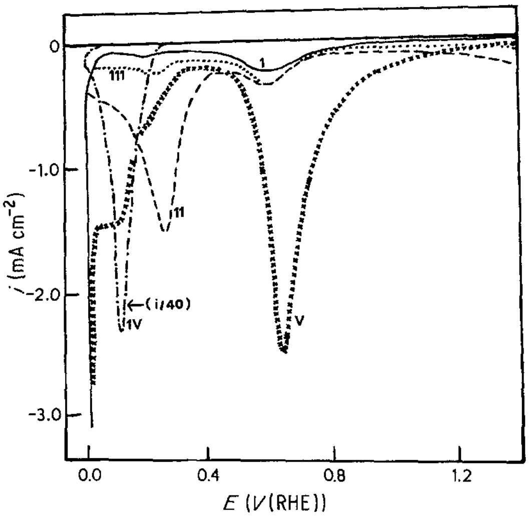

Fig. 3. Cathodic reduction sweeps for platinum in $1.0\,\mathrm{mol\,dm^{-3}}$ NaOH at 25° C; curve I (——), prior to cycling; II (– – –), after cycling, 0.44 to 2.70 V, $4.52\,\mathrm{V\,s^{-1}}$ for 10 min, in $1.0\,\mathrm{mol\,dm^{-3}}$ NaOH: III (. . . . .), second reduction sweep after allowing the electrode to stand on open-circuit in $1.0\,\mathrm{mol\,dm^{-3}}$ NaOH for a further 15 min; IV (–·–·–·–), next cathodic sweep recorded after transferring the electrode to $1.0\,\mathrm{mol\,dm^{-3}}$ H_2SO_4, V (xxxx), next consecutive reduction scan recorded immediately after curve IV without removing the electrode from the acid or reforming the hydrous layer.

$$\mathrm{Pt_l} \rightleftharpoons \mathrm{Pt^*} = \mathrm{Pt(IV)} \qquad (17)$$

At higher potential (0.6 V) this set of equilibria will shift to the right, i.e. the oxidized state will be favoured, the activity of Pt* will be low and some more surface metal lattice atoms (which for a polycrystalline metal are not homogenous) will tend to oxidize. It is evidently this increasing level of Pt(IV) species that causes the progressive increase in oxidation current with increasing potential above about 0.2 V(RHE).

3.3. *Evidence for an intermediate oxide layer in electrochemically produced thick oxide films grown on platinum in base*

With thick oxide layers grown on platinum in acid by the potential cycling technique [1] only two peaks are observed on reduction, one at about 0.6 V which is assumed to correspond to the removal of Pt(II) monolayer-type species and the other at about 0.2 V corresponding to the removal of Pt(IV) hydrous oxide species. With films grown in a similar manner on platinum in base the first peak is again observed but – as outlined here earlier – the yellow hydrated Pt(IV) material is not reduced above 0 V(RHE) during the cathodic sweep. However, a *small* peak was observed just above 0.2 V on the reduction sweep in base (curve II, Fig. 3). The yellow film was still on the surface after this sweep and its reduction gave rise to the very large, sharp cathodic peak at about 0.12 V(RHE) when this electrode was subsequently transferred to acid (curve IV, Fig. 3). The charge associated with the small peak at about 0.25 V in base (Fig. 4) corresponded to about 2% of that for the subsequent

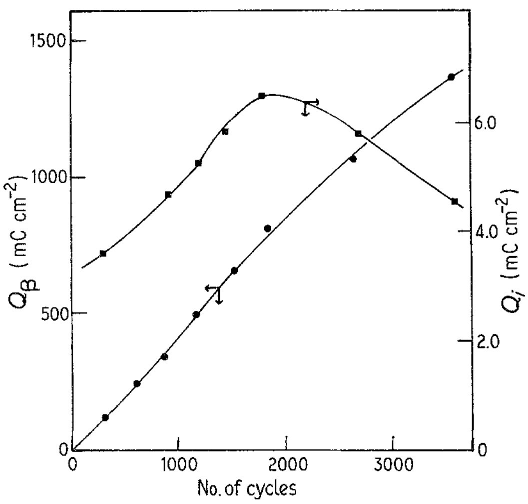

Fig. 4. Variation of the charge values for a base-grown film on platinum (0.44 to 2.70 V, 4.52 V s^{-1}) as a function of the number of oxide growth cycles (T = 25° C); the analytical scan in each case was 1.50 to 0 V at 40 mV s^{-1}. Q_i is the charge associated with the peak at about 0.25 V (see curve II, Fig. 3) in base (1.0 mol dm^{-3} NaOH). Q_β is the charge associated with the reduction of the hydrous films, grown in base in an identical manner to those involved in the Q_i determinations, after transferring the electrode to 1.0 mol dm^{-3} H_2SO_4.

reduction in acid of the bulk of the hydrous oxide material. This minor reduction in base above 0 V is also evident in the work of Shibata [14] where the oxide material on platinum was produced by d.c. techniques and in the reduction of palladium oxide layers grown by potential cycling [30].

The film grown in base is assumed to be composed of three components; a monolayer, Pt(II), oxide on the metal surface, a thick, Pt(IV), hydrous oxide layer in contact with the solution, and a thin, possibly Pt(IV), oxide layer of virtually anhydrous material (perhaps PtO_2) formed at the boundary between the monolayer and the hydrated material. The material reduced at 0.25 V in base evidently exists beneath the yellow hydrous film because after the small reduction peak in base the remaining hydrous material, especially with quite thick films, did not adhere well to the metal surface. Furthermore, where adhesion was adequate to allow reduction after transfer to acid the resulting active platinum layer frequently gave erratic currents in the hydrogen adsorption region in subsequent monolayer oxidation–reduction sweeps. Evidently this layer lacked good adhesion – the behaviour of similar surfaces produced by reduction of acid-grown films was much better in this respect. It is worth noting that the peak at 0.25 V in base could only be recorded on the first reduction sweep after the oxide growth process, i.e. little further reduction was observed in this region on subsequent cathodic sweeps even after allowing the electrode to stand, with its residual yellow coating of hydrous material intact, for quite considerable periods of time.

The presence of an intermediate oxide layer was also postulated recently [31] in connection with similar films grown on iridium in base. Local pH changes were found to be important during the oxide growth reaction in the latter case. However, such pH variations are unlikely to be responsible for the peak at 0.25 V in the present case for platinum in base. The latter peak was observed on the cathodic sweep where oxide reduction gave rise to OH$^-$ ions, i.e. the pH change would be in the alkaline direction and likely to be insignificant in a 1.0 mol dm^{-3} NaOH solution.

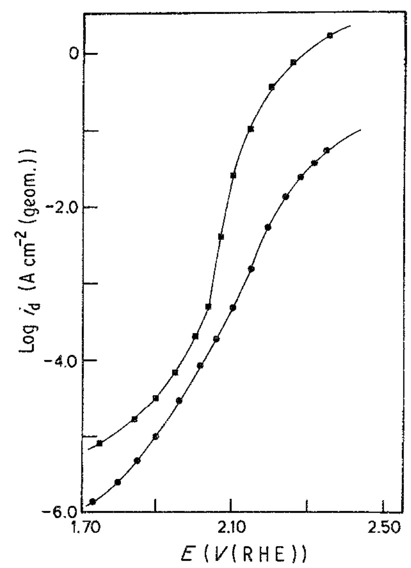

Fig. 5. Effect of enhanced oxide growth on the Tafel plots for oxygen evolution at an originally bright platinum electrode in 1.0 mol dm^{-3} H_2SO_4 at 25° C: (●), uncycled electrode; (■), oxide grown under potential cycling conditions (0.58 → 2.10 V; 100 V s^{-1}) for 9860 cycles.

3.4. *Influence of the hydrous oxide layer on the oxygen gas evolution and other processes at platinum electrodes*

It is well established with other metals [32–34] that the presence of a hydrous oxide film at an electrode surface tends to enhance the rate of anodic reactions such as oxygen or chlorine gas evolution as compared with the corresponding anhydrous oxide. The effect is usually attributed [35] to the increased surface area and greater access of water molecules to the electrocatalytic oxymetal species in the more dispersed material. As outlined in Fig. 5 a similar effect is observed with platinum; in terms of geometric surface area the current density for oxygen gas evolution is significantly higher on the hydrous layer generated by multicycling as compared with the conventional d.c. oxide grown *in situ* on polarizing at increasing anodic values. Typical values were as follows: at 2.15 V the rate of oxygen evolution for uncycled platinum was 1.58 mA cm^{-2}, while with the cycled substrate (see Fig. 5) the corresponding value was 100 mA cm^{-2}. Difficulty was encountered with thicker films; these tended to become detached from the surface at potentials above 2.0 V.

Ideally the current densities for these electrodes should be compared in terms of real (as opposed to geometric) surface area. However, it is not easy to determine the area of the hydrated gel (or hyperextended) film produced on the platinum surface by potential cycling. In similar experiments with iridium [2] the metal area (or hydrogen capacity) usually altered little as the thickness of the hydrous oxide increased under potential cycling conditions. There has been no report to date of *in situ* surface area determination of hydrous oxide coated electrodes; the validity of *ex situ* techniques is debatable in view of possible structural changes accompanying water removal from these systems. The enhanced activity of the cycled electrode for oxygen gas evolution seems to involve more than an increase in roughness or surface area – as outlined below the change in Tafel slope also suggests a significant change in mechanism.

With the uncycled electrode the Tafel slope at 2.00 V was about 120 mV decade^{-1}. However, the value decreased slightly (e.g. to about 103 mV decade^{-1} at 2.12 V) as the potential was increased to the region where hydrous oxide growth is known to occur on platinum [10, 13] under d.c. conditions. A much lower Tafel slope, about 40 mV decade^{-1}, was observed with the cycled, hydrous oxide coated platinum in the region of 2.07 V. Clearly platinum is not a good catalyst for oxygen gas evolution as the reversible potential for this reaction is at 1.23 V. In terms of high-field theory the high overpotential is due to the low conductivity of the surface layers, while according to the low-field approach it is due to a combination of two related factors, (a) inability of the surface to stabilize discharged hydroxyl radicals and (b) the need to generate higher oxidation states, e.g. Pt(V) or Pt(VI), in interfacial oxyspecies. The high-field interpretation appears, from the work of Kuhn and Randle [4], to be invalid as far as the compact oxide is considered – this material has no influence on simple charge transfer kinetics at platinum anodes. Their subsequent work with the hydrated oxide material [36] will be discussed here later. Above 1.80 V, presumably due to the layer becoming somewhat non-stoichiometric, significant oxygen gas evolution occurs. A Tafel slope of 118 mV decade^{-1} is usually regarded [37] as being indicative of rate control due to the first electron transfer step – which of course also involves hydroxyl radical formation and problems associated with stabilization of the later, namely

$$H_2O = H^+ + e^- + OH_{ads} \qquad (18)$$

With the hydrous films, especially in the case of the thick layers grown by cycling, the drop in Tafel slope value clearly indicates that the first electron transfer step is no longer rate-determining, possibly because this electron is now being supplied by an anionic platinate group. By analogy with the scheme given earlier for oxygen evolution on RuO_2 [38], where a 40 mV slope was also observed at 25° C, the following mechanism is suggested for hydrous platinum oxide substrates

$$[Pt(OH)_6]^{2-} + H_2O = [PtO(OH)_5]^{2-} + H_3O^+ + e^- \qquad (19)$$

$$[PtO(OH)_5]^{2-} = [PtO(OH)_5]^- + e^- \text{(r.d.s.)} \qquad (20)$$

$$[PtO(OH)_5]^- = Pt(OH)_4 + O_2 + H^+ + 2e^- + 2H_2O - 2H^+ \qquad (21)$$

The basic difference between the compact and hydrated oxide films with regard to oxygen gas evolution is that in the latter the degree of oxygen coordination is greater, this oxygen is present largely in terminal (-OH) rather than bridging (Pt–O–Pt) form, the structure is more open, and solvent molecules can penetrate to a significant extent into the surface layer. On the compact layer the first step, Equation 18, is inhibited as the OH radicals formed probably have to be stabilized on the compact oxide, not on the metal itself. However, on the hydrated material the OH species are already coordinated to the cations: the first oxidation step, Equation 19, is rapid as it is accompanied by a rather facile proton loss reaction. It is the second step, Equation 20, that is rate-limiting in this case – presumably due to the difficulty of generating the Pt(VI) state. The nature of the subsequent steps is unknown. There may be interaction, e.g. formation of peroxy species, between OH groups coordinated at adjacent sites of the same metal cation or between such groups coordinated at neighbouring cations.

The increase in Tafel slope at the upper end of the potential scale used in these experiments is probably due to a combination of factors, e.g. the effect of the increasing rate of evolution of gas bubbles which screen the surface – thereby decreasing the effective surface area (or increasing the current density) – and increase the resistance in the solution, especially close to the interface. Also, at the high current densities involved in this region, water penetration into the inner region of the film – to compensate for that lost in the electrolysis reaction – may be inadequate, i.e. the evolution reaction at high current densities becomes restricted to the external surface of an oxide layer that becomes progressively more anhydrous. All the phenomena associated with bubble formation are expected to increase the Tafel slope – as observed, Fig. 5, above a potential of about 2.1 V for the hydrous oxide coated electrode. The interesting section of this plot, however, is the low current density region, 1.0 to 50 mA cm^{-2}, where the marked *decrease* in Tafel slope seems to be a genuine electrocatalytic effect for this reaction.

The influence of oxide films on apparently simple electron transfer processes, e.g. Ce(III)/Ce(IV) and Mn(II)/Mn(III) transitions [4, 36], at platinum electrodes is quite interesting. The reactions in question were selected originally on the basis of their simplicity (no adsorption steps or chemical interaction with the oxide); the basic idea was to test the electron transfer properties of the surface layers. As mentioned earlier, Kuhn and Randle [4] found in the first part of their work that the compact material (oxide 1) had no influence on the charge transfer kinetics for the above reactions. However, the presence of a hydrated oxide film (oxide 11) has a severe inhibiting effect [36] which the authors found difficult to explain. It was suggested that the observed behaviour was associated with inhibition of charge transfer through the relatively thin films of the hydrated oxide material – yet the authors pointed out that the expected electron tunnelling behaviour was not observed, e.g. ln *i* did not decrease in a systematic linear manner with increasing oxide thickness. Furthermore, the inhibition became significant when there was less than a monolayer of hydrated oxide on the surface.

These results may be explained by taking into account the difference in charge character of the two different types of oxide material. The compact oxide is not strongly charged and has little influence on the redox behaviour of the solution cations. However, as outlined here earlier, the hydrated material is anionic and the solution cations, e.g. Ce^{3+}, may be assumed to adsorb quite strongly on the latter – the forces involved being largely electrostatic and the reaction may be considered as an ion-exchange type process in which the multivalent cation replaces protons (the reactions were carried out at low pH). The initially bound Ce^{3+} ion probably oxidizes readily but the product, Ce^{4+}, will remain at (or within) the hydrated anionic oxide material and inhibit further reaction – thus (as observed) the steady-state current is low. For both processes investigated the inhibition was more severe for the cathodic reaction, i.e. Ce^{4+} or Mn^{3+} reduction. This suggests that Ce^{3+} or Mn^{2+} was more strongly bound than Ce^{4+} or Mn^{3+}; this may not be too surprising as the more highly charged ions are likely to be more extensively hydrated and therefore less firmly attached to the charged hydrous oxide. The interpretation given here emphasizes once again the importance of the charged character of hydrous oxide materials. While the latter has been largely ignored for insoluble oxide materials in electrochemistry until quite recently, it is a well established feature in their ion-exchange behaviour which has significant technological applications [39].

In conclusion it may be pointed out that support for the views expressed here with regard to the behaviour of platinum hydrous oxide, and especially the role of the latter in electrocatalysis, is provided by the recent work of Goodenough and coworkers [40]. XPS investigation of a Pt–Ru alloy electrode, even prior to methanol oxidation, revealed the presence of a Pt(IV) species which the authors formulated as $PtO_2 . nH_2O$ or $Pt(OH)_4$; the latter assignments were taken from earlier work [7, 8, 11] where – as pointed out here earlier – acid–base effects of these oxides were not taken into account. The role of ruthenium in such systems is considered to be that of a co-catalyst, i.e. it promotes the level of 'active oxygen' at the interface. However, the authors [40] concluded that Pt(IV), not Pt(II), is the active ingredient with regard to oxidation processes, even at low potentials, at platinum surfaces in aqueous media; the present authors are obviously in agreement with this viewpoint.

4. Addendum

In line 23, page 317 of [1] the sentence should read as follows: 'For such conditions the mean value for the ratio $Q_\alpha/2Q_H$ (where Q_H is the charge recorded for monolayer hydride formation in the same experiment – the approach used here was that recommended by Woods [12]) was found to vary from 1.25 to 1.10 as the upper limit of the analytical scan was varied from 2.0 to 1.5 V (RHE); in these experiments the electrode was not held constant at the upper limit of the scan for any significant period of time'.

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