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The stability of hydrous oxide films on platinum

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The stability of hydrous oxide films grown on platinum in both acid and base was investigated as a function of holding potential in solutions of different pH. In contrast to similar films grown on gold – whose behaviour was described earlier – the stability of the bulk of the hydrous oxide deposits on platinum was not very dependent on solution pH. This was attributed to a rather facile rearrangement, in the case of platinum, of the initially anionic oxide species to a virtually neutral state. However, there was invariably a minor component in these deposits that was difficult to reduce in base; this probably involves an outer layer of oxide material (the latter being in contact with the aqueous phase) which retained its hyperextended, anionic form. Reduction of the bulk hydrous oxide in base showed a marked degree of inhibition in the region of 0 V(RHE); the effect seemed to be related to the presence of weakly bound hydrogen on the platinum surface. The hydrous oxide growth process on platinum showed a marked dependence on electrode history – this is a topic for further investigation.

1. Introduction

It is well known [1] that two types of oxide films may be grown on platinum in aqueous media, (a) a thin monolayer-type deposit usually formulated as PtO or $Pt(OH)_2$ and (b) a hydrous oxide, frequently multilayer in character, considered to be either a hydrated oxide, e.g. $PtO_2 \cdot nH_2O$ [2], or, more recently [3], a deposit of hexahydroxyplatinate, $([Pt(OH)_6]^{2-})_n$, with counterions (e.g., H^+ or Na^+) intercalated in aqueous regions of the low density aggregate. The platinum hydrous oxide film appears to behave anomalously; while thermodynamic data [2] indicate that none of the conventional oxides of this metal are stable below ~ 1.0 V(RHE), the hydrous oxide deposits are difficult to reduce at potentials above ~0.5 V(RHE) in acid and even at zero volts in base (the latter has been established by both galvanostatic [4] and potential sweep [5] techniques). This type of behaviour may be rationalized by assuming that the hydrous oxide exists as a metastable species whose reduction is inhibited due to the formation of a high energy intermediate, the hydrated adatom; the overall reduction process in acid has been represented [3] as a two-step reaction, *viz.*

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

$$Pt^*(hyd.) \longrightarrow Pt_l \qquad (2)$$

At potentials below ~0.5 V(RHE) Equation 1 is assumed to be fast and reversible whereas the adatom (Pt*) incorporation into the surface lattice, Equation 2, may also be fast but irreversible. This model explains the irreversible nature of the overall reduction process, and the difficulty involved in reducing the film in base (as pointed out earlier [3] the reversible potential for the process shown in Equation 1 drops by 0.5 (2.3 RT/F) volts (RHE scale) per unit increase in solution pH).

The aim of the present work was to examine the stability of platinum hydrous oxide films at constant potential, for a range of different values of the latter. As outlined recently for similar work with gold [6] the rate of reduction was monitored by recording the cathodic current as a function of time for a period of 200 s; at that stage the rate of reduction was generally quite small and the residual oxide was then estimated by stripping it from the surface using a cathodic sweep. This type of investigation should be of interest to other researchers; for example when examining hydrous oxide films using *in situ* spectroscopy techniques it may be necessary to hold the electrode at a fixed potential to allow for data acquisition over a significant period of time. It will be demonstrated here that in fact the major portion of the hydrous oxide layer on platinum is significantly less stable in base than expected from previous work [4, 5].

2. Experimental details

The working and counter electrodes consisted of platinum wires (1 mm diameter, ~0.5 cm² exposed geometric area, Johnson Matthey Chemicals, Puratronic grade) sealed directly into soda glass. The potential of the working electrode was measured, and is quoted here, with respect to a hydrogen reference in the same solution. The solutions were made up using Analar grade chemicals and triply distilled water; the solution in the working compartment of the cell was usually stirred with a flow of purified nitrogen gas.

The potentiostat used for this work (Wenking,

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LT 78) was controlled using a function generator (Thompson Electrochem., Model DRG 16). Currents were recorded as a potential drop across a standard resistor using a potentiometric chart recorder (Ridadenki, Model BW-133). Hydrous oxide deposits were produced using the potential cycling technique outlined earlier [5]; typically this involved either (a) cycling (0.58 to 2.10 V, 80 V s^{-1}) for 5 min in 1.0 mol dm^{-3} H_2SO_4 or (b) cycling (0.45 to 1.95 V, 40 V s^{-1}) for 5 min in 1.0 mol dm^{-3} NaOH (T = 25° C). Oxide coverage values were determined coulometrically using a cathodic stripping technique, i.e. from a cathodic scan, typically 0.80 to 0 V at a sweep rate of 4 mV s^{-1}; this was usually carried out with the platinum electrode in 1.0 mol dm^{-3} H_2SO_4 as quantitative hydrous oxide reduction is not readily achievable in base [5].

3. Experimental results

A typical cyclic voltammogram for platinum in acid is shown in Fig. 1. The usual three peaks, H_w, H_i and H_s can be seen below 0.4 V on the anodic sweep but only two, H'_w and H'_s, are usually seen in the same region of the cathodic sweep. Significant monolayer oxide formation occurred in the region above 0.8 V on the anodic sweep and the reduction of this material gave rise to the rather symmetrical cathodic peak at ~0.75 V on the cathodic sweep. As pointed out recently [7] hydrous oxide growth on platinum in aqueous H_2SO_4 solution by the potential cycling technique can yield two products, one of which reduces at ~0.37 V and the other (which is assumed to contain incorporated electrolyte, e.g. HSO_4^-, species) at ~0.20 V. The effect is illustrated here in Fig. 2; in curve (a) in this case, which was obtained using a hydrous oxide film grown on a fresh platinum electrode (used without any other pretreatment apart from that needed to produce the oxide layer) the two hydrous oxide reduction peaks, C_1 and C_2, were of approximately equal magnitude. The subsequent changes in behaviour of this electrode system with use are illustrated in this diagram. The magnitude of peak C_1 increased while that of C_2 decreased; further changes after the fifth hydrous oxide growth and reduction experiment (curve (e) in Fig. 2) were quite small. In the present case a brief aqua regia etch was used after each experiment to remove the outer layers of disturbed metal atoms. While consistent data was obtained after the fifth run the marked influence of surface pretreatment and morphology on hydrous oxide growth and reduction behaviour was considered worthy of further investigation; the results of the latter will be presented when the work is completed.

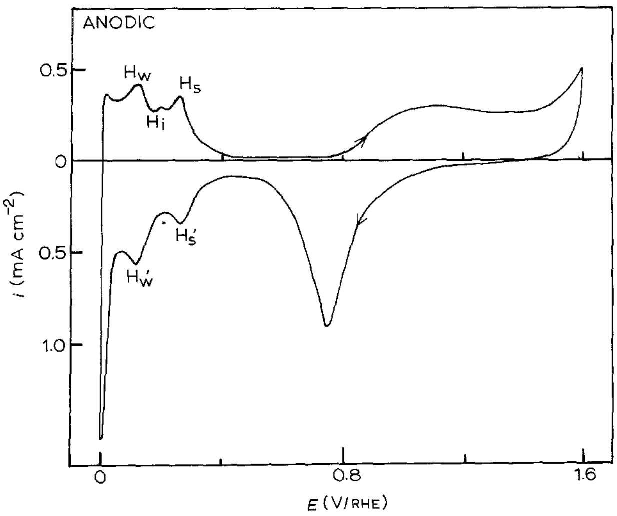

Fig. 1. Typical cyclic voltammogram (0 to 1.60 V, 50 mV s^{-1}) for a platinum electrode in N_2-stirred 1.0 mol dm^{-3} H_2SO_4 at 25° C.

H_w and H'_w, and H_s and H'_s, Fig. 1, are attributed to the formation and removal of weakly and strongly bound surface hydrogen, respectively; H_i is assumed to be the anodic counterpart of C_2 while the corresponding anodic peak for C_1 is assumed to be contained within the tail of H_s, i.e. over the range 0.3 to 0.45 V. It was pointed out earlier [8] that organic oxidation processes, involving oxygen insertion from water, usually commence on Pt at ~0.2 V(RHE), i.e. in the region of peak H_i where incipient hydrous oxide formation is assumed to commence on the anodic sweep. The region for the most marked rise in current for the oxidation of species such as N_2H_4 that do not deactivate the surface is observed [8] at ~0.4 V(RHE), i.e. at approximately the potential of peak C_1. The conclusion drawn earlier was that low coverage, incipient hydrous oxide species formed at adatom sites were important mediators in electrooxidation processes on platinum (it is worth noting here that a similar mechanism was suggested quite recently by Angerstein-Kozlowska and coworkers [9] to explain the mechanism of hydrogen oxidation at gold single crystal electrode surfaces): the low response for hydrous oxide generation on the anodic sweep,

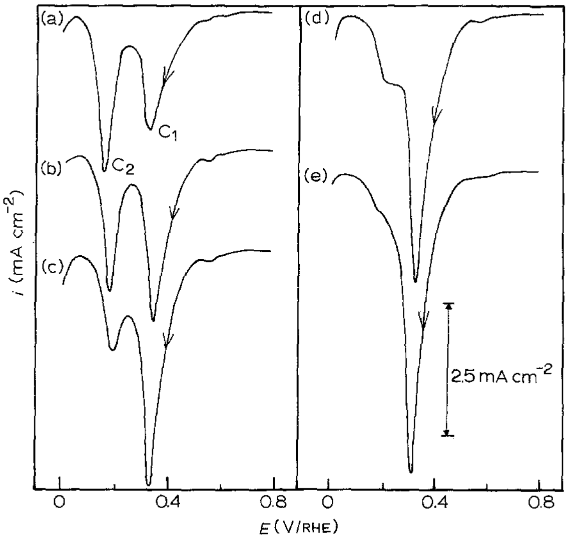

Fig. 2. i-E profiles for hydrous oxide reduction, 0.8 to 0.0 V at 4.0 mV s^{-1}, for a platinum electrode in 1.0 mol dm^{-3} H_2SO_4 at 25° C. In the first case, (a), the film was grown by cycling (0.58 to 2.10 V, 80 V s^{-1} for 5 min) on a fresh electrode. In subsequent experiments, (b) to (e), the oxide growth and reduction procedure was repeated in the sequence shown here: after (a) the electrode was pretreated before each run by immersion for 30 s in warm aqua regia.

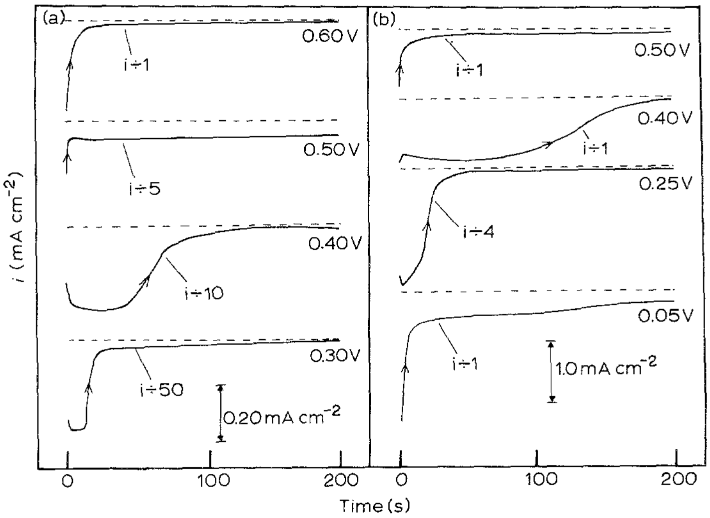

Fig. 3. Current decay plots recorded under potentiostatic conditions for duplex oxide coated platinum electrodes in (a) 1.0 mol dm^{-3} H_2SO_4 and (b) 1.0 mol dm^{-3} NaOH, $T = 25°C$; the different holding potential values are given in the diagram. The oxides were produced by (a) cycling between 0.58 and 2.10 V, 80 V s^{-1} for 5 min, in 1.0 mol dm^{-3} H_2SO_4, and (b) cycling between 0.45 and 1.95 V, 40 V s^{-1} for 5 min, in 1.0 mol dm^{-3} NaOH. The dashed line above the cathodic curve in each case is the zero current line.

compared with C_1 and C_2, is attributed to post-electrochemical adatom decay ($Pt^* \rightarrow Pt_l$). A final point worth noting in the case of Fig. 2 is the location of the monolayer oxide reduction peak on the first sweep after growing the thick film (the electrode, after cycling, is usually coated with a duplex deposit – an inner monolayer oxide film and an outer multilayer hydrous oxide deposit); the peak potential for this process dropped from ~0.75 V to ~0.55 V, Fig. 1; however, this is not unusual as the potential for monolayer oxide reduction is generally dependent on the thickness or potential of formation of the film and in this case the layer was produced using an upper limit of 2.1 V.

Some typical current–time profiles recorded on imposing various fixed potentials on duplex oxide coated platinum electrodes in acid are shown in Fig. 3a. A more complete summary of the data obtained in such experiments is shown in Fig. 4a where the charge for oxide reduction, integrated over the first 200 s, is plotted (curve A) as a function of holding potential. The charge for the residual oxide, estimated from a single sweep recorded after the 200 s holding period is also shown in this diagram (curve B) – along with the net charge for oxide reduction (curve C) – as a function of the holding potential. According to the data shown in curve C the initial oxide coverage was approximately the same in all these experiments. On lowering the holding potential some loss of oxide could be detected below ~0.7 V, quite significant loss was observed on holding between 0.55 to 0.45 V while total oxide reduction was achieved in less than 200 s on holding the potential at, or below, 0.4 V.

The first two curves in Fig. 3a show that on holding at 0.6 or 0.5 V the oxide reduction process is quite slow and the process is incomplete at the end of the 200 s holding period. The two lower curves in this diagram show that the oxide reduction process is quite rapid at 0.4 or 0.3 V; the bulk of the oxide is reduced at a constant rate, the magnitude of the latter increasing on lowering the value of the applied potential, Fig. 5.

Similar data for platinum in base is shown in Figs 3b and 4b; it is important to note here that the data for the residual oxide (curve B, Fig. 4b) was obtained by reducing the film, after holding for 200 s in base, in acid solution. The oxide in this case again showed some indication of reduction on holding at potentials in base between 0.5 to ~0.7 V; on lowering the potentials to within the range 0.5 to 0.3 V the reduction was more vigorous; maximum (though never complete) oxide reduction was observed on holding the potential between 0.15 to 0.3 V. The three surprising features of the results shown here were: (a) at first glance the oxide film in base was not very much more stable than in acid (compare curve A in Fig. 4a over the range 0.6 to 0.3 V with its equivalent in Fig. 4b); (b) it was not possible in any of these experiments with base to attain *total* oxide reduction;

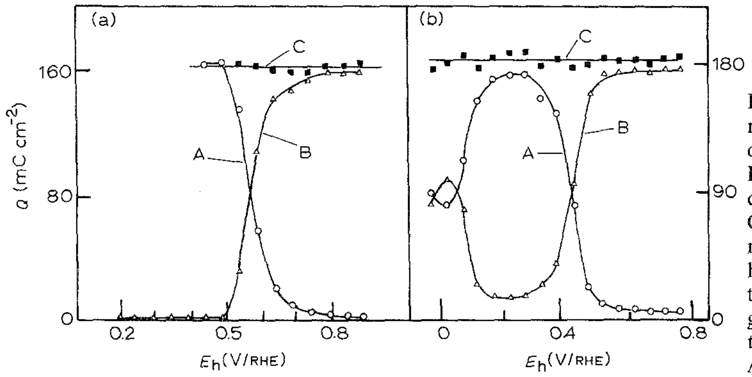

Fig. 4. Effect of the holding potential (E_h) on the charge recorded over a holding period of 200 s (curve A) due to oxide film reduction on platinum in (a) 1.0 mol dm^{-3} H_2SO_4 and (b) 1.0 mol dm^{-3} NaOH, $T = 25°C$; the duplex films were produced as outlined in Fig. 3. Curve B shows the charge for the reduction of the residual oxide in 1.0 mol dm^{-3} H_2SO_4 (quantitative hydrous oxide reduction was not achievable in base), i.e. the quantity remaining after the 200 s polarization at a given E_h value. The charge values for total oxide reduction (curve C) were got by summing the values for curves A and B.

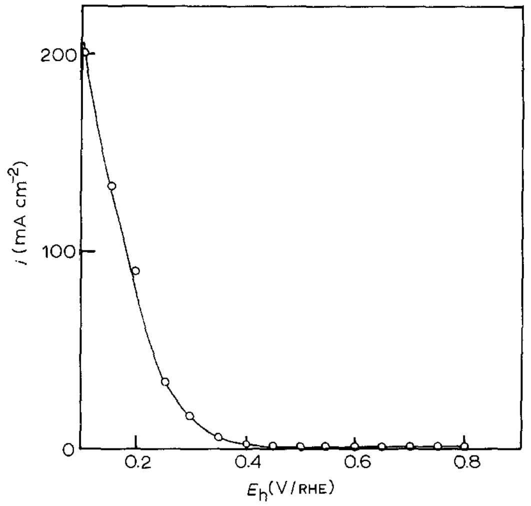

Fig. 5. Effect of holding potential (E_h) on the plateau current associated with oxide film reduction on platinum in 1.0 mol dm^{-3} H_2SO_4, $T = 25°C$. The oxide films were produced by cycling between 0.58 and 2.10 V, $\nu = 80\,V\,s^{-1}$, for 5 min in 1.0 mol dm^{-3} H_2SO_4.

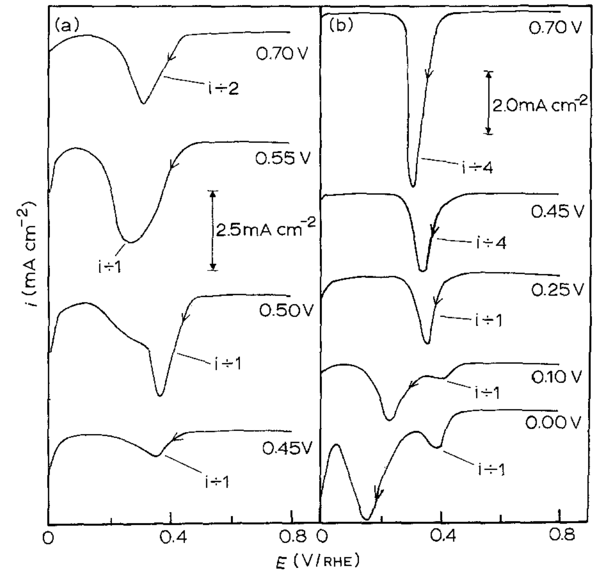

Fig. 6. i–E behaviour for residual oxide reduction at a platinum electrode in 1.0 mol dm^{-3} H_2SO_4 at 25°C. The oxide films were grown in acid (a) and base (b) as outlined in Fig. 3, then held at the potential values stated in this diagram (in acid (a) and base (b)) for a period of 200 s prior to the single sweep reduction (0.80 to 0.0 V, 4 mV s^{-1}) experiments, the responses for which are shown here.

there was always a significant residue (even after holding at 0.15 to 0.3 V) evident in oxide stripping experiments (curve B) carried out in acid; and (c) the oxide reduction over the 200 s period in base was surprisingly inefficient on holding the electrode at potentials lower than 0.15 V.

Some examples of current–time curves for reduction in base are shown in Fig. 3b. There was again evidence in such experiments, e.g. on holding at 0.40 to 0.25 V, that the bulk of the oxide reduction process occurred at a constant rate. At lower values of the holding potential (0.10, 0.05 or 0.00 V) the rate of oxide reduction was low, it decayed with time and was still significant at the end of the 200 s holding period.

Some examples of the stripping curves recorded for the removal of residual oxide after holding the potential constant for 200 s are shown in Fig. 6. The curves for oxide deposits held in acid were usually relatively broad, with a peak maximum at ~0.32 V; they frequently had a shoulder on the cathodic side, i.e. at a potential lower than the above value. However, for films grown and held in base and then stripped in acid the reduction peak was usually significantly sharper; indeed at high coverages of residual oxide, e.g. after holding at 0.8 to 0.5 V, the drop after the peak maximum (again at ~0.3 V) was quite dramatic. A significant difference was noted on stripping residual oxide after holding these films in base at potentials less than 0.15 V; following transfer to acid such residual films gave rise to two reduction peaks, one at ~0.4 and the other at ~0.2 V. Data for a more extensive, separate series of residual oxide stripping experiment are shown in Fig. 7; this confirmed the fact that the oxide reduces rapidly (though not completely) on holding the potential in the region of 0.2 to 0.35 V in base; the process was quite inefficient on holding at 0 V but became more effective again as the potential was held at significantly more cathodic values.

Some data for oxide reduction obtained on holding the potential of base-grown hydrous oxide deposits at constant potential in phosphate buffer solutions of different pH are shown in Fig. 8. Significant reduction was observed on holding the potential at values less than ~0.4 V; this was just slightly lower than that required for significant reduction in acid or base; however, the effect of solution pH in such experiments seemed to be surprisingly small – particularly in view of the marked dependence observed recently [6] in the case of similar experiments carried out with gold.

4. Discussion

The most surprising feature of the present results was the apparent difference in stability of the hydrous platinum oxide films in base under steady state

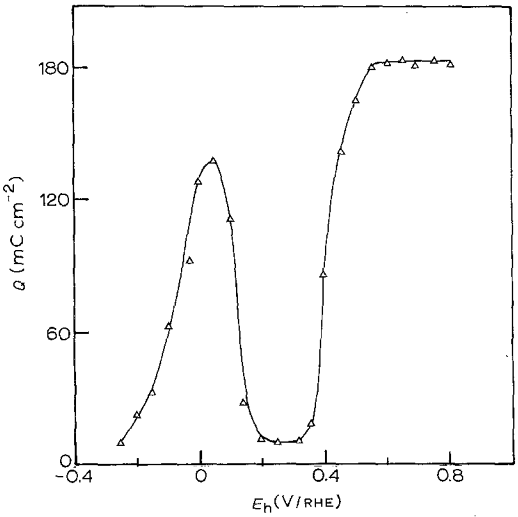

Fig. 7. Residual oxide values (Q) recorded in cathodic sweep experiments, following transfer to acid, after holding the potential of duplex oxide coated Pt electrodes for 200 s at various holding potentials (E_h) in 1.0 mol dm^{-3} NaOH at 25°C. The films were grown by multicycling in base, 0.45 to 1.95 V, 40 V s^{-1} for 5 min.

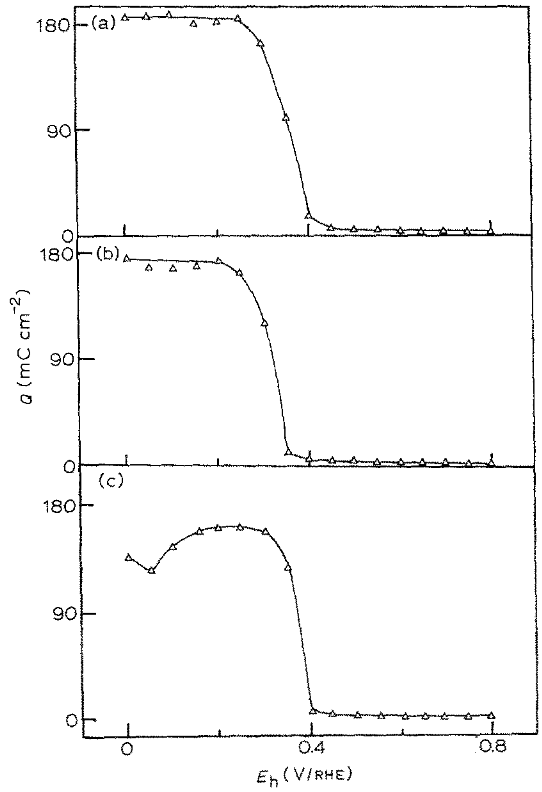

Fig. 8. Effect of holding potential (E_h) on the charge recorded over a holding period of 200 s due to oxide film reduction on platinum in 0.10 M phosphate buffer solutions of different pH values: (a) 3.5, (b) 7.0, and (c) 10.5 at $T = 25°$ C. The duplex films were produced as outlined in Fig. 7 (for pH 7.0 there was no difference in behaviour between acid-grown and base-grown deposits).

polarization, as compared with cyclic voltammetry, conditions. Although there is a report [3] that a minor component of the layer reduces under cathodic sweep conditions, the bulk of the material was found to be stable at potentials well into the hydrogen gas evolution region [4, 5]. However, the data shown here in Fig. 4 demonstrate that at ~ 0.4 V there is little difference in stability between acid and base; the material is apparently slightly more difficult to reduce at this potential in base but the difference is much less than expected in terms of a 0.5 ($2.3\,RT/F$) V/pH unit (RHE scale) shift in reduction potential (as observed and discussed recently for similar films on gold [6]) with change in solution pH. The other noteworthy feature in these experiments is that under conditions of constant polarization in base, Fig. 4b, it was never possible, even on polarizing for example at 0.2 V, to achieve complete reduction of the thick hydrous oxide layer. The presence of the residual oxide was easily established in subsequent potential sweep experiments – see the peak(s) just below 0.4 V in Fig. 6b. This effect can scarcely be attributed to low reactivity of the oxide material; at a potential of 0.25 V, Fig. 3b, most of the oxide was removed during the first 20 s of polarization. Despite the fact that the cathodic current for the remaining 180 s was virtually negligible, there was a significant hydrous oxide response when this electrode was subsequently reduced (see the curve for 0.25 V in Fig. 6b) in acid.

The simplest explanation of the effect reported here is that these hydrous oxide films are not uniform. The material is probably only poorly crystallized, with the outer regions of the microparticles more dispersed, hydrated – and therefore more accessible to hydroxide ions – in base, than the interior. Strong evidence to support this view of oxide systems was obtained [10] in recent electron microscopy studies of battery grade PbO_2. It was suggested earlier [6] that the following type of equilibrium may be involved in the case of platinum, *viz.*

$$Pt(OH)_6^{2-} + 2H^+ \rightleftharpoons H_2Pt(OH)_6 \rightleftharpoons PtO_2 \cdot 4H_2O \qquad (3)$$

There may be loss of water from the hydrated oxide in the interior of the microparticles as the material partially crystallizes. However, the exterior of the microparticles is exposed to the highly basic solution and in this region the oxide is likely to remain stabilized in the anionic form. Support for this view can also be found in recent work on hydrous iridium oxide films [11]; the well-known electrochromic effect in such deposits may be removed or quenched by exposure to UV light. In the latter case the quenching is effective even though less than 30% of the charge storage capacity of the film is lost at the same time due to the irradiation. Evidently only a certain percentage of the material in this type of deposit, presumably the highly hydrated outer portion, is active with regard to the electrochromic effect. In the case of platinum the uncharged oxide reduces at virtually the same potential in base as in acid, *viz.*

$$PtO_2 \cdot xH_2O + 4H^+ + 4e^- = Pt + (x + 2)H_2O \qquad (4)$$

whereas the residue of more dispersed anionic material should reduce, see Equation 1, at a considerably lower potential at high pH. It is evidently this dispersed material that can withstand reduction in base at ~ 0.25 V and give rise to the peak at ~ 0.37 V, Fig. 6b, when the electrode is subsequently subjected to a cathodic sweep in acid.

The other, quite unusual feature of the hydrous oxide reduction process in base is the increase in resistance of the deposit to reduction as the polarization potential of the electrode is lowered below ~ 0.15 V, Figs 4b and 7. The origin of this effect is uncertain; it is assumed to be due to the influence of chemisorbed hydrogen at the interface which is quite significant below 0.2 V, see Fig. 1. It was demonstrated recently [12] that other cathodic reactions such as acetone hydrogenation on platinized platinum also exhibit inhibition effects at high hydrogen coverage; possibly the hydrous oxide species in the present case only reduce when present at the interface in a chemisorbed state – and such chemisorption is inhibited at high hydrogen coverage. Other factors to be borne in mind here are the effect of hydrogen chemisorption on both the activity and rate of decay of adatom species (see Equations 1 and 2), as well as the state of charge of the chemisorbed hydrogen. If the presence of hydrogen impedes the adatom decay process, Equation 2, then the presence of a high adatom activity at the interface should inhibit the formation of such adatoms which in the present case are produced by the reversible reaction shown here in Equation 1. Alternatively, if the hydrogen is present at the interface in a protonic form hydrous oxide species interacting with the latter are more likely to exist as anions, e.g. $Pt(OH)^{2-}_{6(ads)}$, and the latter are less readily reduced in base than their neutral equivalents. The loss of oxide at potential below 0 V (Fig. 7) may well entail reduction of such anionic species – the potential estimated for the latter in base is assumed to be somewhat less than 0 V. The value estimated previously [3] for $Pt(OH)^{2-}_6$ reduction was approximately -0.2 V; this was based on a peak value for the same reaction in acid being at ~0.2 V: however, since under certain conditions there is a further major oxide reduction peak for acid [7] at ~0.37 V, the corresponding value for base may have to be revised upwards to ~0 V.

The bulk of the hydrous oxide material reduced in acid, under conditions of constant polarization, i.e. Fig. 3a, at a constant rate; however, the value of the latter, Fig. 5, was highly dependent on the applied potential. Such behaviour may be rationalized in terms of the scheme outlined here in Equations 1 and 2. The slow step is the adatom decay process, Equation 2, whose rate is independent of the quantity of oxide remaining on the surface. Lowering the reduction potential, especially in the region below 0.4 V, raises the adatom activity at the interface which in turn raises the rate of adatom decay, hence the rapid rise in the plateau current, Fig. 5, with increasing value of the reduction potential. Essentially the same type of behaviour is observed in base, Fig. 3b and thus the same explanation is assumed to be valid.

The responses for residual oxide stripping experiments in the case of acid-grown films, Fig. 6a, show that the material involved in peak C_1 (see Fig. 2) is the main component in the layer. However, the peak in many instances was quite broad (with occasional indications of a shoulder at lower potentials, i.e. in the region of peak C_2 as, for example, the response for 0.5 V in Fig. 6a); it may well be that there are usually traces of sulphate species incorporated into films grown by cycling in aqueous H_2SO_4 solution. The peaks recorded for residual oxide reduction in the case of base-grown films, Fig. 6b, were much sharper (at least for holding potential values above ~0.2 V) and generally in the region of peak C_1. The responses for residual oxide reduction for holding potentials below 0.2 V (lower region of Fig. 6b) were significantly different as here two peaks were noted, with the magnitude of C_2 exceeding that of C_1. This is the region, 0.2 to 0.0 V, where anomalous behaviour was noted in the oxide stripping experiments, Fig. 7. Assuming that C_2 corresponds to oxide containing incorporated sulphate species, which is unexpected in this case considering that these films were grown and polarized in sulphate-free base, it seems that polarizing in the hydrogen adsorption region (below 0.2 V) maintains the film in the hyperextended (or low density) state which can then absorb HSO_4^- or SO_4^{2-} ions on transfer to acid. Possibly above 0.2 V the metal surface can interact strongly with the oxide species – promoting crystallization and partial dehydration of the latter; such interaction is assumed to be impeded below 0.2 V due to the high hydrogen coverage at the interface.

The data recorded for oxide film reduction, under constant polarization conditions, in solutions of intermediate pH, Fig. 8, support the view that the stability of the bulk of the material is not very dependent on solution pH. There was also an indication here, in Fig. 8c, that at high pH there was increased resistance to reduction, in a minor component of the film, as the polarizing potential dropped below 0.2 V.

5. Conclusions

The conclusions from this work are as follows:

(1) The major portion (100% in acid and *ca.* 95% in base) of the thick hydrous oxide film formed *in situ* on platinum by the potential cycling technique reduces rapidly below ~0.65 V in acid and ~0.5 V in base. At a given potential this reduction, for most of the reaction, occurs at a constant rate which is probably determined by the adatom decay process.

(2) The hydrous oxide reduction process at constant potential in base exhibits an unusual degree of inhibition at potentials below ~0.2 V, i.e. when weakly bound hydrogen is present at the interface; while such inhibition is probably due to the presence of such hydrogen, a fundamental interpretation of this phenomenon is yet to be developed.

(3) Incomplete reduction of the hydrous oxide deposit at a potential of 0.2 to 0.4 V in base seems to be related to a more dispersed form of the oxide, probably present initially at the oxide film/solution interface, which exists in an anionic form, e.g. as platinate ions.

(4) The difference in oxide reduction behaviour between acid and base (in terms of *E*–pH shift) is less dramatic (as least for the bulk of the oxide) in the case of platinum as compared with gold [6]. Evidently the bulk of the hydrous oxide formed on platinum can rearrange more easily to the uncharged state.

(5) The growth of the hydrous oxide material, and in particular the ratio of the two possible products identified by the cathodic peaks – Fig. 2, shows a curious dependence on the electrode history; this aspect of platinum behaviour is currently being more extensively investigated.

(6) The non-uniform nature of the hydrous oxide deposits, with neutral and anionic regions present plus the likelihood of loss of bound water, are features to be borne in mind when attempting to characterise these films using ultra high vacuum spectroscopy techniques [13, 14].

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