JOURNAL OF APPLIED ELECTROCHEMISTRY **25** (1995) 913–922

Formation and reduction of hydrous oxide films on platinum in aqueous solution at 273 K

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Received 29 September 1994; revised 16 March 1995

Although the conventional cyclic voltammetry behaviour of platinum in aqueous acid media is not markedly dependent on temperature there is one quite interesting temperature effect in the hydrous oxide growth reaction. In multilayer oxide growth under potential cycling conditions at 273 K the optimum lower limit was found to be about 0.25 V (not 0.58 V as demonstrated earlier for the same reaction at room temperature). This suggests that partial retention of the monolayer oxide is not required for hydrous oxide growth; one of the main functions of the multicycling procedure is to repetitively activate the metal surface so that continued hydrous oxide growth can take place. With such a negative value for the lower limit the multilayer oxide deposit obtained is virtually pure HO2 material; HO1 (or mixtures of HO1 and HO2) were produced by using a more positive value for the lower limit. Some interesting anomalies in platinum oxide electrochemistry are outlined that again highlight the fact that this is a more complex system than is generally realized.

1. Introduction

The electrochemistry of hydrous oxides [1] of the noble metals has been the subject of increasing interest in recent years. The behaviour of platinum hydrous oxides has received considerable attention [2–14], partly due to the fact that submonolayer coverages of such deposits on platinum may have an important influence on the electrocatalytic performance of this metal [10, 13]. Deposits suitable for electrochemical investigation may be produced on the parent metal by subjecting the latter to d.c. anodization [15, 16], potential cycling [17] or potential pulsing [18] techniques. Since hydrous oxides generally tend to be poorly crystalline, water swollen, gel-type materials, details of their composition and structure are frequently lacking. As discussed elsewhere [11] the formation and reduction of hydrous oxide deposits on platinum occur under highly irreversible conditions; this has been attributed [11, 13] to the influence of the lattice coordination number (or stabilization energy) of surface metal atoms.

Most of the work to date on hydrous oxide films has been carried out at room temperature, i.e. at about 298 K. The effect of temperature is interesting. One example, from recent work in this laboratory [19], has been to demonstrate that with platinum in acid solution at 333 K there are frequently three hydrous oxide reduction peaks. Evidently the hydrous (or β) oxide film may contain up to three components (HO1, HO2 and HO3). Normally at room temperature only two cathodic peaks (corresponding to reduction of HO1 and HO2 [10, 20]) are observed (at 333 K the peak for HO3 reduction occurred at about 0.0 V). The present work involved a survey of the formation and reduction of hydrous oxide films on platinum in acid at 273 K. One of the surprising features was the fact that these deposits could be produced on the parent metal using a lower cycling limit value, during multilayer oxide growth, that was significantly more negative (at about 0.25 V) than the potential range involved in monolayer oxide film reduction. Evidence was also obtained for the presence of a platinum oxide species that is not easily reduced in acid at a potential of about 0 V.

2. Experimental details

The equipment and approach used in this work were outlined in a recent publication [9]. Generally, the cell, including the reference electrode compartment, was suspended in a stirred ice/water mixture. The electrolyte temperature was measured directly with the thermometer bulb immersed in the cell solution. All potentials were measured, and are quoted, with respect to a hydrogen reference electrode (RHE) in the same solution. Since the hydrous oxide growth process is influenced by the electrode pretreatment (or history), especially the number of previous hydrous oxide film growth and reduction experiments [21] with a given surface, the usual pretreatment of the bright platinum wire (1.0 mm diam.) surface was a brief etch in aqua regia, a wash with distilled water, mild abrasion with fine emery paper, followed by a second wash with distilled water.

3. Results

3.1. *Effect of lowering the temperature on the cyclic voltammetry of platinum in acid solution*

Typical cyclic voltammograms for platinum in acid are shown for 298 K (full line) and 273 K (dotted

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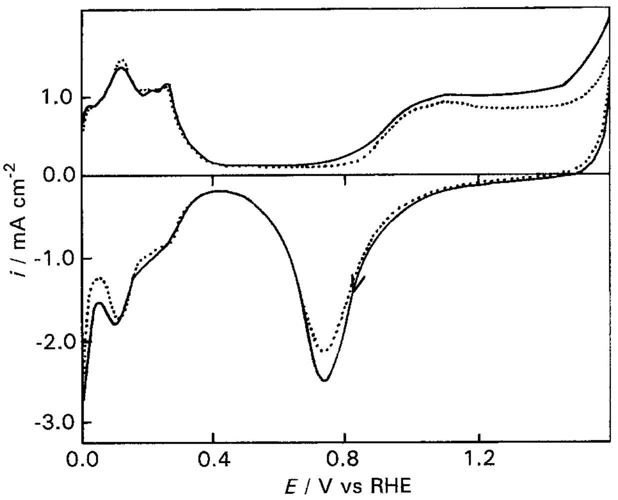

Fig. 1. Cyclic voltammograms (0–1.6 V, 50 mV s^{-1}) for bright Pt in 1.0 mol dm^{-3} H_2SO_4 at (—) 273 K and (●●●) 298 K.

line) in Fig. 1. The effect of the temperature change, especially in the hydrogen region, was not dramatic. In the monolayer oxide (or OH_{ads} and O_{ads}) formation/reduction region the current (or charge) values were lower at 273 K (the formation of the film is evidently a slow process that proceeds to a somewhat lesser extent at the lower temperature) but the peak maximum potential for the oxide removal process was virtually independent (over the rather short range involved here) of temperature.

3.2. *Effect of the upper limit for oxide growth in acid solution at 273 K*

Some typical examples of oxide reduction profiles for films grown on bright platinum in acid at 273 K by the potential cycling technique are shown in Figs 2 and 3. In this series of experiments the lower limit during oxide growth was maintained at a constant value of 0.58 V (this being the optimum value [17] for oxide growth on Pt in acid at 298 K) while the upper limit was varied. With an upper limit $\leqslant$ 2.1 V three peaks, Fig. 2(c), were usually observed. The first (C_1), attributed to reduction of the inner monolayer oxide, usually overlapped with the second (C_2). C_2 and C_3 were attributed to reduction of the hydrous oxide species, HO1 and HO2, respectively. Typical peak maximum values in these experiments, taken from Fig. 2(c), were 0.55 V (C_1), 0.35 V (C_2) and 0.16 V (C_3), the dominant feature in the sweeps shown in Fig. 2 being peak C_2 (i.e. the main product on cycling in these experiments was the HO1 oxide). On increasing the upper limit for oxide growth to values within the range 2.2 to 2.9 V peaks C_2 and C_3 seemed to merge. In such experiments, see Fig. 3, the monolayer oxide removal peak occurred at about 0.5 V while the single (possibly composite, a shoulder was evident in some cases) hydrous oxide removal peak appeared within the region 0.25 to 0.10 V (see Fig. 4). In this work where the lower limit was 0.58 V, all the hydrous oxide material appeared to be removed by the end of the first negative sweep; there was no cathodic response on the subsequent positive sweep. The charge for oxide growth did not alter dramatically with the upper limit (Fig. 4) for values of the latter above 2.0 V: it varied from 61 (at 2.0 V) to 80 (at 2.9 V) mC cm^{-2}; the maximum, about 98 mC cm^{-2}, being observed with an upper limit of about 2.2 V. The data for the upper limit shown in Fig. 4 were recorded using only one value for the lower limit (0.58 V): as outlined later (in Fig. 9) much larger charge values were observed using a much lower value, 0.25 V, for the lower limit during the oxide-growth cycling process. The influence of the lower limit was more complex than expected, the detailed interaction between these two limits with regard to oxide growth and reduction behaviour was not investigated in the present work in an exhaustive manner.

3.3. *Effect of the lower limit for oxide growth in acid solution at 273 K*

A number of interesting observations were made during the course of this aspect of the work, namely,

(i) For a given set of oxide growth conditions the reduction profile (and evidently the nature of the oxide film) varied significantly over the first few experiments with an initially fresh electrode surface

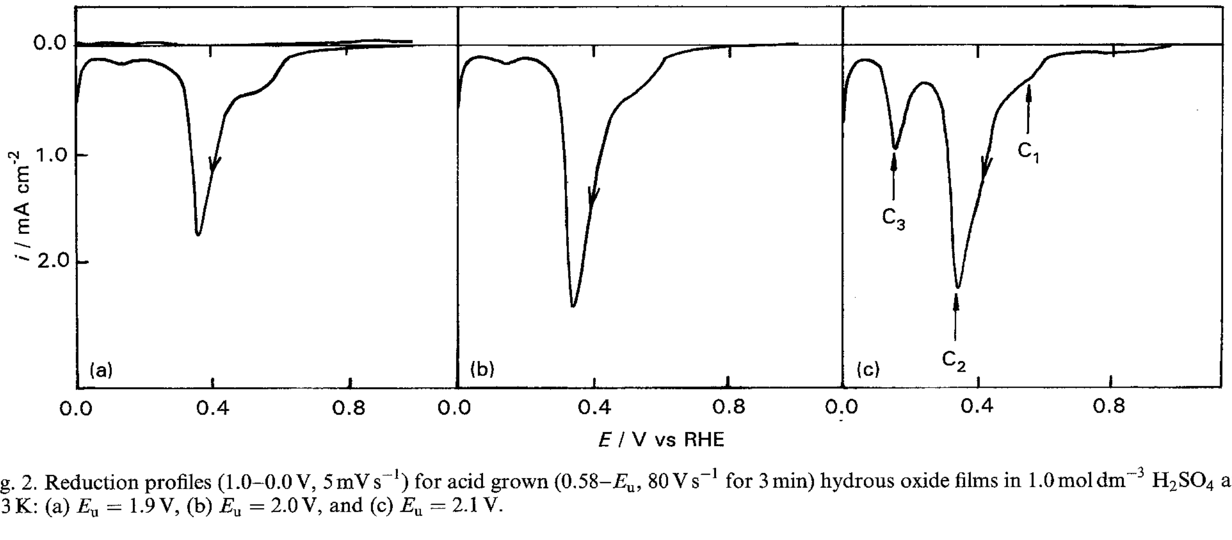

Fig. 2. Reduction profiles (1.0–0.0 V, 5 mV s^{-1}) for acid grown (0.58–E_u, 80 V s^{-1} for 3 min) hydrous oxide films in 1.0 mol dm^{-3} H_2SO_4 at 273 K: (a) E_u = 1.9 V, (b) E_u = 2.0 V, and (c) E_u = 2.1 V.

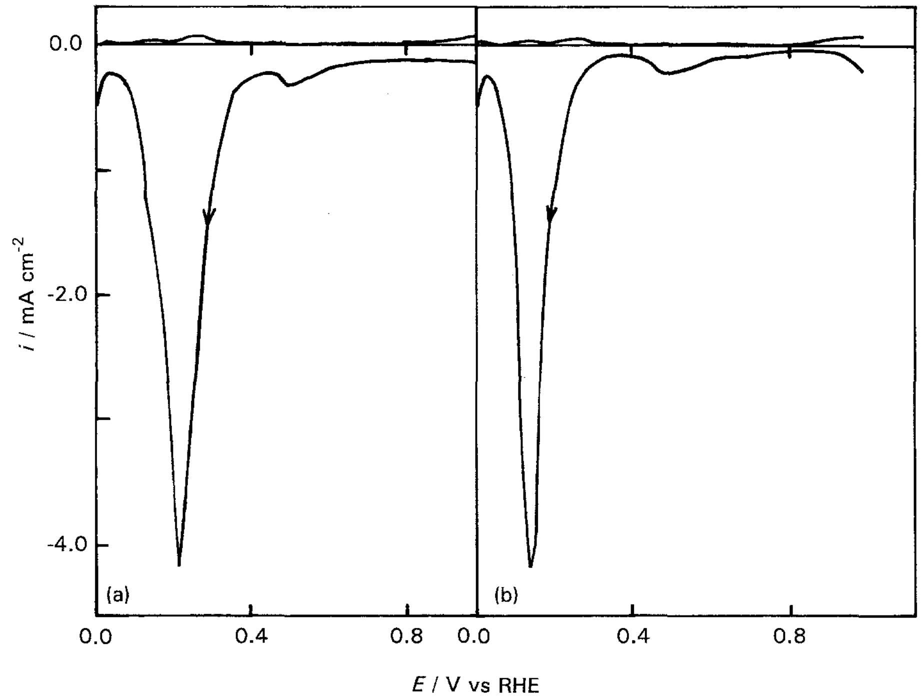

Fig. 3. Reduction profiles (1.0–0.0 V, 5 mV s^{-1}) for acid grown (0.58–E_u, 80 V s^{-1}, 3 min) hydrous oxide films in 1.0 mol dm^{-3} H_2SO_4 at 273 K: (a) E_u = 2.2 V; (b) E_u = 2.7 V.

(Fig. 5). This effect, described earlier [21] for work carried out at room temperature, was more marked with thicker oxide deposits.

(ii) With a fresh electrode it was usually necessary, therefore, to repeat the oxide growth and reduction experiment a few times in order to obtain a reducible reduction profile. It became apparent during such experiments that in some cases not only was the oxide not fully reduced on the first negative sweep, e.g. Fig. 5(b), but there was an accumulation on the surface of an oxide species that appeared to be quite difficult to reduce. One manifestation of the presence of such a species are the cathodic currents at the lower end of positive sweeps in the cyclic voltammograms shown

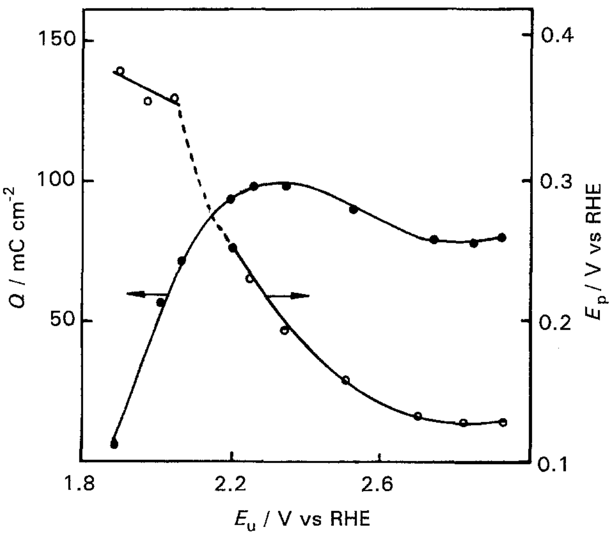

Fig. 4. Effect of the upper limit (E_u) used during oxide growth on both the reduction charge density (Q) and the reduction peak potential (E_p) for hydrous oxide films grown (0.58–E_u, 80 V s^{-1} for 3 min) and subsequently reduced (1.0–0.0 V, 5 mV s^{-1}) in 1.0 mol dm^{-3} H_2SO_4 at 273 K.

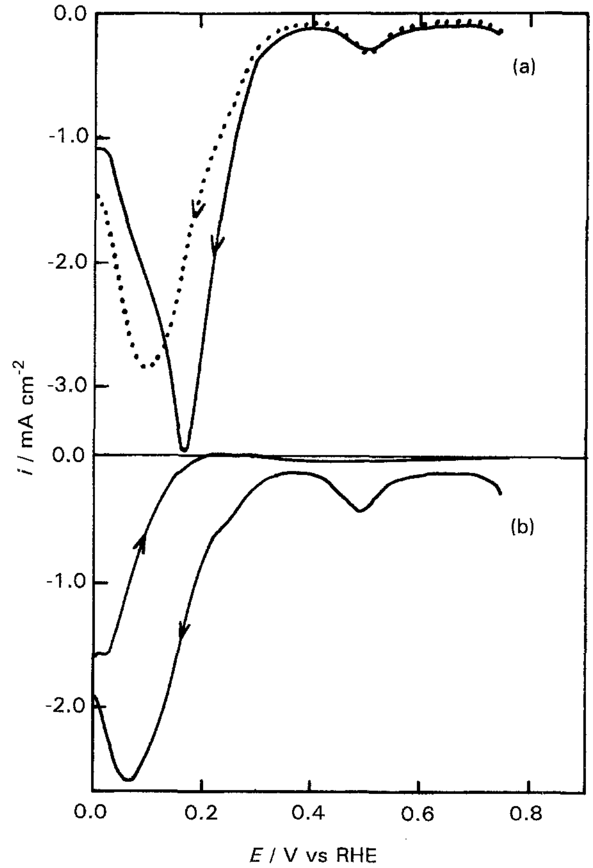

Fig. 5. Reduction profiles (0.8–0.0 V, 5 mV s^{-1}) for acid-grown (0.46–2.3 V, 80 V s^{-1} for 3 min) hydrous oxide films on bright Pt in 1.0 mol dm^{-3} H_2SO_4 at 273 K: (a) (—), reduction of 1st oxide film on a fresh electrode; (●●●), reduction sweep for the 2nd oxide film; (b) reduction sweep for the 3rd oxide film. These were repeat experiments with the same electrode with no intermediate surface treatment, apart from oxide growth.

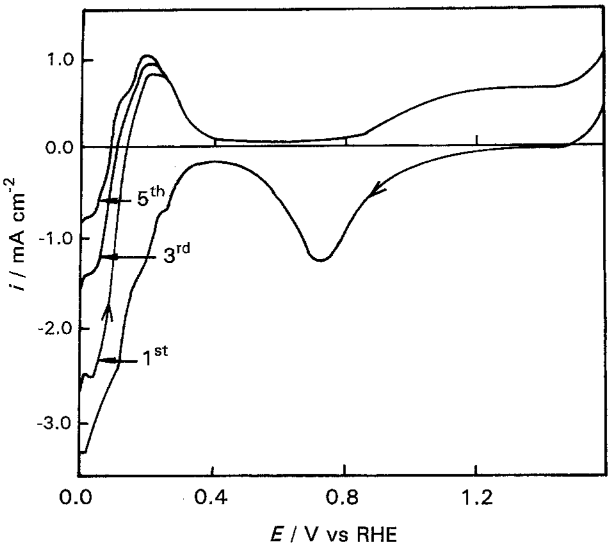

Fig. 6. Examples of repeated cyclic voltammograms (0.0–1.60 V, 50 mV s^{-1}) for a bright Pt electrode recorded after the latter had been subjected to three hydrous oxide growth/reduction experiments (the films were grown at 0.3–2.3 V, 80 V s^{-1}, for 3 min) in 1.0 mol dm^{-3} H_2SO_4 at 273 K. The response on the negative sweep remained virtually unaltered; the gradual changes at the negative end of the positive sweep are illustrated here.

in Fig. 6 (such an unusual response was reproduced later with a different electrode). To avoid such complications the oxide deposits, after growth in acid at 273 K, were frequently reduced in acid at 298 K. It is interesting to note that behaviour very similar to that shown in Fig. 6 was observed recently [22] for platinum in acid at room temperature during the course of work that also involved reduction of thick oxide layers.

(iii) It was assumed in earlier work [17] of a similar nature, carried out using acid solution at 298 K, that thick hydrous oxide growth by the potential cycling technique was possible only when the lower limit was set at a value such that the major portion, but not all, of the inner monolayer oxide film was reduced–this was the reason for selecting the value of 0.58 V in the investigation of the effect of the upper limit (Section 3.2). However, in the present case it was found that multilayer oxide growth in acid at 273 K was possible even with the lower limit set as low as 0.20 V: the lower limit also had an important influence on both the type and thickness of the film produced.

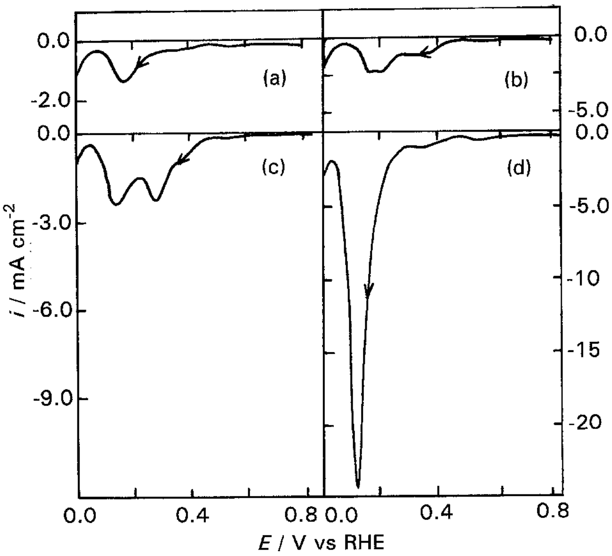

Fig. 7. Reduction profiles (0.8–0.0 V, 5 mV s^{-1}) for acid-grown Pt hydrous oxide films in 1.0 mol dm^{-3} H_2SO_4 (the films were grown at 273 K but reduced at 298 K): (a) fresh electrode, oxide growth conditions were 0.20–2.30 V, 80 V s^{-1} for 3 min; (b) repeat of (a) without intermediate electrode pretreatment; (c) fresh electrode, film growth conditions were 0.24 to 2.30 V, 80 V s^{-1} for 3 min; (d) sweep recorded for reduction of the third oxide deposit grown (without intermediate pretreatment) under the same conditions as in (c).

As is clear from the reduction response shown in Fig. 7(a) hydrous oxide (largely HO2, E_{max} $\sim$ 0.17 V) formation was observed, although at low level, with the lower limit of cycling set at 0.20 V. A significantly higher yield of oxide was observed on raising this level even slightly to 0.24 V, Fig. 7(c). In general a high upper limit, e.g. 2.30 V, favoured formation of the HO2 oxide: this was certainly true of steady state behaviour (i.e. for about the third, or later, oxide growth and reduction experiment with the same specimen) even with the lower limit as high as 0.58 V. Predominant formation of the HO1 oxide was observed, Fig. 8(a), following cycling with a low upper limit, e.g. 1.90 V, and a high lower limit, e.g. 0.6 V. As outlined in Fig. 8(b) and 8(c) reducing the lower limit for cycling favoured the formation of the HO2 oxide, even with an upper limit of 1.90 V. The dotted curve (for the first reduction sweep) in Fig. 8(c) is an interesting illustration of the complexity of the oxide-coated platinum reduction process: four maxima are present; the following are the E_{max} values 0.54 V (monolayer oxide), 0.36 V (HO1), 0.20 V (HO2) and 0.02 V (the latter peak is attributed to an indefinite oxide species, see also Figs 6 and 10(c)). A synopsis of the effect of the lower limit used in cycling on both the type of oxide produced (the full line relates to HO2, the dashed line to HO1) and the charge value associated with their reduction is shown in Fig. 9. Quite thick HO2 films were produced with a lower limit, during oxide growth by cycling, of about 0.25 V.

3.4. *Behaviour of platinum in base at 273 K*

Examples of cyclic voltammograms for clean polycrystalline platinum in 1.0 mol dm^{-3} NaOH and 1.0 mol dm^{-3} H_2SO_4, both at 273 K, are shown in Fig. 10(a) and (b), respectively. As pointed out previously [23] the hydrogen peaks in base occur at a significantly more positive potential than in acid. Furthermore, with platinum in base faradaic current, evidently associated with the formation of surface oxyspecies (i.e. premonolayer oxide formation phenomena) seemed to commence in the positive sweep, Fig. 10(a), at about 0.52 V, with minor maxima at about 0.65, 0.84 and 1.06 V. On the subsequent negative sweep the maximum of the monolayer oxide removal peak appeared at about 0.68 V and, in the hydrogen region, the charge in the strongly bound hydrogen region ($E_{max} \approx 0.38$ V) was much lower

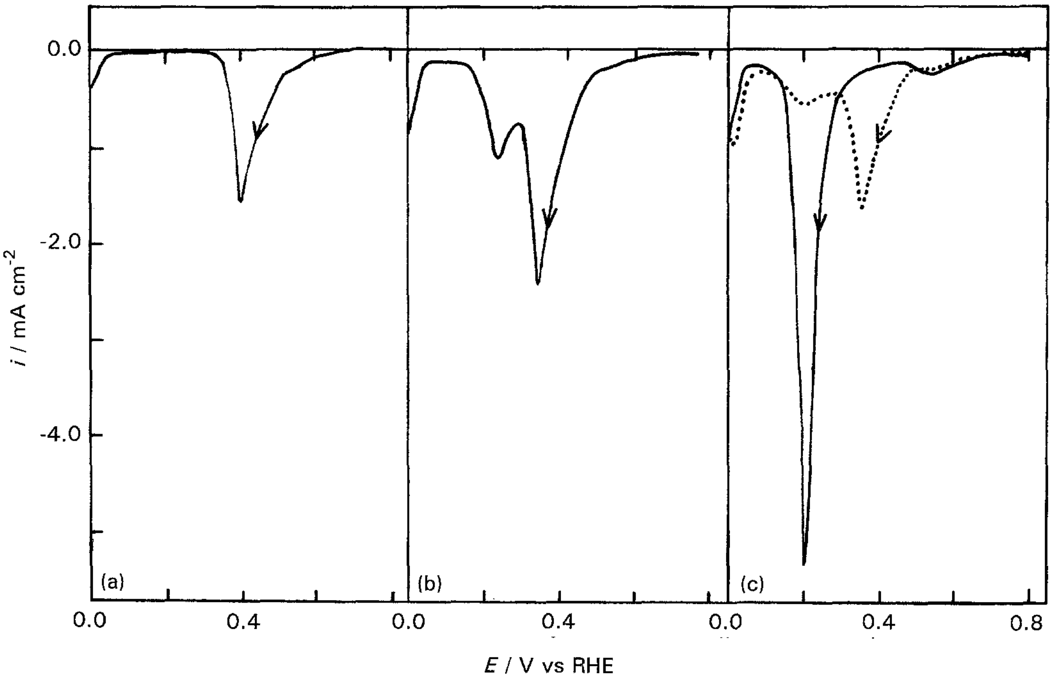

Fig. 8. Reduction profile (0.8–0.0 V, 5 mV s^{-1}, $T = 298$ K) for acid grown ($E_L \rightarrow 1.9$ V, 80 V s^{-1} for 3 min at 273 K) hydrous oxide films in 1.0 mol dm^{-3} H_2SO_4: (a) $E_L = 0.55$ V; (b) $E_L = 0.48$ V; (c) $E_L = 0.40$ V. The full line in (c) is from the 3rd oxide growth/reduction experiment (representing steady-state behaviour). The dotted line in (c) is from the 1st experiment where 4 reduction peaks were observed, $E_{max} = 0.54$ V (monolayer oxide), 0.36 V (HO1), 0.20 V (HO2) and 0.02 V (the nature of the process involved in the latter case is not quite clear). In each case the electrode, after oxide growth at 273 K, was transferred, prior to reduction, to a second solution at 298 K.

than that in the weakly bound hydrogen region ($E_{max} \approx 0.26$ V). Also, the cathodic charge in the hydrogen region of the negative sweep seemed to be significantly larger than its anodic equivalent in the positive sweep.

In the positive sweep for acid, Fig. 10(b), the intermediate (H_3) peak, which is generally absent in base, reappeared. The current over most of the double layer region of the positive sweep in acid was far lower than in base. It is interesting to compare the response for the fresh platinum electrode in acid, Fig. 10(b), with that of a similar electrode which had been subjected to several hydrous oxide growth and reduction runs, Fig. 10(c). The resolution of some of the peaks in the hydrogen region was rather poor in the case of the used electrode but five maxima or shoulders were evident in this region in the positive sweep and four on the negative sweep. Points to note here are (i) the presence of the pair of peaks $H_3/H_{3'}$ (usually with an acid solution only the anodic peak, H_3, is observed; $H_{3'}$ is normally absent in the negative sweep), (ii) $H_{3'}$ (at ~0.19 V) was significantly more pronounced than $H_{4'}$ (at ~0.27 V in this case), (iii) peak X (at ~0.03 V) is rarely seen for platinum in acid, some of the few exceptions being Figs 6 and 8(c) (dotted line) in the present work.

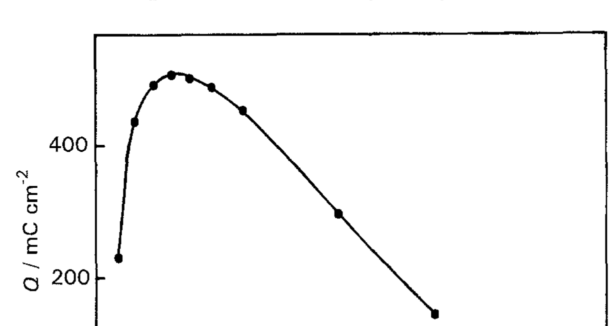

Fig. 9. Effect of the lower limit (E_L) on the charge density for hydrous oxide reduction: the films were grown (2.30 V–E_L, 80 V s^{-1}, 3 min, $T = 273$ K) and reduced (1.0–0.0 V, 5 mV s,5^{-1}, $T = 298$ K) in 1.0 mol dm^{-3} H_2SO_4. The full and dashed lines correspond to HO2 and HO1 material, respectively.

The study of the growth and reduction of hydrous oxide films on platinum in base is complicated by the difficulty [9] of totally reducing the hydrous oxide (especially the HO2 component) under such conditions. When an acid-grown film was reduced in acid, Fig. 11(a), two main reduction peaks ($E_{max} = 0.3$ and 0.13 V, respectively) were observed. When the film was regrown in acid but reduced in base, full line in Fig. 11(b), only one reduction peak ($E_{max} = 0.28$ V) was observed. On repeating the negative scan, following transfer of the electrode back into acid, dashed line in Fig. 11(b), a further major oxide reduction peak ($E_{max} = 0.12$ V) was observed, along with a lesser response in the region about 0.3 V.

There was no difficulty in growing a hydrous oxide film on platinum in base at 273 K. Figure 12(a) shows the reduction response (in acid) for a deposit produced by multicycling the potential of a platinum electrode between 0.45 and 1.95 V in 1.0 mol dm^{-3} NaOH at 273 K. The monolayer oxide reduction peak in this case appeared at about 0.54 V but the major feature was the HO1 reduction peak at about 0.34 V. The two minor peaks at lower potentials

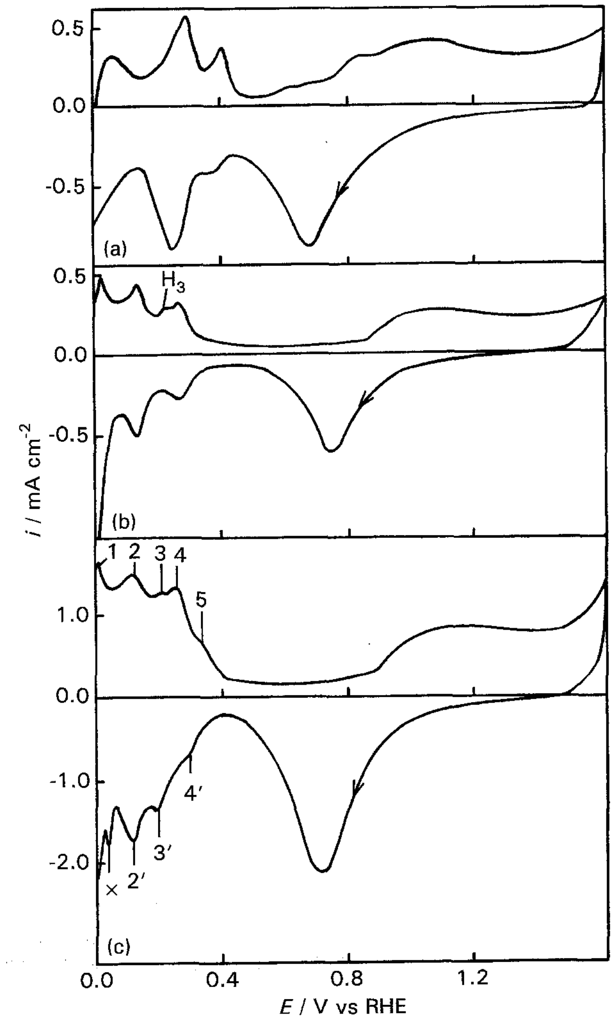

Fig. 10. Cyclic voltammograms (0–1.6 V, 50 mV s^{-1}) for bright Pt in (a) 1.0 mol dm^{-3} NaOH at 273 K, (b) 1.0 mol dm^{-3} H_2SO_4 at 273 K, (c) 1.0 mol dm^{-3} H_2SO_4 at 273 K after three hydrous oxide growth and reduction experiments had been carried out with this particular Pt electrode.

(~0.25 and ~0.14 V) also appeared in the blank, Fig. 12(b), and are assumed to be due to deposition of strongly bound and weakly bound hydrogen, respectively.

4. Discussion

4.1. *Effect of temperature on the cyclic voltammetry of platinum*

The effect of temperature on the cyclic voltammetry behaviour of platinum, especially in the hydrogen adsorption/desorption region (where, for moderate sweep rates, reversible behaviour is frequently assumed [24]), is not dramatic. This is in agreement with the conclusion drawn earlier by Florit and Arvia [25] who investigated the voltammetric behaviour of platinum in acid over a wider temperature range (189–292 K) and in greater detail than in the present investigation which was concerned primarily with hydrous oxide behaviour. The current values at the beginning of the monolayer oxide formation region (at ~0.8 V on the positive sweep) were appreciably lower at 273 K. There is evidence of unusual behaviour in this region; for example, a peak has been reported at about 0.7 V at 353 K (see Fig. 1(b) in [10]). Such a response has been attributed [10, 13] to oxidation of some active, poorly lattice stabilized, platinum atoms on the electrode surface in a process referred to as premonolayer oxidation. The reactivity (and coverage) of these active species is assumed to be highly temperature dependent. The difference in anodic currents over the range 0.9 to 1.1 V in Fig. 1 is less marked: over this range the metal atoms being oxidized are of relatively high lattice coordination number, the reaction is more an adsorption of OH

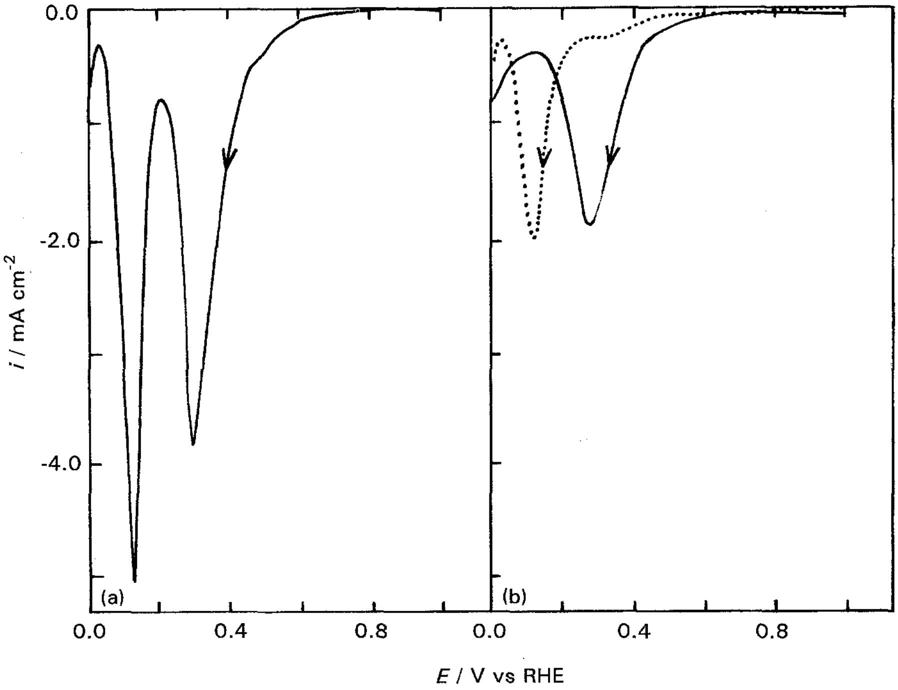

Fig. 11. Reduction profiles (1.0–0.0 V, 5 mV s^{-1}, 273 K) for acid grown (0.58–2.1 V, 80 V s^{-1} for 10 min at 273 K) hydrous oxides in (a) 1.0 mol dm^{-3} H_2SO_4 at 273 K and (b) (—) 1.0 mol dm^{-3} NaOH at 273 K, (●●●) reduction profile for the remaining hydrous oxide in 1.0 mol dm^{-3} H_2SO_4 at 273 K recorded following transfer of the electrode from base to acid.

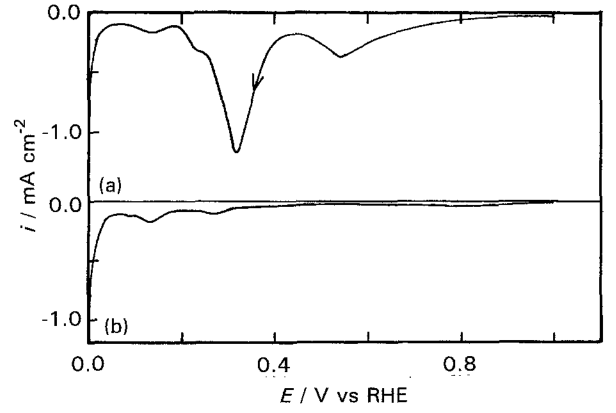

Fig. 12. (a) Reduction profile (1.0–0.0 V, 5 mV s^{-1}, 298 K, 1.0 mol dm^{-3} H_2SO_4) for a base grown (0.45–1.95 V, 40 V s^{-1}, 3 min, 1.0 mol dm^{-3} NaOH at 273 K) hydrous oxide deposit on Pt. (b) Repeat reduction profile (or blank) in acid (298 K) run immediately after (a).

species on a rigid lattice and this is evidently less temperature sensitive. Over the range 1.1 to 1.5 V (positive sweep) place-exchange processes are assumed to be significant [24] and the lower currents at 273 K are assumed to reflect the appreciable temperature sensitivity of this type of reaction. The lower height (or charge) associated with the peak at about 0.75 V (negative sweep) at 273 K is assumed to reflect the reduced oxide coverage (due to inhibition of the place-exchange reaction on the positive sweep) attained at the upper limit of the sweep at the lower temperature. At the lower temperature there is also better resolution on the negative sweep between the peak for deposition of weakly adsorbed hydrogen ($E_{max} \approx 0.1$ V) and the hydrogen gas evolution currents below about 0.05 V, evidently due to the slower rate of gas evolution at the lower temperature.

4.2. *Hydrous oxide growth in acid*

The results shown in Figs 2 and 3 of the present investigation confirm previous data [20, 21] obtained at 298 K, namely that hydrous oxide growth carried out with an upper limit less than 2.1 V favours HO1 formation whereas that carried out with an upper limit greater than 2.1 V favours HO2 formation. The assignments of the different oxides here as based on peak maximum potential values ($\sim$0.37 V for HO1 and $\sim$0.17 V for HO2: see Fig. 2(c)). The data shown in Fig. 4 support the conclusion that the thinner films (of lower oxide reduction charge, Q) consist mainly of the HO1 component ($E_p \approx 0.37$ V). With thicker films (produced with $E_u \geqslant \sim 2.2$ V) the peak potential for hydrous oxide reduction dropped from about 0.25 to 0.13 V with increasing value of E_u. This suggests that with 2.2 V $< E_u <$ 2.4 V a layer of intermediate composition is formed at 273 K, with the HO2 form predominating when the film is produced at a high ($\geqslant$ 2.6 V) E_u value.

What is not clear at this stage is precisely what factors (or contributions) determine the peak reduction potentials. Since no oxide of platinum is thermodynamically stable below about 1.0 V [26] reductions are clearly occurring under very irreversible conditions. The low potential values observed for hydrous oxide reduction have been attributed to the active state (or high energy) of the initially discharged metal atoms [11], but clearly the nature of the hydrous oxide film also influences the course of the reaction. The overall process, reduction of the Pt(IV) oxycomplexes to lattice stabilized platinum (Pt_l), is obviously very favourable from an energy viewpoint below, e.g. 0.5 V. The inhibition or barrier is evidently associated with formation of the active intermediate form of platinum (Pt^*). The overall reaction may be considered as a two-stage reaction, namely,

$$\mathrm{Pt(IV)} + 4e^- \overset{(i)}{\rightleftharpoons} \mathrm{Pt}^* \xrightarrow{(ii)} \mathrm{Pt_l} \qquad (1)$$

in which the equilibrium potential for stage (i) is influenced by the ligand sphere about the Pt(IV) ion and the general structure of the oxide.

A novel feature of the present work was the observation, Fig. 7(a), that hydrous oxide growth was possible with a lower cycling limit of 0.2 V. The latter value is far lower than the potential range for the monolayer oxide reduction peak in Fig. 1 (where the upper limit was 1.60 V) or Fig. 3(b) (where the upper limit was 2.70 V). However, the latter responses were recorded at quite slow sweep rates (5–50 mV s^{-1}) whereas hydrous oxide growth in acid was carried out at 80 V s^{-1}. It is unlikely that monolayer oxide reduction on cycling at 80 V s^{-1} occurred at a very negative potential (close to 0.2 V) as the extent of monolayer oxide formation on the positive sweep is probably also quite low at this fast sweep rate. It is assumed here that the monolayer oxide film is not directly involved in hydrous oxide film growth on platinum. This view is supported by earlier work on gold in base [27] where the optimum lower limit for hydrous oxide growth by multicycling, $\sim$0.75 V, was also significantly lower than the peak for regular monolayer oxide reduction, $\sim$1.0 V, for this system.

According to an earlier explanation of multilayer hydrous oxide growth on noble metals under repetitive potential cycling conditions [17] application of the positive sweep results in the formation of hydrous oxide (usually as a minor product in any given sweep) and monolayer oxide species at low coordination and high coordination surface metal atoms, respectively. The function of the subsequent negative sweep is to reduce the initially predominant, rather inert, monolayer oxide deposit, but not the slightly more reduction-resistant hydrous oxide species. With an upper limit $\geqslant$1.9 V extensive place-exchange is assumed to occur in the monolayer deposit so that on reduction of the latter a significant coverage of low coordination metal atoms is generated at the surface. Repetitive cycling in this manner, using appropriate limits, leads to an accumulation of a multilayer hydrous oxide deposit at the interface. Quartz crystal microbalance data for gold and other metals [28, 29] provide evidence that potential cycling, i.e. monolayer oxide formation/reduction treatment, induces changes in surface morphology. An active, roughened, surface state is generated that in some instances persisted for a significant period of time (occasionally several hours were required to reestablish the initially smooth state).

In earlier work with platinum in acid at 298 K (see Fig. 5(a) in [17]) the optimum lower limit for oxide growth was about 0.58 V and the yield of hydrous oxide was quite low when the lower limit was $\leqslant 0.5$ V. In the present case the optimum lower limit, Fig. 9, was about 0.25 V. The resulting deposit in this case was predominantly the HO2 oxide as, during oxide growth, the HO1 formed on a positive cycle is reduced at the lower end of the negative cycle. The lowering of the optimum lower limit in the present case is assumed to be due to the fact that the active metal atoms formed on reduction of the oxide monolayer persist for a longer period at 273 K (as compared with 298 K). The decay in question probably involves processes such as loss of water molecules and anions attached to displaced surface atoms, surface atom diffusion, adatom incorporation at defect sites etc., all of which occur at a slower rate at 273 K. The inability to produce a hydrous oxide deposit using a lower limit, on multicycling, of less than 0.2 V is evidently due to the instability of the HO2 material at such a low potential.

The major influence of the limits used in the oxide growth process with platinum in acid solution is clear from Figs 8 and 9. With a low upper limit value of 1.9 V preferential formation of the HO1 oxide is expected [20]. This was observed when the lower limit was 0.55 V, Fig. 8(a). However, as is clear from the dashed line in Fig. 9 the yield of HO1 was generally rather small, possibly with such a lower limit value (0.55 V) the monolayer oxide film was incompletely reduced at the lower limit of the fast ($80\ \mathrm{V\,s^{-1}}$) oxide growth cycle. The combination of fast cycling, low upper limit value and deactivation due to a significant residue of unreduced monolayer oxide is assumed to inhibit the HO1 formation process.

Reducing the lower limit for growth to 0.48 V, Fig. 8(b), is assumed to have two effects: (i) more complete monolayer oxide reduction in the negative sweep during the growth process, and (ii) slight reduction of some of the HO1 deposit as the latter material commences reduction, Fig. 8(b), just below 0.5 V. In this case HO1 is still a major product but (possibly due to more complete monolayer reduction, or greater surface activation, at the lower end of the oxide growth sweep) some HO2 is also formed. Finally, with a lower limit of 0.4 V, Fig. 8(c), both the monolayer oxide and apparently any HO1 species present are reduced at the lower end of the oxide growth cycle. Activation of the surface in this case is rather effective and a significant amount of the HO2 oxide was generated. The data shown in Fig. 8(c) is significant as it demonstrates: (i) the influence of the state of the surface on the hydrous oxide growth process (compare the reduction response shown by the full line for steady state behaviour and that given by the dashed line for the first oxide growth/reduction experiment) and (ii) it is obviously the basis of a method for generating thick films of relatively pure HO2 material. It is clear from Fig. 9 that the optimum conditions for thick HO2 film growth under potential cycling conditions entail the use of a high positive (e.g. 2.3 V) and a low negative (~ 0.25 V) limit.

4.3. *Anomalous behaviour of platinum at low potential*

Hydrous oxide growth on platinum seems to be quite strongly influenced by the defect state of the metal; it probably only occurs at sites where metal atoms are of low lattice coordination number. One of the main factors influencing the defect state of the metal is the past history or pretreatment of the electrode. This is clear for instance from the much earlier work of James [15] who observed that hydrous oxide growth on platinum under d.c. conditions became progressively easier (at least on a temporary basis) with increasing number of preceding multilayer oxide growth and reduction experiments. Another manifestation of the influence of electrode history is the change in the HO2/HO1 ratio in repeated experiments with the same electrode [21]. The behaviour shown in Fig. 6, in particular the large cathodic responses at the early stages of the positive sweeps in the first few cycles with an extensively worked (or disrupted) electrode surface, is unusual but not unique. A reduction peak in the same region, about 0.05 V, can be seen also in the negative sweep in the case of the dotted line in both Fig. 8(c) and in Fig. 10(c). A larger peak in the region of 0 V (attributed, as mentioned here earlier, to a new hydrous oxide component, HO3) was observed recently [19], in a more consistent manner, in the reduction of hydrous films on platinum in acid at 60 °C. An unusual hydrous oxide reduction response (which they designated the β' peak) in the hydrogen adsorption region was reported independently by Birss and Goledzinowski [7]; a more detailed discussion of this topic is given in a related paper [22]. Furthermore, this type of behaviour is not restricted to platinum. A large sharp negative peak was observed recently [30] following hydrous oxide growth on gold in base (no foreign anions, e.g. HSO_4^- or SO_4^{2-}, were involved) at a potential significantly lower than 0 V, i.e. at about 1.5 V more negative than that at which any regular oxide of gold is thermodynamically stable [26].

The reduction of any oxide of platinum or gold at a potential of 0 V (RHE) clearly occurs in an irreversible manner. Two unusual features of the response at low potentials in Fig. 6 are worth noting. First, since the reduction occurs irreversibly, i.e. at a large negative overpotential, it may be expected to occur rapidly, giving rise to a large cathodic peak (as in the case of HO1 and HO2 in Figs 2 and 3), in the first negative sweep. However, this is not the case in the experiment outlined in Fig. 6 as there was still a trace of a residual oxide response at low potentials even in the 10th positive sweep. This may be explained in terms of the view expressed elsewhere in the case of the HO3 oxide [19]. HO3 itself is not readily reduced above 0 V but it decays gradually to HO2 which is reduced above 0 V. Therefore HO3 may act as a limited source or reservoir supplying the HO2 that reduces over the range 0 to 0.1 V in the sweeps shown in Fig. 6 (since there is little indication of HO3 formation at 273 K, the species being reduced below 0.1 V may be a less reactive HO2 species that at higher temperature alters to the HO3 state).

Second, the departure from conventional behaviour for platinum in the case of Fig. 6 arises only at low potentials (about 0 to 0.25 V); there is little indication of oxide reduction over the double layer region (despite the thermodynamically unstable oxide being still obviously present, it reduces again at low potentials). Support for this notion of a quasi-stable state for HO2 at $E \geqslant \sim 0.25$ V is given in Fig. 9 where the optimum lower limit for HO2 growth is seen to occur also at 0.25 V; as the lower limit is made more negative than the latter value much of the HO2 product is reduced.

The quasi (or anomalous) stability of HO2 at low potentials is an important question both in platinum electrochemistry [11] and electrocatalysis [13]. There is in the present case, Fig. 6, significant electrochemical evidence for the existence of a platinum oxide species that shows little tendency, in repeated scans, to reduce in the region of the strongly bound hydrogen peak (or at more positive potential values). Anomalous behaviour of this type was reported recently for this system in several papers [11, 31] from this laboratory. The effect may be rationalized on the basis of a poorly stabilized, reactive state of the initial reduction product, see Equation 1.

It is interesting to note in connection with the fundamental electrochemistry of polycrystalline platinum in aqueous media that the five peaks (labelled 1 to 5) in the hydrogen desorption region in Fig. 10(c) were previously identified by Conway (([24] p. 75); he used a slightly different notation). Peak 1 is probably due to oxidation of locally dissolved hydrogen (and perhaps any hydrogen bubbles attached to the electrode surface). Peaks 2 and 4 are generally attributed to oxidation of weakly and strongly adsorbed hydrogen, respectively. The interpretation of peak 3 (which in [24] p. 71, Conway described as 'the well known *anomalous* "third" peak') is controversial. It has been attributed recently [13] to formation of a low level of the HO2 oxide at highly active sites on the metal surface and, by analogy, peak 5 (which Conway [24] denoted as H_0) may well be due to formation of a submonolayer level of HO1. As already discussed elsewhere [13] it is virtually impossible to explain the oxygen transfer reaction

$$CO_{ads} + H_2O = CO_2 + 2H^+ + 2e^- \qquad (7)$$

that commences on platinum in acid [32, 33] at about 0.2 V, followed by an upsurge in rate at about 0.45 V, without assuming the intervention of active oxide (or oxygen transfer) species, e.g. low coverage HO2 and HO1 entities, at the interface.

The counterpart of peak 3, i.e. peak 3′, is rarely observed–its appearance on the negative sweep in Fig. 10(c) is one of the very few exceptions. It may be noted also that the appearance of peak 3′ is coupled with some loss of definition of peak 4′. The electrode surface involved in this experiment (after three prior hydrous oxide growth/reduction experiments) is assumed to be highly disordered. Also, the low temperature may inhibit rearrangement. It is assumed, therefore, that after the monolayer oxide reduction in this case some active metal sites that would normally be involved in strong adsorption of hydrogen exist in the oxidized, hydrous oxide, state. This view, at least, explains the small 4′ and large 3′ peaks in the present case, i.e. peak 3′ is assumed to involve reduction of a low level of a HO2 species.

The cyclic voltammogram for platinum in base at 273 K, Fig. 10(a), is rather similar to the response reported earlier for this system at 298 K (full line in Fig. 1(b), or Fig. 3(a), in [23]). The intermediate peak 3 is not observed with base, as spontaneous HO2 formation is assumed to occur (due to super Nernstian E/pH effects [1]) at lower potentials at high pH. The charge associated with the adsorption of strongly bound hydrogen (at about 0.4 V, negative sweep), both in Fig. 10(a) here, and in the earlier work with Pt in base [23], is surprisingly small while the currents in the region below about 0.3 V on the negative (as compared with the positive) sweep are large (as indeed are those at the end of the double layer region of the negative sweep). Again it is assumed that the low response associated with uptake of strongly adsorbed hydrogen, plus the greater net charge on the negative as compared with the positive sweep in the region below about 0.5 V, are due to the presence of some hydrous oxide species that persist on the surface after the monolayer oxide removal process and are reduced slowly only at lower potentials. It was demonstrated earlier, Fig. 3 in [34], that the component of a base-grown platinum hydrous oxide deposit that is reduced at high pH also reacts only after monolayer removal, i.e. again in the region below about 0.5 V.

4.4. *Hydrous oxide growth in base*

Hydrous oxide growth on platinum in base at 298 K has already been investigated [17, 35]. A detailed study of the same process in base at 273 K was not carried out here; it was merely demonstrated that a deposit of the HO1 oxide could be produced on cycling the potential of a platinum electrode between suitable limits in alkaline solution, Fig. 12. One of the disadvantages of working with base is that the platinum (HO2) hydrous oxide deposit, as demonstrated here in Fig. 11, is not readily reduced in this medium. A detailed discussion of this topic was published recently [9].

5. Conclusions

(i) The conventional cyclic voltammetry behaviour of platinum metal in acid solution, as already known from previous work [25], is not markedly dependent upon temperature.
(ii) Platinum hydrous oxide deposits, produced by potential cycling techniques in acid solution at 273 K, gave rise to two reduction peaks that were attributed to the presence of the two oxide components, HO1 and HO2. A novel feature of the results was the ability to produce such deposits using an unusually low value, e.g. 0.20 V, for the lower limit involved in the oxide growth cycling at 273 K. Such a result, together with earlier data for the optimum lower limit for hydrous oxide growth on gold in base [27], suggests that even partial retention of the monolayer oxide deposit is not necessarily a prerequisite for hydrous oxide growth on noble metal electrode surfaces (the important factor seems to be the morphological/surface metal atom activity changes induced by the repetitive monolayer oxide formation/reduction processes). Displacement of surface metal atoms under potential cycling conditions has already been demonstrated, for platinum single crystal plane surfaces, by the STM experiments of Itaya and coworkers [36].
(iii) Quite thick hydrous oxide films were produced at 273 K using a lower limit of about 0.25 V; the use of such a low limit resulted in a virtually pure HO2 deposit as any HO1 species formed was reduced at the negative end of the oxide growth cycles. Thinner deposits of either HO1 or mixtures of HO1 + HO2 were produced using a more positive value ($> \sim 0.45$ V) for the lower cycling limit.
(iv) The complexity of the behaviour of platinum in this area was again demonstrated. The hydrous oxide reduction profile, and hence the nature of the deposit formed on cycling, was strongly influenced by electrode history (or pretreatment). This is assumed to reflect the important role of the defect structure of the outer layers of the metal (a factor that, while very important in practice, e.g. in supported Pt electrocatalysts, rarely receives adequate attention). All the hydrous oxides reduced at potentials far below the thermodynamically reversible value, the HO2 oxide in particular being incompletely reduced in base even in a slow sweep ($5\,\mathrm{mV\,s^{-1}}$) extending to 0 V. A quite novel feature (also observed in related work at 298 K that will be reported shortly) were the indications of the formation, with an extensively disrupted Pt outer layer, of an oxide deposit that was not readily reduced in acid solution at 0 V, e.g. Fig. 6, and that showed very little inclination to reduce above about 0.2 V.
(v) Although hydrous oxide films could be grown on platinum in base at 273 K, total reduction of HO2 deposits was again shown to be difficult to achieve at 273 K (as at 298 K) in solutions of high pH.

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