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## Redox behaviour of thermally activated platinum electrodes with particular reference to operation at elevated temperature

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**Abstract** The present work is a continuation of an earlier investigation of the effect of severe thermal pretreatment on the redox properties of platinum electrodes in aqueous media. The most interesting observation was that raising the solution temperature to ca. 75 °C resulted in a dramatic anodic response in the positive sweep at ca. 0.25 V (RHE). Such behaviour was noted earlier at room temperature but only when the thermally pretreated sample was further activated by cathodic polarization. This transition at 0.25 V was partially reversed on the negative sweep, but the cathodic process involved was subject to severe inhibition. There is independent evidence for similar behaviour for gold in aqueous acid solution. The relevance of the present results to the operation of fuel cell anodes is outlined.

**Key words** Platinum · Thermal pretreatment · Premonolayer oxidation · Active sites · Electrocatalysis

### Introduction

The electrocatalytic behaviour of noble metals, and their mixtures or alloys with one another, has become a topic of widespread interest in recent years in connection with fuel cell development [1]. One of the major problems or challenges in the ambient or slightly elevated temperature fuel cell area is the removal of strongly adsorbed, deactivating CO<sub>ads</sub> species [2] from platinum-based anodes operating either directly or indirectly on methanol (the fuel may consist of CO-contaminated hydrogen gas produced from methanol in an on-board reformer [3]). The present project is concerned with the background to CO<sub>ads</sub> oxidation, in particular as to how the oxygen required for this reaction, viz.



is transferred from water to the surface deactivating species at a platinum electrode surface at low potentials (within the double layer region) in aqueous acid solution.

In a novel approach to noble metal electrocatalysis, referred to as the incipient hydrous oxide/adatom mediator (IHOAM) model, which was discussed in some detail recently in this journal [4], it was suggested that the important oxygen donor or transfer agent involved in the type of reaction shown in Eq. 1 is a hydrous oxide species formed by oxidation of active platinum atoms at the electrode/solution interface. The background to this new approach has been outlined in several papers from this laboratory [5–7]. It is assumed that all metal surfaces contain active sites, in the form of defects, whose important component (from a catalysis viewpoint [8]) are low coordination surface metal atoms (it is worth noting that Kolb and Schneeweis [9] pointed out recently that even monocrystalline metal surfaces contain many such imperfections). Such atoms are assumed to have a low lattice stabilization energy and hence an unusually high activity and low redox potential, i.e. they undergo oxidation well within the double layer region. Furthermore, because of their exposed coordination sites, they can coordinate an unusual number of ligands, e.g. OH<sub>2</sub> and OH<sup>-</sup> species, i.e. the product is assumed to be a hydrous oxide species.

It is generally accepted, since the original proposal by Taylor [10], that surface active site coverages are usually quite low, ca. 1–2% of a monolayer. It was demonstrated recently [11] that such coverages may be enhanced by appropriate thermal pretreatment. The principle involved, as discussed recently [4], is quite simple: some of the energy inserted electrically into the sample during the pretreatment process is retained in the final active state in the form of high energy, frozen-in (or metastable) low coordination surface atoms; the latter yield an enhanced premonolayer oxidation response when the electrode is subsequently examined under cyclic voltammetry conditions.

In the earlier work with thermally pretreated platinum electrodes [11] in acid solution at room temperature

it was demonstrated that while enhanced premonolayer oxidation responses were observed, the behaviour was complex. Frequently three unusual anodic peaks were observed in the first positive sweep, one at ca. 0.25 V (this was assumed to be due to an unusually high energy Pt atom state; at room temperature an appreciable occupancy of this state occurred only when the thermal pretreatment was used in combination with subsequent cathodic pretreatment [11]), another at ca. 0.45 V and a final one at ca. 0.75 V. These unusual anodic responses decayed on repeated cycling; it seemed that these enhanced premonolayer oxidation reactions were not very reversible. It is worth noting that quite similar behaviour was reported recently [12] for gold, activated by severe cathodic pretreatment, in acid solution; again there was a substantial anodic response, at ca. 0.35 V, which was attributed to the oxidation of active gold atoms at the electrode surface, but, as with thermally pretreated platinum, the subsequent cathodic response on the negative sweep was quite sluggish.

In the present work with thermally pretreated platinum electrodes in acid solution at elevated temperature, ca. 75 °C, it was found that the dominant feature in the positive sweep was the anodic response at ca. 0.2 V (RHE). There was a corresponding cathodic response in the same region of the negative sweep when the latter was run at a slow sweep rate. It may be noted that the presence of such an unusual anodic transition at ca. 0.2 V was postulated earlier [6] for this electrode system in a controversial paper from this laboratory. The implication of this result with regard to noble metal electrochemistry and fuel cell electrocatalysis is briefly outlined.

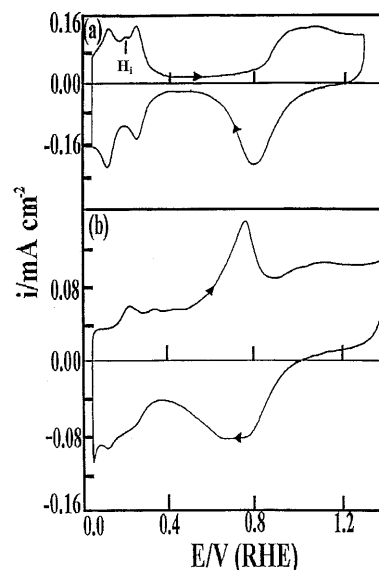
## Experimental

The equipment and technique used in the present investigation were outlined earlier [11]. In the present case the electrochemical cell and the reference electrode compartment were maintained in a water bath in which the temperature was controlled electronically ( $\pm 0.1$  °C). The platinum wire loop (which, as in previous work [11], consisted of a 20 cm long, 0.5 mm diameter, sample of Johnson Matthey, Puratronic grade, Pt wire) was heated electrically in a 5% H<sub>2</sub> + 95% N<sub>2</sub> gas mixture and, after cooling, was brought into contact with the electrolyte (without exposure to air) and investigated using cyclic voltammetry without further pretreatment. The solution in the cell was made up using triply distilled water and Analar grade acid (either H<sub>2</sub>SO<sub>4</sub> or HClO<sub>4</sub>). The cell had a sealed glass lid which prevented the ingress of oxygen from the air, the gases flowing through the cell were maintained at slightly elevated pressure with the aid of gas bubblers in the outlet streams. Most of the responses shown here correspond to the first cycle, commencing with the positive sweep.

## Results

Cyclic voltammetric data for platinum in aqueous solutions at room temperature

Typical responses for the wire loop electrode are shown, first in its unheated state (Fig. 1a) and then immediately



**Fig. 1** Cyclic voltammograms for a polycrystalline platinum electrode in 1.0 mol dm<sup>-3</sup> H<sub>2</sub>SO<sub>4</sub> at ca. 16 °C: **a** 0.05–1.3 V, 50 mV s<sup>-1</sup>, no thermal pretreatment; **b** 0.05–1.4 V, 50 mV s<sup>-1</sup>, after thermal pretreatment in 5% H<sub>2</sub>/N<sub>2</sub> gas atmosphere (9 A, 25 s,  $T \approx 1310$  °C)

after thermal pretreatment (Fig. 1b); in both cases the response was recorded when the electrode was immersed in acid solution at ca. 16 °C. The response shown in Fig. 1a is quite conventional for polycrystalline platinum electrodes in acid. Attention is drawn here to one feature in this diagram, namely the small anodic peak, labelled H<sub>i</sub>, in the lower region (at ca. 0.2 V) of the positive sweep. An enhanced version of this peak was usually the dominant feature of positive sweeps recorded in the present work for thermally pretreated platinum in solutions at elevated (70–80 °C) temperature. The presence of peak H<sub>i</sub> in Fig. 1a is highlighted here to emphasize the fact that the enhanced peak in this region observed in later experiments reflects a response or transition that is associated (obviously at a low level) with conventional polycrystalline platinum/aqueous acid solution interfaces even at room temperature [6].

After thermal pretreatment the response for the same electrode at room temperature (Fig. 1b) was considerably different. Most of the observed changes, e.g. the disappearance of a discrete double layer region, the excess anodic (positive sweep) to cathodic (negative sweep) charge, and the larger cathodic compared with anodic current values in the adsorbed hydrogen region (below ca. 0.35 V) have been noted and discussed earlier [11]. One of the most intriguing features of the work with these thermally pretreated electrodes is that the oxide grown in the positive sweep is not completely reduced at the lower end of the negative sweep. This is evident from the general charge imbalance in Fig. 1b, but it is much more obvious in other voltammograms shown here later, e.g. in Fig. 4a and Fig. 5, where higher solution temperatures and slower sweep rates were involved.

It is a basic assumption in the present work, and this view is supported by earlier work [13] (including

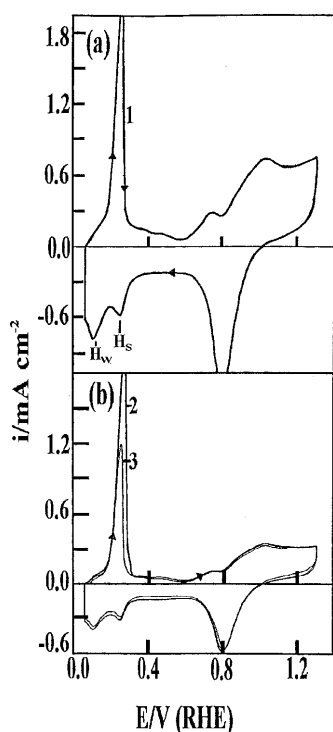
investigations involving platinum electrodes activated by severe cathodic polarization [14]), that it is possible to grow an oxide on platinum which is reluctant to undergo reduction (obviously for kinetic rather than thermodynamic reasons) at  $E = 0.0$  V.

Cyclic voltammetry data for thermally pretreated platinum in aqueous solutions at elevated temperature

An example of the initial (first cycle) response for a thermally pretreated platinum electrode in  $\text{H}_2\text{SO}_4$  solution at elevated temperature is shown in Fig. 2a; further sweeps for the same electrode are shown in Fig. 2b. The most interesting feature is the marked anodic peak at 0.2 V in the positive sweep. There were indications of this peak in Fig. 1a and b, but this feature is much more dramatic in Fig. 2.

In some respects the remainder of the sweep in Fig. 2a was reasonably normal, e.g. there was a monolayer oxide formation response above ca. 0.8 V, an equivalent monolayer oxide reduction peak at ca. 0.8 V, plus the two usual hydrogen adsorption peaks ( $H_s$  and  $H_w$ ) at low potentials (negative sweep). The main discrepancies in Fig. 2a compared with the normal response for platinum are:

1. The characteristic hydrogen desorption peaks in the positive sweep for platinum in acid solution are not evident; it is clear from further examples shown here



**Fig. 2** Cyclic voltammograms ( $0.05\text{--}1.3$  V,  $50$   $\text{mV s}^{-1}$ ) for a polycrystalline platinum wire electrode in  $1$   $\text{mol dm}^{-3}$   $\text{H}_2\text{SO}_4$  at ca.  $80$   $^\circ\text{C}$ ; this wire was thermally pretreated in  $5\%$   $\text{H}_2/\text{N}_2$  gas atmosphere ( $9$  A,  $25$  s,  $T \approx 1310$   $^\circ\text{C}$ ): **a** first sweep and **b** second and third successive sweeps

later that the nature of the responses at low potentials in the positive and negative sweeps, and evidently the reactions giving rise to these peaks, are quite different from those observed with conventional platinum. As outlined earlier [11], the sharp anodic peak at ca.  $0.2$  V is assumed to be due to an active metal/hydrous oxide,  $\text{Pt}^*/\text{Pt}(\text{HO}_2)$  oxide, transition.

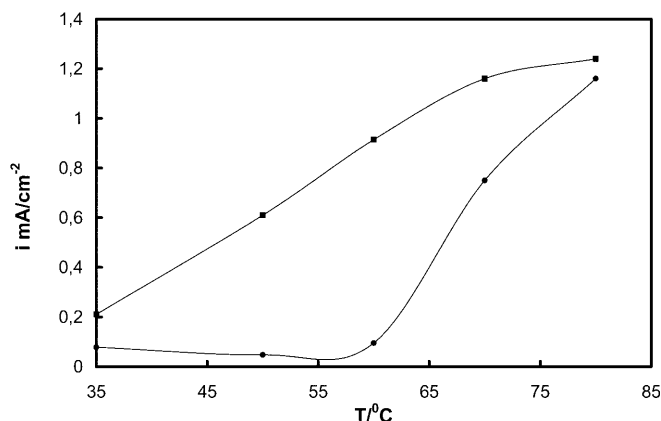
2. There are unusual features in the double layer region (from ca.  $0.35$  to  $0.55$  V and at  $0.75$  V) of the positive sweep which are rather similar, though less pronounced, in the same region in Fig. 1b.
3. The cathodic currents below ca.  $0.65$  V in the negative sweep seem unusually large. In the case of second and third scans (Fig. 2b) the voltammetric response seemed to have stabilized, with the exception of the sharp anodic peak in the positive sweep; the charge associated with this feature, at ca.  $0.25$  V, continued to decrease quite significantly on repeated scanning.

Effect of cell solution temperature on the anodic response at low potentials

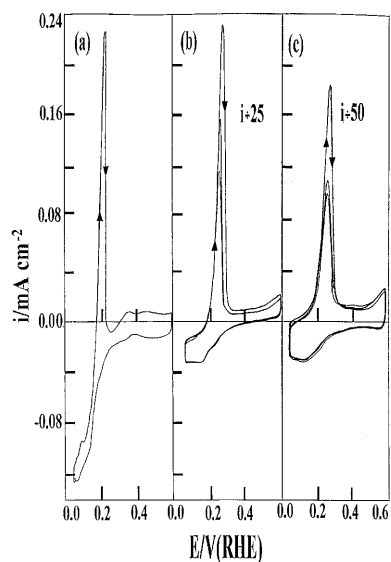
The effect of the cell solution temperature on the anodic response at ca.  $0.2$  V was investigated for two different electrolytes,  $\text{H}_2\text{SO}_4$  and  $\text{HClO}_4$ . The results are summarized, in terms of peak current density, in Fig. 3. Each point represents a separate experiment with its own thermal pretreatment stage. The response involved increased more readily, with increasing temperature, in the presence of perchloric acid. However, at  $80$   $^\circ\text{C}$  the height of the peak was rather similar for both acid solutions.

Effect of sweep rate

Examples of the effect of sweep rate on the voltammetric behaviour of thermally pretreated platinum in acid



**Fig. 3** Variation of the maximum anodic response (first positive sweep) for the peak at ca.  $0.25$  V as a function of solution temperature in  $1.0$   $\text{mol dm}^{-3}$   $\text{H}_2\text{SO}_4$  (●) and  $1.0$   $\text{mol dm}^{-3}$   $\text{HClO}_4$  (■) solution for the platinum wire which was thermally pretreated under the same conditions as Fig. 2



**Fig. 4** Effect of sweep rate on the cyclic voltammetric response (first cycle 0.05–0.60 V) for a platinum wire electrode in 1.0 mol dm<sup>-3</sup> H<sub>2</sub>SO<sub>4</sub> at ca. 80 °C; the wire was pretreated thermally in 5% H<sub>2</sub>/N<sub>2</sub> gas atmosphere (9 A, 25 s,  $T \approx 1310$  °C): **a** 10 mV s<sup>-1</sup>; **b** 50 mV s<sup>-1</sup>; **c** 200 mV s<sup>-1</sup>

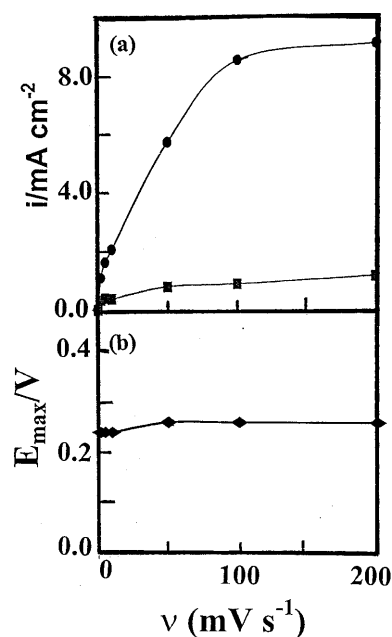
solution at 80 °C are shown in Fig. 4. The sharp anodic peak at ca. 0.2 V is evident in all three cases and the peak shape and position scarcely altered on changing from 10 mV s<sup>-1</sup> (in Fig. 4a) to 200 mV s<sup>-1</sup> (in Fig. 4c). Note also that in these three experiments the current sensitivity was changed to keep the anodic peak on scale at the different sweep rates.

The most interesting feature of these sweep rate experiments is that it is quite clear from the data at slow sweep rates, e.g. at 10 mV s<sup>-1</sup> in Fig. 4a, that the sharp anodic peak at ca. 0.2 V has a cathodic counterpart on the reverse sweep. The unusual feature here is that for some reason the current density associated with the cathodic feature at ca. 0.2 V on the negative sweep reaches a limiting value, i.e. there is some barrier or inhibition involved that severely limits the rate of the cathodic reaction.

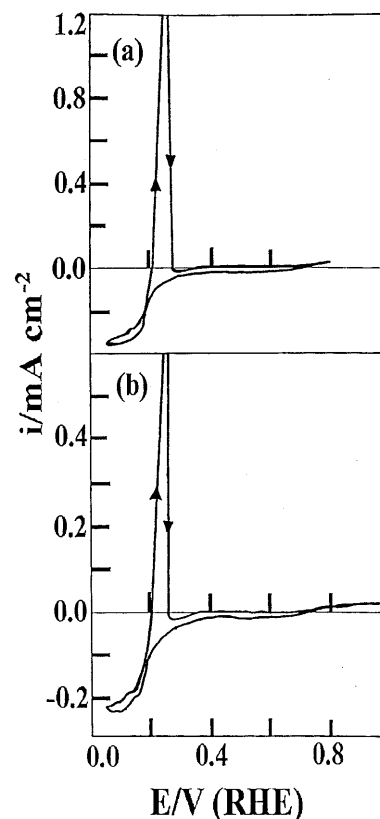
The results of a more extended series of sweep rate experiments are outlined in Fig. 5. The height of the anodic peak increased dramatically (upper curve in Fig. 5a), though not quite linearly, with increasing sweep rate up to values of the latter in the region of ca. 100 mV s<sup>-1</sup>. The plateau current below 0.2 V on the negative sweep (lower curve in Fig. 5a) increased only very slightly with increasing sweep rate. The variation of peak maximum potential for the main feature in the positive sweep is shown in Fig. 5b. Apart from a slight increase at low sweep rates, the potential value involved seemed to be independent of sweep rate.

Effect of the upper limit of the sweep

Two examples illustrating the effect of upper limit of the sweep are shown in Fig. 6. The responses in this case



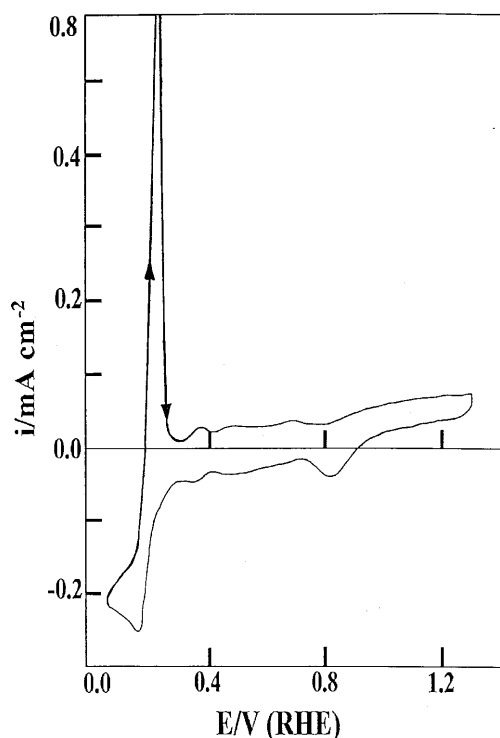
**Fig. 5** Variation of the peak current density (●) and peak potential (◆) for the anodic response at ca. 0.25 V (positive sweep, first cycle) as a function of sweep rate; each sweep rate value entailed a separate thermal pretreatment (conditions are given in Fig. 4). The variation of the magnitude of the cathodic response below 0.2 V on the subsequent negative sweeps in these experiments (■) is also shown in **a**



**Fig. 6** Effect of the upper limit on cyclic voltammograms for a platinum wire electrode in 1.0 mol dm<sup>-3</sup> H<sub>2</sub>SO<sub>4</sub> at ca. 80 °C; the wire was pretreated thermally in 5% H<sub>2</sub>/N<sub>2</sub> gas atmosphere (9 A, 25 s,  $T \approx 1310$  °C): **a** 0.05–0.8 V, 10 mV s<sup>-1</sup>; **b** 0.05–1.0 V, 10 mV s<sup>-1</sup>

were recorded at a rather low sweep rate ( $10 \text{ mV s}^{-1}$ ) and the dominant features are the anodic peak just above  $0.2 \text{ V}$  (positive sweep) and the cathodic current plateau in the region below  $0.2 \text{ V}$  (negative sweep). Slight cathodic currents, also evident in Fig. 4a, are observed at ca.  $0.3 \text{ V}$ , i.e. after the main anodic peak, in these positive sweeps recorded at  $10 \text{ mV s}^{-1}$ . The upper regions of these sweeps in Fig. 6 are not very dramatic; there is a minor flow of anodic current above ca.  $0.75 \text{ V}$  and the cathodic current below this value, but the dominant response for the interface is the active metal/hydrous oxide transition below  $0.3 \text{ V}$ .

The response for the same electrode at a faster sweep rate ( $50 \text{ mV s}^{-1}$ ) is shown in Fig. 7. There is some similarity in this case in the response above  $0.3 \text{ V}$  to the cycles shown in Fig. 2. However, the lower region of the negative sweep is quite different; in Fig. 7 this seems to be predominantly an oxide reduction response whereas in Fig. 2 there seems to be a combination of oxide reduction and hydrogen adsorption reactions taking place simultaneously, probably on different regions of the surface. Note that the cathodic current density value below  $0.2 \text{ V}$  in the negative sweeps in Fig. 7 and Fig. 6b are approximately equal, despite the substantial difference in sweep rate. This supports the view that the cathodic reaction involved in this region is quite sluggish.



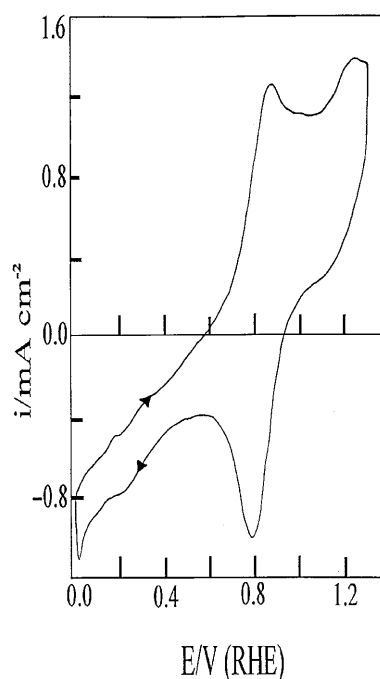
**Fig. 7** Repeat of the type of sweep shown in Fig. 6; same conditions as the latter, apart from the range ( $0.05\text{--}1.30 \text{ V}$ ) and sweep rate ( $50 \text{ mV s}^{-1}$ )

Responses recorded for thermally pretreated platinum electrodes in base

A typical cyclic voltammogram recorded for a thermally pretreated platinum electrode in base is shown in Fig. 8. The anodic peak at ca.  $0.2 \text{ V}$  in the positive sweep, as invariably observed in the present work with such an electrode in acid solution at elevated temperature, is absent in this case. The most unusual feature is the marked cathodic currents recorded, even during the first positive sweep, in the region below  $0.6 \text{ V}$ . It seems that monolayer (or  $\alpha$ ) oxide formation occurred in the positive sweep above  $0.6 \text{ V}$  and indeed a typical cathodic monolayer oxide reduction peak appeared on the negative sweep. However, a major charge imbalance is evident between the two regions, the anodic charge in the positive sweep being much larger than its cathodic counterpart. Evidently some of the anodic charge above  $0.6 \text{ V}$  results in  $\beta$ , rather than  $\alpha$ , oxide formation, and the reduction of platinum hydrous oxide species is already known [15] to be quite a sluggish reaction in base.

The stability of the highly active state of platinum

Most of the cyclic voltammograms reported here are the first sweeps recorded shortly after thermal pretreatment. The anodic feature at ca.  $0.2 \text{ V}$  is assumed to be due to the oxidation of active platinum atoms (or clusters of

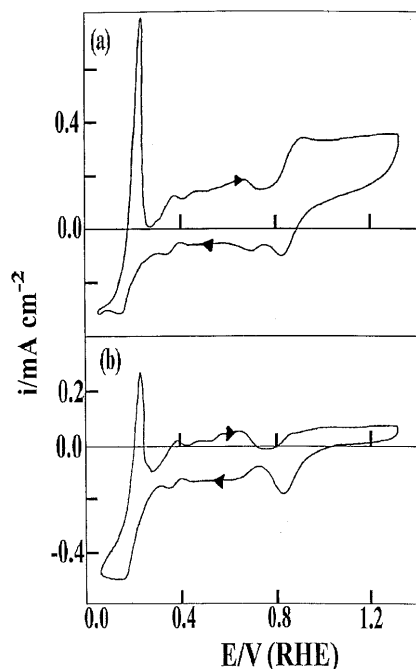


**Fig. 8** Cyclic voltammogram ( $0.0\text{--}1.3 \text{ V}$ ,  $50 \text{ mV s}^{-1}$ ) for a platinum electrode in  $1.0 \text{ mol dm}^{-3}$  NaOH solution at ca.  $70 \text{ }^\circ\text{C}$ ; the wire was pretreated thermally in  $5\% \text{ H}_2/\text{N}_2$  gas ( $9 \text{ A}$ ,  $25 \text{ s}$ ,  $T \approx 1310 \text{ }^\circ\text{C}$ )

same) [11], i.e. a thermodynamically unstable, but frozen-in, state of the metal is apparently involved. Such an active state is expected to decay with time, but the rate of decay is evidently not dramatic.

For example, two responses are shown in Fig. 9 for an electrode pretreated in a similar manner. In the first case (Fig. 9a) the response was recorded 1 h after the electrode had cooled, whereas in the second case (Fig. 9b) the response was recorded 4 days after the electrode had cooled. It is clear that in both cases the metal surface had not relaxed to that of conventional platinum. However, there were apparently some changes: the anodic response for active platinum at ca. 0.2 V is lower while the cathodic response for stable Pt at ca. 0.8 V (monolayer oxide reduction) is greater in Fig. 9b, as compared with Fig. 9a. Thus it seems that while the conversion of the active to the regular state of platinum tends to occur, this process is quite slow at room temperature. The anodic response at 0.2 V in Fig. 9b confirms the existence of a substantial quantity of active Pt at the interface.

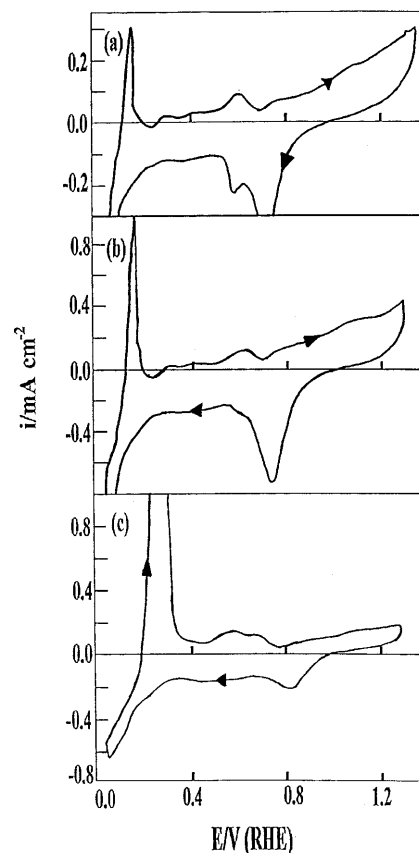
The results of similar experiments are shown in Fig. 10. In this case the thermal pretreatment was the same for all three experiments. In the first part of Fig. 10a, the response was recorded after the electrode was allowed to rest, after thermal activation, for 5 days in contact with air; the anodic response at ca. 0.2 V for the active state is still evident. For the sake of comparison, the same electrode was then subjected to the same thermal pretreatment as in Fig. 10a but the response was



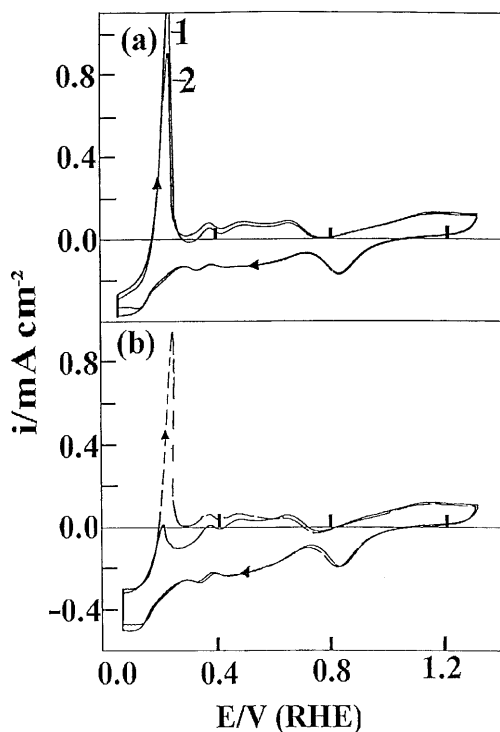
**Fig. 9** Effect of resting time after the thermal pretreatment (9 A, 25 s,  $T \approx 1310^\circ\text{C}$ ) on the response (0.05–1.3 V,  $50\text{ mV s}^{-1}$ ) recorded for platinum in  $1.0\text{ mol dm}^{-3}\text{ H}_2\text{SO}_4$  at  $80^\circ\text{C}$ ; the electrode was allowed to rest in the 5%  $\text{H}_2/\text{N}_2$  atmosphere for **a** 1.0 h and **b** 95.5 h

recorded, Fig. 10b, immediately after the wire had cooled (in this case the surface was not exposed to air). The curve in Fig. 10c is the response recorded on repeating the experiment outlined in Fig. 10b. The anodic response for the active state is much larger in Fig. 10c, as compared with Fig. 10b, and the monolayer oxide reduction response is correspondingly smaller. This highlights one of the difficulties in working with active states of metals: the ratio (or occupancy [11]) of the different states is not easily controlled.

It was demonstrated in Fig. 2, and illustrated again here in Fig. 11a, that the anodic response at ca. 0.2 V for the highly active state of platinum decayed on repeated scanning; however, it is not clear whether such decay is due to conversion of the active platinum to (1) a less reactive form of the metal or (2) to an oxide species that is not readily reduced. In either event, the highly active state (or a least the appropriate anodic response at ca. 0.2 V) may be restored (Fig. 11b) without resorting to further thermal pretreatment; all that is required is to subject the surface to a short period of cathodization at low potentials.



**Fig. 10** The electrode was pretreated as in Fig. 9 and then allowed to rest in air for 5 days prior to transfer to  $1.0\text{ mol dm}^{-3}\text{ HClO}_4$  solution where it gave the response (0.05–1.3 V,  $50\text{ mV s}^{-1}$ ) shown in **a**. Subsequent consecutive responses (after thermal pretreatment in each case but no exposure to air and no long arrest) are shown in **b** and **c**



**Fig. 11** First and second sweeps **a** for a thermally pretreated (as in Fig. 9) platinum wire electrode in  $1.0 \text{ mol dm}^{-3} \text{ H}_2\text{SO}_4$  at  $80 \text{ }^\circ\text{C}$ . The potential cycling was continued until the anodic peak at ca.  $0.25 \text{ V}$  became quite small (*full line* in **b**). The *dashed line* in **b** was then recorded after holding the electrode at  $-0.05 \text{ V}$  for 2 min; note the reappearance of a strong anodic response at ca.  $0.25 \text{ V}$ . In each case the cycling conditions were  $0.05\text{--}1.3 \text{ V}$ ,  $50 \text{ mV s}^{-1}$

## Discussion

The relationship between hydrous oxide reduction behaviour, premonolayer oxidation responses and electrocatalysis for metal electrodes in aqueous media was outlined diagrammatically in a recent publication in this journal [4]. While the responses shown here for platinum may seem quite unusual, they are in excellent agreement with the general scheme outlined in this earlier work, i.e. in Fig. 1 of [4]. There is a major component, labelled Pt(HO<sub>2</sub>), in multilayer platinum hydrous oxide films which undergoes reduction in acid solution at ca.  $0.2 \text{ V}$  [6, 15, 16]. It was demonstrated earlier that, at platinum in aqueous acid solution, species such as dichromate or nitrite [17] undergo a major increase in reduction response (in a negative sweep) at  $0.2 \text{ V}$ , whereas hydrazine undergoes a major increase in oxidation rate in a positive sweep at about the same value [18, 19]. It was suggested earlier [6], and the topic was discussed in some detail in the latter publication, that peak H<sub>i</sub> in Fig. 1a corresponds to a premonolayer oxidation reaction; the response for this process appears in much more dramatic form (due to the highly active state of the Pt surface at elevated temperature) in several diagrams in the present work. In some of the diagrams shown here, e.g. Fig. 4a, there is a degree of reversibility

in this redox response at ca.  $0.2 \text{ V}$ , although (as reported also recently for a similar reaction for gold in acid [12]) there is some inhibition of the cathodic reaction. In our opinion the novel response at ca.  $0.2 \text{ V}$  in the present work is due to an active metal Pt\*/hydrous oxide, Pt(HO<sub>2</sub>), transition and this electrode system fulfils the basic criteria outlined earlier [4] with regard to the IHOAM approach to electrocatalysis.

The underlying assumption in the present work is that on heating the metal the platinum atoms, especially on the surface, become mobile so that on rapid cooling many of these atoms become frozen-in in a low-coordination, high-energy state. Such a surface, in which many of the metal atoms are assumed to be present as discrete species or small particles (which are known [20] to be unusually electropositive), is intrinsically unstable. Some movement of atoms at the surface is assumed to occur even at room temperature (giving rise, for instance, to Ostwald ripening or cold sintering effects [21]); however, such movement or rearrangement is expected to be enhanced by raising the temperature. Since the moving atoms are of quite low coordination number, and hence very active from a thermodynamic viewpoint, the increase in anodic response at ca.  $0.2 \text{ V}$  on increasing the cell temperature (Fig. 2; compared with the behaviour described earlier [11] for similarly activated electrodes at room temperature) is understandable. In simple terms, increasing the temperature increases the probability of surface platinum atoms attaining the higher energy state and thus reacting at the unusually low potentials in the positive sweep. This promotion occurs more readily in HClO<sub>4</sub>, as compared with H<sub>2</sub>SO<sub>4</sub> solution (Fig. 3) as ClO<sub>4</sub><sup>-</sup> anions are much less strongly adsorbed on the platinum electrode surface.

It seems from the response shown in Fig. 6b that at the elevated temperature the dominant anodic response for a highly active platinum surface is the premonolayer or hydrous ( $\beta$ ) oxide, rather than the conventional monolayer ( $\alpha$ ) oxide, formation reaction. This premonolayer oxidation reaction is evidently quite rapid as the peak potential (Fig. 5b) did not alter appreciably with sweep rate. However, there are complications, e.g. the height of the anodic peak did not increase linearly with increasing sweep rate (Fig. 5a) and the cathodic response at ca.  $0.2 \text{ V}$  on the negative sweep was quite sluggish.

The limiting peak height value of the anodic response at high sweep rates (Fig. 5a) is assumed to be due to the slow rate of promotion of the active metal atoms to the very high energy state (in simple terms this limiting reaction, which precedes electron transfer at  $0.2 \text{ V}$ , may be regarded as promotion of metal atoms from kink or ledge sites to terraces). The cathodic response at  $0.2 \text{ V}$  (negative sweep) is clearly quite sluggish, as the peak, or plateau, current for this process (see the lower curve in Fig. 5a) altered very little with sweep rate. As suggested recently in connection with similar behaviour in the case of gold [12], there may be poor contact between the low-density hydrous oxide film and the metal surface, this

contact getting progressively worse as the inner region of the oxide film undergoes reduction; however, it is worth noting that similar inhibition is not usually observed when thick multilayer hydrous oxide films are reduced [16] under negative potential sweep conditions.

Anodic responses in the double layer region of noble metal electrodes in aqueous solution are frequently attributed to an accumulation of oxidizable impurities at the interface. However, as in previous publications from this laboratory, dealing with platinum [11], palladium [22] and gold [12], this view is rejected; the detailed argument given in these earlier works will not be repeated here. This does not imply that the presence of impurities, or the need to minimize or eliminate same, should be ignored. In our opinion the anodic responses, e.g. at ca. 0.2 V in Fig. 2, are too large to be due simply to impurities and the fact that electrocatalytic processes (as mentioned here earlier) commence and terminate at this same value (oxidations above and reductions below 0.2 V) clearly demonstrates that there is a vital transition for the Pt/aqueous acid electrode system at the potential in question. The type of behaviour involved was discussed in a generalized manner recently in the case of copper in base [4] and attention was drawn to independent evidence (based on Raman spectroscopy [23] and contact resistance [24] data) for the presence of hydroxy species at the interface in questions at potentials that are well within the double layer region. Oxide coverages at low potentials in the case of conventional platinum are obviously extremely small and hence difficult to detect (only ca. 1% of the surface, i.e. the active site regions, may be involved). The problem of detection of the oxide species is exacerbated in the fuel cell anode area (which has been the focus of much work in Pt electrochemistry in recent years) as the surface is often  $\text{CO}_{\text{ads}}$  contaminated [3]; the presence of  $\text{CO}_{\text{ads}}$  alters the redox behaviour of the Pt/solution interface, i.e. the presence of  $\text{CO}_{\text{ads}}$  inhibits the premonolayer oxidation reaction.

As pointed out earlier [11, 25], thermal or electrochemical activation of platinum not only enhances the premonolayer oxidation response but also reduces (if not eliminates) the normal anodic response due to the oxidation of adsorbed hydrogen in the positive sweep see (Fig. 2a). There are two possible explanations of this effect. In the first case, the highly active surface may undergo oxidation when the thermally pretreated electrode is brought into contact with the aqueous phase. In several of the voltammograms shown here. e.g. Figs. 4a and 6, cathodic currents were observed at  $E < 0.2$  V in the first positive sweep, suggesting that the metal surface is covered with a recalcitrant (difficult to reduce [13]) oxide which severely inhibits  $\text{H}_{\text{ads}}$  formation. On the other hand, if active but unoxidized Pt atoms are present, these are usually electropositive species. Usually hydrogen adsorption on Pt is assumed to involve at least partial electron transfer from the hydrogen atoms to the d-band vacancies in the metal; this is less likely to occur when the surface metal atoms are in an unusually active,

very electropositive state. Also, if there is some hydrogen adsorbed on the less active regions of the surface, the highly active regions of the same surface being oxidized, the hydrogen may be removed from the surface via a local cell reaction, i.e. the  $\text{H}_{\text{ads}}$  removal reaction may not entail a significant flow of external current.

Some evidence for the presence of a recalcitrant oxide (possibly of a slightly different character to  $\text{HO}_2$ ) is evident in some of the voltammograms shown here, e.g. in Fig. 4a there is a minor cathodic response in the positive sweep at ca. 0.26 V. It is important to note this feature is not due to conventional reduction of dissolved oxygen on platinum. If the latter reaction was involved, the flow of cathodic current should continue on the positive sweep to ca. 0.8 V. It is worth noting also that at any stage of the present work (with either acid or base electrolyte) the responses for a conventional platinum electrode showed no abnormal features. It is interesting also that the potential region for the sharp anodic response in the positive sweep did not alter significantly with the nature of the acid. This supports the view [11] that the product of the reaction is some type of oxide or hydroxide species. The presence of anions at the interface should not be ignored, and they may well be incorporated subsequently into the oxide product in a post-electrochemical step above ca. 0.25 V.

From a catalysis or electrocatalysis viewpoint, the model of surface reactivity (or active site behaviour) that emerges from the present work is rather novel. Active sites are often regarded as static defects [26], e.g. kinks or ledges. Such entities are still regarded as important; they are assumed to be centres of intermediate activity and the retention of material in this form at the interface is probably the reason why a significant response at ca. 0.2 V is still observed (Fig. 9b) and Fig. 10a, even after allowing the thermally activated electrodes to rest for several days either in an inert gas atmosphere or in air. However, for many electrocatalytic processes the most important surface species are low-coordination platinum atoms, generated via thermal vibrations, at these static defects (since such adatom species are mobile, they may migrate, and react, at a significant distance from their source, i.e. they may react on a terrace some distance away from the defect). The notion that an active surface site may be virtually a single surface metal is not novel; it is a view proposed earlier by Rooney and co-workers [27, 28] in connection with the  $\pi$ -bond theory of heterogeneous catalysis and was also proposed recently by Ertl and co-workers [8] on the basis of STM data. The redox properties of active metal surfaces are probably very difficult to control; they are assumed to be influenced by the detailed microstructure of the outer layers of the metal sample (i.e. the past history of the disordered solid), the defect distribution (type and coverage) of the surface, the energy and geometric arrangement (adsorption energy, degree of agglomeration, etc.) of active surface atoms – plus the fact that the active state is intrinsically unstable. However, the need to understand and study such ill-defined, reactive systems is highlighted

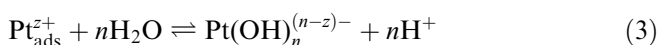


by Somarjai's recent claim [29] that "rough surfaces do chemistry", i.e. they are usually the most active catalysts.

The realization of the fact that single crystal surfaces "have plenty of imperfections" [9], plus the fact that surface microscopy techniques have difficulty in imaging mobile surface metal atoms [30, 31], has interesting implications for surface electrochemistry. It suggests, for instance, that cyclic voltammetry is one of the few techniques that provide information with regard to the presence, distribution and reactivity of these apparently vitally important mobile (or potentially mobile) species at noble metal surfaces. A common assumption [1] with the regard to oxidation of  $\text{CO}_{\text{ads}}$  at platinum in aqueous media is that the oxygen transfer species, at 0.2–0.5 V (RHE), is the  $\text{OH}_{\text{ads}}$  radical. However, this seems improbable; the  $E^0$  value [32] for this reaction, viz.



is 2.85 V (RHE), i.e. it is over 2.0 V more positive than the observed  $\text{CO}_{\text{ads}}$  oxidation potential region [33]. The most likely species to undergo oxidation at the interface at low potentials are the highly active Pt adatoms, and the product,  $\text{Pt}_{\text{ads}}^{z+}$ , on combining with  $\text{H}_2\text{O}$  or  $\text{OH}^-$  species, viz.



is assumed to yield an adsorbed hydrous oxide entity which is apparently the oxygen-transfer mediator for  $\text{CO}_{\text{ads}}$ . The involvement of a platinate ion, i.e.  $\text{Pt}(\text{OH})_6^{2-}$ , in such a reaction [6] has yet to be unambiguously established. However, such an anionic species is in agreement with the result shown in Fig. 8, i.e. with both the absence of the sharp anodic peak at 0.25 V and the sluggish nature of the oxide reduction response (even at 70 °C) at low potentials in the case of active platinum electrodes in base [15]. The absence of the sharp anodic peak at ca. 0.25 V for active platinum in base (Fig. 8) is attributed to the involvement of a super-Nernstian  $E/\text{pH}$  shift [6], i.e. the active metal/hydrous oxide transition for this reaction shifts in the negative direction by ca.  $0.5(2.3RT/F)\Delta\text{pH}$ . On changing from acid to base ( $\Delta\text{pH} \approx 13$ ), the expected decrease is assumed to be ca. 0.44 V, i.e. from ca. 0.25 V in acid to ca. -0.19 V in base; hence the sharp anodic peak does not appear with platinum in base (Fig. 8) because the active metal is already oxidized at 0.0 V (a diagrammatic representation of this aspect of Pt electrochemistry is given in Fig. 8 of [25]).

Confirmation of the above effect even in the case of conventional platinum in base is provided by Marichev [24] who reported, on the basis of contact electrical resistance data, that platinum surfaces (or evidently the active sites on same) in 1.0 mol  $\text{dm}^{-3}$  NaOH commence oxidation at ca. -0.1 V (RHE). Since Marichev's data for premonolayer oxidation of copper in base [24] (which commences at ca. -0.4 V) is in agreement with spectroscopic data [4, 23], his result for platinum in base is assumed to be valid. The cathodic responses below

0.6 V in Fig. 6 are attributed to slow reduction of a recalcitrant (but thermodynamically unstable) oxide. It is unlikely that the unusual nature of the response shown in Fig. 8 is due to an ohmic effect as the monolayer oxide reduction peak in the negative sweep occurs at the conventional value of ca. 0.8 V.

With regard to  $\text{CO}_{\text{ads}}$  deactivation of platinum-based fuel cell anodes, it is interesting to note that oxidation of this adsorbate on a porous platinum electrode in acid solution at room temperature also commences [33] (in agreement with the IHOAM approach, as mentioned here earlier for the oxidation of hydrazine) just above 0.2 V, evidently due to the involvement of a  $\text{Pt}(\text{HO}2)$  oxide mediator. Unfortunately, the reaction in this region is quite slow, the major  $\text{CO}_{\text{ads}}$  oxidation peak [33] occurring above 0.5 V, evidently due to the involvement of a  $\text{Pt}(\text{HO}1)$  oxide mediator [11]. It appears therefore that the primary objective in fuel cell anode development work should be directed towards enhancing the coverage and activity of the  $\text{Pt}(\text{HO}2)$  mediator system. This may explain the role of Ru in mixed Pt/Ru electrocatalyst systems which are more effective than pure Pt for  $\text{CO}_{\text{ads}}$  oxidation at low potentials [33]. Ruthenium is more susceptible to oxidation than platinum and it is possible that, in a mixture of these two metals, oxidation of the former has an activating effect on the latter, i.e. promotes  $\text{Pt}(\text{HO}2)$  oxide formation. However, the precise role of ruthenium in these systems is not well understood, although it seems that an unusually active state of the platinum is involved.

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## Conclusions

1. The present work supports the view that unusually active, non-equilibrium, states of metal surfaces exist or may be produced at an electrode surface. It provides strong support for the earlier claim [6] that there is an important redox transition in the case of platinum in aqueous acid solution at ca. 0.2 V (RHE). With regard to simple electrocatalytic processes, the behaviour of platinum in acid is in excellent agreement with the general scheme proposed recently [4] in terms of the IHOAM approach to such reactions. There is a complication in the case of processes where  $\text{CO}_{\text{ads}}$  is involved; CO is assumed to coordinate to active platinum atoms and inhibit both the formation of the oxidative mediator and the oxidative removal of the inhibitor species.

2. The active site model proposed here is somewhat unusual. The active entities or sites are not necessarily assumed to be static surface defects such as steps or kinks, although these are probably a major source or sink for the metal adatoms. The vital reaction site species are assumed to be high-energy, thermally promoted, relatively mobile surface metal atoms. The latter are regarded as quite low coverage, difficult to detect or control, rather transient species whose properties are quite different from those of

well-embedded surface (or bulk) metal atoms. Active atoms are assumed to exist at room temperature at all real metal surfaces; they are assumed to be associated with unavoidable defect features and, for many processes, they apparently dominate electrocatalytic behaviour. The importance of active sites in surface electrochemistry was stressed again recently by Savadogo [34] in a survey of the hydrogen gas evolution reaction.

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