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Anomalous electrochemical behaviour of palladium in base

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Abstract Noble metal hydrous oxides are known to be recalcitrant systems, i.e. they either undergo reduction at high overpotential or fail to undergo this reaction, due to the intervention of high-energy, virtually isolated atom or nanocluster states of the element as primary reduction products. Hydrogen absorption by activated palladium in base results in enhanced levels of surface activation and eventually to the spontaneous generation of recalcitrant hydrous oxide species which deactivate the electrode surface. Hydrous oxide behaviour at palladium in base is significantly more complicated than in acid; the deposits in question are less readily formed in base, and the main component of a multilayer oxide film grown in acid (HO2) seems to alter to a more readily reducible form (HO1) on transferring the electrode to base. However, evidence was obtained serendipitously in the present work for the formation of a recalcitrant oxide deposit on palladium in base; the involvement of metastable metal and hydrous oxide states provides the basis of energy storage and anomalous heat emission behaviour which is a controversial topic in the case of this electrode system.

Abbreviations

HO1 multilayer hydrous oxide 1
HO2 multilayer hydrous oxide 2
EMS equilibrated metal surface
MMS metastable metal surface

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Introduction

The electrochemical behaviour of polycrystalline Pd surfaces in aqueous media was discussed in a number of publications [1–8] from this laboratory. Considerable work has also been devoted to the behaviour of Pd single crystal surfaces [9–14] and Pd deposits on Au [15–17] and on Pt [18–22] single crystal surfaces; a detailed review of the electrochemical (though not electrocatalytic) properties of Pd was carried out recently by Jerkiewicz et al. [23]. Since Pd and Pt occur in the same group of the periodic table and have similar outer electron configurations, they exhibit similar electrochemical properties [24]. However, two major differences may be noted: (1) Pd has a remarkable tendency to absorb hydrogen in the region below 0.1 V vs RHE (reversible hydrogen electrode); the resulting equilibrated hydride (for p_{H2}=1.0 atm and 25 °C) has been formulated [25] as $PdH_{0.69}$; (2) the hydrous oxide electrochemistry of Pd in base (which is the major topic of the present investigation) is significantly more complicated than that of Pt.

Monolayer (α) oxide formation/reduction on Pd in aqueous acid and base is similar to that of Pt [24]. Hydrous (β) oxide formation and reduction on these metals usually occur under much more irreversible conditions, i.e. this reaction generally exhibits much greater hysteresis than the corresponding reactions for the monolayer deposit. According to Pourbaix [26], Pd should be oxidised to PdO (anhydrous or hydrated) at ca. 0.9 V, PdO_2 (hydrated) at ca. 1.27 V and PdO_3 at ca. 2.03 V vs RHE. However, as pointed out earlier [27], the growth of the multilayer hydrous oxide film, which may be regarded as $PdO_2 \cdot nH_2O$ under potential cycling conditions, requires an upper potential cycling limit in excess of ca. 2.40 V. It is clearly difficult with all the noble metals to convert the surface layers from the compact metal to the dispersed hydrous

oxide state, especially when (as in the case of Pd above 1.0 V) much of the surface is coated with a deactivating monolayer oxide deposit.

Reduction of the Pd hydrous oxide deposits in acid solution, even at quite slow sweep rates (2–20 mV s^{-1}), usually gives rise to two cathodic peaks [7], one at ca. 0.55 V and the other at ca. 0.24 V, which were attributed to the presence of two components (labelled as HO1 and HO2, respectively) in the hydrous oxide deposit. These potential values have no thermodynamic significance as the reactions occur under very irreversible conditions. The inhibition of the reduction processes was attributed earlier [6, 7] to the formation of highly active adatom or cluster atom states as the primary products of the reduction reaction.

Rather similar data was observed [28] for the reduction of multilayer hydrous oxide films on Pt in acid solution at 25 °C. However, with a similar acid-grown film in base, it was found [29] that, while the HO1 component was reduced readily, the reaction of the HO2 component was quite sluggish, e.g. ca. 25% of the deposit remained on the Pt surface after the latter had been polarised in base at 25 °C in the hydrogen gas evolution region at $E=-0.25$ V vs RHE for a period of 1.0 h. A negative shift in reduction potential—even in terms of the RHE scale, on increasing the solution pH, is quite common for hydrous oxide systems. The effect is sometimes referred to as a super-Nernstian E/pH shift [27] and is associated with the anionic nature of the hydroxy complexes present in many hydrous oxide deposits.

The behaviour of hydrous oxide-coated Pd electrodes in base should be quite interesting. If, as expected, the same type of behaviour is observed as for the corresponding Pt system [29], then the Pd (HO2) oxide deposit should exist at $E<0.0$ V on a hydrided Pd substrate—clearly a rather unstable situation. Furthermore, Pd in base is rather similar to the system which gave rise to the initial reports [30] of anomalous heat generation or cold fusion. While we have no strong opinion (or heat data to report) on the latter topic, we have observed some unusual effects which indicate that the behaviour of this electrode system is considerably more complex than is generally realised.

Materials and methods

The equipment and techniques used in this work were described earlier [7]. The hydrous oxide deposits were produced on bright Pd wire electrodes (0.5 mm diameter, ca. 0.3 cm^2 exposed area, Johnson Matthey plc, Puratronic grade, sealed into soda glass) by triangular potential cycling [2, 27], typically in either 1.0 mol dm^{-3} H$_2$SO$_4$ (0.68→2.82 V at 10 V s^{-1}) or in 1.0 mol dm^{-3} NaOH

(0.48→ 2.82 V at 10 V s^{-1}) at 25 °C. After such cycling, the phase boundary arrangement, extending outwards from the metal surface, was as follows [27]: metal/α oxide/β oxide/ aqueous solution; the β oxide is a porous, often heterogeneous, gel layer which does not inhibit access of solution species to the electrode surface. The oxide deposits were reduced subsequently in deoxygenated solution using a slow negative sweep, typically 1.0 to 0.1 V at 10 mV s^{-1}; all current density values are quoted in terms of geometric surface area. Usually, the electrodes were given a brief etch in diluted (25 vol.% in water) aqua regia, to remove any active metal from the surface between experiments. All potential are quoted in terms of the RHE scale, i.e. with respect to hydrogen ($p=1.0$ atm) in the same solution.

Results

Basic cyclic voltammetry of Pd

Typical examples of cyclic voltammograms recorded for bright Pd electrodes in acid (full line) and base (dashed line) are shown in Fig. 1. The responses in the oxide film formation region are rather similar to those observed with Pt, and, as discussed earlier [1], the onset potential for monolayer (or α) oxide film formation occurs at an appreciably lower potential (as also mentioned by Woods [24]) in base (ca. 0.64 V) as compared with that in acid (ca. 0.80 V). The peak maximum for the oxide reduction process on the negative sweep occurred at considerably closer potential values in acid and base. Another significant
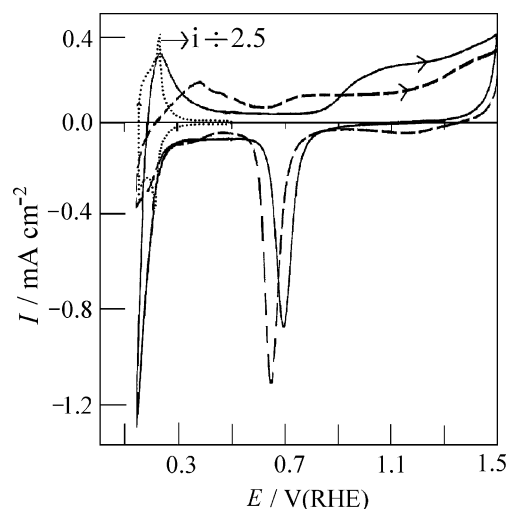

Fig. 1 Cyclic voltammograms (0.15 → 1.5 V, 50 mV s^{-1}) for bright Pd in 1.0 mol dm^{-3} H$_2$SO$_4$ (*full line*) and 1.0 mol dm^{-3} NaOH (*dashed line*) at 25 °C; the *dotted line* shows the response (0.15 → 0.5 V, 50 mV s^{-1}) for the same electrode in acid after disrupting the Pd surface (the disruption involved growth and reduction of a multilayer hydrous oxide film as outlined earlier—see Fig. 3a in [7])

difference between the responses for acid and base is the broad anodic response from ca. 0.3 to 0.6 V in the positive sweep recorded for Pd in base. There is no equivalent response in the case of Pd in acid [7], but there is a more marked anodic response in this case at low potential (E_p = 0.23 V, positive sweep, full line). As pointed out earlier [6, 7], it is possible to generate a pair of conjugate peaks (indicated by the dotted lines in Fig. 1) at ca. 0.23 V by disrupting the Pd surface—this reversible response, which is discussed again here later, was attributed to the formation and reduction of hydrous oxide species at active regions of the Pd surface.

Reduction of acid-grown hydrous oxide films

Typical responses for the reduction of thick acid-grown hydrous oxide films on Pd are shown in Fig. 2. In acid solution (Fig. 2b), a small peak was usually observed at ca. 0.6 V which is assumed to be due to the reduction of the monolayer (α) oxide deposit: this peak, recorded at a much higher current sensitivity, is much more clearly evident in Fig. 1. This was normally followed by two further cathodic peaks, one (C_1) with a maximum at ca. 0.52 V and another (C_2) with a maximum at ca. 0.24 V. Similar behaviour was observed earlier [6, 7], and the peaks involved were attributed to the reduction of two different components in the β-oxide deposit which were designated as HO1 and HO2, respectively. In terms of this approach, it seems that thick hydrous oxide films produced on Pd in acid consist predominantly of HO2-type material.

When these acid-grown oxide films on Pd were reduced following transfer of the electrode to base (Fig. 2a), unexpected behaviour was observed. The first hydrous oxide reduction peak ($C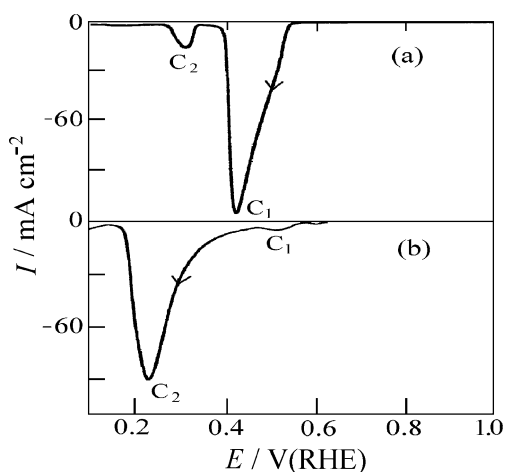_1$, $E_p \approx 0.42$ V) was the dominant cathodic feature, while the second peak (C_2, $E_p \approx 0.3$ V) was quite small. In these experiments with base, the monolayer oxide reduction peak was usually absent; the material involved is apparently reduced at the early stage of the main hydrous oxide reduction peak, i.e. below 0.54 V. Another surprising feature of the response in base is that, unlike the behaviour observed in similar experiments with Pt [29], where total reduction of the β-oxide film in base is difficult to achieve, reduction of similar acid-grown films on Pd in base normally went to completion (interesting exceptions to the latter are described here later). The completeness of reduction in base was demonstrated in two ways:

1. At the end of the sweep in base, the electrode was transferred back into acid, and another negative sweep was recorded. No major hydrous oxide reduction response was observed in the latter case; there was a minor cathodic feature at ca. 0.23 V, but this may be observed with a disrupted Pd surface that was never exposed to base.
2. Values for the total hydrous oxide reduction charge, for films of various thicknesses grown in acid under similar conditions, were virtually independent of whether the reduction was carried out in acid or base. This is illustrated here in Fig. 3 where charge values recorded for acid-grown films, reduced in acid or base, are shown as a function of film growth time. The two sets of values are quite similar in magnitude and demonstrate a linear increase in oxide coverage with increasing cycling time.

Fig. 2 Typical oxide reduction sweeps, $1.0 \rightarrow 0.1$ V, 10 mV s^{-1}, for acid-grown multilayer hydrous oxide deposits in **a** 1.0 mol dm^{-3} NaOH and **b** 1.0 mol dm^{-3} H$_2$SO$_4$ at 25 °C. The films were grown on Pd in acid by multicycling ($0.68 \rightarrow 2.82$ V at 10 V s^{-1} for 5.0 min)
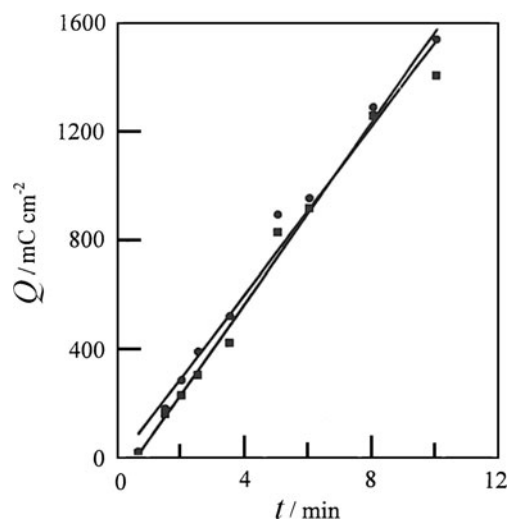

Fig. 3 Variation of the net charge for oxide reduction as a function of the oxide growth time in acid (the growth and reduction conditions, apart from the cycling time, were similar to those given in Fig. 2): *filled square* and *filled circle* refer to reductions carried out in 1.0 mol dm^{-3} H$_2$SO$_4$ and 1.0 mol dm^{-3} NaOH at 25 °C, respectively

A synopsis of the trends observed for acid-grown Pd hydrous oxide films in the course of reduction in acid and base is given in Figs. 4 and 5. In terms of charge density, the dominant features are C_2 in acid and C_1 in base (Fig. 4); the E_p values for these two dominant peaks showed a linear decrease with oxide film thickness or growth time (Fig. 5). No data is given here for short growth times as in such circumstances the peaks were poorly resolved, especially in acid. The charge values for peaks C_1 in acid and C_2 in base were rather small and varied in an unusual manner with growth time; the peak potential values for these two features showed only minor variations with overall film thickness values.

Reduction of base-grown hydrous oxide films

The growth under potential cycling conditions of hydrous deposits on Pd in base was much slower by nearly an order magnitude, as indicated in Fig. 6, than for growth under cycling conditions in acid as indicated in Fig. 3. The reduction patterns for such films in base and acid are illustrated in Fig. 7. The behaviour in base was unusual; for growth times less than ca. 6.5 min a small, very sharp, cathodic response was observed at ca. 0.35 V which overlapped with a larger, but again quite sharp, peak at ca. 0.33 V. However, with films grown for longer times (>6.5 min) the larger peak appeared before the smaller peak; however, the difference between the two peak
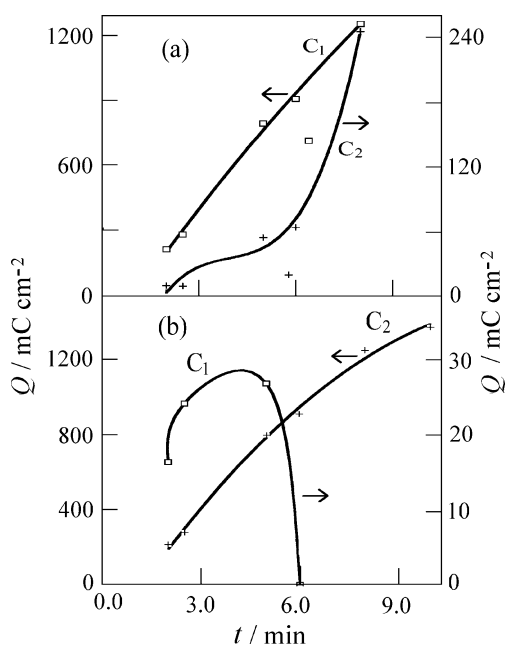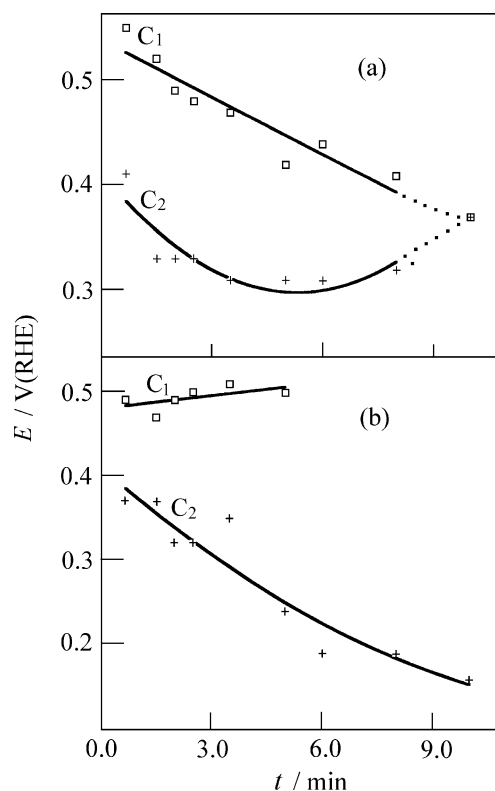

Fig. 5 Variation of peak potential values with net oxide (acid-grown) film thickness—data taken from the experiments described in Fig. 3; **a** and **b** refer to reductions in base and acid, respectively

potential values (ca. 0.36 and 0.34 V) in the latter case was again quite small. The variation of peak potential with film thickness for the reduction of these base-grown deposits is shown for base and acid solutions in Fig. 8. In the case of acid solution (Fig. 8b), the peak potential decreased with increasing thickness (similar behaviour was observed for the corresponding reaction in the case of the
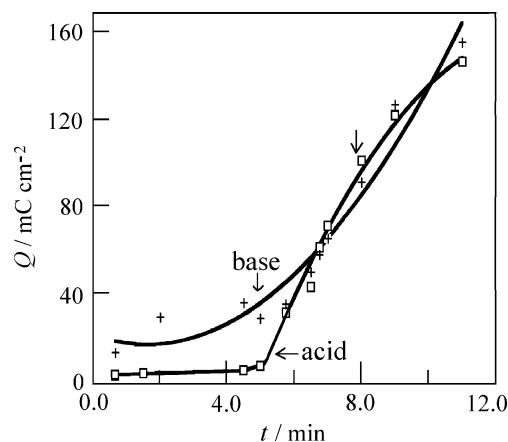

Fig. 4 Variation of the charge values for the individual hydrous oxide reduction peaks, C_1 and C_2 (see Fig. 2), as a function of the growth time—the oxide was produced in acid solution. The conditions involved are given in Fig. 3, the data taken from the same experiments; **a** and **b** refer to reductions in base and acid, respectively

Fig. 6 Variation of the net charge for reduction of base-grown films (produced by cycling, $0.48 \rightarrow 2.82$ V, 10 V s^{-1}; reduced at 10 mV s^{-1}, $1.0 \rightarrow 0.1$ V) as a function of oxide growth time; the films were reduced in either 1.0 mol dm^{-3} NaOH (*plus sign*) or 1.0 mol dm^{-3} H$_2$SO$_4$ [*open square*] at 25 °C
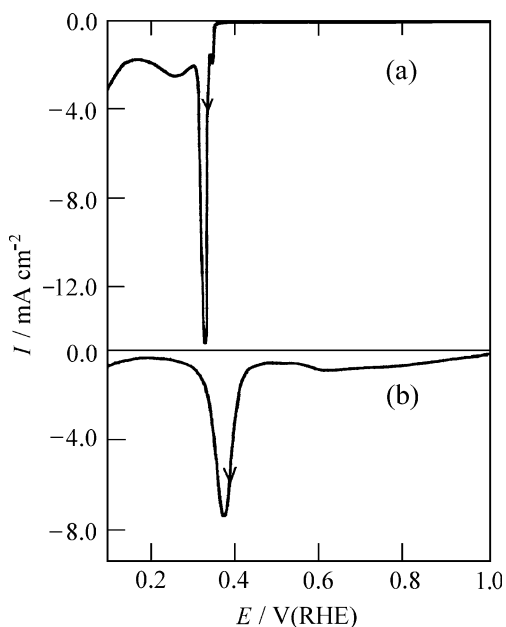
Fig. 7 Typical reduction profiles (1.0 to 0.1 V, 10 mV s^{-1}) for base-grown (cycling time=6.0 min) hydrous Pd oxide films in **a** base and **b** acid (conditions similar to those outlined in Fig. 6)

main peak, C$_2$ in Fig. 5b, with acid-grown films). The trend in the case of the base-grown films reduced in base (Fig. 8a) was unusual. While the peak potential initially decreased in value with increasing thickness (the normal behaviour), this trend was reversed for $Q \geq$ ca. 40 mC cm^{-2}.
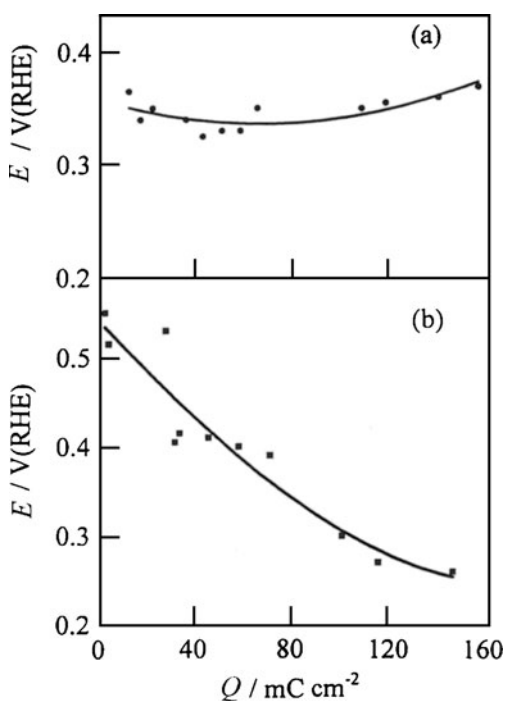

Fig. 8 Variation of the peak potential values with oxide film thickness for the reduction of base-grown Pd hydrous oxide deposits in **a** base and **b** acid: data taken from the experiment described in Fig. 6

Significant cathodic currents were observed in the negative sweeps in base after the appearance of the sharp peaks shown in Fig. 7a. Evidently, oxide reduction continued right down close to, or into, the hydrogen adsorption region. This meant that the assessment of charge associated with oxide reduction in base was not very accurate. Usually, the charge for oxide reduction in base was got by assuming that the reaction was completed at ca. 0.2 V, i.e. at the minimum in Fig. 7a after the small peak at ca. 0.26 V. The values thus obtained, especially for longer growth times, agreed reasonably well (Fig. 6) with the corresponding data for similar base-grown films when these were reduced in acid. An apparent exception here is the case of base-grown films of low thickness (or short, <ca. 5 min, growth times), as indicated in Fig. 6. The charge values recorded were significantly lower when reduction was carried out in acid solution. Loss of oxide from the surface due to either dissolution or particle detachment in acid solution may be involved. The response for reduction in acid (Fig. 7b) showed that this reaction gave rise to a single peak (E_{max}=0.39 V). There was an indication of a monolayer oxide reduction response in this case in the region just above 0.6 V.

Anomalous reduction behaviour in base

In general, the reduction of acid-grown Pd hydrous oxide films in base gave reproducible behaviour, i.e. a large cathodic peak (C$_1$) and a minor cathodic peak (C$_2$), as shown in Fig. 2a. Such behaviour was observed repeatedly when the electrode was used for several days; after each experiment the electrode was dipped for a short period (ca. 15 s) in diluted aqua regia to remove much of the active outer layer of metal (this active deposit was generated on reduction of the previously grown oxide deposit).

However, it was noted (and this observation was checked on several occasions) that a film could be grown in acid that was not reduced readily in base. The deposits in question were usually obtained with electrodes that had been used for repeated oxide growth, and reduction followed by a brief etch after each reduction sweep. When such an electrode was allowed to rest overnight, or for several days, the oxide film generated in acid was quite reluctant to undergo reduction in base in the course of the usual negative sweep (1.0 to 0.1 V, 10 mV s^{-1}).

These results were so unusual that the experiments involved will be described here individually in some detail, viz.

Case 1 The Pd electrode was used for 1 week in experiments involving hydrous oxide growth in acid solution and reduction in either acid or base. Between successive experiments, the electrode was cleaned by brief immersion

in diluted aqua regia. This electrode was allowed to rest for 2 days and then used for three hydrous oxide growth (each of which involved 6 min of cycling) and reduction experiments, all carried out using acid solution, with the usual results as outlined here in Fig. 2b. The oxide deposit was then regrown in acid solution, and the electrode transferred to base. Application of three successive reduction sweeps (1.0 to 0.10 V) at decreasing sweep rates, 10, 5 and 2 mV s^{-1}, failed to yield a hydrous oxide reduction response. However, a major response for this process (E_{max}=0.22 V) was observed in the usual manner, see Fig. 2b, on the first sweep recorded after transferring the electrode back into acid solution.

The electrode was again cleaned in the diluted aqua regia; an oxide deposit was regrown in acid solution (6 min of cycling), and the electrode was transferred to base. The first reduction sweep (1.0 to 0.10 V, 10 mV s^{-1}) yielded no reduction response. The potential was then held at 0.20 V and the current/time response recorded (Fig. 9a). After 8 min of no apparent reaction, a sharp cathodic peak (the width at half height was ca. 1.9 s) was observed; the charge involved in the peak, ca. 0.95 C cm^{-2}, corresponded quite closely to that expected for total reduction of the oxide film (similar films had been reduced earlier in acid solution).

The absence of oxide on the surface after this event was verified by recording a further reduction sweep (which was featureless) after transferring the electrode to acid.

Efforts to repeat the process, i.e. to regrow an oxide deposit in acid that was reluctant to undergo reduction in base, with this electrode at this stage were unsuccessful. It appears that disturbing the surface by growing and reducing hydrous oxide films is not sufficient as a pretreatment process to produce the recalcitrant oxide. It seems that allowing the electrode to rest for an extended period of time is an important feature in attaining the unusual precursor
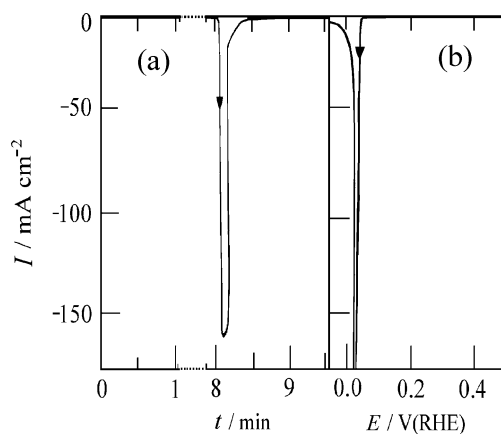
state that yields the recalcitrant oxide, i.e. an acid-grown oxide deposit that is difficult to reduce in base.

Case 2 This was observed with a different Pd electrode which was pretreated in a manner similar to that outlined here in Case 1—the resting period in this case was 3 days. On transferring the acid-grown film to base, no oxide reduction response was observed on the first two sweeps (1.0 to 0.0 V, 10 mV s^{-1}). In the third sweep, with the lower limit reduced to −0.1 V (this was probably of little significance), an unusually sharp cathodic peak (the peak width at half height was equivalent to ca. 5.75 s) was observed at 0.03 V, Fig. 9b. Total oxide reduction was achieved in this case as no oxide reduction peak was observed in a subsequent scan carried out after transferring the electrode to acid solution.

Case 3 The electrode was pretreated in a manner similar to that outlined for case 1, except that the rest period was shorter, ca. 14 h. When the acid-grown deposit (6 min of cycling) was transferred to base, significant oxide reduction (64% of the total) was observed on the first negative sweep (1.0 to 0.1 V, 10 mV s^{-1}), full line in Fig. 10a. However, the reaction was incomplete at the lower limit as a significant oxide (36% of the total) reduction response,
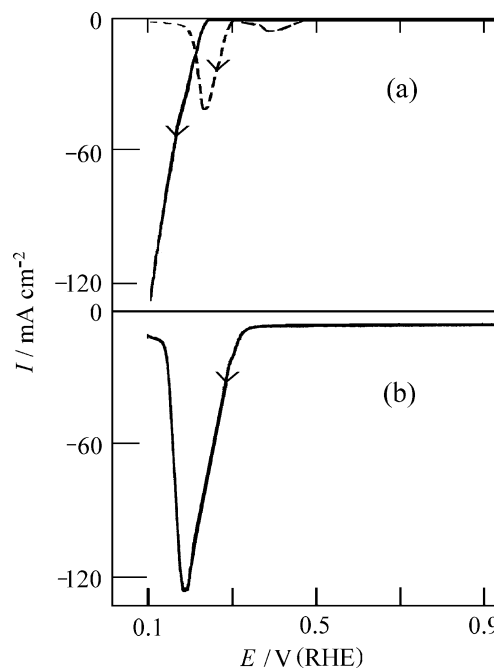

Fig. 10 Reduction of base-grown hydrous oxide films in 1.0 mol dm^{-3} NaOH at 25 °C: **a** (*full line*), first and (*dashed line*), second, negative sweep (1.0 → 0.1 V, 10 mV s^{-1}) for a film grown (t=6.0 min) by potential cycling (the electrode had been allowed to rest for 14 h prior to oxide growth—details are given in the text): **b** repeat of the oxide growth and reduction experiment in base; the electrode was not allowed to rest before this experiment, and the film was totally reduced in the first negative sweep

Fig. 9 Current spikes recorded for the reduction of base-grown Pd hydrous oxide deposits in 1.0 mol dm^{-3} NaOH at 25 °C under **a** potentiostatic and **b** potential sweep conditions. Details of these unusual responses (cases 1 and 2, respectively) are given in the text

dashed line in Fig. 10a, was observed when the negative sweep was repeated in the same electrolyte. The peak potential values in the case of this dashed line are quite similar to those shown in Fig. 2a—even though the charge values are quite different. At the conclusion of this experiment, the hydrous oxide film was regrown on the same electrode in base. This film was totally reduced on the first negative sweep in base, Fig. 10b. Attempts to immediately produce equivalent base-grown oxide deposits, which were reluctant to undergo reduction in base, were unsuccessful; such regrowth required that the disrupted electrode be subjected to an intervening period of extended rest.

Inhibition of hydrogen absorption into Pd in base

This aspect was part of a separate investigation, but the main feature seems worthy of inclusion here. It was carried out with the same equipment, as described here earlier, except that a thinner Pd wire (0.12-mm diameter) was employed to reduce the time taken to saturate the sample with hydrogen, i.e. to attain a potential of 0.0 V. Usually the electrode was activated in situ by growing and reducing three multilayer hydrous oxide films on the surface. After this, hydrogen gas was bubbled through the solution, and the potential was recorded as a function of time.

The lower curve in Fig. 11 is the response recorded during the course of hydrogen absorption in acid solution. As described elsewhere [25], the potential dropped rapidly to a plateau value of ca. 0.045 V—this being the region where the α/β hydride transition occurs for this system. When this

transition was completed after ca. 2.0 h, the potential decreased to 0.0 V, at which point the non-stoichiometric hydride, $PdH_{0.69}$ [25], is assumed to be present.

When this experiment was repeated in base, as shown in the upper curve in Fig. 11, similar behaviour was observed initially, i.e. the potential dropped to a plateau value which was slightly higher, at ca. 0.07 V, than in acid; in this case, there was a slightly negative slope. However, the potential never reached 0.0 V (this experiment was repeated several times); instead, at some unpredictable stage of the experiment, the potential started to drift rather sharply upwards (in the positive direction). Evidently, the surface became deactivated or poisoned so that equilibrium between hydrogen in the Pd and hydrogen in the solution no longer existed. Such behaviour occurred only with rather active Pd surfaces; when the activation pretreatment steps were omitted, the electrode in hydrogen-saturated base normally attained a final equilibrium potential value (as in acid) of 0.0 V.

An interesting aspect of this work was that hydrogen absorption/desorption work with the Pd seemed to activate the electrode surface; note the large premonolayer oxidation response in Fig. 12a, together with the corresponding reduction peak at ca. 0.23 V on the subsequent negative sweep. The process involved here seemed to be formation and reduction of incipient hydrous oxide species, as the charge associated with the reduction sweep in Fig. 12b, c increased significantly with increasing upper limit of the scan; however, this limit in Fig. 12c was below the potential required for the onset of conventional monolayer oxide formation.

Discussion

Anomalous behaviour of metal surfaces

There is an increasing awareness at the present time that the properties of solid metal surfaces, especially those of the noble metals, are more complex than was assumed earlier. This is particularly clear in the case of gold; the latter is the noblest and most inert of metals, an extremely weak chemisorber, and thus, in terms of the activated chemisorption model of catalysis should be a very poor catalyst. However, about two decades ago, Haruta et al. [31] demonstrated that under certain conditions, gold possesses unrivalled catalytic activity for room temperature oxidation of carbon monoxide. This triggered worldwide interest in the catalytic properties of gold, and a survey of this work is now available in book form [32]; an overview of the interesting electrocatalytic properties of gold in aqueous media has also been published [33]. The underlying theme of the present work is that this unexpected behaviour outlined here for gold extends to all solid metal surfaces.
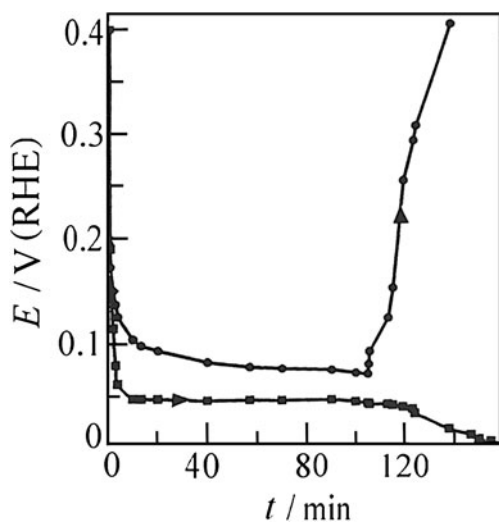

Fig. 11 Variation of potential with time during the course of hydrogen absorption by a Pd wire (diameter=0.122 mm) electrode in H_2-stirred (*filled square*) 1.0 mol dm^{-3} H_2SO_4 and (*filled circle*) 1.0 mol dm^{-3} NaOH at 25 °C. The surface of the electrode was disrupted (or activated) initially by a few hydrous oxide growth/reduction experiments
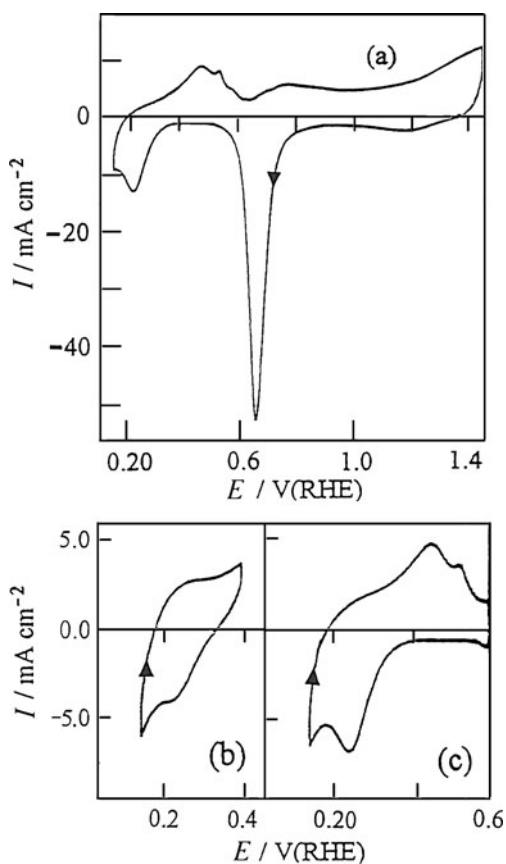
Fig. 12 Cyclic voltammograms for a Pd wire (diameter=0.122 mm) in 1.0 mol dm^{-3} NaOH at 25 °C (the wire was activated initially by saturating it with H$_2$ in 1.0 mol dm^{-3} H$_2$SO$_4$; the H$_{abs}$ was then removed by polarising at 1.0 V until i=0): **a** 0.15 → 1.50 V, 20 mV s^{-1}; **b** 0.15 → 0.4 V, 10 mV s^{-1}; **c** 0.15 → 0.6 V, 10 mV s^{-1}

responsible for the catalytic behaviour of metals. In the case of the group 11 metals (Au, Ag and Cu), the reduced and oxidised form of the MMS states function as mediators for the reduction and oxidation, respectively, of species present in the liquid or gaseous phase; the same mechanism may operate in the case of a Pt metal surface, although, in this case, there is an alternative (the activated chemisorption) mode of catalysis. Recent theoretical work by Friend et al. [36] on the influence of "undercoordination" on the interaction of atomic oxygen with defective Au(111) surfaces highlights the increasing interest in the properties of MMS states.

The use of highly dispersed metal nanoparticles in catalytic, e.g. fuel cell systems is obviously advantageous from a materials utilisation viewpoint; also, the high percentage of surface (as compared with bulk) metal atoms in nanoparticle systems should favour MMS, active site and electrocatalytic behaviour. This is borne out by the work of Hayden et al. [37] who observed that the specific activity of TiO$_x$-supported gold nanoparticles for the anodic oxidation of CO in acid solution increased as the particle size was reduced over the range 6 to 3 nm.; however, such particles were found to be inactive at diameters<2 nm. This loss of activity at very small particle sizes was attributed recently by O'Mullane et al. [38] to over-oxidation of very high-energy metal surfaces. It seems that optimum electro-catalytic performance at nanoparticle metal surfaces requires surface states of intermediate activity where the mediator or active site activity and specific surface area are high, but detrimental factors such as surface over-oxidation and particle sintering behaviour are minimised.

Anomalous behaviour of palladium

One of the main factors restricting our understanding of the surface electrochemistry of palladium (and indeed all the noble metals) is the presence at the metal/solution interface of indefinite amounts of EMS and MMS states. Attempts to circumvent this problem by employing single crystal plane electrodes are frustrated by the fact that all real single crystal surfaces contain defects [39], i.e. MMS states, which are generally the basis of surface active site and catalytic behaviour. As illustrated in Fig. 1, monolayer oxide formation commences in the positive sweep (presumably at EMS sites) at ca. 0.80 V in acid (full line) and ca. 0.65 V in base (dashed line); as discussed earlier [1], this variation in onset potential (in terms of the RHE scale) with change in solution pH is unexpected and was attributed to the initial stages of the monolayer oxide being of a significantly hydrated character. In the negative sweep, the monolayer oxide reduction peak occurred at ca. 0.7 V, but the charge for reduction of this oxide is significantly smaller than that apparently involved in its formation. This discrepancy may

The conventional behaviour of the noble metal electrode surfaces, summarised for instance by Woods [24], is assumed to relate to low-energy, equilibrated metal surface (EMS) states of the metals. Such states usually predominate; the vast majority of surface metal atoms are well embedded, highly lattice-coordinated (or highly lattice-stabilised) species which provide anchor points for adsorption but are otherwise often not very reactive; this is the state which gives rise to the well-known adsorbed hydrogen, discrete double layer and monolayer oxide cyclic voltammetry response for Pt in aqueous media. There is a second, less well-defined surface state in the case of solid metals known as the metastable metal surface (MMS) state; for a given metal, there may be a range of such states. The MMS state involves protruding, low-lattice coordination, high-energy surface metal atoms or clusters; it is a difficult state to investigate experimentally as it usually involves low coverage, inherently unstable, typically defect species which cannot be produced in a well-defined, reproducible form. The importance of MMS states lies in the fact that, as discussed recently for gold [34] and copper [35], they often constitute surface active sites and are thus

be attributed to a number of factors, e.g. the oxide formation may be accompanied by some Pd dissolution [40]; some of the discharged oxygen may enter the outer layers of the metal lattice and this subsurface oxygen may not readily undergo reduction [41], and some of the oxide formed above 0.8 V may undergo hydration, forming a hydrous (HO2-type) oxide which only undergoes reduction at ca. 0.25 V [7].

The behaviour of Pd in acid in the hydrogen region (below 0.4 V) is complex, especially with regard to the pair of sharp conjugate peaks at ca. 0.24 V (see the dotted line in Fig. 1). These peaks usually appear in a well-defined manner in work involving single crystal electrodes [9, 10, 16, 20] in H_2SO_4 but not $HClO_4$ [10, 11] or base [14] electrolyte. The absence of the response in base tends to rule out an explanation of the peak behaviour in terms of adsorption/desorption of H as in such a case the sharp peaks should appear at about the same potential (in terms of the RHE scale) in both acid and base. It also appears that that surface order is not an essential requirement as the conjugate peak response has been observed by two groups [7, 42] using deliberately disordered Pd surfaces. Furthermore, Petrii et al. [43] observed a sharp anodic peak at ca. 0.27 V in the positive sweep (the negative sweep is not shown in Fig. 1 of [43]) recorded for Pd nanoparticles electrodeposited on polycrystalline Pt. Hu and Wen also reported a conjugate pair of peaks at ca. 0.24 V (a_1/c_1 in Fig. 6, [44]) for Pd electrodes prepared by reduction of PdO films on Ti; they attributed these peaks to adsorption and desorption of α-PdH, but the latter is a phase (or bulk), not a surface, hydride [25]; hence, an active state surface redox transition, as outlined below, is assumed to be involved.

There is a significant amount of charge associated with these voltammetric peaks at ca. 0.23 V which are assumed to be of faradaic origin. In the positive sweep, the species most likely to undergo oxidation at low potentials (assuming the absence of H_{ads}) are high-energy (MMS) Pd atoms (the absence of such species at a relaxed (undisturbed) Pd surface explains the non-appearance of the peaks in question in most work with polycrystalline Pd). The anodically produced cations (Pd^{n+}) at the electrode surface attracts counterions, e.g. previously adsorbed $H_2SO_4^-$ and OH^- (from H_2O_{ads}) anions. Thus, a layer of sulphate, bisulphate and oxide (or a mixture of these species) may be generated at the interface at low potentials (the formation of mixed adsorption layers at a metal/solution interface was discussed earlier by Conway [45]). In earlier work with Pd in acid [7], a number of correlations were pointed out between the sharp peaks in the H region, observed with activated Pd and the multilayer HO2 reduction peak; the maximum reduction rate occurred in both cases at ca. 0.23 V and, for the same electrode, the charge for the active state response (after disruption) increased linearly

with that for reduction of the associated prior multilayer HO2 deposit (the source of disruption); see Fig. 5 in [7]. The HO2 deposit produced by potential cycling in acid solution is assumed to be predominantly a Pd(IV) oxide or hydroxide, e.g. $PdO_2·nH_2O$; in this extended material, there may well be sulphate and bisulphate ligands present, and the conjugate pair of peaks at 0.23 V are assumed to relate to a quasi-reversible Pd(MMS)/Pd(HO2) transition (the important role of these active surface state transitions was discussed recently for Au [34] and Cu [35]).

Behaviour of acid-grown multilayer Pd oxide films

The reduction response of an acid-grown multilayer oxide film in acid solution, shows, as usual (Fig. 2b) [7], two cathodic peaks, C_1 and C_2, attributed to the reaction of two different hydrous oxide states, designated as HO1 and HO2, respectively. Such behaviour was reproducible in so far as the reduction charge for C_2 was invariably much larger than for C_1 when deposits of different thicknesses were grown and reduced in acid solution.

When similar acid-grown deposits were reduced in base, as shown in Fig. 2a, two unusual effects were noted. In contrast to the reaction in acid, reduction in base gave rise to a peak C_1 which was much larger than peak C_2; the reason for this change in behaviour is unknown, but it appears that immersing an acid-grown Pd hydrous oxide film in base (in which the bisulphate ion activity is extremely low) results in a major alteration of HO2 to HO1. This may be due to loss of bisulphate anions from the HO2 state which thereby transforms to HO1; however, the nature of these hydrous oxide films and their transformation merit further investigation. The second interesting feature, highlighted here in Fig. 3, is that, with these acid-grown Pd oxide films, the net charge for reduction in base is approximately the same as for acid; evidently, the entire oxide film is reduced in base in the course of a single negative sweep. This was somewhat surprising as, under similar conditions with Pt [29], the HO2 component of an acid-grown hydrous oxide film is virtually impossible to reduce totally (even at $E ≤ 0.0$ V) under electrochemical conditions in aqueous base. This pseudo-stability of acid-grown Pt(HO2) species in base was attributed mainly to a super-Nernstian E/pH shift [27], the HO2 oxide being base-stabilised and consequently, quite difficult to reduce (obviously for kinetic reasons) in alkaline solution. Gold exhibits a similar trend; this metal has no oxide that is thermodynamically stable below ca. 1.4 V (RHE); yet, it yields an anodically generated oxide deposit in base [46] which contains a major component that undergoes rapid reduction in alkaline solution only below 0.0 V (RHE). With Pd, most of the acid-grown HO2 deposit apparently alters readily to the HO1 state on immersion in base, and

the latter type of oxide (even in the case of Pt [29]) readily undergoes total reduction in alkaline solution at a potential well above 0.0 V in the course of a single negative sweep.

It is interesting to note that there is little indication of inhibition of the oxide film growth process on Pd, on potential cycling in acid solution, with increasing oxide coverage (Fig. 3); this suggests that the deposit formed is quite porous, the underlying metal surface remaining quite accessible. According to the data summarised in Fig. 4b, the dominant component in a film grown in acid (at least under the conditions used in the present work) was HO2, giving rise to reduction peak C_2. While little indication of peak C_1 (or oxide HO1), especially after long oxide growth times, was observed on reduction in acid, this HO1 deposit (or peak C_1) was the main feature (Fig. 4a) observed when reduction of essentially an identically produced deposit was carried out after transferring the electrode to base. The peak potentials for the dominant cathodic responses, C_2 in acid and C_1 in base (Fig. 5), showed a regular decrease in value with increasing oxide growth time, oxide thickness or peak charge for reduction. The potential maxima for the minor oxide reduction processes, C_1 in acid and C_2 in base, were virtually constant, the values for C_2 in Fig. 5a occurring mainly just above 0.3 V.

Behaviour of base-grown multilayer Pd oxide films

The behaviour of base-grown multilayer Pd oxide films (Fig. 6) is considerably different from that of their acid-grown counterparts (Fig. 3). The extent of oxide growth on potential cycling of the metal in base is considerably lower than for similar oxide growth experiments with acid solution, and the rate of increase in the quantity of oxide with cycling time in base is also more complex. In the case of base-grown films, the reduction behaviour in acid (Fig. 7b) is relatively simple; the initial, low-level response over the range 1.0 to 0.6 V evidently corresponds to reduction of an inner α or compact monolayer oxide film; the broadness of the response in this case is unusual and suggests that there may be a mixture of compact oxide species involved. The main hydrous oxide reduction process occurs in acid in a reasonably symmetrical manner below 0.5 V but, as summarised in Fig. 8b, the peak maximum potential decreased quite significantly with increasing amount of oxide.

The response for the reduction of a base-grown oxide deposit in base (Fig. 7a) is unusual. There is very little indication in this case of a cathodic response above 0.4 V. A sharp increase in cathodic current, overlapping with a discrete sharp peak, was observed at ca. 0.33 V; the maximum of this peak altered little with net film thickness; see Fig. 8a. It is assumed that this sharp response is due to the reduction of a monolayer-type oxide film, the sharpness

of the peak being due to the process occurring under high overpotential conditions, the reaction, once started, being quite facile. After the sharp peak, reduction continued in a sluggish manner, evidently due to the reaction of hydrous oxide species. The sluggish nature of this reaction in base, as compared with acid, is assumed to reflect a degree of super-Nernstian behaviour, i.e. the Pd cations in the hydrous oxide deposit coordinate a variable excess of hydroxide ions and consequently, undergo reduction in anionic form at a lower and more extended range of potential in base as compared with acid.

Multilayer oxide growth and reduction on Pd in aqueous media has received significant attention from previous authors [47–52]. Reduction of Pd β oxide deposits grown at constant potential ($E \geq 2.0$ V) in acid solution gave rise to a number of reduction peaks [48, 51] above 0.9 V in subsequent reduction sweeps also carried out in acid solution. Such peaks are less marked with films also grown in acid but under repetitive potential cycling conditions, presumably as the high oxidation state species involved, e.g. Pd(VI) or PdO_3, is less likely to accumulate in the β oxide deposit when the latter was grown using a lower cycling limit of 0.48 V. Pd electrodes polarised at ca. 2.8 V (RHE) in base [47] yielded rather simple reduction responses, an α oxide reduction response appearing at ca. 0.5 V and a β oxide reduction peak with a maximum at ca. 0.3 V; this was followed by a cathodic plateau or shoulder extending to ca. 0.1 V. Such a response for β oxide reduction at Pd in base is similar to that shown here for the same type of reaction in Fig. 7a and also in Fig. 3 in [52].

Hydrogen activation of Pd

Hydrogen activation of solid metal surfaces is a form of hydrogen embrittlement in which the outer layers of the lattice are extensively disrupted and the surface properties appreciably altered; the effect has been described earlier in some detail for both iron [53] and gold [34, 54]. For example, in the case of gold in acid, oxidation of the stable (EMS) surface normally commences at ca. 1.36 V; however, following cathodic pretreatment [54], the surface (partly converted to an MMS state) undergoes significant oxidation at ca. 0.4 V. Similar behaviour evidently occurs with Pd; in this case, hydrogen enters the metal lattice where it forms a metal hydride; stress induced by the latter process causes Pd atoms to move from the bulk to the surface [55], thereby generating an MMS state which is unusually susceptible to oxidation.

The lower curve in Fig. 11 is a typical response for H uptake by Pd from a H_2-stirred acid solution. The plateau potential of ca. 0.04 V corresponds to the region of coexistence of α and β Pd hydride phase [25]. After an immersion period just in excess of 2 h in this case, the

phase conversion is completed, and the H_2/H^+ equilibrium is eventually achieved at 0.00 V at the Pd hydride surface. The Pd surface is assumed to become activated to some degree in the course of this reaction, but in acid solution, none of the active atoms are converted to the hydrous oxide state. The most stable (or reduction resistant) Pd oxide is the HO2 state; however, this undergoes reduction in acid at ca. 0.24 V (Fig. 2b) and is thus unlikely to be generated (even at the activated surface) in the plateau region at ca. 0.04 V.

The plateau potential for the absorption of hydrogen at Pd in base (upper curve in Fig. 11) is at ca. 0.07 V, and with an initially unactivated Pd electrode, H absorption occurs normally, the potential dropping to 0.0 V after ca. 2 h. However, with a severely disrupted Pd surface, passivation was observed; as illustrated in Fig. 11, the potential, instead of moving downwards to an equilibrium value of 0.00 V, suddenly began to drift rapidly in the positive direction, i.e. neither the H absorbed in the metal or dissolved in the electrolyte had any further influence on the electrode potential—the surface was effectively poisoned. It seems that, with an already activated surface, the energy level of some of the protruding Pd atoms is further promoted under H absorption conditions in base so that spontaneous oxide formation takes place. It is most unlikely that the oxide in question is HO1 since the latter, as illustrated in Fig. 2a, undergoes reduction in base above 0.4 V. The most likely candidate to act as a surface deactivating species is the anionic form of HO2, formulated earlier [2] as an agglomerate of $[Pd(OH)_6]^{2-}$ species (the bulk agglomerate state may be uncharged, the anionic state being an oxide reduction precursor species). Such a species, formed gradually at the H-activated Pd surface in base, eventually deactivates the surface, encasing the latter, or perhaps just the active sites, in a coating of recalcitrant (difficult to reduce) oxide. Such an oxide species, which is only metastable, is not readily produced and investigated electrochemically in the case of Pd; however, their behaviour was described earlier for Pt [28, 29], Ru [56] and Ir [57].

The voltammetric response for a Pd surface activated by prior formation and removal of a saturated level of H_{abs} in base (Fig. 12a) shows two types of oxidation responses. Regular monolayer oxide formation/reduction (or EMS/α oxide interconversion) occurs above 0.6 V, the oxidation response being quite protracted while the reduction peak is quite sharp or narrow (similar behaviour observed with Pt has been discussed in considerable detail by Conway [45]). Active state oxide formation/reduction (MMS/β oxide interconversion or premonolayer oxidation/reduction) occurs at a lower potential range, the anodic peak on the positive sweep occurring at ca. 0.45 V, followed by a shoulder at ca. 0.52 V and a cathodic peak in the negative sweep with a maximum at ca. 0.23 V; a broad cathodic

peak in the same region is evident in the response for the reduction of base-grown hydrous oxide films in alkaline solution (Fig. 7a). The degree of hysteresis in the premonolayer oxidation for Pd in base (Fig. 12) seems rather unusual; this may reflect an initial rapid decay in the active state, i.e. the metal atoms undergoing premonolayer oxidation are appreciably less active than the metal atoms generated initially in the subsequent oxide reduction process. It may be noted that unusual premonolayer oxidation/reduction responses were reported earlier by Hu and Wen (see Fig. 2, [58]) for polycrystalline Pd surfaces in base; similar behaviour for Pd single crystal surfaces in base was described by Hoshi et al. [14]. Scanning electron microscopy data for Pd surfaces produced by reduction of Ti-supported PdO deposits indicated that the metal films thus produced were much more extensively cracked when the reaction was carried out in base, as compared with acid [44], suggesting that the metal films obtained in base (which may not be fully reduced) were highly stressed.

Energy storage in Pd electrodes in base

According to Pourbaix's thermodynamic data [26], which relates only to equilibrated bulk phases, Pd should begin to undergo oxidation to PdO at ca. 0.9 V (RHE). The observed value for the onset of oxidation of Pd in acid solution under CV conditions (Fig. 1) is ca 0.8 V; this slightly lower value is not surprising as the activity or chemical potential of surface metal atoms is assumed to be higher than that of their bulk equivalents. The significantly lower onset potential value for the onset of oxidation of Pd in base, ca. 0.65 V, was attributed earlier [1] to the effect of hydrolysis on the initial oxidation product, the latter becoming progressively more stable with increasing solution pH. Reduction of the monolayer oxide film in the negative sweep in both acid and base (Fig. 1) gave rise to a sharp peak at ca. 0.7 V; this is appreciably lower than Pourbaix's value for the Pd/PdO transition, but the effect may be attributed to the generation of initially rather active metal atoms in the course of oxide reduction.

The multilayer hydrous oxide deposit produced by potential cycling in acid solution is assumed to be composed of hydrated palladium dioxide species $PdO_2 \cdot nH_2O$. Direct reduction of the latter to the metal, viz.

$$PdO_2 \cdot nH_2O + 4H^+ + 4e^- \rightarrow Pd + (n+2)H_2O \qquad (1)$$
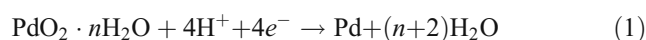
should occur (on the basis of thermodynamic data provided by Pourbaix [26]) at 1.09 V. In practice, this reaction, multilayer β oxide reduction at Pd in acid solution, occurs vigorously (peak C_2 in Fig. 2b) only below 0.3 V. The main source of inhibition of this type of reaction [56, 57] seems to be that the metal atoms involved are generated initially in

a highly active, virtually discrete atom state. Thus, for the reaction

$$PdO_2 \cdot nH_2O + 4H^+ + 4e^- \rightarrow Pd_g + (n+2)H_2O \qquad (2)$$
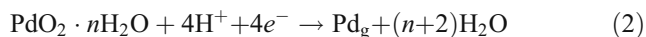
$E°$ (at 25 °C) is 0.21 V (RHE); in this case, the initial reduction product is assumed to be an isolated, virtually gaseous, Pd atom of chemical potential, $\mu^0(Pd_g)$, of approximately 339.74 kJ mol^{-1} [59]. This approach may explain the low potential range for Pd hydrous oxide film reduction in acid solution but does not account for the generation of the oxide blocking species at $E \leq 0.1$ V for Pd in H$_2$-stirred base (Fig. 11) or the reluctance in some instances (as described here earlier) of Pd β oxide films to undergo rapid reduction at 0.0 V in alkaline solution. However, hydrous oxide films frequently exhibit a super-Nernstian E/pH shift [27], i.e. a decrease in redox potential, in the RHE scale of ca. 0.5 (2.3RT/F) V (or ca. 30 mV at 25 °C) per unit increase in solution pH. Thus, the Pd$_g$/PdO$_2 \cdot n$H$_2$O transition, which is estimated to occur at ca. 0.21 V (RHE) in acid, should occur at ca. 0.21−13 (0.03)=−0.18 V (RHE) in base (for the transition from acid to base ΔpH is assumed here to be 13 pH units). Hence, provided that the reduced form of the metal/metal oxide couple is in a very highly active state, the metal can undergo oxidation at abnormally low potentials.

With regard to the assumptions made in the present work, it is worth noting that

(a) Metastable states are quite common in chemistry in general and in metals in particular [60]. The states in question are intrinsically unstable and prone to spontaneous decay; however, such decay may be reversed by extensive disruption of (or expenditure of energy on) the sample using techniques such as multilayer hydrous oxide growth and reduction [7], rapid thermal quenching [8], hydrogen absorption/desorption (Figs. 11 and 12) and cathodization [34].

(b) Recalcitrant (difficult to reduce) oxides are well established in the case of noble metals and, in some cases, coatings of these materials have applications, e.g. as metastable metal oxide cathodes for H$_2$ gas evolution [56, 57]. However, such coatings are intrinsically unstable and, as illustrated here in Fig. 9a, uncontrolled collapse, i.e. reduction, of the coating may occur in some instances. The response in Fig. 9b is less clear-cut; the reduction of the oxide deposit in this case was also severely inhibited initially, but, once the reaction commenced, there was a rapid burst of cathodic current which at E=0.03 V probably involved a mixture of oxide reduction and Pd hydride formation.

(c) Multilayer β oxide deposits have been described as anionic polymers [2, 52] with counterions present in intercalated water; however, the majority of the oxide species may be present in a neutral state, e.g. as Pd (OH)$_4$ or PdO(OH)$_2$, with only the electroactive species present at the interface (i) existing in an anionic form due to coordination of excess hydroxide ions, viz.

$$PdO(OH)_2(i) + 2OH^-(aq) \rightarrow \{PdO(OH)_4\}^{2-}(i) \qquad (3)$$
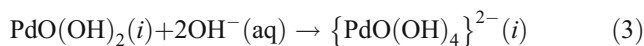
The assignment of anionic character to the β oxide species is necessary to account for the super-Nernstian E/pH shift and the increased reluctance of β oxide films to undergo reduction in base.

A schematic representation of the gradual accumulation and intermittent release of energy by a palladium electrode in base is outlined in Fig. 13. Under cathodic conditions, hydrogen is produced at the Pd surface, and much of it is absorbed by the latter resulting in palladium hydride formation. Depending on the initial state or pretreatment of the electrode, this leads to enhanced activation, resulting in the formation of virtually isolated Pd atoms. Normally, such a state would rapidly decay, the energy being released or dissipated in a steady-state manner in the form of heat. However, the formation of the recalcitrant HO2 oxide provides an energy storage mechanism. The superactive state of the metal, Pd*, is assumed to be gradually, but spontaneously converted to the recalcitrant form of HO2, viz.
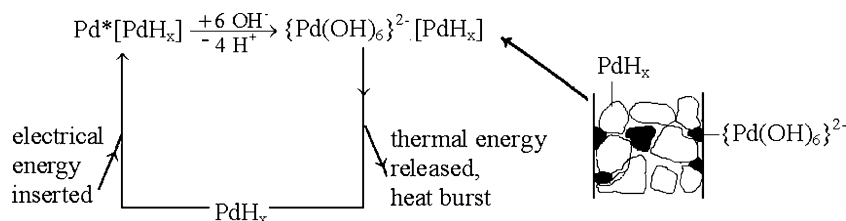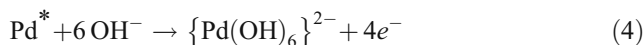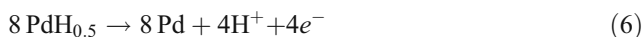
$$Pd^* + 6\,OH^- \rightarrow \{Pd(OH)_6\}^{2-} + 4e^- \qquad (4)$$
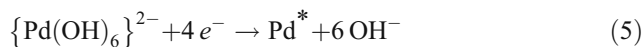

Fig. 13 Schematic cycle for the gradual accumulation and intermittent release of energy by a palladium hydride electrode in base (in practice H may be replaced by D). As outlined in the text, the electrically driven cathodization activates some of the palladium (or its hydride) to such a degree that recalcitrant oxide is formed which is assumed to react in an intermittent manner with the hydride releasing heat bursts

so that Pd oxide accumulates in the Pd hydride cathode (see the right hand side of Fig. 13). Such a situation may seem improbable, but is little different in principle to the behaviour of noble metal oxide cathodes used for hydrogen gas evolution [56, 57] or the apparent ability of Pt hydrous oxide deposits to resist reduction in base [29] at $E \leq 0.0$ V.

The mixture of hydride and oxide in the same sample of Pd (Fig. 13) is unstable, and the following local cell reaction is likely to occur (in an uncontrolled manner), viz.

$$\{Pd(OH)_6\}^{2-} + 4e^- \rightarrow Pd^* + 6OH^- \qquad (5)$$

$$8\,PdH_{0.5} \rightarrow 8\,Pd + 4H^+ + 4e^- \qquad (6)$$

$$\{Pd(OH)_6\}^{2-} + 8PdH_{0.5}$$
$$\rightarrow Pd^* + 8\,Pd + 4\,H_2O + 2OH^- \qquad (7)$$

(the stoichiometry of the hydride used here, $PdH_{0.5}$, was chosen solely for convenience). Thus, a burst of energy may be released due to the local cell reaction (Eq. 7); alternatively, the oxide reduction may occur suddenly, as in Fig. 9b, in a direct cathodic manner (Eq. 5) in which case energy will be released due to the decay of the high-energy state of the metal $Pd^* \rightarrow Pd$. Once the oxide reduction reaction has gone to completion (even locally), the energy storage process can recommence.

The present work does not relate directly to that of Fleischmann and Pons [30]: in particular, the latter employed deuterium oxide (and deuterium gas) which may be a significant factor in their experiments. It has been demonstrated here, in agreement with Fleischmann and Pons, that there is an energy release mechanism in the case of Pd electrodes in base; however, in the present case, this release is attributed to an unusual energy storage mechanism involving the intervention of a high-energy, unstable form of the metal cathode, i.e. the effect is not of nuclear origin.

Fig. 14 Overview of the active state/hydrous oxide behaviour of palladium in aqueous media; details are outlined in the final section of the text
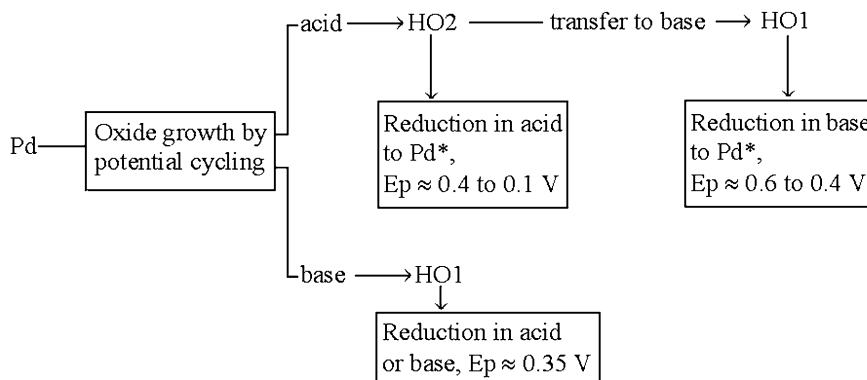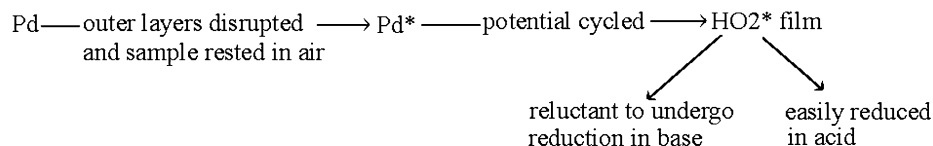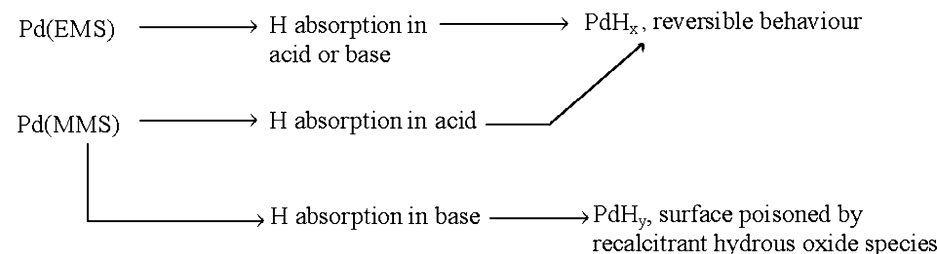
Summary

Pd is assumed to exhibit two basic types of surface electrochemistries, one relating to the EMS and the other to the MMS state. The EMS state is dominant in the case of hydrogen adsorption, conventional double layer and mono-layer oxide formation, and the electrochemistry involved has been summarised by various authors [23, 24, 26, 45]; the absorption of hydrogen by Pd (this is basically a bulk phenomenon, although it apparently affects surface activity indirectly; Fig. 11) has been described in detail by Lewis [25]. A synopsis of the MMS/hydrous oxide electrochem-istry of Pd, based on the present and earlier work [7] by the current authors, is given in Fig. 14. Attention is drawn to the following points:

(a) Two hydrous oxide species, HO1 and HO2, may be produced by potential cycling Pd in aqueous solution; the main product in acid [7] is HO2, but on transferring such a cycled electrode to base, an unexpected major HO1 oxide reduction response is observed; see Fig. 2. Hydrous oxide growth on Pd under potential cycling conditions in base is more sluggish than in acid. The oxide deposit involved is assumed to be more stable and possibly less hydrated when grown in base and, on transfer to acid, such deposits underwent reduction (Fig. 7b) at a higher potential than similar acid-grown deposits (Fig. 2b).

(b) The recalcitrant oxide is difficult to generate electro-chemically on Pd (certainly more difficult than for the same type of deposit on Pt [29]); however, it can be produced on electrodes which, after activation, are allowed to rest for a few days in air (the latter is assumed to favour processes such as formation of subsurface oxygen or oxide nanoparticles). Subse-quent potential cycling of such an electrode in acid solution yielded a recalcitrant oxide deposit whose eventual reduction at low potentials in base yielded quite unusual cathodic responses (Fig. 9).

It is indicated here that using a highly active state of palladium results in the generation of a recalcitrant hydrous oxide species (this was done via hydrogen absorption in base, Fig. 11; it would be interesting to see if the same result could be achieved via prolonged cathodization instead of H_2 gas absorption); a slow, energy-demanding process is involved, and this forms the basis of an unusual mechanism of electrode energy storage. The oxide, however, is unstable at low potentials and undergoes spontaneous rapid reduction in a random manner accompanied by the release of stored energy, as outlined here in Fig. 13. It would be interesting to explore the anomalous activation behaviour of Pd using a deuterium-based, rather than hydrogen-based, electrolyte system.

(c) Pd wire electrodes readily absorbed hydrogen when immersed in H_2-saturated acid solution and eventually, for $p(H_2)$=1.0 atm and 298 K, attained an equilibrium potential value of 0.0 V (RHE). Similar behaviour was observed with clean unactivated Pd electrodes in base. However, with a disrupted, MMS-type Pd surface in base, absorption of hydrogen eventually resulted in severe surface deactivation (Fig. 11) due to the formation of recalcitrant HO2 oxide species; the recalcitrant nature of this oxide in base is attributed to the intervention of a super-Nernstian E/pH shift.

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