JOURNAL OF APPLIED ELECTROCHEMISTRY 23 (1993) 573–582

# The electrocatalytic behaviour of palladium in acid and base*

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Received 9 July 1992; revised 28 October 1992

Anomalous oxidation of noble metals such as platinum is now an established feature of metal cluster/oxygen gas reactions. The same type of process at polycrystalline metal electrodes in aqueous media is assumed to give rise to incipient hydrous oxide formation. This approach was used here to rationalize the electrocatalytic behaviour of palladium, with regard to both oxidations and reductions, in aqueous acid and base. The activity of palladium was not dramatically different to that of platinum, and the presence of an unusual peak at about 0.23 V vs RHE in the case of palladium in acid is rather similar in character to the so-called anomalous hydrogen peak previously described for platinum under similar conditions. For both metals (and a similar claim was made recently for gold) an adatom/incipient hydrous oxide transition is assumed to be involved, and it is interesting that the onset/termination potential for hydrazine oxidation under potential sweep conditions virtually coincided with the potential for this minor peak or transition.

## 1. Introduction

The electrocatalytic behaviour of noble metal electrodes is of considerable importance both from a fundamental and technological viewpoint. In several recent publications from this laboratory [1–5] it was suggested that such reactions involve premonolayer oxidation, i.e. low lattice coordination surface metal atoms oxidize at unusually low potentials (significantly lower than the onset potential for regular monolayer oxide, or $OH_{ads}$, formation) to yield incipient (or low coverage) hydrous oxide species that mediate oxidation processes [2] or inhibit reduction processes [4]. Both a generalized scheme [1] and a kinetic treatment [5] for such reactions have been published; also, a review of hydrous oxide electrochemistry of the noble metals (which was a largely ignored topic until quite recently) is available [6]. It may be noted that a similar approach was used, in the case of gold, by Conway and coworkers [7–9]: they also assumed that premonolayer oxidation involved formation of an anionic hydroxy species [7, 8], which mediated an oxidation process [9], in the potential region prior to the onset potential for monolayer oxide formation. The particular case of gold (which is a convenient model system) in both acid and base was discussed extensively in a number of recent publications from this laboratory [10–13]. The objective here is to expand this approach to other noble metals.

It was postulated earlier [2] that platinum in acid can undergo very low coverage premonolayer oxidation at potentials as low as 0.2 V vs RHE. It was subsequently demonstrated [14] that this process may become the dominant reaction in the cyclic voltammetry behaviour of platinum in acid following extensive pretreatment of the electrode surface. There is independent evidence [15] that platinum metal clusters can exhibit the same type of anomalous oxidation with oxygen gas (in the absence of the liquid phase), the main difference being that with the latter the product is an anhydrous, rather than hydrous, oxide species. Such anomalous behaviour was attributed [15] to the unusual electronic properties of low lattice coordination, as compared with regular bulk lattice (or high lattice coordination), metal atoms.

The results of a survey of the electrocatalytic behaviour of a wide range of noble metals (including palladium) in both acid and base have already been published [3] and the data obtained was in reasonable agreement with the incipient hydrous oxide–adatom model approach. In the present work the behaviour of palladium was selected for more detailed investigation. Since platinum and palladium occur in the same group VIII subgroup of the periodic table it is usually assumed that they have similar electrochemical properties [16, 17]. Yet there are quite significant differences. Palladium at room temperature absorbs quite large quanitites of hydrogen [18]. In the present investigation such behaviour was avoided by restricting the lower limit of the sweep to values in the region of about 0.15 V. It is also more prone to dissolution [19, 20] and possibly oxygen uptake, at high potentials [21], into the outer layers of the metal. Some basic work on the electrochemistry of palladium in acid and base was described earlier [22–24]. The main emphasis here is on electrocatalysis: the techniques used were d.c. and

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* This paper is dedicated to Professor Brian E. Conway on the occasion of his 65th birthday, and in recognition of his outstanding contribution to electrochemistry.

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a.c. cyclic voltammetry and essentially it represents a continuation of earlier work on gold [10, 11] with the intention of investigating the performance of palladium in terms of the incipient hydrous oxide/adatom approach to electrocatalysis.

## 2. Experimental details

Both the working and counter electrodes consisted of lengths of palladium wire (1.0 mm diam., about 0.25 cm and 3.0 cm exposed length, respectively, Johnson Matthey, Puratronic grade) sealed directly into soda glass. Smooth working electrodes were pretreated before use by mild abrasion with fine grade emery paper followed by washing with triply distilled water. Such electrodes were coated with palladium black (when this was required) by cathodizing them at 50 mA cm$^{-2}$ for 1 min in a solution of 1 g of $PdCl_2$ in 100 ml of 0.1 M aqueous HCl at room temperature. All electrodes were cycled before use (0.2–1.3 V, 50 mV s$^{-1}$) for a few minutes in the acid or base electrolyte to ensure that the expected cyclic voltammetry behaviour [16, 22] of the system was observed. The potential of the working electrode was recorded (and is reported) with respect to a reversible hydrogen electrode in the same solution.

Solutions were made up using high purity (Analar grade) chemicals and triply distilled water; the solution in the working compartment of the cell was stirred with a flow of purified nitrogen gas. A.c. cyclic voltammetry experiments were carried out by superimposing a small sine wave signal (20 mV peak to peak, 300 Hz) on the regular triangular sweep. The potentiostat used for this work (EG & G, Model 273) was controlled using headstart software (EG & G Parc); the in-phase or faradaic a.c. response was selectively extracted and amplified using a lock-in amplifier (EG & G, Model 5208) and was recorded using an IBM PC XT. D.c. voltammograms were recorded using either the same equipment or its analogue equivalent (a Wenking, Model PGS 81, potentiostat, Metrohm, Model E 612, VA scanner, and a Rikadenki, Model RW-21, X–Y recorder).

## 3. Results

### 3.1. *Behaviour of palladium at low pH*

Typical examples of the d.c. and in-phase a.c. behaviour of a palladized (or Pd black) surface are shown in Fig. 1. Monolayer oxide (or $OH_{ads}$) formation commenced in this case at ~ 0.75 V (positive sweep, Fig. 1(a)) and the process involved gave rise to a plateau current extending from about 0.85 V to the upper limit of the sweep, 1.3 V. Reduction of this anodic film on the subsequent negative sweep gave rise to a symmetrical cathodic peak with a maximum at ~ 0.75 V. The hydrogen adsorption and desorption processes commenced and terminated (negative and positive sweep, respectively) below 0.4 V. An interesting feature was the appearance of the reversible pair of peaks at ~ 0.25 V, Fig. 1(a). Usually these did not appear (at least in a regular well defined manner) in voltammograms recorded for unpalladized (bright) palladium surfaces in acid; however, there was an overlapping pair of peaks in this region for both palladized, Fig. 1(b), and bright electrodes in a.c. voltammograms recorded under similar conditions.

An interesting feature in the a.c. response for palladium in acid, Fig. 1(b), is that, compared with platinum under similar conditions [25], the current in part of the hydrogen region, e.g. just below 0.2 V, was rather low (especially when compared with the values at the peaks at ~ 0.25 and 0.8 V in Fig. 1(b)). A distinct bulge or shoulder may be seen in the region above the maximum at the start of the monolayer oxide formation region in Fig. 1(b). In several instances (not shown here) a.c. voltammograms recorded between 0 and 1.2 V for bright electrodes exhibited a small peak, only on the negative sweep and not with a low upper limit (e.g. 0.9 V), at ~ 0.14 V. Although in such cases there was no

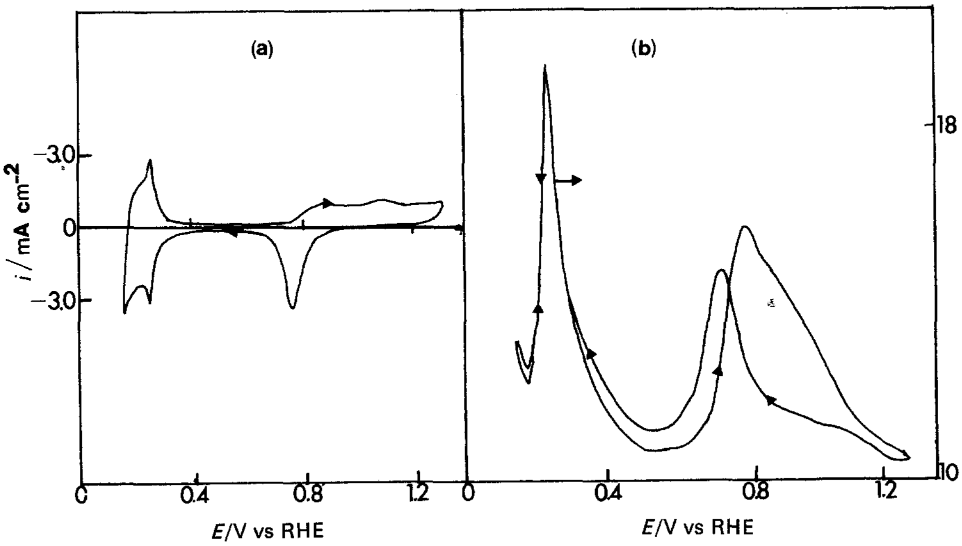

Fig. 1. Typical d.c. (a) and in-phase a.c. (b) cyclic voltammograms (0.15 to 1.3 V, 5 mV s$^{-1}$) for palladized palladium in 1.0 M $H_2SO_4$ at 25° C.

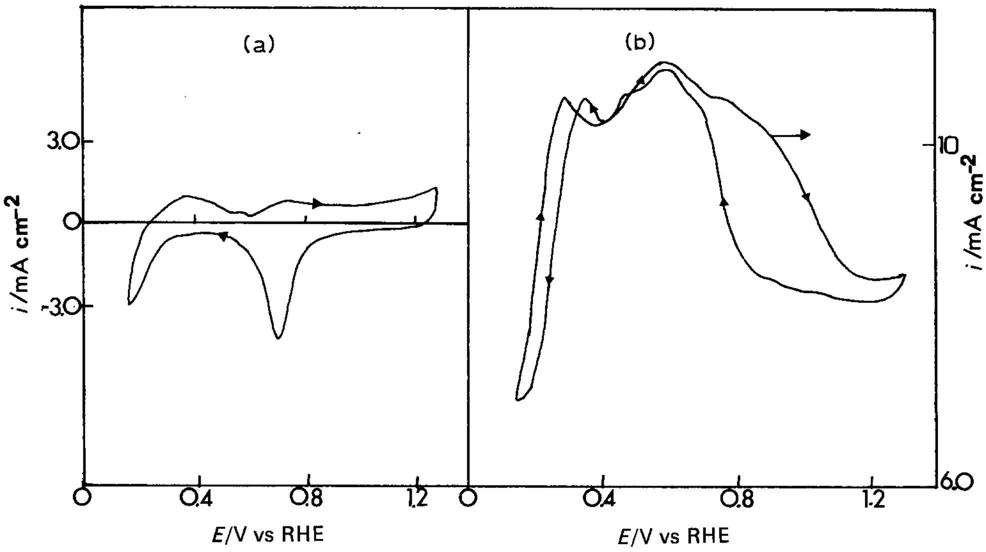

Fig. 2. Repeat of the experiments outlined in Fig. 1 using palladized palladium in 1.0 M NaOH, $T = 25°$ C.

obvious counterpart on the positive sweep the a.c. current in the latter showed an increase commencing at about the same potential and there was an indication also of a slight bulge or shoulder on the negative side of the sharp peak at ~ 0.25 V.

### 3.2. *Behaviour of palladium at high pH*

Similar responses for palladized palladium electrodes in base are outlined in Fig. 2. The d.c. monolayer oxide formation response commenced in this case at a significantly lower value, ~ 0.62 V. There was even an indication of a premonolayer peak, e.g. in the positive sweep in Fig. 2(a), at ~ 0.56 V. There was no trace in Fig. 2(a) of the reversible pair of peaks at ~ 0.24 V (compare with the response for acid in Fig. 1(a)).

The corresponding a.c. response, Fig. 2(b), is unusual in that the a.c. current in the double layer region (the latter, quite well defined in the negative d.c. sweep, extended from 0.55 to 0.35 V) was quite high – much larger than, for instance, the value at the lower end of the sweep, 0.15 V, which is well within the reversible hydrogen adsorption region. The peaks at the early stage of the hydrogen adsorption region in base (which in this case have no d.c. equivalent) seemed to be of different character to those observed in the same potential range in acid. These two peaks just below 0.4 V for base are quite small (compare the peak current density values for the palladized surface in base, Fig. 2(b), with their equivalent (also below 0.4 V) for acid, Fig. 1 (b)), occur at a slightly more positive potential as compared with acid, and exhibit significant hysteresis. The highest a.c. response for base occurred at the onset of the monolayer oxide formation process, i.e. at ~ 0.6 V.

### 3.3. *Electrocatalytic behaviour of palladium at* 20° *C*

As pointed out earlier [2] hydrazine is a useful compound for the investigation of electrocatalytic oxidation processes at noble metal electrode surfaces as, unlike the behaviour of most organics, its reaction is free of $CO_{ads}$ deactivation effects. The observed response was influenced by the state of the surface. With a palladized surface the d.c. response in acid, Fig. 3(a), commenced (positive sweep) and terminated (negative sweep) just above the reversible pair of peaks at ~ 0.22 V (it is difficult, because of the overlap, to locate precisely the onset/termination value – it may well be within the peak region). The oxidation current rose rapidly, to a limiting value, over the range 0.25 to 0.4 V and this trend was retraced on the subsequent negative sweep.

The corresponding behaviour for bright palladium in acid is shown in Fig. 4(a). Hydrazine oxidation commenced and terminated in this case at a more positive potential, ~ 0.35 V, and the region of rapid increase was ~ 0.4 to 0.6 V. Monolayer oxide deactivation of the surface was more evident in this case, especially above ~ 0.95 V on the negative sweep. After removal of this oxide material at ~ 0.8 V (negative sweep) the surface was unusually reactive but the behaviour below 0.6 V was quite similar with regard to electrocatalytic oxidation on the forward and reverse sweeps.

The a.c. response for the palladized electrode is shown in Fig. 3(b). After the peak at ~ 0.25 V (positive sweep) an increase in response commenced at ~ 0.37 V: after a maximum at 0.52 V there was a slight decrease until ~ 0.7 V and then a further maximum at ~0.83 V (it may be noted also that there was a minor increase in d.c. current in the corresponding curve, above ~ 0.75 V, in Fig. 3(a)). In the subsequent negative sweep there was a peak, Fig. 3(b), in the monolayer oxide removal region: the responses during the forward and reverse sweeps were quite similar in the region below ~ 0.55 V. The a.c. response for the bright electrode, Fig. 4(b), was rather similar in appearance to that in Fig. 3(b), the main differences were the lower current density values and the sharpness of the peaks in the double layer region in Fig. 4(b). In particular, in the negative sweep in the latter

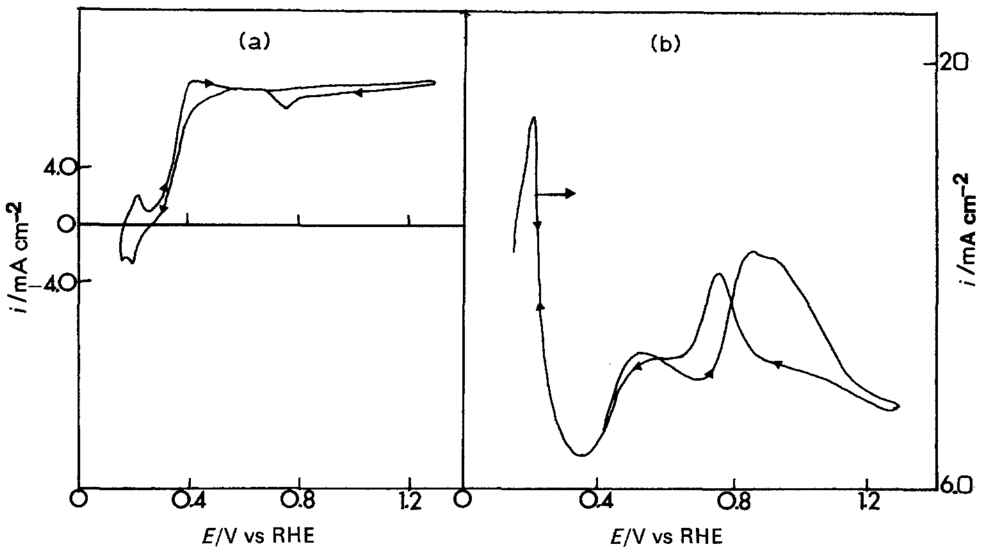

Fig. 3. Repeat of the experiments outlined in Fig. 1 using palladized palladium in 1.0 M $H_2SO_4$ + 0.1 M $N_2H_4$, $T = 25°$ C.

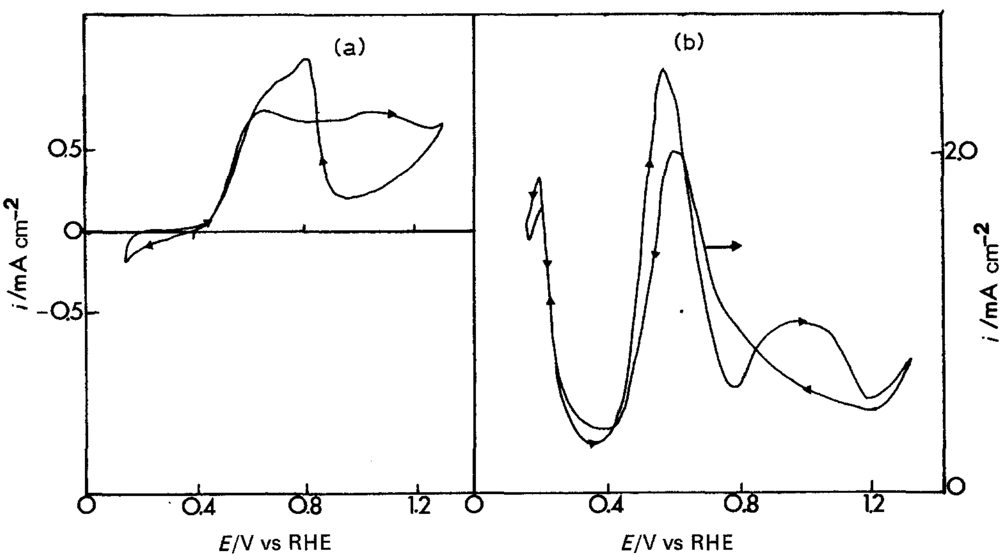

Fig. 4. Repeat of the experiments outlined in Fig. 3 using bright palladium, $T = 25°$ C.

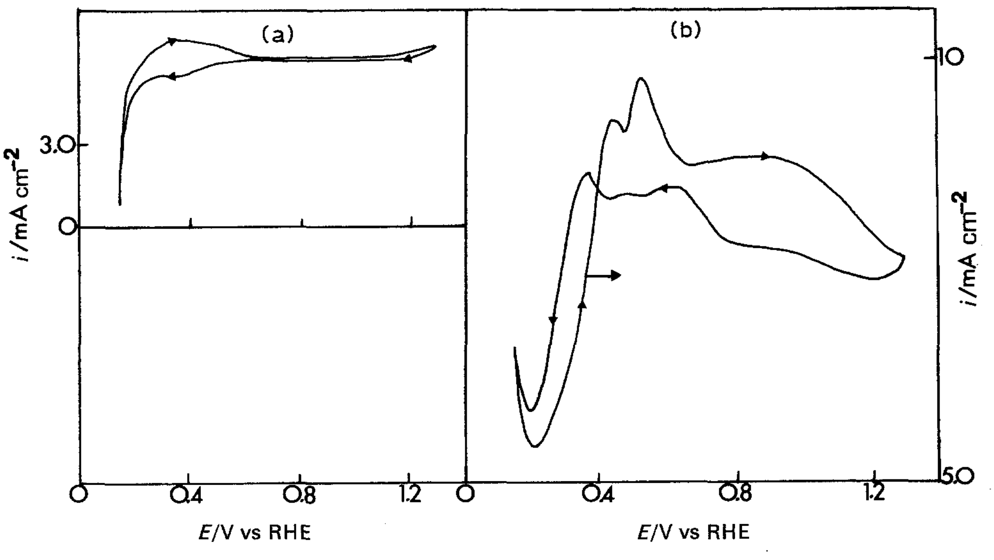

Fig. 5. Repeat of the experiments outlined in Fig. 1 using palladized palladium in 1.0 M NaOH + 0.1 M $N_2H_4$, $T = 25°$ C.

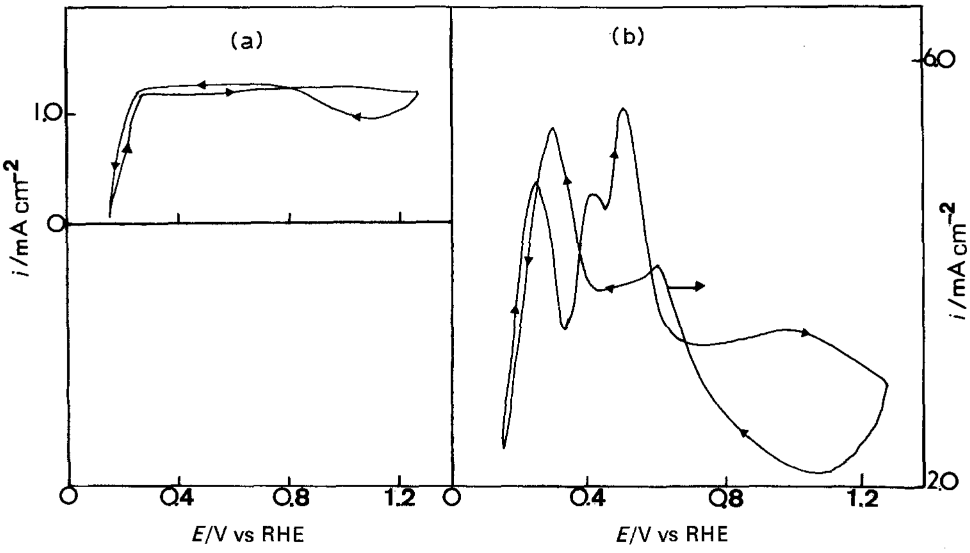

Fig. 6. Repeat of the experiments outlined in Fig. 5 using bright palladium, $T = 25°$ C.

diagram the poorly resolved peak or shoulder associated with the monolayer oxide reduction process at ~ 0.8 V was only a minor feature on the much larger peak at ~ 0.6 V.

The responses for hydrazine oxidation on both palladized, Fig. 5, and bright, Fig. 6, palladium electrodes in base were also investigated. The main differences, as compared with the behaviour in acid, were a lower onset/termination potential in base, a lower potential to attain the limiting rate of oxidation, and less difference with regard to these potential values between palladized and bright surfaces. The a.c. curves recorded for hydrazine oxidation in base were rather complex, with maxima at ~ 0.43, 0.5, 0.85 V (positive sweep) and ~ 0.6 and 0.35 V (negative sweep) in Fig. 5(b). The main difference in a.c. responses between palladized and bright electrodes in the case of hydrazine oxidation in base was the peak at ~ 0.24 V (positive sweep) for the smooth electrode, Fig. 6(b). However, there was also a minor inflection or shoulder at ~ 0.3 V in the positive sweep for the palladized surface, Fig. 5(b).

The d.c. response for reduction of dissolved nitrous oxide on palladized palladium in acid is shown, for two different temperatures, in Fig. 7. Reaction in this case commenced (negative sweep) and termi-

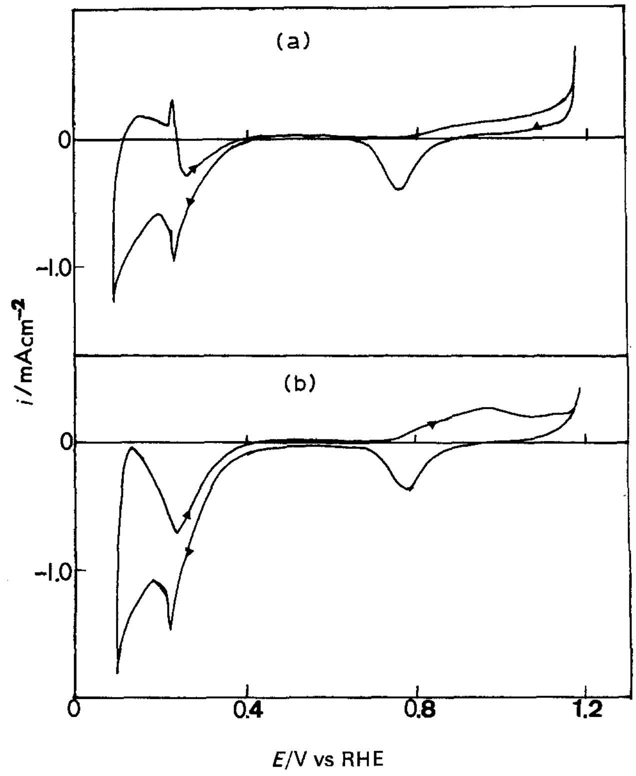

Fig. 7. Typical d.c. cyclic voltammograms (0.1–1.2 V, 5 mV s$^{-1}$) for a palladized palladium electrode in $N_2O$-stirred 1.0 M $H_2SO_4$ at (a) 20° C and (b) 60° C.

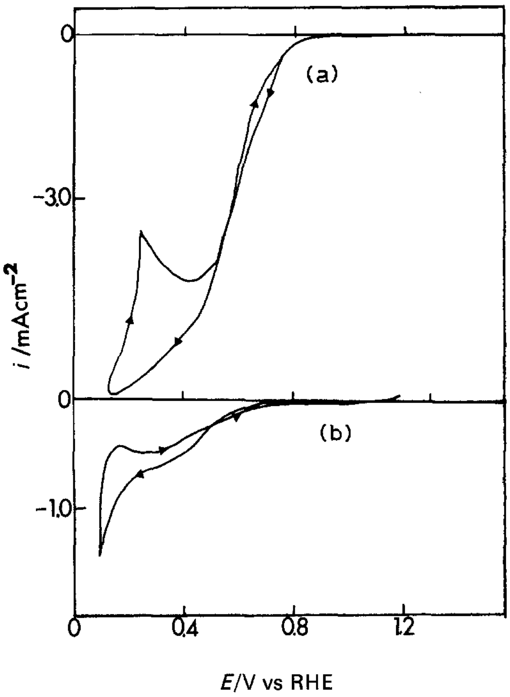

Fig. 8. Typical d.c. cyclic voltammograms (0.1–1.2 V, 5 mV s$^{-1}$) for bright palladium in 1.0 M $H_2SO_4$ at 20° C containing (a) 0.02 M $K_2Cr_2O_7$, and (b) 0.02 M $K_2S_2O_8$.

nated (positive sweep) at ~ 0.4 V, the same potential at which hydrazine oxidation under similar conditions, Fig. 3(a), reached a limiting rate. Also, the nitrous oxide reduction rate increased, Fig. 7 – while the hydrazine oxidation rate decreased, Fig. 3(a) – as the electrode potential was lowered in value over the range 0.4 to 0.2 V.

Palladized palladium, in general, did not appear to be a very active electrocatalyst. There was little indication of an oxidation response with 0.1 M isopropanol, or a reduction response in the presence of 0.05 M sodium nitrate, present in 1.0 M $H_2SO_4$ at 20° C. On bright palladium under similar conditions various reductants, e.g. dichromate and persulphate, Fig. 8, showed a significant drop in reduction rate during the positive sweep at potentials well before the start of the monolayer oxide formation process at ~ 0.75 V. Thus, in the case of dichromate, Fig. 8(a), the reduction current in the positive sweep showed a dramatic drop commencing at ~ 0.4 V, i.e. well before any regular monolayer oxide was produced at the interface.

### 3.4. *Behaviour at 60° C*

D.c. cyclic voltammograms for both bright and palladized palladium in 3.0 M $H_2SO_4$ at 60° C showed a reversible pair of peaks at ~ 0.21 V, similar to the behaviour shown at ~ 0.25 V in Fig. 1(a). In such experiments anodic currents were generally observed over the double layer region (0.75 to 0.35 V) of the negative sweep and there was a substantial a.c. response (in the form of a plateau) over the range 0.4 to 0.55 V. The d.c. response for hydrazine oxidation on bright palladium in acid at 60° C is shown in Fig. 9(a). Reaction commenced on the positive sweep at ~ 0.25 V and reached a first maximum at ~ 0.65 V, then (after a short plateau) a second maximum at ~ 0.97 V, followed by a further increase commencing at ~ 1.15 V. On the subsequent negative sweep there was a minimum at ~ 1.15 V, a maximum at ~ 0.96 V, and then a regular decline (with an indication of an inflection at ~ 0.8 V) until ~ 0.45 V. Oxidation finally ceased at ~ 0.25 V. The corresponding a.c. response, Fig. 9(b), was also complex with maxima at ~ 0.2, 0.6 and 1.1 V (positive sweep), and ~ 1.05, 0.65 and 0.15 V (negative sweep).

The effect of various other reductants and oxidants on the cyclic voltammetry of bright palladium in 1.0 M $H_2SO_4$ at 60° C was also investigated. Formaldehyde appeared to strongly deactivate the surface: the only significant oxidation response was an anodic peak on the negative sweep in the monolayer oxide reduction region at ~ 0.8 V: the a.c. response below 0.4 V was also unusually small. Formic acid was more active: in this case oxidation commenced

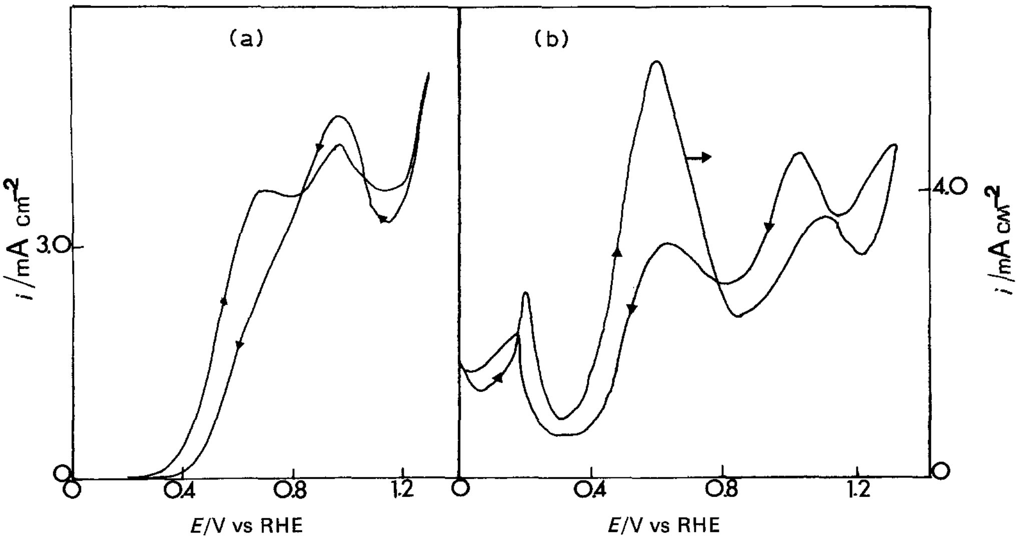

Fig. 9. Typical d.c. (a), 0.1–1.3 V, 5 mV s$^{-1}$, and a.c. (b), 0.0–1.3 V, 5 mV s$^{-1}$, cyclic voltammograms for bright palladium in 1.0 M $H_2SO_4$ + 0.05 M $N_2H_4$ at 60° C.

on the positive sweep at ~ 0.1 V and a large a.c. response was observed in the region below 0.4 V. Persulphate ($S_2O_8^{2-}$) ions were reduced below ~ 0.9 V: while the rate was surprisingly low over the range 0.2 to 0.9 V, the a.c. response for bright palladium in 1.0 M $H_2SO_4$ + 0.02 M $K_2S_2O_8$ at 60° C was rather similar to that shown in Fig. 1(b). With hydrogen peroxide or dichromate at 60° C the major inhibitor with regard to reduction appeared to be the monolayer oxide deposit. Virtually no reaction was observed with either compound above ~ 0.8 V.

## 4. Discussion

### 4.1. *The electrochemistry of palladium in acid and base*

Palladium, according to Pourbaix [26], is stable (or resistant to oxidation) in aqueous media at 298 K to ~ 0.9 V vs RHE. The values quoted [26] for the first oxidation step, namely

$$Pd + H_2O = PdO + 2H^+ + 2e^- \qquad (1)$$

range from 0.897 to 0.917 V, the product involved (PdO) being either the hydrated or anhydrous oxide, respectively. The increase in anodic current, corresponding to the onset of monolayer oxide formation on the positive sweep, Fig. 1(a), commenced at a somewhat lower value, ~ 0.75 V. However, this is scarcely surprising as the initial products of oxidation are probably $OH_{ads}$ species which were not considered in Pourbaix's work. The other features of the response in the oxide film region, e.g. the plateau above 0.9 V (positive sweep in Fig. 1(a)) and the hysteresis between the monolayer oxide formation and reduction regions, are quite well established features of both palladium and platinum electrochemistry [16, 27] and will not be discussed in detail here.

The unusual feature in Fig. 1 is the reversible pair of peaks at ~ 0.25 V: it is worth noting that such peaks are also evident in the earlier work of Perdriel and coworkers [28]. It is assumed here that, as in the case of both gold [11, 13] and platinum [2, 28], these are due to an adatom/incipient hydrous oxide transition. The low potential involved is due to the low lattice coordination number of the metal adatoms, i.e. to the reaction of a low coverage, highly active, form of the metal. A simple calculation to illustrate the lowering of the potential of the metal/hydrous oxide transition in the case of adatoms may be made as follows (the hydrous oxide is assumed to be a Pd(IV) species [22], $PdO_2$(hyd) or $Pd(OH)_6^{2-}$), namely

$$PdO_2(hyd) + 4H^+ + 4e^- = Pd + 2H_2O \qquad (2)$$

Taking the standard chemical potential values for $PdO_2$(hyd) and $H_2O(l)$ from Pourbaix [26], the standard potential ($E^0$) for this reaction is ~ 1.09 V. However, the same type of calculation may be carried out for the case where the product is highly active, non-lattice stabilized, palladium atoms. In this case the standard chemical potential of palladium may be taken as the vapourization energy of the metal, ~ 372.4 kJ mol$^{-1}$ [29]: this yields a standard potential ($E^0$) value of 0.13 V. The reversible peaks at low potential in Fig. 1 occurred at a more positive value, ~ 0.25 V: however, this is scarcely surprising since the palladium atoms formed on reduction at the interface are probably hydrated and have some further stabilization due to contact with the electrode surface. The high reversibility of the transition (and the high activity of adatom species with regard to electrocatalysis) is understandable as the majority of the adatom coordination sites are directly exposed to solution species. With a similar atom in the surface of a terrace most of these coordination sites are inaccessible due to the large number of neighbouring metal atoms.

It is worth noting also that anomalous oxidation of metals was demonstrated recently, in totally independent work, by Parmigiani and coworkers [15]. They observed that platinum clusters reacted with oxygen gas more readily, i.e. at a much lower temperature, than bulk (or continuous) platinum. Their explanation had a similar thermodynamic basis to that outlined here for palladium. Clusters have unusual structures: the metal atoms present have lower lattice coordination number values: occupancy of the outer 6sp orbital was assumed to increase, while that of the 5d decreased, as the cluster size decreased, leading to a limiting value of $5d^9$ $6sp^1$ in the case of the platinum adatom (as compared with $5d^{9.6}$ $6sp^{0.4}$ for the bulk metal). The adatoms oxidized more readily (or in an anomalous manner as compared with bulk platinum) due to the greater ease of donating an electron from the more diffuse 6sp, as compared with the less diffuse 5d, orbital. The main difference between this metal cluster/oxygen gas work and similar processes at metal/solution interfaces is that the oxidation product in the latter case is a hydrous, rather than anhydrous, oxide. Parmigiani and coworkers also pointed out that reversible formation of oxyspecies may be an important aspect in catalytic cycles; this is essentially the basis of the incipient hydrous oxide/adatom mediator model of electrocatalysis [1, 30].

The much lower response due to the reversible transition at ~ 0.25 V in the case of bright palladium electrodes is evidently due to the absence of a significant quantity of active palladium on this type of surface. In the palladized case the outer layer of metal atoms were deposited in a virtually random manner at room temperature to form a microcrystalline (or cluster) layer; such deposits have difficulty in annealing or rearranging to form the regular bulk structure. The combination of high surface area and high surface defect density would explain their more dramatic premonolayer oxidation response as compared to the bright surfaces; however, these bright surfaces did give a reversible response in acid at ~ 0.25 V when examined using the more sensitive a.c. technique.

The absence of the reversible pair of peaks at low potentials in the case of palladized palladium electrodes in base, Fig. 2(a), is also understandable in terms of an adatom/incipient hydrous oxide transition. As discussed recently for gold [13] such a transition should occur at a much lower potential at high pH; the decrease should be by ~ 0.35 V, i.e. from ~ 0.25 V in acid to ~ −0.1 V in base. At such a low potential the premonolayer oxidation response may be masked by the hydrogen gas evolution current; also, to observe the response below 0 V in base in cyclic voltammetry experiments the sweep would have to be extended to potentials well below the hydrogen absorption/desorption region, and there may well be interference due to the presence of large quantities of hydrogen both on and within the metal lattice.

What is evident in Fig. 2(a) is the appearance of a broad peak on the positive sweep at ~ 0.3 V with no obvious counterpart on the negative sweep at this potential. It may well be that there is some premonolayer oxidation of the surface in this region, the metal atoms involved being of slightly higher lattice coordination number (and hence somewhat less active) than adatoms. The negative shift in potential on transferring the electrode from acid to base is evident in the monolayer oxidation reaction (this effect was also pointed out earlier [23]): in acid, the monolayer oxidation reaction, positive sweep in Fig. 1(a), commenced at ~ 0.75 V whereas the same process in base, Fig. 2(a), commenced at ~ 0.6 V.

It may be observed also that on the positive sweep in Fig. 2(a) there is a small intermediate peak just below 0.6 V. Indeed both the d.c. and a.c. responses in Fig. 2 suggest that there is considerable interfacial reactivity from ca. 0.2 to 0.7 V; the decay in a.c. response, positive sweep in Fig. 2(b), above ~ 0.7 V is in agreement with the earlier suggestion [23] that the monolayer oxide becomes more anhydrous and less reactive in character with increasing coverage.

### 4.2. *Oxidation of solution species on palladium*

According to the incipient hydrous oxide/adatom model of electrocatalysis [1] oxidation of a reactive, oxidizable solution species should commence (positive sweep) and terminate (negative sweep) at the potential corresponding to that of the adatom/incipient hydrous oxide transition. For acid solution, Fig. 1(a), this evidently corresponds to the reversible peaks at ~ 0.25 V. However, as is clear from Fig. 3(a), the hydrazine oxidation response commences (and terminates) just above this pair of peaks. Either no oxide is involved in the peak-related processes or the oxide produced is not reactive.

The solution to this dilemma can be found in the work of Parmigiani and coworkers [15] who have pointed out that below a certain particle size the oxidation activity of metal clusters catalysts decreases with decreasing particle size (despite the increase in specific surface area); the more finely divided metal is over-reactive and too readily converted to the inactive oxide. The same type of behaviour is assumed to occur with the palladium black layer in the present work. This layer is likely to be an aggregate of poorly crystalline metal particles of different sizes. The very reactive material (minute particles with a highly distorted, if any, structure) oxidizes, in a reversible manner, at low potentials, giving rise to the peaks at ~ 0.25 V. However, this very reactive material is apparently extensively (if not totally) converted to the hydrous oxide state which is a poor electrocatalyst.

As pointed out independently [15], the occupancy of the outer sp orbital, and hence the ease of oxidation, decreases with increasing cluster or particle size (clusters or particles in the case of the palladium surface may be viewed as regions of the surface of different defect density and, hence, activity). Therefore, above the peak at ~ 0.25 V, positive sweep in Fig. 3(a), some of the slightly less active surface palladium atoms oxidize. The products in this case are low coverage incipient hydrous oxide species that are still attached to the metal lattice (and not to further oxide species). Such active oxide may continue reacting in a rapid, reversible, manner as follows:

$$[\mathrm{Pd(OH)_6^{2-}}]_{\mathrm{ads}} + 6\mathrm{H^+} + 4\mathrm{e^-} = \mathrm{Pd^*} + 6\mathrm{H_2O} \quad (3)$$

As pointed out earlier [3] partial replacement of OH species by $N_2H_4$ molecules in the coordination sphere of the Pd cation may be the crucial factor in the electrooxidation of the solution species. The positive electric field around the cation may well be a vital factor in promoting both electron loss to the metal and proton loss to the solution (both species being lost from the coordinated hydrazine molecule). The general kinetic ($i/E$) behaviour shown in Fig. 3(a) is in excellent agreement with the theory outlined previously [5] for this type of mediated interfacial reaction.

With the less active, bright palladium surface in acid solution, Fig. 4(a), the main increase in current due to hydrazine oxidation occurs (positive sweep) above 0.4 V. This, together with the absence in this case of the reversible peaks at ~ 0.25 V, reflects the lower activity of metal atoms at the unpalladized surface. The a.c. behaviour of the two surfaces, Figs 3(b) and 4(b), are not dramatically different: note for instance that a major increase in response in both cases commences on the positive sweep just below 0.4 V. The mediating species is evidently the same for both surfaces but the coverages is greater, and the limiting value attained at a lower potential, in the case of the palladized surface. The larger oxidation currents on the negative (as compared with the positive) sweep in Fig. 4(a) over the range 0.8 to 0.6 V evidently reflects the greater coverage of adatoms (and hence incipient hydrous oxide mediator species) on the bright surface after reduction of the oxide monolayer. Direct evidence for such displacement of surface metal atoms due to formation and reduction of monolayer oxide films on platinum was obtained recently [31, 32] in scanning tunnelling microscopy (STM) experiments.

The responses for hydrazine oxidation in base, Figs 5(a) and 6(a), are similar to those for acid in that limiting rates of oxidation were observed over most of the sweep. However, three significant differences may be noted: (i) the onset/termination potential for hydrazine oxidation was significantly lower in base, (ii) the value for this potential was virtually the same for both palladized and bright surfaces in base, and (iii) the variation in current with potential in the region just above the onset of oxidation was quite dramatic for both types of surface in base. Such behaviour may be explained in terms of the assumption, already discussed here, that the reversible potential for the generation of the incipient oxide mediator is lower in base, coupled with the fact that adsorbed hydrogen, at a high coverage of the latter, inhibits either the mediator formation process or some stage in the subsequent hydrazine oxidation reaction. (The inhibiting effect of $H_{ads}$, at high coverages of this species, has already been demonstrated [33] for other electrode reactions, e.g. acetone reduction on platinum.) As the potential traverses the hydrogen region on the positive sweep in base the source of the inhibition ($H_{ads}$) is largely removed at ~ 0.15 V. As the potential is well above the reversible value for incipient hydrous oxide formation, the coverage of the mediator either is, or rapidly becomes, quite significant, even on the bright palladium surface: hence the dramatic increase in the rate of hydrazine oxidation in this region. Similar behaviour with regard to the shift in onset/termination potential with pH has already been described for gold [13] (where there is no complication due to adsorbed hydrogen) and platinum [3] (whose behaviour is quite similar to palladium).

Palladium generally appeared to have a low activity with regard to the oxidation of organic species; this may be due to the fact that (as is well known [34] for platinum) strongly adsorbed intermediates or products, e.g. $CO_{ads}$, tend to poison the surface. The exception in this case was formic acid which on bright palladium in 1.0 M $H_2SO_4$ at 60° C commenced oxidation at a lower potential (~ 0.1 V) on the positive sweep than hydrazine (~ 0.3 V, Fig. 9(a)). However, formic acid reacts via a different mechanism: this compound decomposes on palladium, that is,

$$HCOOH = 2H_{ads} + CO_2 \qquad (4)$$

The hydrogen thus produced is absorbed, under open-circuit conditions, into the metal lattice. (This is one method [35] for producing palladium hydride.) The species being anodically oxidized in this case is surface hydrogen produced in the preceding, nonelectrochemical, catalytic decomposition step, Equation 4: the hydrous oxide mediator plays no role in the oxidation of formic acid.

The comparison of the behaviour of hydrazine with that of formic acid on palladium is interesting from a mechanistic viewpoint. It may be considered that hydrazine, towards the end of the hydrogen region on the positive sweep, decomposes to yield adsorbed hydrogen which is then oxidized. Thus,

$$N_2H_4(aq) = N_2(g) + 4H_{ads} \qquad (5)$$

$$4H_{ads} = 4H^+(aq) + 4e^- \qquad (6)$$

To test this approach a palladized palladium electrode was immersed for 30 min in 1.0 M NaOH, containing $5 \times 10^{-3}$ M $N_2H_4$, at 25° C. At the end of this period the electrode was tested in $N_2H_4$-free solution for the presence of adsorbed hydrogen. The presence of such hydrogen should enhance the anodic currents on the positive sweep: as no increase in the anodic response was observed, the active oxide mediator route seems to be one that is involved in the case of hydrazine oxidation.

### 4.3. *Reduction of oxidants*

The reduction of nitrous oxide, Fig. 7, on palladized palladium in acid commenced (negative sweep) and terminated (positive sweep) at ~ 0.4 V, the same value at which hydrazine oxidation under similar conditions, Fig. 3, reached a limiting value. Such behaviour is in agreement with the adatom-incipient hydrous oxide view of electrocatalysis [1]. The $N_2O$ reduction is evidently an inhibited process that occurs largely at metal adatom sites. The latter are no longer available, in their reduced state, on the palladized surface above 0.4 V. Reducing the potential, in the region below 0.4 V, on the negative sweep progressively reduces the coverage of hydrous oxide, generating more adatoms which in turn are reoxidized by the $N_2O$, i.e. an interfacial electrocatalytic redox cycle is set up that can operate at an increasing rate as the potential is decreased. Reduction continued to occur below the reversible peaks at ~ 0.23 V, but perhaps not at the rate expected. In this region there is significant coverage of adsorbed hydrogen at the surface which, as already pointed out here, is a source of inhibition of electrocatalytic processes at noble metal surfaces.

The reduction of the other oxidants, dichromate and persulphate, Fig. 8, appears to be less inhibited in so far as reduction commenced/terminated on removal/formation of the monolayer oxide deposit. Note, however, that on the positive sweep in the case of dichromate (and to a lesser extent with persulphate) significant inhibition of the reduction process commenced in the region of 0.4 V: the latter is also the value at which, on bright palladium in acid (Fig. 4), hydrazine oxidation commenced on the positive sweep. The major change in dichromate oxidation rate, Fig. 8(a), occurred over the range 0.5 to 0.7 V; it is clear from Fig. 1(a) that this is the double layer region for palladium in acid. The obvious explanation of such behaviour is that reduction is confined to quite low coverage active palladium atoms at the interface (not necessarily the more active adatoms which remain oxidized to ~ 0.4 V) whose coverage varies with potential over the double layer region due to variation in the potential for the active Pd atom/incipient hydrous oxide transition.

The behaviour of dichromate on palladium, Fig. 8(a), and gold (see Fig. 9 of [13]) in acid is remarkably similar in that for both metals a dramatic change in reduction rate occurs within the double layer region. The source of this change is clearly not the monolayer hydrogen or oxide deposit, nor the dichromate itself as the region over which the variation occurs is different for the two metals in question, ~0.5 to 0.7 V for palladium (positive sweep, 8(a)) and ~1.05 V for gold [13]. Since dichromate in acid is a strong oxidant, $E^0(Cr_2O_7^{2-}/Cr^{3+}) = 1.33\,V$, some other, quite minor (from a coverage or charge viewpoint), change at the interfaces in question must be involved in the inhibition of reduction at these lower potentials. The active metal atom/incipient hydrous oxide (or premonolayer oxidation) viewpoint seems to be the most logical approach to account for such behaviour.

## 5. Conclusions

(i) The assumption made in this work is that premonolayer oxidation (or incipient hydrous oxide formation) plays a major role in noble metal electrocatalysis, a view also expressed by Conway and coworkers in the case of gold in acid [7–9]. Anomalous oxidation of platinum has been established in metal cluster-oxygen gas interaction studies [15]; it was postulated earlier on the basis of electrochemical investigations [2] and both groups attribute the effect to the unusual reactivity of low lattice coordination metal atoms. Differences in responses between bright palladium and electrodeposited palladium black surfaces were attributed to the presence of a much higher content of reactive metal atoms, possibly as clusters of different size, in the electrodeposited layer. There is analogy between the unusual reversible peaks at ~0.23 V in the case of palladized palladium in acid and the so-called 'anomalous hydrogen peak' ($H_i$) for platinum in acid [2]: in both cases premonolayer oxidation of unusually reactive metal atoms at the interface is assumed to be involved. The large a.c. response in the double layer region for palladium black electrodes in acid, and more especially in base, supports the view that a very reversible (but low coverage) adatom-incipient hydrous oxide transition is involved in this region.

(ii) The electrocatalytic activity of palladium is not dramatically different to that of platinum. In many cases the activity of palladium is lower and its stability in acid [24] significant lower. However, at a fundamental level the three metals, gold [10–13], platinum [2, 4, 25] and palladium, show unusual similarities. In all cases minute faradaic responses (at ~0.2 V for platinum [2] and palladium (Fig. 1(a)), and at higher values [12] for gold) have been reported. Such features (which in earlier work were usually ignored) often occur at potential values where dramatic changes in current densities associated with electrocatalytic processes occur and a basis for rationalizing such behaviour has been published [1, 5].

(iii) One minor problem with the adatom/incipient hydrous oxide approach, again evident here in the case of palladium, is that the reversible transition rarely occurs at a discrete value. This again is understandable as (a) the activity of surface metal atoms varies with lattice coordination number [15], and (b) hydrous oxides can occur in different forms [6]. This seems particularly true for palladium in base [24].

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