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## An investigation of the electrochemical responses of superactivated gold electrodes in alkaline solution

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**Abstract** It is now well established that gold, in the form of oxide-supported microparticles or even as conventional macroelectrodes, displays inexplicably high catalytic activity for some reactions. In the present work, gold surfaces were superactivated by a combination of thermal and cathodic pretreatment and such electrodes in base yielded up to five distinct, and quite marked, premonolayer oxidation responses within the double layer region, over the range 0.0–1.0 V (RHE). As outlined in earlier publications, such unusual behaviour is important from an electrocatalytic (and heterogeneous catalysis) viewpoint. A new mode of active site adsorption, involving highly localized electron transfer from active surface atoms to either the external circuit (in electrocatalysis) or an adsorbing reactant (in heterogeneous catalysis), is proposed. Such localized (active site) adsorption, which is based on surface quantum confinement effects, is virtually independent of (or only indirectly related to) the electronic properties of the bulk metal.

**Keywords** Gold · Active states · Premonolayer oxidation · Adsorption · Electrocatalysis

### Introduction

Gold is the noblest and most inert of metals [1] and is often used in fundamental studies in electrochemistry; since it is a very weak chemisorber [1] it has traditionally been regarded as a poor catalyst or electrocatalyst. However, this assumption was contradicted recently by the work of Haruta and co-workers [2] (work on this topic was reviewed recently by Thompson [3, 4]), who

observed that oxide-supported gold microparticles are the most active catalyst for ambient and sub-ambient temperature oxidation of carbon monoxide. It is also well established in electrochemistry that gold displays considerable electrocatalytic activity, especially in base [5, 6].

The combination of high catalytic activity and weak chemisorbing power for a metal surface is rather unusual. Such behaviour was interpreted recently [6, 7] in terms of the involvement of active states of metal surfaces. The vast majority of real surfaces are regarded as being somewhat disordered or structurally heterogeneous; at certain sites at the surface, gold atoms (or microclusters) exist in a non-equilibrium, highly active state; such atoms are regarded as severely lacking in lattice stabilization energy or exhibiting quantum confinement effects and are thus capable of undergoing oxidation, or adsorbing oxygen, under unusually mild conditions. According to this approach, d-band vacancies and associated covalent bonding are not essential for surface adsorption and catalysis. Highly localized electron transfer may occur between superactive metal atoms and the adsorbing molecules, resulting in the formation of an ionic or polar covalent bond. Such interactions, based on the existence of low-coverage, non-equilibrium states of surface metal atoms (and independent of the bulk electronic properties of the solid), are assumed to be of major importance in catalytic processes occurring at surface active sites.

The behaviour of metal atoms at surface active sites is extremely difficult to investigate as such atoms are in very low coverage, non-equilibrium and poorly ordered states. Electrochemical techniques have advantages for investigating such species because they may be used [8] to enhance the coverage (or occupancy) of such states, monitor their redox behaviour in a sensitive manner and investigate electrocatalytic processes which are often confined to such sites. There is independent evidence of premonolayer (or anomalous) oxidation of gold surfaces in base from earlier, independent work involving surface-enhanced Raman spectroscopy (SERS) [9], contact

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electrical resistance (CER) [10] and radioactive tracer [11] techniques. None of these seem to have the level of sensitivity displayed in the present work by cyclic voltammetry, where up to five easily distinguishable anodic responses (or peaks) were observed, depending on the degree of surface activation, in the double layer region of the positive sweep.

The activation of gold surfaces by thermal [12] and cathodic [8] pretreatment was reported earlier. The redox behaviour of the activated surfaces in acid solution was found to be quite unusual (it has recently come to our attention also that preliminary work of a similar character was carried out much earlier by Ives [13]). The present work involved an investigation of the redox behaviour of activated gold electrodes in base. In some respects this is a more interesting system than gold in acid; the electrocatalytic behaviour of gold is more marked in base [5, 6] and advantage is taken of the latter in pulsed amperometric detector systems where gold in base is often the electrode of choice [14]. A remarkable feature of the present work is the range or diversity of the anodic responses in the double layer region for this electrode system.

## Experimental

The type of cell and the equipment used in the present work were described in some detail in an earlier report dealing with thermally pretreated platinum [15]. The working electrode consisted of a loop of gold wire, 18 cm in length, 0.5 mm diameter (Johnson Matthey, Puratronic grade), both ends of which were attached to heavy copper leads (the latter were required to pass the relatively large heating or pretreatment current which in some instances was 12.5 A). The method used to estimate the pretreatment temperature of the gold wire was outlined earlier [12]. Prior to the heating process the solution was withdrawn from the cell and during the heating and cooling process the working compartment was subjected to a flow of 5%  $H_2/N_2$  gas at a slightly positive pressure. After the cooling process the deoxygenated electrolyte was allowed to return to the cell (the surface was not allowed to contact the air after the start of the pretreatment process until all the electrochemical measurements were completed). To avoid copper contamination from the leads, only the lower portion of the gold loop was immersed in the cell electrolyte. As in the earlier work with platinum [15], most cyclic voltammograms shown here are from the first cycle which commenced at the lower limit of 0.0 V.

All solutions were made up using doubly distilled water and Analar grade chemicals. In most cases the electrolyte used was sodium hydroxide; however, to demonstrate that the unusual behaviour in the double layer region was not specific to this electrolyte (or an impurity therein), some experiments were also carried out using an organic base (tetraethylammonium hydroxide) electrolyte. All potential values were measured, and are reported, with respect to a hydrogen reference electrode in the same solution, i.e. in terms of the RHE scale.

## Results

### Effect of the thermal pretreatment temperature

A typical example of the response for an unpretreated gold electrode in base is shown in Fig. 1a. The main

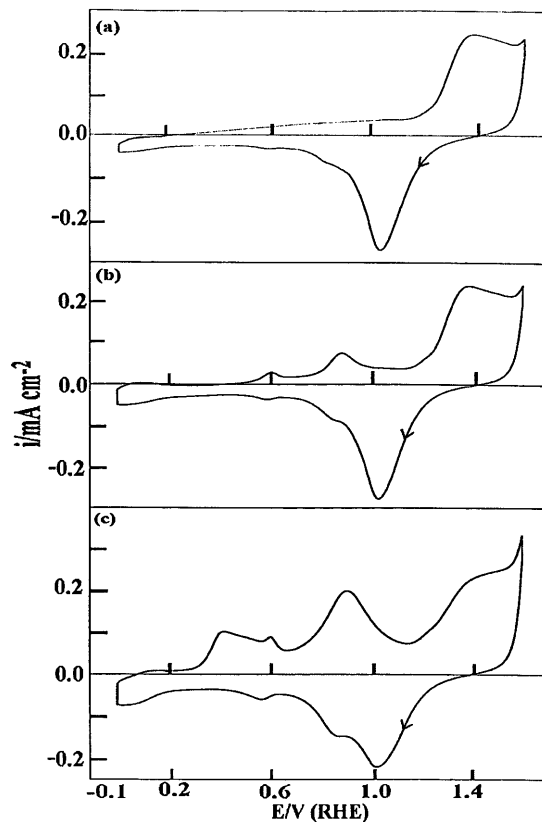
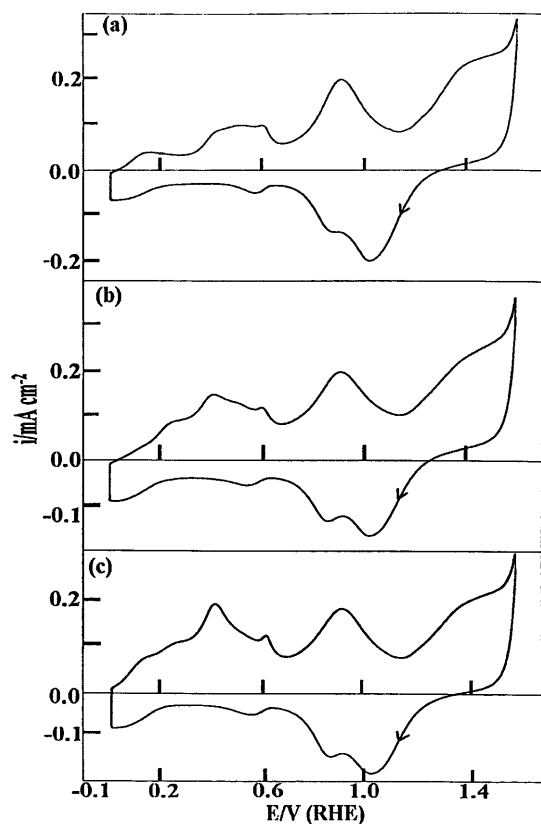


Fig. 1 Cyclic voltammograms ( $0.0\text{--}1.6\text{ V}$ ,  $50\text{ mV s}^{-1}$ ) for a gold wire electrode in  $1.0\text{ mol dm}^{-3}$  NaOH at  $18\text{ }^\circ\text{C}$ : **a** unheated metal; **b** preheated for 20 s at 6 A ( $430\text{ }^\circ\text{C}$ ); **c** preheated for 20 s at 8 A ( $570\text{ }^\circ\text{C}$ )

features are the usual increase in anodic current due to onset of monolayer oxide formation at ca. 1.20 V in the positive sweep and the cathodic peak at ca. 1.05 V due to the reduction of this deposit in the negative sweep. Pretreatment of the electrodes at  $430\text{ }^\circ\text{C}$  for 20 s resulted in significant, reversible responses (Fig. 1b) in the double layer, one at ca. 0.6 V and another at ca. 0.9 V. Raising the pretreatment temperature to  $570\text{ }^\circ\text{C}$  for 20 s (Fig. 1c) resulted in a shift in the onset of oxidation in the positive sweep to ca. 0.3 V and a significant increase in the magnitude of the reversible peaks at ca. 0.9 V. Further examples, recorded on increasing the pretreatment temperature (to 655, 815 and  $905\text{ }^\circ\text{C}$ ) are shown in Fig. 2. Attention is drawn here in particular to the positive sweep in Fig. 2c: there are six discrete anodic peaks or oxidation responses involved. The first two (one at ca. 0.1 V and the other at ca. 0.25 V) are not well defined in this case but the remainder (the peaks at ca. 0.4 V, 0.6 V and 0.9 V, plus the plateau above 1.2 V) are quite evident in this diagram; more dramatic versions of most of these peaks (especially those appearing at low potentials) were recorded later, e.g. Fig. 6a, on combining thermal with cathodic activation. The anodic peaks above 0.5 V in Fig. 2 have cathodic counterparts, but these (as pointed out earlier for gold in acid [8, 12]) are frequently absent in the case of the peaks below 0.5 V.

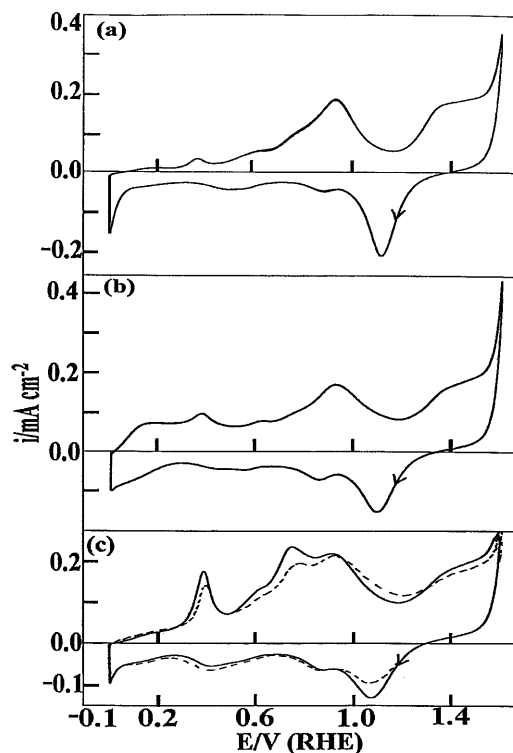


**Fig. 2** Cyclic voltammograms (0.0–1.6 V, 50 mV s<sup>-1</sup>) for a gold wire electrode in 1.0 mol dm<sup>-3</sup> NaOH at 18 °C; the wire was preheated for 20 s at **a** 9 A (655 °C), **b** 11.5 A (815 °C) and **c** 12.5 A (905 °C)

The effect of raising the cell solution temperature is outlined in Fig. 3. The most notable change is evident in the case of Fig. 3c, where the pretreatment temperature used was 905 °C (the corresponding room temperature response is that shown in Fig. 2c). In the positive sweep in Fig. 3c, a relatively sharp peak is evident at ca. 0.4 V and above this, from ca. 0.5 to 1.0 V, there is a large anodic response which consists of three broad, overlapping peaks.

#### Effect of combined, thermal followed by cathodic, pretreatment

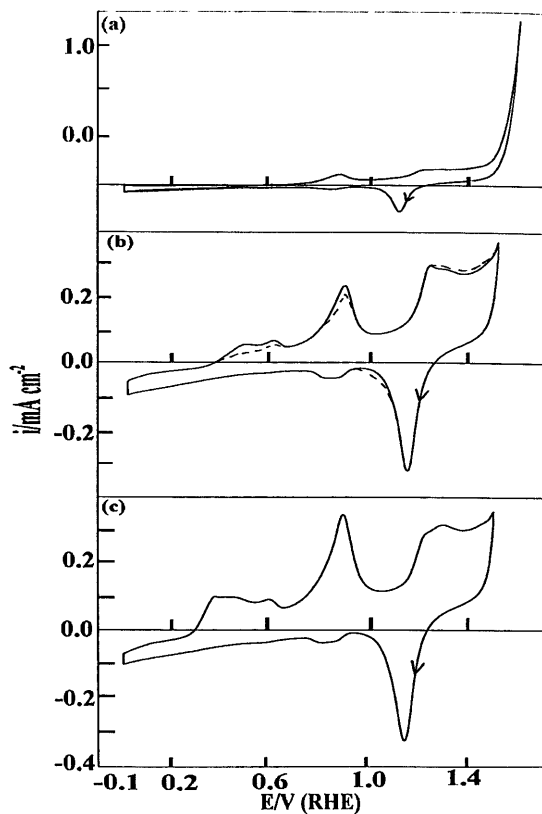
Most of these experiments were carried out at a cell temperature of 70 °C. The basic response of the electrode after thermal pretreatment is shown in Fig. 4a; the main unusual feature was the anodic peak at ca. 0.9 V in the positive sweep. This appeared in all voltammograms recorded for active gold in base; the corresponding cathodic response for its counterpart in the negative sweep (especially at 70 °C) was usually rather low. It is clear from the remaining data shown in Fig. 4 that subjecting the gold electrode to a combination of thermal followed by cathodic activation (even at 0.0 V) significantly enhanced the anodic responses observed at the early stages, 0.3 < E < 0.7 V, of the positive sweep.



**Fig. 3** Cyclic voltammograms (0.0–1.6 V, 50 mV s<sup>-1</sup>) for a gold wire electrode in 1.0 mol dm<sup>-3</sup> NaOH at 70 °C; the gold was preheated for 20 s at **a** 8 A (570 °C), **b** 10 A (700 °C) and **c** 12.5 A (905 °C); the *dashed line* in **c** shows the response for the second cycle

Intensifying the cathodic pretreatment to -0.3 V for 1 min (Fig. 5a), or especially for longer periods, e.g. 3.0 min (Fig. 5b), significantly enhanced the anodic responses in the double layer region of the positive sweep. Note the appearance of a peak at ca. 0.8 V in Fig. 5b, this feature existing only as a shoulder at the same potential in Fig. 5a. There are a total of five anodic peaks in the double layer region in Fig. 5b, the charge associated with the premonolayer oxidation reaction in this case significantly exceeding the monolayer oxide reduction response. Reduction over the double layer region of the negative sweep was surprisingly small and the main changes in the second, as compared with the first, positive sweep (dashed line in Fig. 5b) was the reduction in the charge for the first three anodic peaks, i.e. the more active gold atoms, which react at low potentials, were the ones that disappeared (or were oxidized) most readily, and were also the least likely to be regenerated in the negative sweep.

On repeating the experiment outlined in Fig. 5, with the same electrode, the existence of five anodic premonolayer oxidation peaks (full line in Fig. 6a) became much more obvious and the last of these peaks, i.e. the one at ca. 0.9 V (which was usually the dominant feature, e.g. in Fig. 5a), was the lowest in peak current density value. The response for the second positive sweep (dashed line in Fig. 6a) resembled the first. On the third sweep (full line in Fig. 6b) the first anodic peak (at ca. 0.2 V)



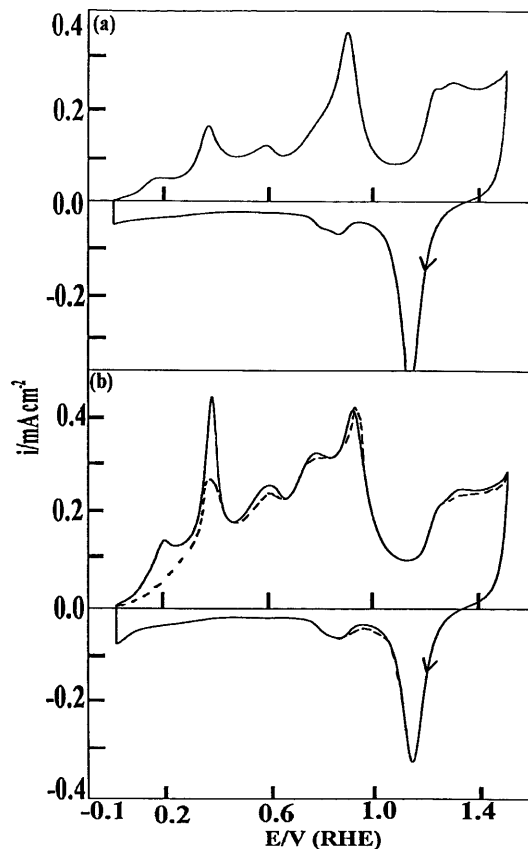
**Fig. 4** Cyclic voltammograms ( $0.0\text{--}1.5\text{ V}$ ,  $50\text{ mV s}^{-1}$ ) for a gold wire electrode in  $1.0\text{ mol dm}^{-3}$  NaOH at  $70\text{ }^\circ\text{C}$ : **a** the wire was preheated for 20 s at 11.5 A ( $815\text{ }^\circ\text{C}$ ); **b** preheated as in **a** plus prepolarized at 0.0 V for 30 s; **c** preheated as in **a** plus prepolarized at 0.0 V for 3 min

was absent, the main features being the second and fifth peak (at ca. 0.35 and ca. 0.9 V, respectively). Finally, in the fourth sweep the sole anodic premonolayer oxidation peak was the one at ca. 0.9 V. In all four negative sweeps in Fig. 6 the cathodic responses are quite low; however, the presence of a reducible species at the interface, which reacts only in a slow manner, is demonstrated by the presence of cathodic currents up to ca. 0.5 V in the fourth positive sweep (dashed line in Fig. 6b).

A further example of the same type of activation and decay is shown in Fig. 7. The cathodic activation conditions were much milder in this case and the decay in the anodic response below 0.8 V was more rapid. Again, cathodic current was observed up to  $E \approx 0.5\text{ V}$  in the second and third positive sweeps, and the magnitude of this response (which is assumed to be determined by a slow oxide reduction step [8]) showed little sign of decay on cycling.

Responses observed in the presence of an organic base

The response of a thermally activated gold electrode in tetraethylammonium hydroxide solution at room temperature is shown in Fig. 8a. The response is not very different from that observed in the corresponding ex-

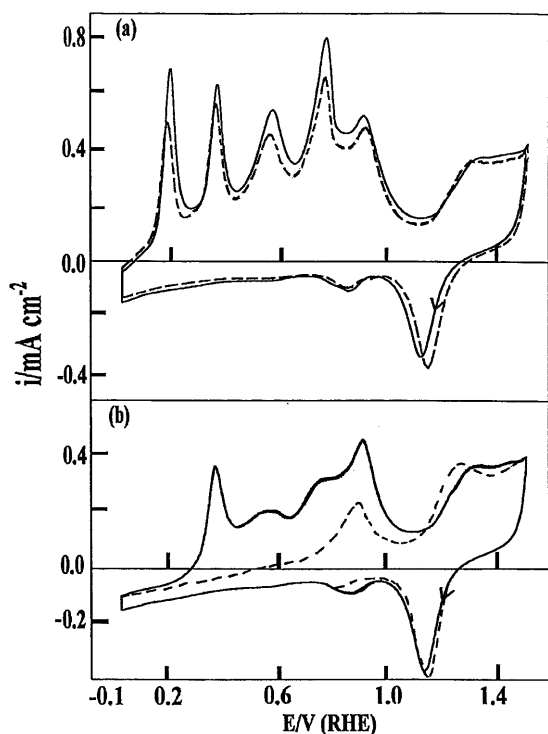


**Fig. 5** Cyclic voltammograms ( $0.0\text{--}1.5\text{ V}$ ,  $50\text{ mV s}^{-1}$ ) for a gold wire electrode in  $1.0\text{ mol dm}^{-3}$  NaOH at  $70\text{ }^\circ\text{C}$ : **a** the gold was preheated for 20 s at 11.5 A ( $815\text{ }^\circ\text{C}$ ) and prepolarized at  $-0.3\text{ V}$  for 1 min; **b** the gold was preheated as in **a** and then prepolarized at  $-0.3\text{ V}$  for 3 min

periment (Fig. 2c) with NaOH solution. On the basis of such behaviour it appears quite unlikely that the unusual responses in the double layer region for activated gold surfaces are due to the presence of an impurity originating in the inorganic base. The effect of a combination of thermal and cathodic pretreatment on the subsequent voltammetric response is shown in Fig. 8b. Once again the cathodic pretreatment enhanced the anodic responses at low potentials; the first major increase in anodic current in the positive sweep occurred in this case at ca. 0.0 V. There is no obvious monolayer oxide formation response above 1.2 V in Fig. 8b; however, its cathodic counterpart appeared as usual at ca. 1.0 V. The presence of a significant cathodic response (two poorly resolved peaks) below 0.4 V in the negative sweep in Fig. 8b is unusual (other examples of such behaviour are shown in Fig. 9). The relevance of such behaviour is discussed later.

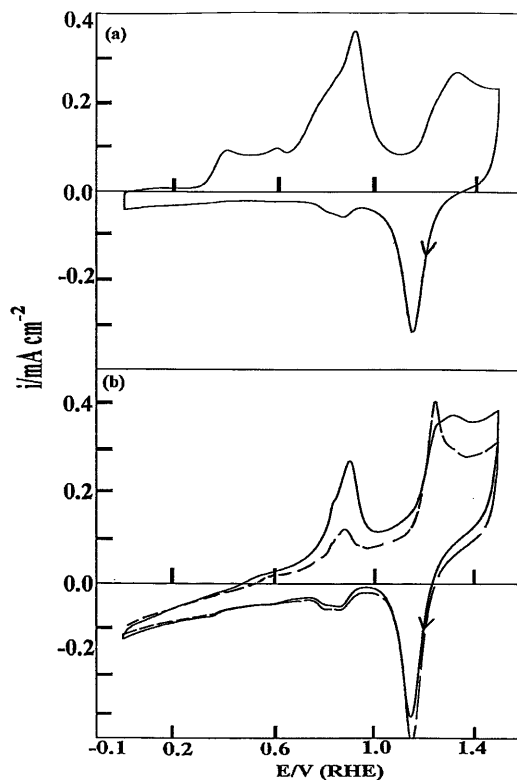
Effect of extended resting period

It has been observed in many instances in this laboratory, even in work involving activated platinum (see



**Fig. 6** Repeat of the experiment shown in Fig. 5b; the thermal and cathodic polarization conditions, and the electrode, were the same: **a** first sweep (full line), second sweep (dashed line) and **b** third sweep (full line), fourth sweep (dashed line)

fig. 4 in [16]), that quite unusual responses are frequently observed after allowing activated metal electrodes to remain at rest (or to relax) for a significant period of time in solution, air or an inert gas atmosphere. Evidently as the active layer of the metal restructures, some of the outermost atoms remain for a considerable period of time in an unusually active state (presumably all attainable lattice vacancies are occupied). An example of a first cycle for an active gold electrode, after restructuring, is shown in Fig. 9a. A major oxidation response was observed in the positive sweep at ca. 0.4 V, with less well-defined anodic maxima at ca. 0.6 and 0.9 V, plus a small shoulder at ca. 0.3 V. Another unusual feature was the absence of the conventional monolayer oxide formation/removal response for this electrode at  $E > 1.0$  V. The first negative sweep in Fig. 9a was also unusual: a total of six cathodic peaks (with maxima at ca. 0.8, 0.55, 0.3, 0.1, 0.0 and  $-0.1$  V; these were minor ill-defined features on a broad background response) were observed in the double layer region. The magnitude of most of these features decreased (especially in the case of the anodic peak at ca. 0.4 V) on repeated cycling (see the dashed line in Fig. 9a). However, unusual redox behaviour in the double layer region was still observed (Fig. 9b) after the electrode was allowed to rest, without further activation, for a period of ca. 24 h; most of the premonolayer features shown in Fig. 9a are evident, at a reduced intensity, in Fig. 9b. After continued cycling for a period of 1 h the responses below 0.8 V in the double

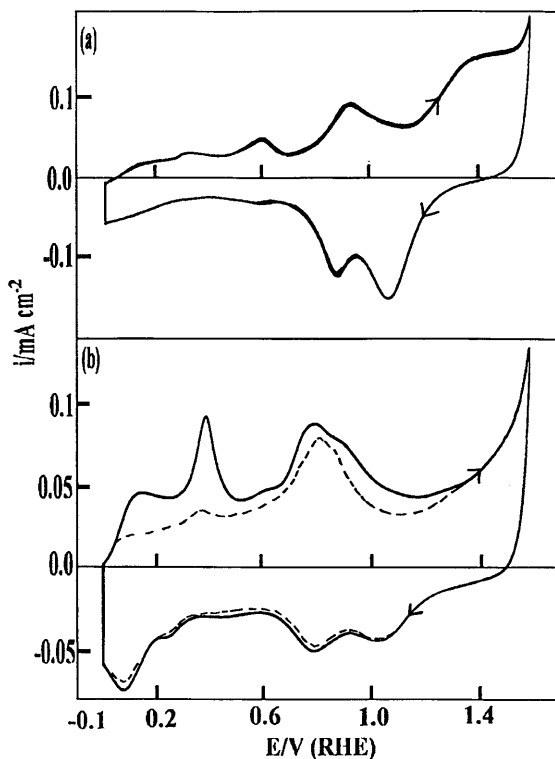


**Fig. 7** Cyclic voltammograms ( $0.0$ – $1.5$  V,  $50$   $\text{mV s}^{-1}$ ) for a gold wire electrode in  $1.0$   $\text{mol dm}^{-3}$  NaOH at  $70$   $^{\circ}\text{C}$ ; the gold was preheated for  $20$  s at  $11.5$  A ( $815$   $^{\circ}\text{C}$ ) and prepolarized at  $+0.2$  V for  $3$  min: **a** first sweep; **b** second sweep (full line) and third sweep (dashed line)

layer region were quite low (Fig. 9c) and the conventional monolayer oxide formation/reduction response above  $1.0$  V was restored. However, the reversible redox transition at ca.  $0.9$  V was still quite marked; there was a minor reversible transition at ca.  $0.6$  V, a minor anodic peak at ca.  $0.3$  V and a final (probably related) set of peaks, of low magnitude, at  $0.1$  and  $-0.1$  V (positive and negative sweep, respectively).

## Discussion

Earlier microscopy investigations showed that both thermal [12] and cathodic [17] activation pretreatment resulted in considerable roughening or disordering of the outer layers of the metal lattice. This is not surprising, since two ways in which metals store energy or become unusually reactive involve the presence of extremely small particle sizes [18] and extended vacancies [19]. Hence, for the same metal, activated surfaces are regarded as quite different in character from idealized, monatomically flat, single-crystal surfaces, e.g. while the metal/solution interface in the latter, single-crystal, case is two dimensional or planar, this is evidently not the case when the metal surface involved is in a highly activated state. Activated metal surfaces are tortuous or irregular; they consist of a variable array of species such

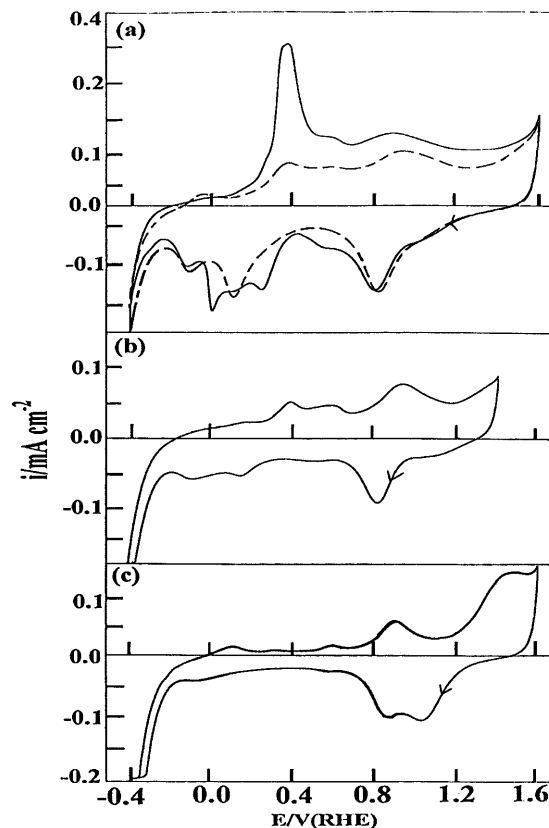


**Fig. 8** Cyclic voltammograms (0.0–1.6 V,  $50 \text{ mV s}^{-1}$ ) for a gold wire electrode in  $1.0 \text{ mol dm}^{-3} \text{ Et}_4\text{NOH}$  at  $18^\circ\text{C}$ : **a** the gold was preheated for 20 s at 12.5 A ( $905^\circ\text{C}$ ) and **b** preheated as in **a** and prepolarized at  $-0.3 \text{ V}$  for 7 min, first sweep (*full line*), second sweep (*dashed line*)

as adatoms, microclusters, small crystallites, numerous defects, etc.; also, the highly active region probably extends to a significant extent into the metal, i.e. an active outer zone, rather than a surface, is assumed to be involved. With highly active metal electrodes the boundary between the metal and solution is not sharp, there is a degree of phase intermingling at the interface and the properties of the metal in the active zone are abnormal.

The importance of rough surfaces with regard to catalysis has been stressed by Somorjai [20]. Highly active metals are difficult to investigate as they tend to be variable, their character depending on pretreatment, age and use (they are essentially unstable). The atoms in the active zone not only undergo oxidation at unusually low potentials, but some of the oxygen involved may enter vacancies in the lattice and exist as subsurface oxygen which may be reluctant to undergo oxidation. Also, some of the surface metal clusters, which expand on oxidation, may yield high hydrated oxide species which are in poor contact with the remaining metal (especially if reduction commences at the particle/metal interface); such behaviour (along with subsurface oxide formation) may contribute to the low oxide reduction responses in the negative sweeps in much of the present work, e.g. Fig. 6a.

In several cases, e.g. in Fig. 2, the degree of irreversibility of the premonolayer oxidation response was



**Fig. 9** Cyclic voltammograms ( $-0.4$  to  $1.6 \text{ V}$ ,  $50 \text{ mV s}^{-1}$ ) for a gold wire electrode in  $1.0 \text{ mol dm}^{-3} \text{ NaOH}$  at  $18^\circ\text{C}$  (the wire in question had been used for several days in carrying out experiments of the type outlined in Fig. 5, i.e. the outer layers of the metal were in an active state): **a** after resting in air for ca. 5 days, first sweep (*full line*), sixth sweep (*dashed line*); **b** response ( $-0.4$  to  $1.4 \text{ V}$ ,  $50 \text{ mV s}^{-1}$ ) for the same electrode on the following morning without any further thermal activation; and **c** response ( $-0.4$  to  $1.6 \text{ V}$ ,  $50 \text{ mV s}^{-1}$ ) for the electrode after cycling under these conditions for ca. 1 h

greater for processes occurring at low potentials, i.e. at  $E < 0.55 \text{ V}$ . It is assumed that the metal atoms undergoing reaction in this region are in a highly active very low coordination state and these are assumed to be totally oxidized, the hydrated oxide product being in relatively poor contact with the bulk metal. Less active atoms, e.g. those that react anodically at ca.  $0.9 \text{ V}$ , are assumed to be in a more highly coordinated state; hence they may not react completely, i.e. there may be an unoxidized metal core (possibly attached to the bulk lattice), or the oxide formed may be different (hydrated gold oxides may exist in at least three different states [21]), e.g. the one involve at  $0.9 \text{ V}$  being more easily reduced and hence the response in this region is of a more reversible character. The sluggish nature of the reduction responses of the premonolayer oxides formed on activated metals at low potentials was discussed earlier for both gold [8] and platinum [8] in acid solution. The absence of a marked cathodic response does not mean that the oxide species are absent (the latter condition could arise if the active metal atoms were

anodically dissolved); cathodic currents (Fig. 7b) and, in some cases, cathodic peaks (Figs. 8b and 9a), at  $E < 0.55$  V in the negative sweep, support this view that there are reducible species, i.e. oxides, present at the interface down to  $E = 0.0$  V.

It is interesting to compare the responses for gold, activated at different temperatures, in base (Figs. 1 and 2) with the corresponding data reported earlier [12] for gold in acid. The diversity of premonolayer oxidation peaks is obviously greater in base and this is clearly highlighted by the positive sweep shown here in Fig. 6a. The major anodic responses within the double layer region occur with gold in acid at  $E < 0.6$  V, whereas in base much of the charge in the double layer region is observed (Fig. 2) at  $E > 0.6$  V. There may be kinetic factors involved; oxides are more stable, or less reactive, in base, e.g. multilayer hydrous oxide deposits can be formed much more readily on gold in acid solution [22]. It is quite possible that the initial product formed on activated gold in base at  $E < 0.6$  V does not readily rearrange, i.e. it blocks the surface and thus impedes the oxidation of underlying reactive gold atoms, giving rise to a more protracted response with an absence (at least in Fig. 2) of sharp anodic peaks.

With activated gold in acid [12], the onset of oxidation in the positive sweep usually commenced above 0.25 V. Occasionally in base the oxidation commenced in the positive sweep (Fig. 5) at ca. 0.0 V and an anodic peak is evident in Fig. 6a with a maximum at 0.20 V. It is assumed that the shift to lower potentials for oxidation in base (as compared with acid) is a reflection of a super-Nernstian  $E/\text{pH}$  shift [23]. Indeed, the extent of this negative shift due to the increase in solution pH is lower than expected and it is possible that some of the highly active gold atoms undergo spontaneous oxidation when the activated gold is first immersed in base (as will be reported later, multilayer hydrous oxide reduction on gold in base in some instances gives rise to sharp cathodic peaks at  $E \approx -0.3$  V).

While thermal pretreatment is an effective procedure for activating gold surfaces, the resulting anodic responses (Figs. 1, 2, 3) usually consist of a series of broad, overlapping peaks. Much better peak resolution is observed (Fig. 6a) when thermal activation is followed by relatively mild cathodic activation. The disadvantage of the thermal procedure, as used in the present work, is that the cooling process is not instantaneous, i.e. some of the more active states (or species) are probably lost due to annealing effects as the sample cools. Subsequent cathodization, even under quite mild conditions (as in Fig. 4), promotes oxidation responses at quite low potentials. The mechanism involved in cathodic activation was discussed recently [8] and is assumed to be related to hydrogen embrittlement effects. Its major advantage is that it is carried out at ambient temperature and, hence, there is far less annealing or loss of the highly active surface states. Thus, as illustrated here in Fig. 4, even mild cathodization promotes anodic responses below 0.6 V. Occupancy of the high-energy surface states is

further enhanced by increasing the intensity of the cathodic pretreatment (Fig. 5).

The data shown in Fig. 6 are a dramatic illustration of the complexity of the premonolayer oxidation behaviour of gold in base. Five anodic peaks are clearly evident, on a broad background response, over the range 0.1–1.0 V. As noted earlier for such behaviour for both gold [8] and platinum [24] in acid solution, the corresponding response on the subsequent negative sweep is often low and featureless. Of these five anodic peaks in the double layer region, the first to disappear on repetitive cycling is the one at ca. 0.2 V, whereas after four cycles (dashed line in Fig. 6b) the only one remaining is the peak at ca. 0.9 V. Such a trend is understandable; of the various active state atoms, the ones that are most likely to be lost (either irreversibly oxidized or converted to a less active state) are those undergoing oxidation at the lowest potential, i.e. at ca. 0.2 V (these are in the most active state). The ones that are most likely to be retained are (as observed) those undergoing oxidation at 0.9 V (the gold atoms involved are in the least energetic of the active states).

It was pointed out earlier [7] that there is a correlation between premonolayer oxidation and electrocatalytic properties of metal electrodes. Low-coverage active atoms at surface-active sites are assumed to react in a reversible manner, the active atoms and their oxidation products (incipient hydrous oxides) functioning as the interfacial mediators in electrocatalytic reduction and oxidation processes, respectively. In his original proposal with regard to active site behaviour, Taylor [25] specifically pointed out (1) the relevance of low lattice stabilization energy in determining surface atom activity and (2) the existence of more than one type of site on the same surface. The type of site involved in a particular reaction seems to be determined by the reaction that is being catalysed; the interaction between the active site and the catalytic process is assumed to be influenced by energy exchange between the reaction and the site; during the catalytic process the atoms of the active site are assumed to be in a dynamic state in so far as, at a minimum, such atoms undergo a repetitive cyclic redox reaction as part of the catalytic reaction [7].

From the data in Fig. 6a it appears that there are five distinct anodic premonolayer oxidation responses, and five different types of active sites (or metal atoms), involved at the gold/aqueous base interface. As outlined here later, the second assumption here may not be valid as the first of these peaks may well be due to an Au(0)/Au(I) transition, the product altering later (at a more positive potential) to yield a second, Au(I)/Au(III), transition, i.e. the same type of active atom may yield two peaks. Furthermore, all premonolayer couples may not be highly active with regard to mediation.

As outlined in a recent review of the electrocatalytic behaviour of gold (see fig. 3 in [6]), oxidation responses for different solution species in base commence and

terminate at different potentials, formaldehyde at ca. 0.1 V, hydrazine at ca. 0.4 V and ethylene glycol at ca. 0.8 V; these potentials evidently coincide with the onset potentials for the first, third and fifth anodic peak in Fig. 3. The fourth peak in Fig. 3 commences at ca. 0.65 V and, as pointed out earlier [26], some organics, e.g. pyrrolidine, commence and terminate oxidation under potential sweep conditions at the latter value. As also outlined earlier [27], the first peak seems to involve AuOH formation; the product is a strong base and is assumed to exist at the interface as an  $\text{Au}^+_{\text{ads}} \cdot n\text{H}_2\text{O}$  species which favours interaction with aldehydes, the latter existing in base as anionic, *gem*-diolate,  $\text{RCH}(\text{OH})\text{O}^-$ , species (electrostatic interaction promotes the aldehyde reaction at the  $\text{Au}^+_{\text{ads}}$  site at low potentials).

An interesting question with regard to the anodic responses in Fig. 6a is what determines the differences between the anodic responses. While it may be due to the differences in active atom ( $\text{Au}^*$ ) environments, e.g. the type of adatom adsorption site (on terraces, kinks and ledges), surface cluster size, etc., the type of hydrous oxide species ( $\text{HO1}$ ,  $\text{HO2}$ , or  $\text{HO3}$  [21]) may also be important; presumably it is the interaction between these two factors that results in the peak diversity. The lack of reversibility in the premonolayer oxidation responses in Fig. 6a is not confined to gold in base [24]. The oxide product is assumed to be hydrated and there may be difficulty in transferring electrons from the metal to the extensively coordinated  $\text{Au}^{3+}$  cation. The same type of inhibition does not arise in electrocatalytic processes occurring at conventional gold surfaces or, more precisely, at active sites on the latter. Recent work in this laboratory (L.D. Burke, A.P. O'Mullane, unpublished results) indicates that at low coverage the surface-active state response occurs in a more discrete, reversible manner. Also, the conditions involved in electrocatalytic processes are different, e.g. the dissolved reactant may enter, and modify, the metal or ion coordination sphere and the interfacial process is of a dynamic, cyclic redox [7], character, i.e. the oxide undergoes repetitive formation and reduction during electrocatalysis. In the type of experiment outlined in Fig. 6 the premonolayer oxide is generated at higher coverage and is not immediately reduced, i.e. it has significant time to alter to a less reducible state.

The type of cathodic responses (even in the positive sweep) at  $E < 0.5$  V in both Fig. 6b and Fig. 7b (dashed line in both cases) are quite similar to that shown earlier (fig. 8 in [24]) for activated platinum in base. It was also demonstrated earlier [8] that while cathodically activated gold gave little response in the double layer region in base, the surface was active as the anomalous responses appeared as usual on transferring the electrode from base to acid solution. It appears that the hydrous oxide/active metal transition (especially at high oxide coverage) is even more sluggish in base than in acid. One of the few cases in the present work where cathodic peaks were observed at  $E \leq 0.6$  V in the negative sweep was in

experiments carried out with the organic base (Fig. 8b). The tetraethylammonium cation is relatively large and hydrophobic; with such cations present at the interface the oxide formed may be less hydrated and thus in more intimate contact with the metal surface; hence the more marked cathodic response.

The results shown in Fig. 9 highlight an important aspect of activated metal surfaces. The latter are labile, non-equilibrium states whose character varies with time as the active zone restructures. Inevitably in such a process the active layer becomes more stable, but this evidently is not true (at least temporarily) in the case of the outermost layer of atoms, which apparently become more active. It is important to note that the type of unusual behaviour shown by the full line in Fig. 9a is not an isolated observation.

In earlier work with platinum (see fig. 4 in [16]) an electrode was activated by intermittent abrasion and repetitive cycling in acid solution. On allowing such an electrode to rest (apart from an occasional potential scan for monitoring purposes), the cyclic voltammetric responses (which appeared rather normal at the beginning of the resting period) became progressively more anomalous with time over a period of a least 24 h. It is assumed that with both platinum and gold the active layers relax by undergoing annealing (or Ostwald ripening) processes, i.e. small particles lose atoms which enter lattice vacancies. However, such a process leaves fewer vacancies to be filled and the atoms remaining in the minute particle more active. Eventually it seems that the outermost layer of the metal is transformed to virtually a lattice vacancy-free surface on which metal atoms move about in a highly active state (many undergoing oxidation at ca. 0.4 V (full line in Fig. 9a) from one kink or ledge site to another. Similar unusual behaviour, basically the transformation, on standing, of the outer region of an active layer of electrodeposited copper to a more active form, will be reported later. Our opinion is that the phenomenon in question is relatively common, i.e. in the process of losing energy via restructuring, some of the atoms in the outermost layer of an active metal deposit attain an unexpectedly high level of activity. Such a view may be controversial but the behaviour of the highly active states of metal surfaces has received little attention and is likely to be quite different from that of low-energy surfaces, e.g. active states are assumed to be dynamic entities.

The earlier work of Ives [13], referred to previously, was concerned with gold in acid. He reported that subjecting the electrode to prolonged heating in a hydrogen atmosphere (up to 800 °C) radically altered its electrochemical behaviour, e.g. it showed a rest potential of 0.4 V (RHE) which was completely insensitive to  $\text{N}_2$  or  $\text{H}_2$  stirring; this is the potential value usually observed for the main premonolayer anodic peak [8] with cathodically activated gold in acid; in many instances also, thermally activated gold in acid [12] exhibits a marked anodic response in the same region. The overpotential with respect to hydrogen gas evolu-



tion was also enhanced due to thermal pretreatment, and in addition increased further with polarization time (the decay in activity of activated gold cathodes, in acid solution, with time was again confirmed recently [17]). Finally, when the hydrogen gas evolution current was switched off the potential decayed in most cases to a rather well-defined plateau at ca. 0.4 V. Ives [13] interpreted his results in terms of thermal deactivation of gold and the involvement of atomic hydrogen (the time dependence of the hydrogen overpotential was ascribed to the effect of penetration of the gold lattice by hydrogen atoms). We consider Ives work as important as it independently supports our claim that the basic electrochemistry of gold in aqueous media is not as simple as usually portrayed. As outlined here and in earlier work [12, 17], our explanation of anomalous behaviour is different (we have activated gold [8] without using thermal pretreatment). We regard the rest potential of 0.4 V (observed by Ives) as being due to a metastable, active gold metal/hydrous oxide  $[Au^*/AuO_x(hyd)]$ , interfacial couple.

In the refereeing of the present work, questions arose as to (1) the possible role of impurities and (2) the stability of the superactive state of the metal. The possible involvement of an impurity was discussed, and discounted, in related earlier work involving superactivated platinum [15]; the detailed arguments will not be repeated here. There is now convincing evidence, e.g. in the case of copper [28, 29], that metals can store energy, or exist in an activated state, owing to the presence of unusual, non-equilibrium, microstructural features. It is not unreasonable to assume that if the activity of metal atoms is raised (artificially), their oxidation potential will be displaced to more negative potentials. Such behaviour, as discussed recently [7], is quite logical but has, as yet, received very little attention in surface electrochemistry.

Superactive states are obviously high-energy, non-equilibrium, virtually transient species; in our opinion the problem is not that their activity decays, but that these unstable states persist on the surface for quite appreciable lengths of time. The objective of our work is to enhance the occupancy of these states so that their behaviour may be investigated by electrochemical techniques. Direct investigation of superactive surfaces, e.g. by STM or AFM, is not simple; these systems are quite rough and labile [12, 17]. The importance of superactive states is that their behaviour evidently mirrors that of active-site atoms which are the vital entities in surface and interfacial catalysis [30]. Active site chemistry, even as outlined by Taylor [25], is very largely based on the reaction of metastable, high-energy, superactive, surface metal atoms. The main features highlighted by the present work (but this again was pointed out earlier by Taylor [25]) is the presence of several distinguishable types of active states (or sites) on the same metal surface. It is worth re-stressing here that we do not regard surface-active site atoms as being arranged in a very rigid, immobile manner.

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## Conclusions

These may be summarized as follows:

1. The conventional view of gold in aqueous base is that this is an extremely simple electrode system; however, this notion is contradicted here and it is now proposed that all metals (including the present system) exhibit two types of electrochemistry: along with the conventional response, which relates to low energy metal surfaces, there is a separate type of electrochemical response associated with high-energy, superactive states of metal surfaces.
2. The active states response for highly activated gold in base (Fig. 6a) is quite complex and this is reflected in the unusual (and unexpected) high electrocatalytic behaviour of gold in base [6]. Surface activation is assumed to enhance the occupancy of high-energy surface states of the metal which exist, but are scarcely occupied, at conventional gold surfaces. Low-coverage active sites are regarded as the key factor in electrocatalysis; the type of site or mediator for a particular reaction seems to be rather specific and the choice is assumed to be influenced by the energy transferred between the reaction undergoing catalysis and the mediator system involved (the greater, or more effective, this transfer, the lower the redox potential of the mediating couple involved). In some cases, unusual factors, e.g. electrostatic interactions in the case of aldehyde oxidation, may be involved.
3. Catalysis at solid metal surfaces and interfaces is assumed to involve non-equilibrium, highly active states. The study of such states is obviously difficult, e.g. they are not easily controlled and reproduced, and (at room temperature or above) are apt to vary with time. Their importance, from a catalytic viewpoint, lies in the fact that, via highly localized electron transfer, superactive surface states provide a route for chemisorption and catalysis that is unavailable at the stable surface of the same metal (such behaviour is also assumed to be the origin of the remarkable activity of oxide-supported gold micro-particle catalysts [2]).

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