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## The effect of severe thermal pretreatment on the redox behaviour of gold in aqueous acid solution

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**Abstract** Severe thermal pretreatment of gold wire electrodes in an inert gas atmosphere resulted in the appearance of dramatic premonolayer oxidation responses, which in some instances commenced at 0.25 V (RHE), for the resulting active gold electrodes in aqueous acid media. Similar behaviour was reported earlier for platinum and gold activated by cathodic pretreatment in acid solution; these active noble metal surfaces are evidently more susceptible to oxidation than bulk copper. Such behaviour was attributed to the effect of surface disorder; many of the metal atoms at the interface are assumed to be in a very active, metastable state possessing quite low lattice stabilization energy. Premonolayer oxidation responses are again correlated with electrocatalytic behaviour and the existence of unusual chemisorption behaviour for molecules reacting at highly active states of metals is outlined.

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

### Introduction

The ability of metals to store energy, or to exist in an active state, is a well-known phenomenon in metallurgy [1]. The basis of such storage is that any process that creates non-reversible defects, e.g. dislocations or grain boundaries, in a metal raises the molar free energy or chemical potential of the solid. Although the resulting non-equilibrium state should decay spontaneously, this

process is often quite slow at temperatures below the melting point, and especially below the Tammann temperature value [2] for the solid, as the atom diffusion process, by which defects migrate and disappear, is often very slow.

The activation of metal surfaces, and in particular its relevance to the redox and electrocatalytic properties of surface metal atoms, was discussed in a number of recent papers from this laboratory [3, 4, 5, 6, 7]. It was demonstrated that with appropriately severe electrode pretreatment, e.g. heat treatment [3, 4], cathodization [5], oxide growth and reduction [6], it is possible to dramatically alter the electrochemical responses of noble metal electrode surfaces in aqueous media. In the present case it was observed that a gold surface in aqueous solution may be thermally activated to such a degree that it undergoes oxidation at a lower potential than a conventional copper surface:  $E^\circ(\text{Cu}/\text{Cu}_2\text{O}, \text{aqueous base}) = 0.47 \text{ V (RHE)}$  at 298 K [8]. Such a major shift in oxidation potential is not considered novel as it was demonstrated earlier for both cathodically activated gold [5] and thermally activated platinum [3, 4] electrodes in aqueous acid media.

The basis of superactivation of noble metal surfaces was interpreted earlier [3] by analogy with Henglein's view [9] of the behaviour of metal microcluster systems. As the outer layers of a metal lattice become progressively more disrupted, the metal atoms present at the surface become more discrete and lose much of their lattice stabilization energy; quantum confinement effects also begin to operate. The resulting changes in electropositive character (and premonolayer oxidation response [4]) tend to be quite dramatic. There is evidence of similar behaviour based on data obtained by non-electrochemical techniques, e.g. it has long been established [10] that the work function of a metal decreases [by ca. 0.6 eV at room temperature in the case of W(110)] when the roughness or disorder of the surface is increased, i.e. when steps and adatoms are generated on the latter.

The highly active (or superactive) surface is assumed to be in an extremely defective, nanoparticle, metastable

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state. The minute grains are thermodynamically unstable; they undergo annealing or cold sintering (Ostwald ripening) by diffusion of metal atoms from smaller to larger particles. Metal atoms undergoing surface diffusion have few neighbours, i.e. they are highly active and prone to undergo oxidation at unusually low potentials; hence the appearance of dramatic premonolayer oxidation effects. At room temperature the diffusion of metal atoms and consequently the sintering of particles (the latter being the source of the highly active atoms) are relatively slow, i.e. the active state is retained for quite considerable periods of time, e.g. for at least 4 days in the case of Pt [4]. The loss of the active state may also be impeded by the fact that even at quite low potentials some of the more active metal atoms present may exist in the oxidized state which does not readily undergo reduction [4, 5].

The importance of the superactive state is that it results not only in dramatic changes in the redox response but also creates new routes for reaction. This was demonstrated recently by Haruta and co-workers [11], who observed that oxide-supported, minute gold particles are the most active catalysts for CO oxidation at sub-ambient temperatures. In conventional terms such behaviour is inexplicable; gold has no vacancies in its d-band and is thus a very weak chemisorber (the absence of a significant adsorbed hydrogen response for gold in aqueous media is well established [12]). Superactive surface gold atoms are very electropositive and by donating an electron to a gas phase species (oxygen and/or carbon monoxide) they provide a route for chemisorption that is unavailable in the case of the conventional surface. The unusual catalytic properties of oxide-supported gold microparticles were reviewed recently by Bond and Thompson [13], who (in the concluding section of their article) stressed the importance of chemisorption at the particle surface. It has been suggested also for both gold [5] and platinum [3, 4] electrodes in aqueous media that superactivation favours hydrous ( $\beta$ ), rather than monolayer ( $\alpha$ ), oxide formation, and a generalized scheme for noble metal electrocatalysis, based on the concept of active state interfacial redox couples, was published recently [7].

## Experimental

The type of cell and the equipment used in this work were described in some detail in earlier reports dealing with thermally pretreated platinum [3, 4]. 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). Prior to the heating process the solution was withdrawn from the cell (the latter, apart from the gas inlet and outlet, was sealed to prevent ingress of air) and during the heating and cooling process the working compartment was subjected to a flow of oxygen-free argon or 5% H<sub>2</sub> in N<sub>2</sub> gas (usually the latter) 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 earlier work with platinum [3, 4], most cyclic voltammograms shown here are from the first cycle which commenced at the lower limit. Confirmation that the unusual responses reported here for thermally pretreated gold were not due to copper contamination from the leads was obtained by experiments carried out with gold electrodes in which the wire was sealed directly into glass; following either thermal pretreatment (heating in a H<sub>2</sub>/O<sub>2</sub> flame) or severe cathodic polarization [5], such electrodes gave similar responses when immersed in acid solution as those outlined here later for electrically pretreated electrodes. The preliminary work in this project was carried out in gold in aqueous H<sub>2</sub>SO<sub>4</sub> solution; at a later stage, when checking most of the results, a switch was made to HClO<sub>4</sub> solution; the change seemed to have little effect on the unusual voltammetric behaviour reported here.

The use of an incandescent filament pyrometer (Hartmann and Braun, Pyropto) to measure the pretreatment temperature of the wire was less successful for gold than in earlier work with platinum [3, 4]. The temperatures used for gold (melting point 1066 °C) were significantly lower and the colour of the metal itself made colour matching difficult. Most of the values quoted here were obtained with the aid of the Stefan-Boltzmann relation [14] (whose applicability was checked using platinum), viz.:

$$\text{Power} = VI = \epsilon CA(T^4 - T_s^4) = \epsilon C(2\pi rL)(T^4 - T_s^4) \quad (1)$$

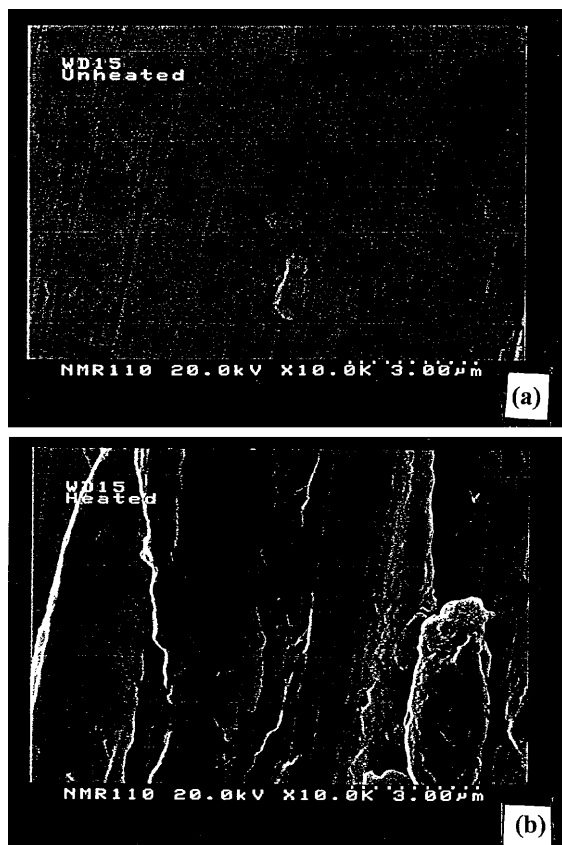
where  $\epsilon$  is the emissivity of gold (the value used, 0.13, was taken from data supplied with the pyrometer),  $C$  is the Stefan-Boltzmann constant (ca.  $5.7 \times 10^{-8} \text{ W m}^{-2} \text{ T}^4$ ),  $A$  is the area [ $2\pi rL$ , where  $r$  = the radius of the wire (ca.  $2.5 \times 10^{-4} \text{ m}$ ) and  $L$  = the length of the gold wire (ca. 0.18 m)],  $T$  is the temperature of the gold wire (K),  $T_s$  is the temperature of the surrounding atmosphere (ca. 300 K),  $I$  is the current applied to the wire during electrical heating (7–12.5 A), and  $V$  is the measured potential drop across the gold wire for a particular applied current value.

The surface microscopy work reported here is of preliminary character; the main objective was to demonstrate that the thermal pretreatment process had a disrupting, rather than ordering, effect on the metal surface. Scanning electron microscope (SEM) images were obtained using a Hitachi S-4000 Field Effect SEM. Atomic force microscopy (AFM) studies of the topographical changes induced by the heating process were carried out using a Topometrix Explorer AFM, fitted with commercial silicon tips, operating in a non-contact mode.

## Results

### Effect of the heat pretreatment on the morphology of the gold surface

A brief survey of the effect of the thermal pretreatment on the surface of the gold wire was carried out using both SEM and AFM. Since the thermal expansion coefficient ( $\alpha$ ) of gold is quite significant (it has the largest value of  $\alpha$  in the noble metal group [15]), it is quite likely that considerable stress is generated in the wire as the sample cools rapidly on switching off the heating current. The outer layers of the wire cool, and shrink, more rapidly than the interior; then, as the interior undergoes the same changes (and the system becomes more rigid) the stresses involved apparently cause delamination of the outer layers of the metal. The result is illustrated in the lower SEM photograph in Fig. 1, where the surface of the thermally pretreated gold wire is seen to be coated with partially detached flakes of the metal.



**Fig. 1** Typical scanning electron microscope images of the surface of a gold wire (amplification factor  $10^4$ ) before (a) and after (b) heating ( $905\text{ }^\circ\text{C}$  for 20 s) in a 5%  $\text{H}_2$  in  $\text{N}_2$  atmosphere (the heating was followed by rapid cooling, i.e. there was little time for annealing as the sample cooled)

Representative AFM images of thermally unpretreated and thermally pretreated gold wires are shown in Fig. 2. The average roughness values ( $R_a$ ) and average height values were significantly greater after thermal pretreatment;  $R_a$  is defined as the arithmetic mean of the deviation in height,  $Z_i$ , from the mean height,

$$R_a = \frac{1}{N} \sum_{i=1}^N |Z_i - \bar{Z}| \quad (2)$$

It is evident from Fig. 2 that the thermal pretreatment significantly increased the disorder or roughness of the gold surface.

#### Effect of the pretreatment temperature on the redox response

A typical example of the response of a gold surface in acid solution at  $18\text{ }^\circ\text{C}$  after a short period of heating at 6.0 A (ca.  $430\text{ }^\circ\text{C}$ ) is shown in Fig. 3a. Three unusual features appeared in the positive sweep: (1) a peak at ca. 0.16 V (this disappeared later on raising the pretreatment temperature; under the latter conditions, cathodic cur-

rents were often observed at the early stages of the positive sweep); (2) a rather broad peak was observed at ca. 0.68 V; (3) a significant current increase, leading to a plateau rather than a peak, commenced at ca. 1.10 V. These three features were relatively small; the main anodic response was that associated with the monolayer ( $\alpha$ ) oxide formation reaction which commenced at ca. 1.30 V. On the subsequent negative sweep the main cathodic features were the  $\alpha$  oxide reduction peak at ca. 1.18 V and a sharp increase in cathodic current (evidently due to the onset of hydrogen gas evolution) just below 0.1 V. Minor, poorly defined, cathodic features were also noted at ca. 0.96 V, ca. 0.65 V and below ca. 0.4 V.

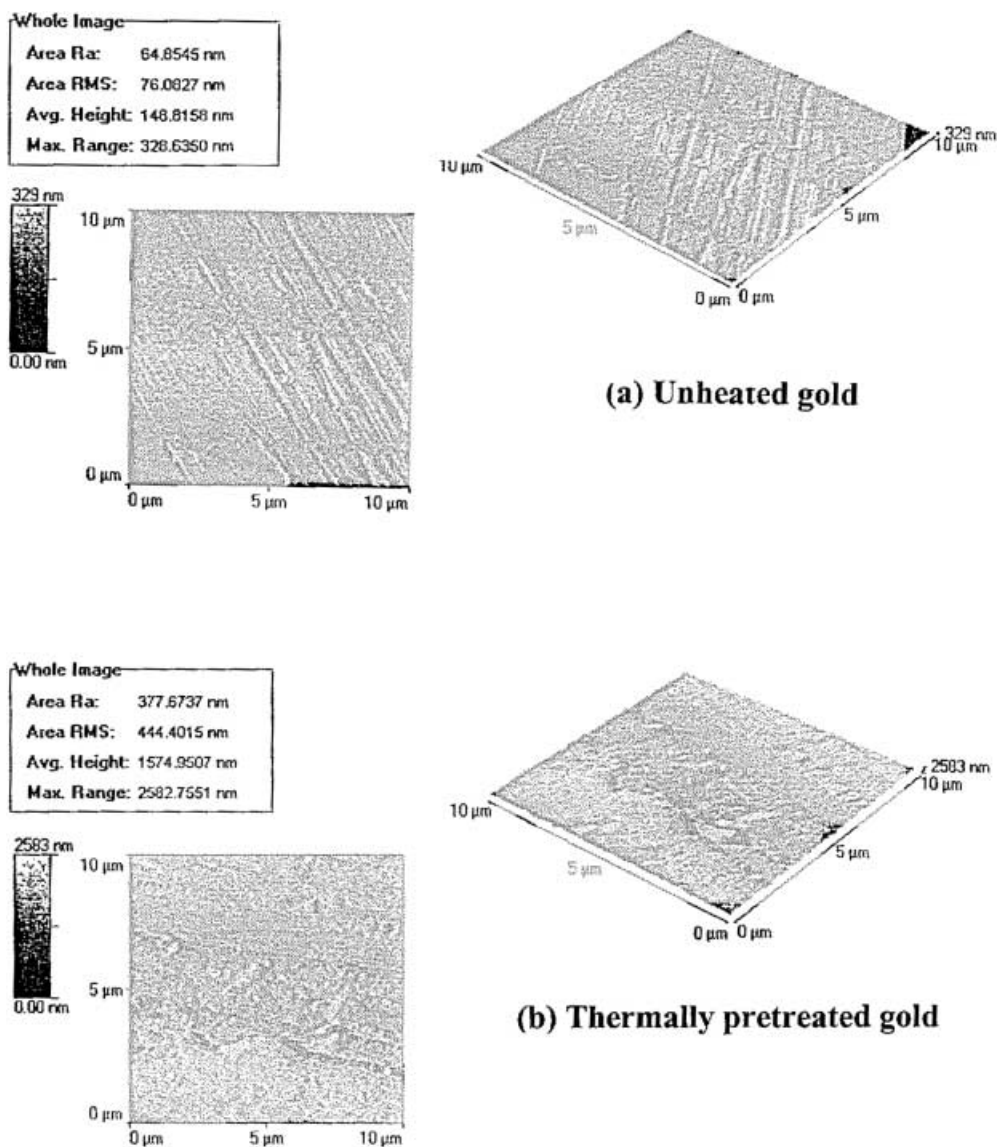
Increasing the pretreatment current to 7.0 A (Fig. 3b) resulted in the loss of the first anodic peak in the positive sweep (at ca. 0.16 V in Fig. 3a) and the emergence of a more marked cathodic shoulder below 0.4 V on the negative sweep. Raising the pretreatment current to 8.0 A (Fig. 3c) gave a response which is remarkably similar to some of those reported earlier by Ling and co-workers [16] [see their figs. A-3 to A-5 for gold in  $\text{H}_2\text{SO}_4$  solution; in particular, the appearance of an overlapping anodic doublet at low potentials in the positive sweep (after mild cathodic polarization) in their fig. A-5 and thermal pretreatment in the present case (Fig. 3c) is worth noting]. Also, the cathodic responses below 0.8 V on the negative sweep in both cases were rather sluggish.

Raising the pretreatment current to 9.0 A (Fig. 4a) resulted in a significant increase in the anodic response in the positive sweep at ca. 0.56 V and the emergence of a relatively sharp anodic peak at ca. 1.38 V, i.e. at the early stage of the  $\alpha$  oxide formation region. Some anodic current, presumably associated with the oxidation of residual active gold atoms, was observed over the range 0.98 to 0.82 V of the negative sweep, but significant cathodic current (and some ill-defined peaks) were observed over the range 0.80 to 0.0 V. Raising the pretreatment current to 11.5 A (Fig. 4b) or 12.5 A (Fig. 4c) resulted in the emergence of a substantial anodic peak at ca. 0.4 V. This first peak disappeared much more rapidly (on repeated cycling or even on allowing the system to rest) than the second anodic peak at ca. 0.56 V (Fig. 4c). In the latter case also the third anodic peak, at ca. 0.8 V, moved to more positive potentials and changed to a plateau format above 1.0 V, similar to that shown in Fig. 4a, on allowing the electrode to rest, after heating, for 20 min.

As illustrated in Fig. 5, rather similar behaviour was observed on raising the cell solution temperature. In the case of Fig. 5c, the first anodic peak ( $E_p = 0.34\text{ V}$ ) was particularly prominent and the anodic charge over the region 0.24–0.65 V of the positive sweep was particularly large, e.g. it greatly exceeded the charge in the  $\alpha$  oxide formation region.

#### Effect of repeated scanning and effect of sweep rate

The degree of activation of the surface, measured in terms of the anodic response at low potentials ( $< 0.7\text{ V}$ ),

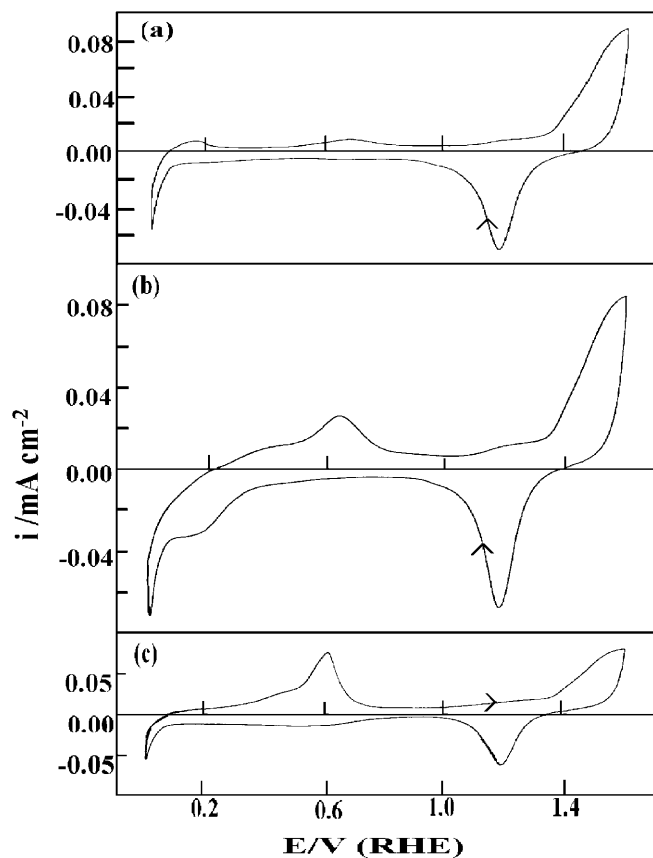


**Fig. 2a, b** Typical atomic force microscopy images of an unheated and heated sample of the same gold wire (the heating conditions are given in Fig. 1). The estimated average ( $R_a$ ) and root mean square ( $R_{rms}$ ) roughness values for both samples are quoted

was particularly large for a pretreatment current of 12.5 A. Detailed investigation of the effect of variables in both the generation and subsequent behaviour of the active states was restricted by the fact that these states, in the first instance, are trapped, frozen-in, metastable systems, i.e. they are not formed each time (even in successive experiments with the same sample) in precisely the same manner. Also, they are not stable at ambient temperature, even though the decay on resting is not particularly rapid. Finally, as outlined here in Fig. 6, the voltammetric peaks decrease in height (or charge) on repeated scanning; this is particularly true of the first anodic peak at ca. 0.4 V; the second anodic peak at 0.52 V is appreciably more persistent (although it also is subject to slow decay). Both the monolayer oxide

response and the cathodic plateau current on the reverse sweep (below 0.8 V) are much more stable.

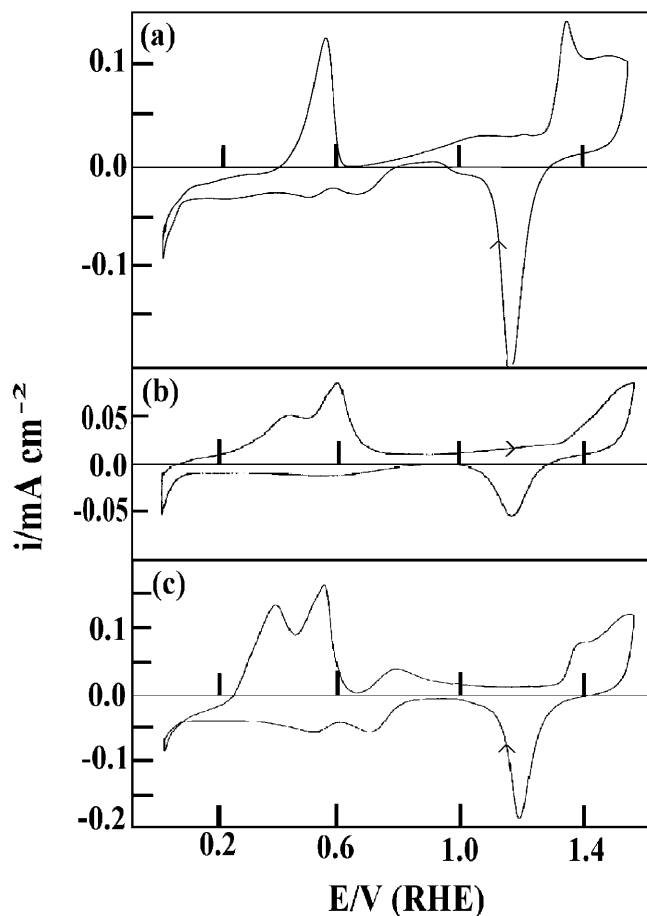
The effect of sweep rate on the voltammetric response is outlined in Fig. 7. At  $10 \text{ mV s}^{-1}$  (Fig. 7a), three to four anodic peaks (the one at ca. 0.5 V seemed to be a doublet) were observed at the early stages of the positive sweep ( $E_p = 0.28, 0.37, 0.49$  and  $0.53$  V). Over the same region of the negative sweep the cathodic response was generally sluggish; a plateau, rather than distinct peaks, was observed and this extended (with a slight increase in current) down to 0.0 V. As noted here earlier (Fig. 4a), some anodic current was observed in the negative sweep in the region just after the monolayer oxide reduction region. The general nature of the responses (Fig. 7) did not alter dramatically on varying the sweep rate, although peak resolution at the lower end of the positive sweep was decreased on increasing the sweep rate. It is interesting also that, in all cases in Fig. 7, cathodic current was observed at the early stages ( $E < 0.2$  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> HClO<sub>4</sub> solution at 18 °C; the gold was preheated electrically for 20 s in an argon atmosphere at **a** 6 A (430 °C), **b** 7 A (515 °C) and **c** 8 A (570 °C)

#### Effect of varying the upper limit

Two examples are shown in Fig. 8 where in the first case the  $\alpha$  oxide film region was not entered and in the second case where the electrode was subjected to both  $\alpha$  oxide formation/removal and oxygen gas evolution. With regard to unusual responses at low potentials ( $E < 0.7$  V, positive sweep) the upper limit had virtually no effect, especially in the first positive sweep since this commenced in both cases at 0.0 V. Even in the same region of the subsequent negative sweep, the difference in the case of the first sweeps was not marked, the reaction involved below 0.7 V being quite sluggish. For both upper limit experiments the magnitude of the first anodic peak at ca. 0.32 V decreased on cycling and the feature was absent in each case in the third sweep. One of the interesting features in Fig. 8b is that the charge (or peak height) at the onset of monolayer oxide formation region is greater in the second sweep. Such behaviour was observed in a much more marked manner recently in the case of copper in base [17]; with both metals the decay in the active state of the metal is accompanied by a decrease in premonolayer, and an increase in regular monolayer, oxidation response.

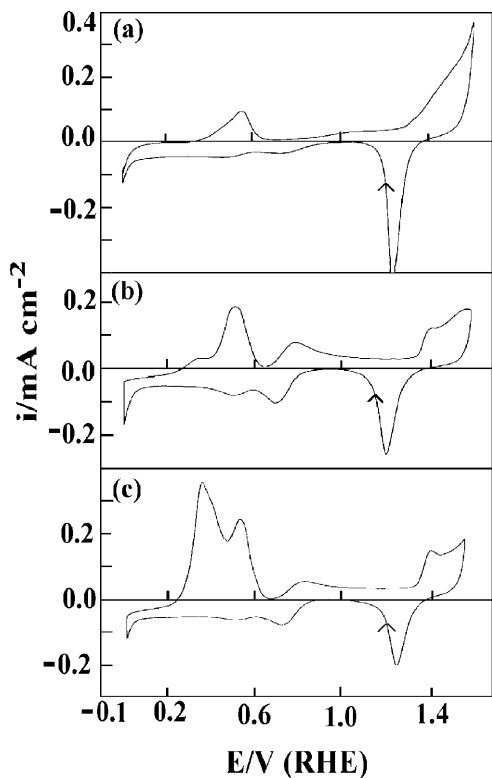


**Fig. 4** Cyclic voltammograms (0.0–1.6 V, 50 mV s<sup>-1</sup>) for a gold wire electrode in 1.0 mol dm<sup>-3</sup> HClO<sub>4</sub> solution at 18 °C; the gold was preheated electrically for 20 s in an argon atmosphere at **a** 9 A (655 °C), **b** 11.5 A (815 °C) and **c** 12.5 A (905 °C)

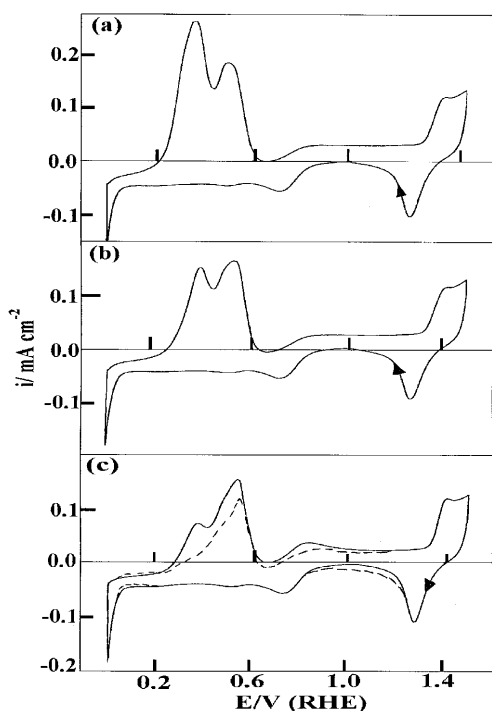
#### Effect of cathodization

The ability to activate a gold surface in acid solution solely by cathodic polarization pretreatment was demonstrated earlier [5]. A similar effect is demonstrated here in Fig. 9. In this case the electrode was first activated by thermal pretreatment (Fig. 9a) and the electrode was then subjected to continuous cycling (0.0–1.6 V at 50 mV s<sup>-1</sup>) for 30 min. During this period the first anodic peak at ca. 0.31 V disappeared and the magnitude of the second, at ca. 0.53 V, was reduced (Fig. 9b). It is also worth noting that the cathodic response below ca. 0.8 V in the negative sweep remained largely unaltered, apart from a slight decrease in magnitude.

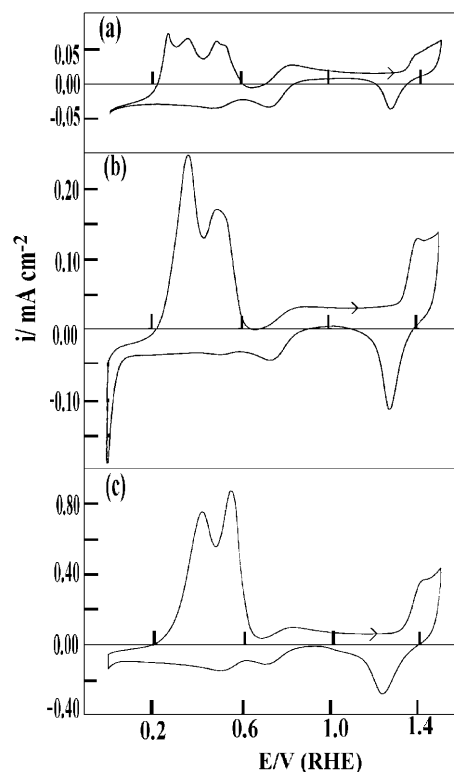
Subjecting this partially deactivated surface (Fig. 9b) to cathodic polarization at -0.1 V (the same effect was observed, but the response or extent of reactivation was lower, on holding at 0.0 V) resulted in the reappearance of the anodic peak at low potentials in the positive sweep (Fig. 9c). Close inspection of these lower peaks in Fig. 9a and c reveal interesting differences. In Fig. 9a the first anodic peak maximum is at ca. 0.31 V and there is a shoulder at ca. 0.40 V. In Fig. 9c the first peak maximum



**Fig. 5** Cyclic voltammograms (0.0–1.6 V,  $50 \text{ mV s}^{-1}$ ) for a gold wire electrode in  $1.0 \text{ mol dm}^{-3} \text{ HClO}_4$  solution at  $50 \text{ }^\circ\text{C}$ ; the gold was preheated electrically for 20 s in an argon atmosphere at **a** 8 A ( $570 \text{ }^\circ\text{C}$ ), **b** 10 A ( $700 \text{ }^\circ\text{C}$ ) and **c** 12.5 A ( $905 \text{ }^\circ\text{C}$ )



**Fig. 6** Cyclic voltammograms (0.0–1.5 V,  $50 \text{ mV s}^{-1}$ ) for a gold wire electrode in  $1.0 \text{ mol dm}^{-3} \text{ HClO}_4$  solution at  $50 \text{ }^\circ\text{C}$ ; the gold was preheated electrically at 12.5 A ( $905 \text{ }^\circ\text{C}$ ) for 20 s in an argon atmosphere: **a** first sweep, **b** second sweep and **c** third sweep (full line) and fourth sweep (dashed line)

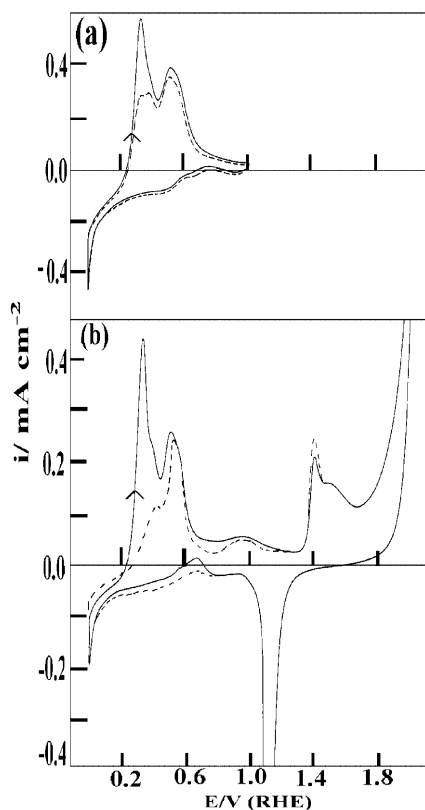


**Fig. 7** Cyclic voltammograms (0.0–1.5 V) for a gold wire electrode in  $1.0 \text{ mol dm}^{-3} \text{ HClO}_4$  solution at  $50 \text{ }^\circ\text{C}$ ; the gold was preheated electrically at 12.5 A ( $905 \text{ }^\circ\text{C}$ ) for 20 s in an argon atmosphere: **a**  $10 \text{ mV s}^{-1}$ , **b**  $50 \text{ mV s}^{-1}$  and **c**  $200 \text{ mV s}^{-1}$

is at ca. 0.42 V and there was an indication of a shoulder on this peak at lower, or more negative, potentials. Evidently, it is possible to reactivate gold surfaces by cathodic polarization but the two states obtained, one by thermal and the other by cathodic pretreatment, may not be identical with regard to the reactivity of the active gold atoms at the surface.

The data shown in Fig. 9b are interesting in that the anodic peak at ca. 0.52 V, i.e. the active gold response, still appeared in the positive sweep after 30 min of continuous cycling (or after 30 cycles), i.e. the layer of active metal atoms is not rapidly lost (or anodically stripped) from the surface. Also the cathodic response below 0.6 V in the negative sweep was present on the 30th cycle. Such behaviour is more typical of oxide formation/reduction, rather than metal dissolution, at highly active gold atom sites; the decay in the anodic response at low potentials ( $E \approx 0.3 \text{ V}$ ) may well be due to these very active atoms attaining a state of greater stability via surface reconstruction effects.

The retention of the active state of the gold surface in the absence of cycling was also investigated. A sample of gold wire was thermally pretreated ( $815 \text{ }^\circ\text{C}$  for 20 s) but allowed to remain in the Ar atmosphere for 48 h prior to allowing the acid solution into the cell. The anodic peak at ca. 0.52 V was still observed in the first positive sweep but the magnitude of the charge in this region was diminished by ca. 90% compared with the response

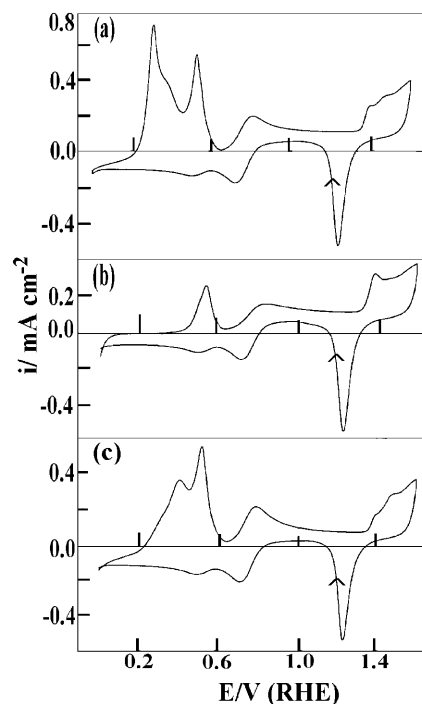


**Fig. 8** Variation of the cyclic voltammetric response ( $50 \text{ mV s}^{-1}$ ; the *full* and *dashed* lines in each case are the first and second cycles, respectively) with upper sweep limit for a gold wire electrode, preheated at  $12.5 \text{ A}$  ( $905 \text{ }^\circ\text{C}$ ) for  $20 \text{ s}$ , in  $1.0 \text{ mol dm}^{-3} \text{ HClO}_4$  at  $18 \text{ }^\circ\text{C}$ : **a**  $0.0\text{--}1.0 \text{ V}$ , **b**  $0.0\text{--}2.0 \text{ V}$

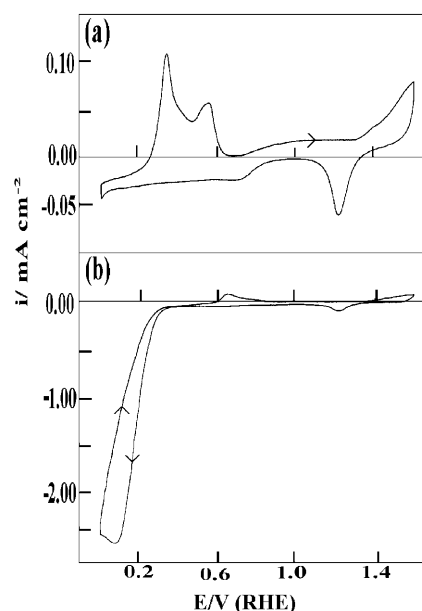
recorded in a similar experiment in which the resting period of the thermally pretreated gold in the inert gas atmosphere was minimal. Obviously the active state of the gold surface is unstable, but the rate of loss of the activity was not particularly rapid.

### Electrocatalysis

The responses for thermally pretreated gold in acid solution, in the absence (a) and in the presence (b) of nitrobenzene, are shown in Fig. 10 (these were separate experiments, i.e. a fresh preheated electrode was used in each case). In the presence of nitrobenzene the anodic response at low potentials was virtually absent in the positive sweep, apart from a minor feature at ca.  $0.65 \text{ V}$  (evidently all the highly active gold atoms were oxidized by the nitro compound). However, below ca.  $0.3 \text{ V}$ , vigorous nitrobenzene reduction was observed. According to the data in Fig. 10a, there appear to be two distinct types of highly active surface gold atoms, one ( $\text{Au}^{**}$ ) undergoing oxidation at ca.  $0.3 \text{ V}$  and the other ( $\text{Au}^*$ ) at ca.  $0.55 \text{ V}$ . In terms of the IHOAM model of electrocatalysis [7], only the former seems to be involved in rapid nitrobenzene reduction as the rate of reaction is



**Fig. 9** Cyclic voltammograms ( $0.0\text{--}1.5 \text{ V}$ ,  $50 \text{ mV s}^{-1}$ ) for a gold wire electrode in  $1.0 \text{ mol dm}^{-3} \text{ HClO}_4$  solution at  $50 \text{ }^\circ\text{C}$ ; the wire was preheated electrically at  $12.5 \text{ A}$  ( $905 \text{ }^\circ\text{C}$ ) for  $20 \text{ s}$  in an argon atmosphere and then subjected to  $30 \text{ min}$  of continuous cycling: the first (a) and last (b) cycles are shown here. The electrode was then polarized at  $-0.1 \text{ V}$  for  $50 \text{ min}$  and the next cycle (c) was then recorded



**Fig. 10** Cyclic voltammograms ( $0.0\text{--}1.6 \text{ V}$ ,  $50 \text{ mV s}^{-1}$ ) for a gold electrode **a** in  $1.0 \text{ mol dm}^{-3} \text{ HClO}_4$  at  $50 \text{ }^\circ\text{C}$ , **b** in  $1.0 \text{ mol dm}^{-3} \text{ HClO}_4 + 0.1 \text{ mol dm}^{-3} \text{ C}_6\text{H}_5\text{NO}_2$  at  $50 \text{ }^\circ\text{C}$ ; in both cases the wire was preheated as outlined in Fig. 6

very slow above ca.  $0.3 \text{ V}$  in the positive sweep. It is assumed that at  $E > 0.3 \text{ V}$  the  $\text{Au}^{**}$  species exists only in its oxidized state (or the main mediator for the

nitrobenzene reduction reaction, the Au\*\* atom, no longer exists at the interface). There is a much slower rate of reduction in the positive sweep over the range 0.3 to ca. 0.55 V; this is assumed to be due to the involvement of a much less effective active gold (Au\*) mediator for nitrobenzene reduction in this region.

The electrocatalytic nature of the nitrobenzene reduction reaction on gold in acid solution was verified by investigating the response for this reaction at other electrode materials, e.g. platinum and carbon. As will be reported later, the observed responses were quite different. Nitrobenzene undergoes reduction at a more positive potential (or at a lower cathodic overpotential) on gold than on platinum; this is not unusual as the same trend was observed [18], in an even more dramatic form, for dichromate reduction on these two metals in acid solution.

Some further electrocatalytic reactions on thermally pretreated gold in acid solution were also investigated (a more detailed account of these will be reported later). Large reduction currents due to hydrogen peroxide reduction were observed over the range 0.0–0.5 V, but rapid oxidation of this compound only occurred above 1.0 V. Reduction of oxygen was also limited to the region  $E < \text{ca. } 0.5 \text{ V}$ . Hydrazine oxidation and dichromate reduction occurred quite rapidly above and below ca. 0.85 V, respectively.

## Discussion

Previous accounts of gold electrochemistry [12, 19] in aqueous media have been concerned largely with the relaxed, relatively low-energy state of the metal surface. In the present work, attention is devoted to high-energy, superactive states of surface gold atoms which, apart from low coverage active sites, are unoccupied in the case of a conventional gold surface. As pointed out in a recent account of cathodically activated gold [5], the type of responses shown here at low potentials, e.g. the sharp anodic peak at ca. 0.5 V and the sluggish cathodic response extending to much lower potentials on the subsequent negative sweep, have been reported previously by other authors who pretreated their gold surfaces by cathodic polarization [16] or thermal annealing [20, 21] techniques.

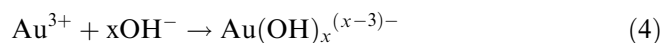
Severe heating of a metal results in the generation of defects in the lattice and movement of atoms in the bulk and especially at the surface. The Tammann temperature of gold, i.e. the value at which metal atoms become mobile [2], is ca. 395 °C for the bulk and 128 °C for the surface. Clearly, when the wire was held at ca. 900 °C there is very considerable movement of gold atoms and a high density of defects present even in the bulk. Switching off the current and allowing the wire to cool rapidly evidently favours trapping of gold atoms in metastable configurations or active states.

It was pointed out recently [5] that while the standard redox potential ( $E^\circ$ ) for the bulk gold/Au<sub>2</sub>O<sub>3</sub> (hyd.) transition is ca. 1.46 V in acid solution, this

value drops to 0.33 V when isolated gold atoms, i.e. atoms with zero lattice stabilization energy, are involved. Despite some uncertainties, e.g. the nature of the hydrous oxide species and the value for its chemical potential ( $\mu^\circ$ ) are rather indefinite, the latter potential value agrees rather well with that for the onset of the first anodic peak in Fig. 4c. Virtually free gold atoms are assumed to exist at the superactive gold surface as high-energy transient species [the first anodic peak is the one that appears least readily under thermal pretreatment conditions (Fig. 4) and is most prone to decay (Fig. 6)]. The entities involved are assumed to be mobile gold atoms on the electrode surface that wander about until eventually they become incorporated into a permanent stable surface feature, i.e. such atoms are the prime participants in the surface reorganization (Ostwald ripening) reaction. The second anodic peak, at ca. 0.53 V (Fig. 4c) evidently reflects the reaction of slightly less active gold atoms. The complexity of the active state response (see Fig. 7a) should not be underrated and the limited data available with regard to the active state at the present time is insufficient to provide a detailed explanation for the origin of the various overlapping anodic peaks.

Cyclic voltammetry is a very useful technique for investigating the active state behaviour of metal surfaces as it provides a useful measure of the amount of material and the number of states involved, plus (with certain assumptions) an indication of energy levels. Its main weakness is the inability to provide any structural, or highly localized, specific data. However, deriving detailed information with regard to the nature of highly active, rather disorganized metal surfaces may be a very challenging task. High-resolution microscopy techniques (STM or AFM) lose resolution when dealing with disordered surfaces and these techniques are unable to detect highly mobile surface atoms [4]. It appears also [3] that some high-vacuum analytical techniques, e.g. low-energy electron diffraction (LEED), are unable to detect discrete surface species such as adatoms.

Many of the anodic premonolayer oxidation responses (below 0.6 V in the positive sweep) observed in the present investigation were quite large and the charge involved was usually on a par with, or exceeded, that for monolayer oxide formation. Hence the premonolayer response is assumed to be of Faradaic, and not capacitive, character. An explanation based solely on OH<sup>-</sup> ion adsorption is improbable (the charge involved is too large) while formation of OH<sub>ads</sub> is unlikely for energetic reasons [22]: the OH radical is extremely electronegative and gold is a very weak chemisorber. The most logical view is that active gold atoms undergo oxidation at low potentials and the resulting gold cations then coordinate hydroxide ions:





Since the active gold atoms are virtually outside the metal lattice, they are assumed to coordinate an unusual number of solvent molecules, and possibly electrolyte anions, on undergoing oxidation. Hence, the product of the premonolayer oxidation reaction is regarded as a hydrous oxide species. These oxide species formed on gold at low potentials are intrinsically unstable and the retention of the deposit depends mainly on the existence of the highly active state of the surface gold atoms ( $\text{Au}^*$ ). Indeed, there is evidence, e.g. in Fig. 7a, of a minor cathodic response above 0.6 V in the positive sweep; this is assumed to arise due to slight reduction of the unstable oxide induced by a decay in activity of a small portion of the highly active state of gold; obviously slow loss of some of the active state of gold will trigger some reduction of the hydrous oxide.

A surprising feature of the response at low potentials is the sluggish nature of this oxide reduction process, especially at low potentials in the negative sweep (such behaviour was also observed for platinum in acid [3, 4] and is evident in independent work for gold [16]). It is evident, e.g. in Fig. 4, that there is an increase in cathodic current at ca. 0.6 V in the negative sweep, but this is followed by more a plateau rather than a major peak. Multivalent cations such as  $\text{Au}^{3+}$  tend to be strongly hydrated [23] and some of the counterions present may be  $\text{HSO}_4^-$  or  $\text{SO}_4^{2-}$ , rather than  $\text{OH}^-$ , species. Slow, potential-independent, reduction down to 0.0 V may be due to the involvement of a preceding chemical reaction, e.g. the hydrous oxide species may have to lose some of its hydration sheath prior to electron transfer.

It appears that when thermally pretreated gold is first brought in contact with the aqueous phase, some of the more active gold atoms ( $\text{Au}^*$ ) undergo spontaneous oxidation (note the cathodic currents,  $E < 0.3$  V, at the beginning of the first positive sweep in many cases reported here). This superficial oxidation is assumed to occur via a local cell mechanism, the cathodic process being the release of a small quantity of hydrogen; the overall reaction may be represented as follows:



Despite its thermodynamic instability, much of this oxide is retained even at 0.0 V (as mentioned here earlier, the cathodic reaction in question is quite sluggish). It is also worth noting that this cathodic feature at the early stages of the positive sweep was observed earlier [5], in several cases in a more dramatic form, using cathodically activated gold. It is suggested here with regard to Eq. 5 that the first anodic peak in the positive sweep in Fig. 3a,  $E_p = 0.16$  V, corresponds to a low level oxidation of highly active gold ( $\text{Au}^*$ ), the lower end of this peak overlapping with the cathodic response due to hydrogen gas evolution, i.e. the two partial reactions in the local cell reaction are distinguishable in this case. Increasing the gold pretreatment temperature, as in Fig. 3b, increases the activity of some of the surface gold atoms; this enables the latter to undergo oxidation at a lower

potential (close to 0.0 V), i.e. the two partial reactions then overlap. The process shown in Eq. 5 does not yield an external current response, the only coulometric feature observed at  $E < \text{ca. } 0.3$  V in Fig. 3b being that due to the sluggish reduction of the unstable oxide species.

According to the IHOAM model of electrocatalysis [7], the importance of the active states of metal surfaces is that the atoms in such states act as the mediators for reduction processes while their oxidation products, i.e. the hydrous oxide species, play a similar role in oxidation processes. Normally the coverage of these mediators is extremely small and their vital role in electrocatalysis is often ignored. In earlier reports from this laboratory [24, 25] it was suggested that at gold surfaces in acid solution there are two types of mediator systems, one commencing reaction at ca. 0.85 V and the other at ca. 1.05 V (the evidence for these conclusions was summarized recently [22, 26]). Some evidence to support these conclusions is provided here even in the case of gold in pure acid, i.e. in the absence of dissolved oxidants or reductants. Thus in Fig. 3b there is a small but significant increase in anodic current, i.e. an oxide mediator generation step, in the positive sweep commencing at ca. 1.1 V. There is also a peak in the positive sweep at ca. 0.8 V in Fig. 5b and Fig. 5c; this feature is also evident in other diagrams, e.g. in Fig. 9 there appears to be a quasi-reversible response in this region. Similar behaviour with regard to the detection of several premonolayer oxidation peaks, and the presence of three different mediator systems (based on different active states of surface metal atoms), was discussed recently [3] in the case of platinum in acid solution. However, under the rather severe activation conditions used in the present work the conversion of surface gold atoms to the most active state, i.e. the one giving the anodic response below 0.6 V, was the favoured process; it therefore appears that there is at least one other electrocatalytic mediator system for gold in acid (in addition to the two mentioned above).

The data for nitrobenzene reduction (Fig. 10b) are included here to demonstrate the complexity of the electrocatalytic behaviour of a gold surface in acid solution. The notion that there are several mediator systems for the same metal is in agreement with Taylor's original idea [27] of the existence of different types of active sites, presumably based on the existence of different levels of surface metal atom activity, at the same surface. The relevant mediator responses or potentials for gold in acid may be summarized as follows:

1. At ca. 1.10 V: many alcohols and organic acids begin to undergo oxidation at the latter value (see tables 1 and 4 in [26]); it was observed in the present work that peroxide oxidation also commenced and terminated (positive and negative sweep, respectively) at ca. 1.1 V.
2. At ca. 0.85 V: it was pointed out earlier [26] that dramatic changes in reaction rate for both hydrazine oxidation and dichromate reduction occur in the case of gold in acid at ca. 0.85 V.

3. At ca. 0.3–0.5 V: it appears from the data shown here (Fig. 10b) for nitrobenzene, and the behaviour mentioned for hydrogen peroxide and oxygen reduction, that there is at least one (if not two) mediator systems in this region. Confirmation of a change in reactivity of the interface in question in this region is provided also by the observation [28] that the onset/termination potential for CO oxidation on gold in acid occurs at ca. 0.2 V (SCE), i.e. ca. 0.45 V (RHE).

Some points are worth noting here, e.g. according to the IHOAM model of electrocatalysis [7], multilayer hydrous oxide film reduction and electrocatalytic behaviour are often closely related. This was pointed out recently for both platinum in acid [3] and copper in base [7]; multilayer hydrous oxide films on gold in acid, on reduction in a negative sweep, also yield three hydrous oxide reduction peaks [29] at potential values not far removed from those quoted here (points 1–3 above). As outlined earlier for platinum [30], it does not necessarily follow that superactivating a metal surface will enhance its electrocatalytic activity (especially with regard to oxidation) as the highly active material may become overoxidized. Superactivation may also not be beneficial with regard to reduction; this was demonstrated recently [31] in the case of the hydrogen gas evolution reaction on gold in acid. During the course of the latter reaction, hydrogen embrittlement of the cathode surface resulted in gradual activation of the latter [5]; the resulting drop in hydrogen evolution rate with time [31], at constant overpotential, was attributed to the change in electronic properties (or coverage and bond strength of the interfacial  $M-H_{ads}$  species) due to the variation of the nature of the outer layers of the metal lattice.

It seems from an electrocatalytic viewpoint that the solution species strongly influences the type of mediator or active site involved in electrocatalysis (e.g. why should oxidation of CO commence at ca. 0.45 V and that of  $N_2H_4$  at ca. 0.85 V?). It may well be that the important factor in the transfer of the energy released in the electrocatalytic process to the active site. If this transfer is efficient, then the atoms will be highly active and the mediation process will occur at quite low potentials. According to this view, the energy change for the electrocatalytic process is not the important factor with regard to the mediator system or onset/termination potential; the crucial factor is the linkage, or energy transfer, between the catalytic process and the active site metal atoms.

It is assumed currently [32] in the case of gold single-crystal electrodes, especially in the case of Au(100) surfaces, that the anodic response at ca. 0.5 V is due to the difference in the potential of zero charge between the two metallic phases involved in the reconstruction process. However, such a non-Faradaic interpretation cannot readily explain the major electrochemical response observed (at about the same potential) for thermally, or cathodically [5], pretreated polycrystalline gold surfaces

in acid solution. It is interesting also that in the course of the Au(100) reconstruction reaction, excess gold atoms (which are presumably highly reactive and thus prone to undergo premonolayer oxidation) are expelled from the lattice [32]. It is apparently accepted (see p. 253 of [32]) that the rate of many individual atomic events on surfaces often exceeds the response time of conventional STM instruments. For example, processes such as kink motion, which may be considered as slow relative to active atom motion on terraces, cannot be clearly imaged or “seen” at the present time. Hence it is debatable as to whether or not the important surface mediator species are detectable in much of the high-resolution microscopy work carried out in the electrocatalysis area at the present time. Furthermore, it seems that with real monocrystalline metal surfaces there are usually plenty of defects present [33] to provide active atoms which may well dominate electrocatalytic behaviour.

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## Conclusions

It is evident that severe thermal (present work) or cathodic [5] pretreatment of gold has a major effect on the redox behaviour of the metal in aqueous acid solution. The novel responses observed are important as they are assumed to reflect the properties of active sites on conventional gold surfaces. The surfaces involved in the current work are quite rough or disordered (Figs. 1 and 2) and this limits (according to Somarjai [34]) the range of techniques suitable for their investigation; however, rough surfaces are of major importance from a practical catalytic viewpoint [34].

For some reactions, and under some conditions, gold possesses almost inexplicable high activity both from a catalytic [11, 13] and electrocatalytic [26] viewpoint. It is suggested that a novel type of chemisorption occurs when surface metal atoms are in a superactive, highly electro-positive state [9]. Gaseous or dissolved atoms or molecules bind to high-energy sites via electron transfer, i.e. a polar, e.g.  $Au_n^+-O_2^-$ , rather than a conventional covalent bond is formed; this provides an unusual route for surface or interfacial catalysis. It is worth noting that tribologically activated gold [35] adsorbs unsaturated hydrocarbons in a dissociative manner; this is remarkable behaviour for a metal that is widely regarded as having very weak chemisorption properties (abrading the surface is assumed to generate some very active gold atoms). It is clear from the present work that more detailed investigation of highly active metal surfaces is an interesting, complex but potentially very useful area of research.

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