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L. Declan Burke · Jean M. Moran
Patrick F. Nugent

Cyclic voltammetry responses of metastable gold electrodes in aqueous media

Abstract Gold is the noblest of metals and it is widely assumed that the surface of a gold electrode only begins to undergo oxidation in aqueous media at ca. 1.36 V (RHE) in acid or ca. 1.25 V in base. However, recent work in this laboratory has shown that, following thermal activation, gold atoms at the surface of a gold electrode may undergo oxidation in acid solution at potentials as low as 0.3 V. In the present work, in which the gold was allowed to cool rapidly from the molten state, oxidation responses were observed for gold in base at $E < 0.0$ V. Such unusual behaviour is attributed to low gold-atom lattice stabilization energy plus the operation of a super-Nernstian E/pH effect. It appears, as outlined recently for silver, that a range of surface active states are available for metals; these give rise to a range of premonolayer oxidation and multilayer hydrous oxide reduction responses; such non-equilibrium surface states are often quite important with regard to electrocatalysis.

Keywords Cooled bead electrode · Electrocatalysis · Gold · Metastable surface · Premonolayer oxidation

Introduction

The metastable (or non-equilibrium) states of metals and alloys are quite well known in metallurgy [1, 2, 3] but have been largely ignored in surface electrochemistry, especially with regard to the basic electrochemical

L. D. Burke (✉) · J. M. Moran · P. F. Nugent
Chemistry Department, University College Cork, Cork, Ireland
E-mail: l.d.burke@ucc.ie
Tel.: +353-21-4902417
Fax: +353-21-4274097

behaviour of the noble metals. The importance of non-equilibrium states in metallurgy is highlighted by Cahn's claim [4] that "the artful control of metastability is the metallurgist's central skill". In the noble metal area, activating an electrode surface usually entails roughening the latter, e.g. by generating a layer of finely divided metal (Pt black in the case of Pt) on the surface. The resulting improved performance appears to be largely due to the increase in real surface area; usually there is no dramatic change in the basic electrochemical response, apart from the increase in current, e.g. a platinum black surface behaves in a similar manner to bright platinum, the oxidation of both surfaces in aqueous acid media usually commencing at ca. 0.85 V (RHE).

The metastable state is unusual in that a metal in such a state has an abnormally high chemical potential or molar free energy value. Essentially a solid metal may be regarded as an energy storage system; at a simple level, when a metal is plastically deformed (or cold worked) at temperatures well below its melting point, a considerable proportion of the applied energy (sometimes in excess of 10%) remains trapped in the metal in the form of various types of defects [2]. At a commercial level, metastable metals and alloys are produced in substantial quantities, mainly by rapid solidification techniques [1, 3]. However, there is a considerable range of other procedures, e.g. various types of vapour deposition, electrodeposition, ion or electron bombardment, laser treatment, etc., which also yield the activated metastable state [3]. The presence of the stored energy is easily demonstrated by differential scanning calorimetry [2]; one of the problems in this area is that the metastable state is ill-defined, intrinsically unstable and difficult to control. Further details of metastable metals, including a section dealing specifically with metastable surface layers, have been published [1].

The metastable (or superactive) state of metal surfaces is a particularly challenging area of research. It was pointed out recently [5] that superactive surface atoms, i.e. metal atoms at solid surfaces that are either mobile (as adatoms) or potentially mobile (ledge and kink

atoms), are high-energy species as they lack much of the lattice stabilization energy of bulk or well-embedded surface atoms. This concept is not particularly novel; similar proposals with regard to the importance of both metastable states and protruding surface atoms, in connection with the vital role of active sites in heterogeneous catalysis, were made much earlier by Taylor [6]. There is also increasing evidence [7, 8, 9] that metal surfaces are not invariably static, e.g. extensive changes in the topography of fresh copper electrodeposits in air, i.e. spontaneous recrystallization (evidently via the generation and movement of adatoms), were observed recently using AFM [9].

Electrocatalysis is currently a popular area of research, largely due to its relevance to fuel cell development. However, in an earlier review of electrocatalysis, Pletcher [10] pointed out the lack of basic understanding of this topic. It appears that there are two types (or basic mechanisms) of electrocatalysis at surfaces. The first involves activated chemisorption which, as pointed out by Pletcher [10], provides a basis for understanding processes such as hydrogen gas evolution, hydrogen oxidation, formic acid oxidation, chlorine evolution, etc.; however, the activated chemisorption viewpoint cannot account for the unusual catalytic [11] and electrocatalytic [12, 13, 14, 15] behaviour of virtually nonchemisorbing metals such as gold.

The second mode of electrocatalysis involves interfacial redox mediator systems and is based on the presence of highly active metal adatom species at the interface (the basic ideas involved were outlined in several recent publications from this laboratory [5, 12, 13, 16]). There is independent evidence (based on cyclic voltammetry [17, 18], SERS [17, 19, 20], XPS [21, 22] and STM [18, 23, 24] data) for the formation of MOH_{ads} species at Group 11 metals (Cu, Ag, Au) in aqueous media at potentials that are well within the double layer region. Cyclic voltammetry is particularly useful in some respects; although it provides no structural data, it yields a measure (in terms of premonolayer peak potential values) of the energy of surface active states and clearly demonstrates, as shown recently for silver in base [16], the existence of several active surface state responses for the same metal. The present work is concerned largely with the active surface state behaviour of gold; surveys of earlier work on this topic were published previously [5, 12, 13].

Experimental

The usual procedure for producing metals in the metastable states on a commercial scale is rapid thermal quenching [3]. The procedure used in the present work was similar, except that the rate of cooling the metal from the molten state was not especially rapid. A gold wire electrode was fabricated in the usual manner, i.e. the wire (1.0 mm diameter, Alfa Aesar, Puratonic grade), with a copper lead attached, was sealed directly into soda glass, leaving ca. 4 mm of gold wire exposed. The end of the wire was heated in a natural gas(or pure hydrogen)/oxygen flame until all exposed metal was melted to form a gold bead or sphere (of geometric area ca.

0.05 cm^2), which was then allowed to cool rapidly in air. Such (working) electrodes are referred to here as cooled bead electrodes (CBEs). In all cases the gold CBEs appeared bright and spherical when viewed with the naked eye; however, scanning electron microscope (SEM) images of their surfaces revealed the presence of considerable undulations plus significant pitting.

The counter electrode was of similar (but unheated) gold wire and the reference electrode was a reversible hydrogen electrode $[p(H_2) = 1.0 \text{ atm}]$ in the same solution. Details of the cell, electrolyte and electrochemical equipment were similar to those reported earlier [25]. It is worth noting that throughout this work a conventional response for a polycrystalline gold electrode could be obtained, using the same solution and equipment, simply by replacing the CBE by a gold wire electrode (the metal in both cases was taken from the same batch of gold wire) which was not subjected to severe thermal pretreatment.

Results

Redox responses of gold CBEs in base

A sequence of cyclic voltammetry responses for a gold CBE in base is shown in Fig. 1. Four regions of current increases or peaks were observed in both the positive and negative sweeps. For the eight peaks labelled in this diagram the peak maximum potentials are as follows: A_1, −0.04 V (a rather broad, low-level response); A_2, 0.07 V (most clearly evident in the first sweep); A_3, 0.33 V (by far the most prominent feature in the positive sweep); A_4, 1.28 V (this is the conventional monolayer oxide formation response); C_4, 1.06 V (monolayer oxide reduction); C_3, −0.04 V (this is the cathodic counterpoint of A_3); C_2, −0.23 V; C_1, −0.30 V. It is not clear that peaks A_1/C_1 and A_2/C_2 represent simple surface redox pairs, although this possibility is not excluded. C_1 decreased in magnitude and shifted slightly in the
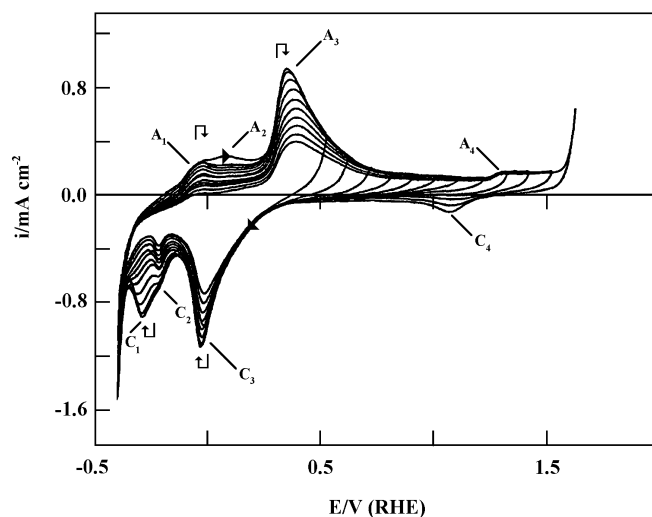

Fig. 1 Cyclic voltammograms (50 mV s^{-1}) for a gold CBE in 1.0 mol dm^{-3} NaOH at 25 °C. The lower limit was constant at −0.4 V; the upper limit was progressively increased above 0.5 V in steps of 0.1 V. All peaks below 0.5 V decreased in height after the second cycle with the exception of peak C_3, which decreased in height only after the fourth cycle

negative direction with increasing number of cycles and increasing upper limit; it eventually disappeared; this loss may be partially due to its overshadowing by the hydrogen gas evolution response. The slight positive shift in peak A_3 with increasing number of cycles, which is accompanied by a decrease in peak charge, may reflect a more rapid loss of the most active gold atoms in the metastable surface state. It is worth stressing that the general appearance (though not the magnitude) of the peaks shown for the gold CBE in Fig. 1 was reasonably reproducible.

It is assumed, as discussed earlier [25], that the redox features observed below ca. 1.0 V in Fig. 1 involve the participation of highly active, protruding, gold atoms at the electrode surface. Such atoms, obviously present at high coverage and in an unstable state, tend to undergo spontaneous decay in activity as the surface atoms rearrange to yield a more stable deposit (direct AFM evidence for such reconstruction behaviour was obtained recently for active copper [9]). This means that the magnitudes of the active state responses tend to decay on cycling, as is clear from Fig. 1, or with resting time. However, after allowing an initially active gold CBE to rest in air for 3 days, the superactive state response, e.g. the anodic peak at ca. 0.3 V in the positive sweep, was still clearly evident (at a reduced level) on resuming potential cycling of this electrode in base. An illustration of the decay in the active state behaviour, on continuous cycling between fixed potential limits, is shown in Fig. 2. Note the unusually large anodic response at ca. 0.0 V in the first positive sweep and a correspondingly large response below −0.2 V in the first negative sweep. However, the main features of the active state response are still evident, at a reduced level, even in the 40th cycle (Fig. 2b).

The degree of retention of the highly active state of the gold CBE in base was often surprising. For example, a surface giving the type of response shown in Fig. 1 was subjected to a cycle between extended potential limits (−0.4 V → 2.1 V → −0.4 V; 50 mV s^{-1}; this entailed both vigorous oxygen gas evolution above 1.6 V, >25 mA cm^{-2} at the upper limit, plus place-exchange associated with the monolayer oxide formation/reduction reaction). The active state response was still quite evident in a subsequent cycle recorded for this electrode using a reduced upper limit.

The sweep rate dependences of the peak current, peak charge and peak potential for the two main features (A_3 and C_3 in Fig. 1) of the active state response were also examined (as illustrated in Fig. 2b, these two peaks reached a stage where, at 50 mV s^{-1}, they became virtually constant, i.e. independent of the number of cycles). The peak potential for C_3 (Fig. 4b) was virtually independent of sweep rate, which is indicative of a rapid reduction reaction. Over the same range of sweep rates the peak potential for A_3 (Fig. 3b) shifted in the positive direction by ca. 60 mV over the range 0–300 mV s^{-1}. Such behaviour is not unusual; monolayer oxide film formation/reduction reactions usually show a similar
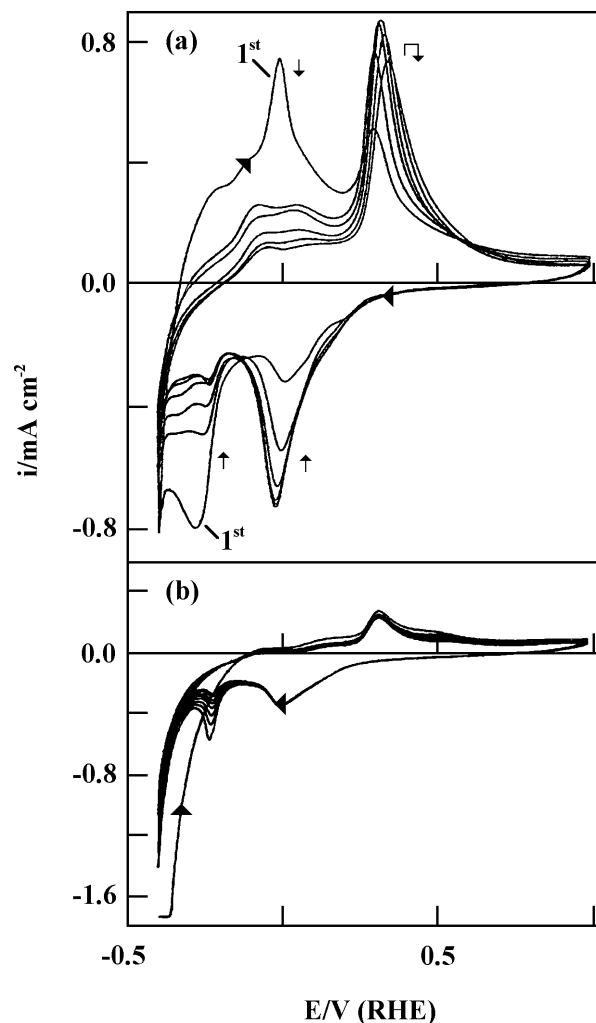

Fig. 2 Cyclic voltammograms (−0.4 V to 1.0 V, 50 mV s^{-1}) for a gold CBE in 1.0 mol dm^{-3} NaOH at 25 °C: (**a**) cycles 1–6, (**b**) cycles 33–40; the cycling in this case was repetitive, with no rest period allowed

trend, the anodic reaction being rather sluggish (probably due to dipole-dipole repulsion and place-exchange behaviour), while oxide reduction yields a much more symmetrical response. An important aspect of the A_3/C_3 redox transitions is that the main participants (active gold atoms and the hydrous oxide) are quite unstable from a thermodynamic viewpoint. The origin of the hysteresis is assumed to be due to slight differences in the species involved, as reactants and products, in the forward and reverse transitions. The peak current densities in both cases increased rapidly, though not quite linearly, with increasing sweep rate. The peak charge for A_3 was almost independent of sweep rate, but dropped significantly with increasing sweep rate for C_3. In the case of C_3 at ca. 0.0 V in Fig. 2b, there is quite substantial reduction over the region just below the peak; the oxide film may be heterogeneous or contact problems may develop as the layer undergoes extensive reduction. However, the constant value for the peak
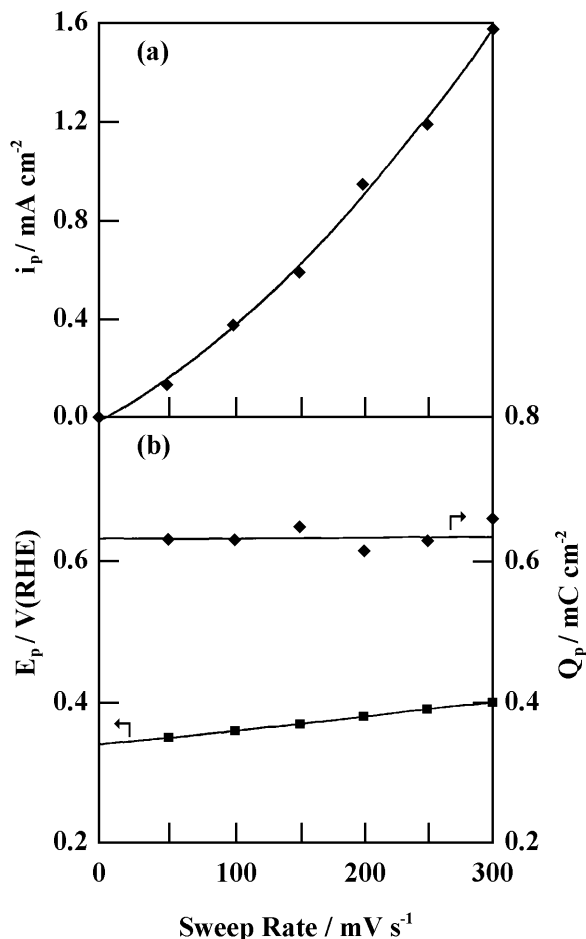
Fig. 3 The effect of sweep rate on (**a**) i_p, peak current density, (**b**) E_p, peak potential, and Q_p, peak charge density, all for peak A_3, in the case of a cooled bead electrode in 1.0 mol dm^{-3} NaOH at 25 °C. Q_p is the charge (above the background) over the potential range 0.22–0.63 V

Fig. 4 The effect of sweep rate on (**a**) i_p, peak current density, (**b**) E_p, peak potential, and Q_p, peak charge density, all for peak C_3, in the case of a cooled bead electrode in 1.0 mol dm^{-3} NaOH at 25 °C; data from the same experiments as in Fig. 3. Q_p is the charge (above the background) over the potential range −0.16 to 0.21 V

potential for C_3 in Fig. 4b suggests that there is an oxide component present that undergoes reduction in a rapid, sweep-rate-independent, manner.

Reduction of multilayer hydrous oxide films grown on a gold wire electrode in base

According to Pourbaix's thermodynamic data [26], which relates only to stable bulk equilibrium metal and oxide phases, gold apparently has no oxide that is stable below ca. 1.4 V. Hence the appearance of oxide reduction peaks below ca 0.0 V in the negative sweep in Figs. 1 and 2 is quite surprising. However, such behaviour is not confined to thermally pretreated, cooled bead electrodes; large cathodic responses below 0.0 V were also observed for the reduction of thick oxide films, grown by either potential cycling or d.c. polarization conditions [27], on conventional gold wire electrodes in base.

The reduction response for an oxide film, grown on a gold wire electrode by potential cycling (using a rather high upper limit, 2.4 V, and a rather long cycling time,
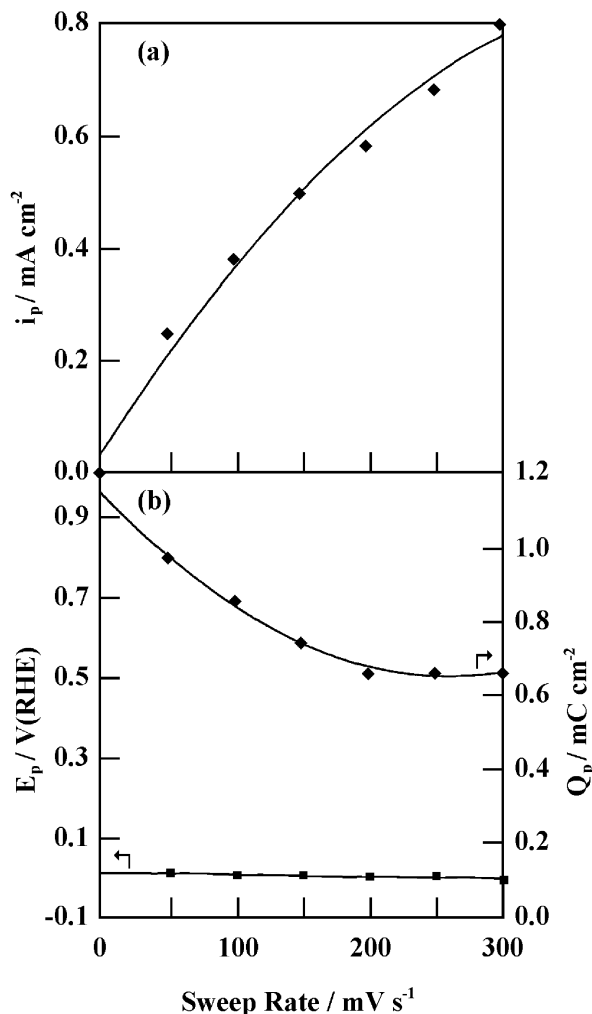
7 min) is shown by the full line in Fig. 5. The sweep rate used for the latter was quite low, 2 mV s^{-1}, the objective being to reduce or minimize peak shifts due to slow kinetics and iR effects. However, one of the most dramatic features was the appearance of a cathodic peak at −0.2 V; this was preceded by a large envelope of charge extending from ca. 1.1 to 0.0 V. The persistent nature of the response below 0.0 V is demonstrated by the result shown by the dotted line in Fig. 5. In this case a hydrous oxide film was grown on gold in the same manner as before. The first negative sweep was applied over the range 1.2 to 0.1 V (this response is not shown here); this was followed by a second negative sweep extending from 1.2 to −0.4 V. As shown by the dotted line in Fig. 5, the main feature of the latter was again a major oxide reduction peak just below −0.2 V; there was also a minor cathodic plateau in this case extending from ca. +0.15 to ca. −0.15 V. This experiment was then repeated, except that in this case the second negative sweep
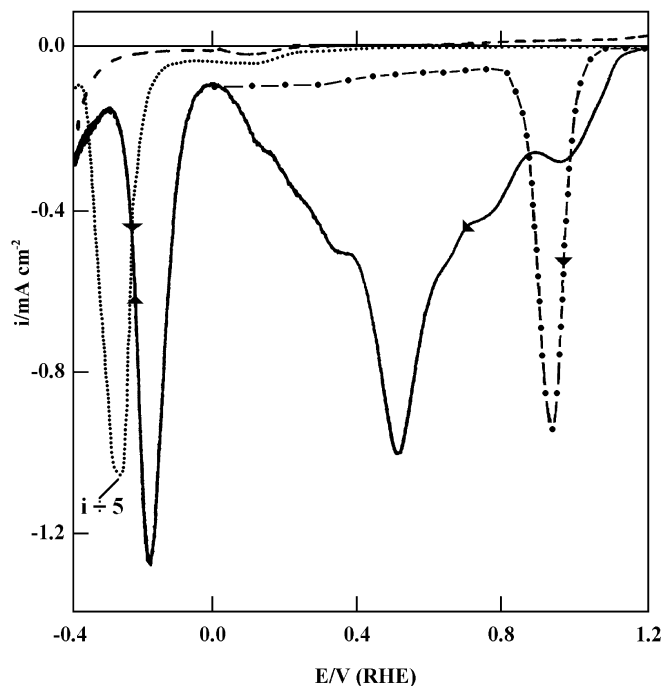
Fig. 5 Reduction profile (*full line*), 1.2 to −0.4 V at 2 mV s⁻¹, for a thick oxide film grown in situ on a mildly pre-abraded gold wire electrode by potential cycling (0.75 to 2.4 V at 50 mV s⁻¹ for 7 min) in 1.0 mol dm⁻³ NaOH at 25 °C. The *dashed line* shows the subsequent positive sweep. The hydrous oxide deposit was regrown; it was then reduced in two stages: an initial sweep (1.2 to 0.1 V at 10 mV s⁻¹; this response is not shown here) and a final sweep (1.2 to −0.4 V, 10 mV s⁻¹); the response in this case, *dotted line*, below 0.0 V, was larger than in the first experiment due to the faster sweep rate. This second experiment was again repeated but the final stage (*dash-dot line*) was carried out after transferring the electrode, plus its partially reduced oxide coating, to 1.0 mol dm⁻³ H_2SO_4

was carried out after transferring the electrode (after the first negative sweep in base, i.e. at 0.1 V) to acid solution. An oxide reduction peak was observed in this case (dashed/dotted line in Fig. 5), just below 1.0 V; this is typical behaviour [27] for the reduction of thin hydrous oxide films on gold in acid solution. This latter sweep for gold in acid commenced at 1.20 V; it is clear that with such a low upper limit, monolayer oxide formation/reduction responses are not involved.

A typical reduction response for a multilayer oxide film, produced in this case under constant polarization rather than potential cycling conditions, is shown in Fig. 6. The major oxide reduction responses occurred below 0.2 V and, as indicated by the arrows, five cathodic features are evident, the peak maximum values being approximately as follows: 1.0, 0.7, 0.45, 0.0 and −0.2 V.

Redox response of a gold CBE in acid solution

Voltammograms recorded for cooled bead electrodes in acid solution (Fig. 7a) were less dramatic than similar
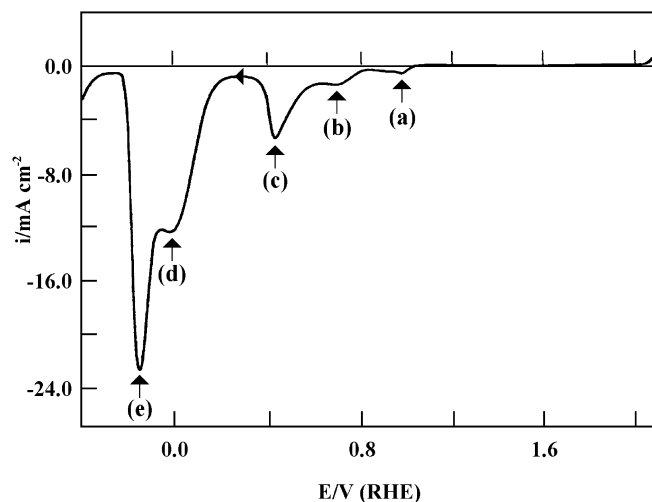

Fig. 6 Reduction sweep (2.1 to −0.4 V, 10 mV s⁻¹) for a thick oxide film on a gold wire electrode in 1.0 mol dm⁻³ NaOH at 25 °C. The film was produced by polarization in base at 2.3 V for 90 min

responses for the same type of electrode in base (Fig. 1). Two rather small peaks were observed in the positive sweep: A_1 at ca. 0.50 V and A_2 at ca. 0.70 V, the latter generally being more pronounced. C_2 in the negative sweep is assumed to be the cathodic counterpart of A_2; A_1 appeared to have no direct cathodic counterpart, but there was a significant flow of cathodic current, even in the positive sweep, over the region 0.0–0.4 V. Investigation of oxide reduction responses (if any) at $E < 0.0$ V was not feasible in this case due to vigorous hydrogen gas evolution current in the latter region. Figure 7b shows a response for a conventional gold wire electrode in acid solution. The main features in this case are the monolayer oxide formation and reduction responses above 1.0 V. A minor irregularity (or inflection) is evident at, or just above, 0.5 V.

Discussion

Cyclic voltammetry of highly activated gold in base

The metastable state of metals is obviously very well known in metallurgy [1, 2, 3], the excess energy being stored in metals due to the presence of a variety of defects at which atoms have a low lattice stabilization energy and are thus unusually active from both a thermodynamic and kinetic viewpoint. Such behaviour is well known in surface chemistry and catalysis, e.g. surface active sites (or centres) are formally defined [28] as protruding atoms (for instance at the apex of a peak) which "share with neighbouring atoms an abnormally small portion of their electrostatic field (or bonding energy) and, therefore, have a large residual field available for chemisorption and for catalysis". The situation at a metastable surface is complicated for a variety of reasons, e.g. (1) control of the state is poor (active states
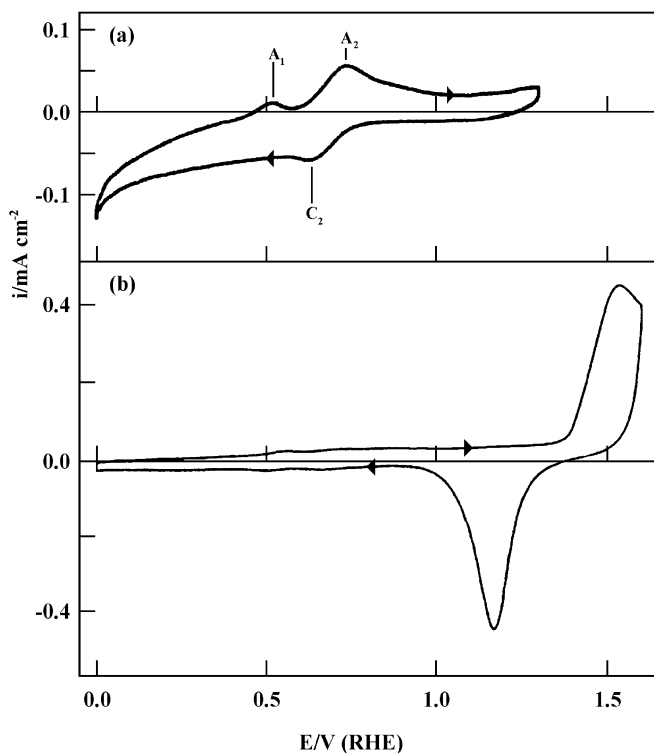
Fig. 7 Cyclic voltammograms (50 mV s^{-1}) for (**a**) a gold CBE in 1.0 mol dm^{-3} H$_2$SO$_4$ at 25 °C (0.0–1.3 V), and (**b**) a conventional gold wire (same batch of metal) under similar conditions (0.0–1.6 V)

are highly variable and intrinsically unstable; precise reproduction of a given disordered state is virtually impossible); (2) the state is likely to alter with time [7, 8, 9] and with use, e.g. on cycling (Fig. 2); (3) at a given surface there are likely to be a range of discrete active species, e.g. terrace adatoms, ledge and kink atoms, surface microclusters [5]; some of these species, e.g. migrating adatoms, may be of a transient character.

Attention may be drawn here to earlier work on both thermally [29, 30] and cathodically [25, 31] pretreated (or activated) gold; in the case of the earlier thermal activation the heating was done electrically, the metal was not cooled from the molten state and hence the activation was less marked. However, in all cases, dramatic premonolayer oxidation, i.e. surface oxidation responses within the double layer region, were observed. Earlier thermodynamic calculations [25] indicated that an isolated gold atom (with no lattice stabilization energy) should undergo oxidation in acid solution (to hydrated Au$_2$O$_3$) at ca. 0.33 V. The maximum for the main anodic peak in Fig. 1 coincides with the latter value, but peaks A$_1$ and A$_2$ clearly occur at lower potentials. However, the response shown in Fig. 1 is for active gold in base and if the oxide is hydrated the transition in question, Au$_1$/Au$_2$O$_3$(hydr.), may exhibit a super-Nernstian E/pH shift [27], i.e. its potential will decrease (in terms of the RHE scale) by $\triangle$pH{0.5(2.3RT/F)}, i.e. from 0.33 V to 0.33−13{0.5×0.059}≈−0.05 V, on changing from an

acidic to a basic solution ($\triangle$pH≈13, T = 298 K). This agrees rather well with the peak maximum potential (−0.04 V) quoted above for A$_1$ in Fig. 1. A degree of caution is required here, e.g. the thermodynamic data for the oxide relates to the bulk state of the latter. However, the agreement between the thermodynamically calculated and observed values is remarkable; in the case of A$_3$ the super-Nernstian E/pH shift may not occur, i.e. the oxide involved may be less hydrated, and the oxide formed may not be anionic [27], due to repulsion effects [the oxide coverage involved in the case of A$_3$ being quite high; under such circumstances the high-energy active state transition should occur at the same potential, ca. 0.33 V (RHE), in base as in acid].

It is evident from the above argument that pre-monolayer oxidation behaviour is a complex topic, this complexity being due not only to the existence of different active states of the metal surface but also due to the possible formation of different types of oxy species. Another surprising aspect in Fig. 1 is the size of the main premonolayer oxidation peak (A$_3$) compared with the conventional monolayer oxidation peak (A$_4$). It appears that the surface coverage of active gold is very high, possibly well above the monolayer level. Such a state may involve a relatively stable surface covered with highly active gold microclusters (microscopy work on the morphology of CBE surfaces is currently in progress; details will be published later). In simple terms, the data shown in Fig. 1 may be regarded as follows. There is an unusually high coverage of highly active gold atoms resting, mainly in cluster form, on a relatively stable gold surface. The latter yields the monolayer oxide response, peaks A$_4$ and C$_4$. The highly active atoms yield peak A$_1$ (and possibly A$_2$, which is more evident in the first sweep in Fig. 2) when reacting under super-Nernstian conditions and A$_3$ when super-Nernstian behaviour is absent. All these transitions display hysteresis behaviour which is not unusual for metal/metal oxide interconversions. It may be noted also that there is a significant difference between the charge versus sweep rate plots (for the same experiments) in the case of oxide formation (Fig. 3) and oxide reduction (Fig. 4) reactions. It seems that in the case of oxidation all the superactive atoms undergo reaction; Q_p is virtually independent of sweep rate over the sweep rate range involved. However, in the case of reduction, Q_p dropped significantly as the sweep rate was increased. Hydrous oxides are rather low density materials [27] and if this material is produced as clusters, reduction at the underlying gold surface may leave residues of the clusters, especially at high sweep rates, in poor contact with the electrode. Note also that the rate of peak current increase with sweep rate for reduction (Fig. 4a) decreases as the sweep rate is increased.

Generally, for a fast reversible surface redox transition, peak potentials and charge values should be independent, while peak current density should be a linear function, of sweep rate [32]. The data shown in Figs. 3 and 4 suggest that the main premonolayer gold responses (peaks A$_3$ and C$_3$) are reasonably rapid with the

following important qualifications: (1) the surface transition is not reversible in the thermodynamic sense as the species involved are in non-equilibrium states; (2) there is significant hysteresis (recent, as yet unpublished, data obtained in this laboratory indicates that such hysteresis is much less marked with less active, or lower oxide coverage, gold surfaces); (3) reduction of high coverage oxide films may be slow to go to completion, apparently due to partial loss of contact at the electrode surface.

The data obtained in the present investigation indicate that the loss of the superactive surface state (especially in the absence of potential cycling) is surprisingly slow. It is assumed that while there is a gradual decay, surface dynamics provides a means of excess energy retention; atoms move to sites of lower energy (adatoms → kink atoms → ledge atoms, and microclusters grow in size); however, such changes may be partially reversed (and hence the elements of the highly active state are retained) due to thermal vibrations. A basic assumption here is that surface active states are never totally absent; they are invariably present, as low coverage active sites, on all real metal surfaces.

Comparison with earlier work

The responses reported here for cooled bead electrodes, e.g. Fig. 1, are considerably simpler than many of those reported earlier [29, 30] for gold wire electrodes activated by electrical heating, especially in the case of a base electrolyte [30]. In some instances in the earlier work the positive sweep for an electrode, heated initially at 815 °C for 20 s and then subjected to cathodization (at −0.3 V for 3 min), exhibited five reasonably well-resolved anodic peaks, on a broad background, extending over the range 0.0–1.0 V (see Fig. 6 in [30]) (the cell temperature in the latter case was 70 °C). Even without cathodic pretreatment and with the cell at room temperature, the anodic response for the thermally pretreated wire in base were still rather complex (Fig. 2 in [30]), anodic currents being especially marked over the ranges 0.3–0.6 V and 0.7–1.0 V (it is evident from the present work that the choice of lower limit used earlier, 0.0 V, was inappropriate as much of the oxide remains unreduced under potential sweep conditions at the latter value).

It seems that in the production of a CBE, melting the metal and allowing it to cool rapidly converted most of the surface gold atoms into a very high-energy state; hence the major anodic response (Fig. 1) at 0.3–0.4 V. Less severe heating, in some cases combined with cathodization (which is an independent method [25, 31] of surface activation), gave a greater range of surface gold atom energy states, and hence more complex anodic premonolayer oxidation responses [20]. In some important respects the behaviour reported earlier is more significant as it highlights the fact that gold, like silver [16], exhibits a wide variety of surface active states and has a complex active state chemistry that, as outlined

earlier [13], is a vital factor in the catalytic and electrocatalytic behaviour of gold surfaces. Virtually all electrocatalytic responses for gold [13, 14, 15] commence at reasonably well-defined potentials within the double layer region, these responses being triggered by surface active state, mediator generation, reactions which, as with silver [16], occur at different potential values.

Response for the gold CBE in acid

The response for the CBE in acid solution (Fig. 7a) was disappointing for a number of reasons. In earlier work with both cathodically [25, 31] and especially thermally [29] pretreated gold wires in acid solution, much more dramatic premonolayer oxidation responses were observed. Also in the earlier work, cathodic responses were observed in the positive sweep over the range 0.0–0.4 V. Such behaviour was also noted in the present work on changing the lower limit to −0.3 V in N_2-stirred solution (the gas purging was used to minimize interference due to dissolved H_2 gas): the three peaks A_1, A_2 and C_2 remained virtually unaltered but there was an indication of a further oxidation peak at ca. 0.25 V {this new feature was often quite marked initially in the earlier work (see Fig. 6 in [29]), but tended to decay rather rapidly}.

The origin of the cathodic current at the early stages of the positive sweep (this was also observed earlier [29]) for a CBE in acid (but not in base) is uncertain. There may have been some oxygen trapped in pores or pits on the surface (oxygen reduction on gold is much slower in acid as compared with base). Some oxide or sulfate may be present, possibly in poor contact (hence the slow reduction rate) with the electrode surface. The low response for the CBE in acid suggests that the amount of highly active metal present was quite low; some dissolution or oxidation of the outer layer may have occurred prior to the sweep.

Multilayer oxide reduction in base

The most surprising feature of the full line scan in Fig. 5 is the major oxide reduction peak at $E < 0.0$ V; this result supports the view that the cathodic peaks (C_1 and C_2) in the same region in Fig. 1 are a genuine part of gold electrochemistry, even though these responses obviously do not involve stable surface gold atoms at any stage. Such behaviour is not unique to gold; it was demonstrated earlier [33] that hydrous oxide films on platinum in base are virtually impossible to reduce totally at $E < 0.0$ V.

The dotted line response in Fig. 5 demonstrates that the component of the oxide film that undergoes reduction below 0.0 V is a discrete species whose existence is independent of the other components in the hydrous oxide deposit. The material involved is assumed to be unstable with respect to reduction even at 1.2 V; yet it remained on the surface for at least 2 min, as the scan

was recorded over the range 1.2 to 0.0 V at 10 mV s^{-1}, exhibiting only a slight trace of a reduction response beginning at ca. 0.2 V. Rapid reduction commenced just below −0.1 V and the simplest interpretation of the result is that (as outlined here earlier) the primary product of reduction is an isolated, highly active, gold atom and the reaction is affected by the super-Nernstian E/pH behaviour of the oxide.

The result shown for the reduction in acid solution in Fig. 5 supports the view that the component that undergoes reduction at $E < 0.0$ V in base is a gold hydrous, rather than compact, virtually anhydrous, oxide. Hydrous gold oxide films in aqueous acid solution usually undergo reduction just after the end of the monolayer oxide reduction reaction [34], although in some cases the response may be more complicated than that observed here. The peak for reduction in acid is rather small compared with its equivalent for base (dotted line in Fig. 5); also, the reduction in acid occurred at a potential higher than expected simply in terms of the super-Nernstian E/pH shift. It is possible that on transfer to acid solution the reactive hydrous oxide deposit (which is assumed to be a hyperextended low-density material [27]) underwent rearrangement and partial dissolution.

The reduction scan for the d.c.-grown multilayer gold oxide deposit shown in Fig. 6 is included to demonstrate that different reactions (based on different states of the metal or oxide), over the range 1.0 to 0.0 V, may occur in a discrete manner; this seems to be especially relevant to electrocatalysis. The latter topic, with regard to gold in aqueous media, was reviewed recently [5, 13, 15] so that only the following points will be made here, viz.:

1. Electrocatalytic processes at gold electrodes, as surveyed using cyclic voltammetry techniques, almost invariably commence and terminate at reasonably well-defined potentials within the double layer region. Premonolayer oxidation reactions occur in the same region and it is not unreasonable to assume that these two quite different types of reaction are interrelated (the latter providing the interfacial mediators for the former [5, 13]). Since electrocatalytic processes are often carried out with conventional (rather than superactivated) gold, it is assumed that there are invariably low-coverage highly active metal atoms present at active sites on gold surfaces and that such atoms are the essence of the electrocatalytic behaviour of this metal.

2. A representative range of electrocatalytic responses for gold in base was outlined earlier (see Fig. 3 in [13]). Oxidation of formaldehyde commenced just above 0.0 V, i.e. in the region of peak (d) in Fig. 6 or peak A_2 in Fig. 1 (in both cases the same active state of gold is assumed to be involved, but the transition evidently occurs in a cyclic manner in the course of electrocatalysis). Oxidation of hydrazine at the same electrode commenced just above 0.4 V, i.e. in the region of peak (c) in Fig. 6. Finally, ethylene glycol

oxidation commenced at ca. 0.8 V, with a steep increase over the range 0.85–1.15 V; note that, in Fig. 6, peak (b) also commences at ca. 0.8 V and there is a definite (but low-level) response over the range 1.0 to 0.8 V. All the responses in Fig. 6 are cathodic; it is assumed that in the electrocatalytic oxidation processes the same type of reactions occur in a reversible manner. The present authors are unaware of any electrocatalytic reaction on gold in base that commences at $E < 0.0$ V, i.e. in the region of peak (e); the level of activity of the gold atoms involved in the latter region is regarded as abnormally high, i.e. this surface state is normally unoccupied.

3. Premonolayer oxidation responses are often very small (the surfaces being unactivated) and tend to be attributed to the presence of trace impurities. We regard the latter view as incorrect: the responses observed in the present work were quite substantial, e.g. the first sweep in Fig. 1; at least one of the features of the CBE response in base (oxide reduction at $E < 0.0$ V) was reproduced using a thermally unactivated gold wire electrode (Fig. 5); premonolayer oxidation and electrocatalytic responses commencing in the double layer region seem to be closely related (as outlined recently also for silver [16]); unactivated gold wire electrodes scanned with our equipment and solution (as in Fig. 1) gave a conventional response (Fig. 7b); there is no evidence (or need to invoke) the presence of an impurity.

Influence of time (and use, e.g. potential cycling) on surface reactivity

The outer layers or surface of a metastable metal electrode may alter with time as the system tends to spontaneously shed its excess energy. As demonstrated in recent AFM investigations [9], this process is not simply just a matter of grain growth; the particle size of the rearranged (and obviously more stable) deposit on the surface was found to be smaller than in the original layer. This is not inexplicable; the initially larger particles may be of quite high energy content due to the presence of many internal defects. In the course of rearrangement (which involves atom migration and also exhibits an induction period [9]), smaller, but less defective (and hence lower energy), grains are produced, but the surface energy may be increased due to (1) increased surface area and (2) an increase in the coverage of high energy atoms on the particle surface.

There are at least two reports (both involving platinum) where abraded, cycled or cathodized, i.e. activated, surfaces underwent dramatic changes in redox [35] and electrocatalytic [36] behaviour following a prolonged rest in air. Dramatic changes in the activity of gold surfaces with regard to oxygen gas reduction in base were also reported by Paliteiro [37]. In the first

instance with gold, the change (or activation) was induced by potential cycling which involved hydrogen gas evolution at the lower limit (with a preabraded surface); in the second case the gold surface was subjected simply to mild hydrogen gas evolution. The change in oxygen reduction behaviour (which in most cases occurred gradually [37], e.g. while the electrode rested in air) may be attributed to decay of the active state generated, e.g. as a result of cathodic activation, in the pretreatment stage. Such independent work highlights the fact that changes in the activity, or metastability, of a metal electrode surface can easily arise (for apparently inexplicable reasons) and significantly affect the electrocatalytic performance of the electrode. Perhaps more importantly, it demonstrates that the electrocatalytic activity of a metal surface is variable. It is assumed to be controlled by the nature and coverage of the active sites present, which in turn are influenced by a wide range of factors, e.g. electrode fabrication, pretreatment, resting time, type of reaction being catalysed, etc.

Paliteiro's work [37] is also interesting from another viewpoint: he pointed out the presence of four small peaks within the double layer region of cyclic voltammograms recorded for polycrystalline gold in base, the peak at ca. 0.3 V (A_3 in the present Fig. 1) becoming more reversible following electrode activation. However, the most dramatic change in his case involved the peak at ca. 0.9 V (the latter transition is quite evident in earlier work, involving relatively mild thermal pretreatment, reported [30] from this laboratory). Paliteiro also accounted for the electrocatalytic activity of gold in base in terms of premonolayer oxidation phenomena.

Conclusions

1. Metastable, intrinsically disordered, states of metals are a major aspect of metallurgy [2] and their importance in surface catalysis has already been stressed [13]. The low level of interest in this active state area of noble metal surface electrochemistry is surprising, especially as the use of electrochemical techniques have much to offer in this field.
2. The unusual catalytic properties of gold nanoparticles, as demonstrated by Haruta and co-workers [38], cannot be explained in terms of the conventional, activated chemisorption, viewpoint. There is a need for a new approach in the area, based on the active surface state behaviour [5], but the latter is in need of much further investigation.
3. The ability to oxidize gold atoms at an electrode surface in base below 0.0 V (or even at 0.3 V, Fig. 1) is remarkable, as is the presence of a major gold oxide reduction peak in the same region (Fig. 5). Conventional accounts of gold electrochemistry are not invalid; however, they relate only to low-energy surfaces and by omitting detailed discussions of topics such as active surface states of the metal,

hydrous oxides, premonolayer oxidation and the role of these in electrocatalysis, they tend to restrict the scope for new developments. In particular, the possibility of modifying, i.e. disordering, metal surfaces with a view to optimizing their performance for a particular electrocatalytic application is a very attractive proposition, especially in the fuel cell area. The upsurge of interest in heterogeneous catalysis by supported gold nanoparticles [11], triggered by the work of Haruta and co-workers [38], is an indication of the scope for similar endeavours in electrocatalysis.

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