

L. Declan Burke · Anthony P. O'Mullane

Generation of active surface states of gold and the role of such states in electrocatalysis

Received: 26 July 1999 / Accepted: 7 September 1999

Abstract The cyclic voltammetry behaviour of gold in aqueous media is often regarded in very simple terms as a combination of two distinct processes, double layer charging/discharging and monolayer oxide formation/removal. This view is questioned here on the basis of both the present results and earlier independent data by other authors. It was demonstrated in the present case that both severe cathodization or thermal pretreatment of polycrystalline gold in acid solution resulted in the appearance of substantial Faradaic responses in the double layer region. Such anomalous behaviour, as outlined recently also for other metals, is rationalized in terms of the presence of active metal atoms (which undergo premonolayer oxidation) at the electrode surface. Such behaviour, which is also assumed to correspond to that of active sites on conventional gold surfaces, is assumed to be of vital importance in electrocatalysis; in many instances the latter process is also quite marked in the double layer region.

Key words Gold · Active states · Hydrous oxide · Premonolayer oxidation · Electrocatalysis

Introduction

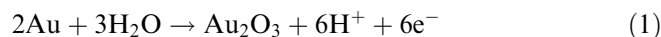
In a number of recent publications from this laboratory [1–4] it was pointed out that the electrochemical responses of solid metal electrodes in aqueous media may be affected (in some cases quite dramatically [1, 3]) by the procedures used for electrode surface pretreatment. The principle involved is simple; the pretreatment processes involve an insertion of energy into the sample and some of this energy is retained by the metal (and espe-

cially by atoms at both the surface and the outer layers of the lattice) in the form of various types of defects, e.g. adatoms, vacancies, microclusters, grain boundaries, etc. These constitute an active, metastable state of the metal and some of these thermodynamically unstable entities yield a most unusual (or anomalous) electrochemical response that correlates quite well with active site behaviour and electrocatalysis [2, 5].

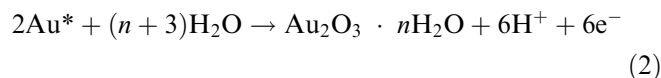
In simple terms, metal surfaces display two types of electrochemical behaviour, viz.

1. The conventional response. This is well known [6] for the noble metals and is assumed to relate to relatively high co-ordination or well embedded surface metal atoms which on anodic oxidation in aqueous media yield a monolayer (or α) oxide species.
2. The anomalous response. This relates to low co-ordination, protruding metal atoms or clusters of same; such active species have a low lattice stabilization energy, undergo oxidation at a low potential, i.e. exhibit premonolayer oxidation behaviour, and are assumed to yield a different oxidation product, namely hydrous (or β) oxide species [7].

With regard to gold, this means that if the surface is non-ideal or heterogeneous there are at least two types of electrochemical transitions involved in surface oxidation, viz.



and



where Au^* symbolizes a protruding active gold atom, Au_2O_3 the α oxide and $\text{Au}_2\text{O}_3 \cdot n\text{H}_2\text{O}$ the β oxide. This is a simplified view; recorded responses may well be more complicated since the lattice co-ordination number (or the activity of Au^*) is quite variable and not easily predetermined or controlled, and the nature of the β oxide is also variable (no distinction is made here

between oxides and hydroxide, i.e. -O- and -OH ligands; at least three distinct forms of gold β oxide apparently exist [8]).

Conventional accounts of gold electrochemistry [6, 9] are concerned mainly with the double layer and Au/ α oxide behaviour (the latter is in reasonable agreement with conventional thermodynamic data for this metal [10]). While such descriptions are apparently valid for low-energy, relaxed gold surfaces, they ignore the possible presence of active gold atoms at the interface, which in many cases are the basis of active site behaviour [11] and electrocatalysis [12, 13]. As outlined in a recent review of gold electrochemistry [12, 13], there is now substantial evidence from reputable independent authors, e.g. Gerischer [14], Weaver [15], Horanyi [16] and Johnson [17], that oxy species may be adsorbed or generated at gold/aqueous solution interfaces at potentials that are significantly lower than the commencement of the α oxide formation reaction.

The present work is concerned with gold in aqueous acid solution. Two independent surface activation techniques were employed. In the first the surface was subjected to extended cathodization, typically -0.20 to -0.60 V for 20–30 min; there is independent evidence involving the use of iron electrodes in base [18] that such pretreatment activates metal surfaces with regard to oxidation at low potentials. In the second case, thermal pretreatment was employed; again there is recent evidence [4] that heating a metal surface, followed by rapid cooling, results in the trapping (or freezing-in) of unusually high-energy surface metal atom states.

Experimental

The working and counter electrodes usually consisted of lengths of gold wire (1.0 mm diameter, ca. 0.8 cm^2 exposed area, Johnson Matthey, Puratronic grade) sealed directly into soda glass. The working electrode was usually pretreated prior to use by mild abrasion with fine grade Emery paper followed by washing the surface with triply distilled water. The gold rotating disc electrode system (EG + G, PAR, model 616) and the pretreatment of the disc surface were described earlier [5]. The electrode potential was usually cycled (0 – 1.80 V at 50 mV s^{-1}) in the acid electrolyte until the conventional cyclic voltammetric response for gold in acid solution (see Fig. 1) was observed.

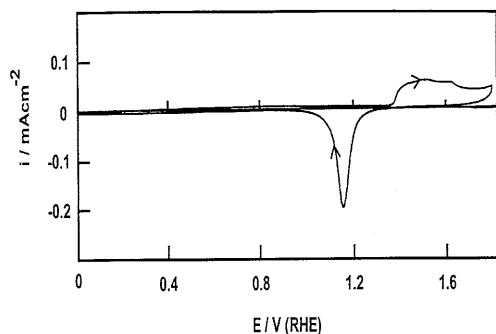


Fig. 1 Cyclic voltammogram (0.00 – 1.80 V, 50 mV s^{-1}) for a non-activated gold wire electrode in $1.0 \text{ mol dm}^{-3} \text{ H}_2\text{SO}_4$ at 25°C

The potential of the working electrode was recorded and is reported with respect to a reversible hydrogen electrode (RHE) [$p(\text{H}_2) = 1.0 \text{ atm}$] in the same solution but in a separate vessel which was connected to the working electrode compartment via a Luggin capillary. Solutions were made up using high-purity (Analar grade) chemicals and triply distilled water. All solutions were purged with oxygen-free nitrogen before and sometimes during use. Cyclic voltammograms were obtained with the aid of a potentiostat (Wenking, model LT-78), a function generator (Metrohm, E612) and an X-Y recorder (Rikadenki, RW21). The plots were subsequently transferred, with the aid of a scanner, to a computer and are reproduced directly here.

Results

Responses for a cathodically polarized gold wire in acid solution

A typical cyclic voltammogram for an untreated gold wire electrode in aqueous acid solution is shown in Fig. 1. This response is conventional [6]; the positive sweep was featureless until the onset at ca. 1.36 V of monolayer oxide film formation. On the subsequent negative sweep this monolayer oxide film was reduced over the potential range of 1.30 to 1.00 V; the hysteresis between the oxide formation and the reduction response is quite evident. This was followed by the usual double layer region extending to the end of the sweep at 0.00 V.

The effect of prolonged cathodic polarization at $E \leq 0.00$ V was investigated using both gold wire and rotating disc electrodes. This electrochemical treatment gave rise to unusual behaviour, an example of which is shown in Fig. 2 for a gold wire electrode prepolarized at -0.60 V for 20 min. On the first positive sweep, cathodic current was observed initially over the range 0.00 – 0.20 V; this was followed by a major anodic peak ($E_p = 0.42$ V) which was quite a broad feature, extending

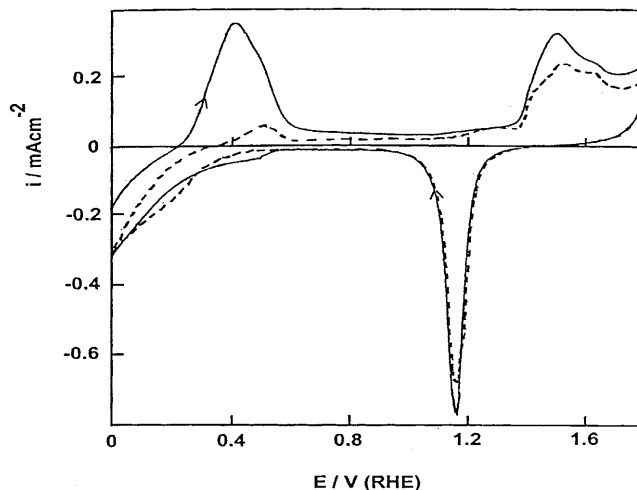


Fig. 2 Cyclic voltammogram (0.00 – 1.80 V, 50 mV s^{-1}) for a gold wire electrode, prepolarized at -0.60 V for 20 min, in $1.0 \text{ mol dm}^{-3} \text{ H}_2\text{SO}_4$ at 25°C . The second sweep for the same electrode is indicated by a dashed line

over the potential range 0.22–0.60 V. A relatively large flow of anodic current was observed over the range 0.60–1.10 V. The significant increase in anodic current at ca. 1.10 V is assumed (as discussed later) to be of relevance with regards to electrocatalysis. Finally, there was a large upsurge in anodic current at ca. 1.36 V which corresponds to the onset of monolayer oxide film formation as observed with conventional, unactivated gold (Fig. 1).

On the subsequent negative sweep the monolayer oxide response was observed at the usual potential of ca. 1.16 V. Below this region the normal double layer response was observed until, at ca. 0.56 V, there was a substantial increase in cathodic current. The magnitude of this response increased with decreasing potential right down to the lower end of the sweep at 0.00 V.

On the second sweep (illustrated by the dashed line in Fig. 2) the anodic peak at ca. 0.50 V was much smaller but this feature was quite persistent in that it continually appeared on repeated cycling of the electrode potential. One procedure for eliminating this feature was extensive repetitive cycling (typically 0.00–1.00 V at 50 mV s^{-1} for 30 min). The premonolayer oxidation response above 1.10 V was more obvious in the second sweep and the overlapping features in the monolayer oxide region were slightly more distinct. The charge in the monolayer oxide formation region was slightly lower in this second sweep but the cathodic response below 0.50 V on both the positive and negative sweeps was still quite evident; in general there was little change in this region on going from the first to the second sweep.

Further examples of responses obtained after subjecting the gold wire electrode to 10 min periods of polarization at various potentials within the range of -0.30 to -0.50 V are shown in Fig. 3. Two anodic peaks, one at ca. 0.30 V and another at ca. 0.51 V, with a minor increase at ca. 0.14 V, are evident in Fig. 3a. Note the absence of cathodic current flow below ca. 0.40 V, evident in Fig. 2, in this case. Only one anodic peak at ca. 0.52 V is present in the double layer region in the other two responses shown in Fig. 3. A notable feature of these responses is that on decreasing the prepolarization potential a significant increase in magnitude of both the anodic peak at ca. 0.52 V on the positive sweep and the cathodic responses from 0.00 to 0.30 V in the positive and negative sweep were observed.

A summary of the effect of sweep rate on the voltammetric response associated with the anodic peak at low potential is illustrated in Fig. 4. The peak charge decreased slightly (Fig. 4a), but the peak maximum potential remained virtually constant (Fig. 4c) with increasing sweep rate. The peak current density (Fig. 4b) increased significantly, though not linearly, with increasing sweep rate. The cathodic current response within the range 0.00–0.30 V on both the positive and negative sweeps increased in a non-linear fashion with increasing sweep rate.

Other unusual responses, which bore a slight similarity (at least at $E < 0.30$ V) to those shown in Fig. 2, are outlined in Fig. 5. These cyclic voltammograms were

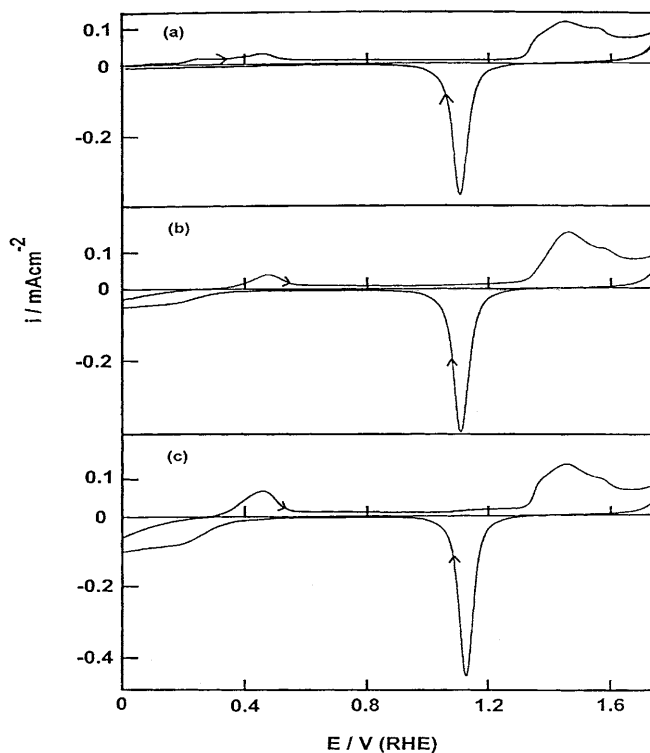


Fig. 3 Cyclic voltammograms (0.00 – 1.80 V, 50 mV s^{-1}) for a gold wire electrode, prepolarized at **a** -0.30 V, **b** -0.40 V and **c** -0.50 V for 10 min in each case, in $1.0 \text{ mol dm}^{-3} \text{ H}_2\text{SO}_4$ at 25°C

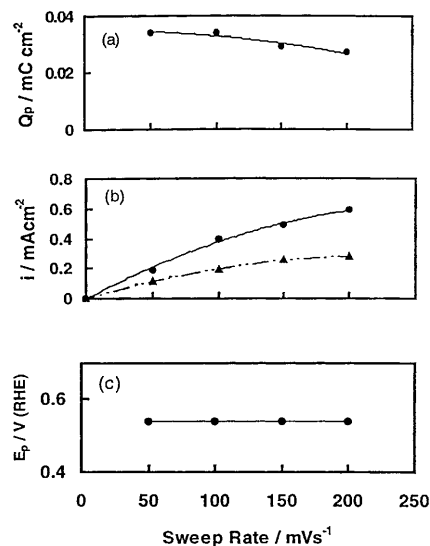


Fig. 4 Effect of sweep rate on **a** peak charge (Q_p), **b** peak current density (i), *full line*, and **c** peak potential (E_p) for the anodic peak in the positive sweep at ca. 0.50 V. The *broken line* in **b** refers to the current density at $E = 0.20$ V in the subsequent negative sweep. All data are from the first cycle and are for a gold wire electrode, prepolarized at -0.30 V for 15 min in each case, in $1.0 \text{ mol dm}^{-3} \text{ H}_2\text{SO}_4$ at 25°C

recorded for a wire electrode which had been used for repeated cathodic polarization and cycling experiments (as summarized here in Fig. 3 and Fig. 4) but then

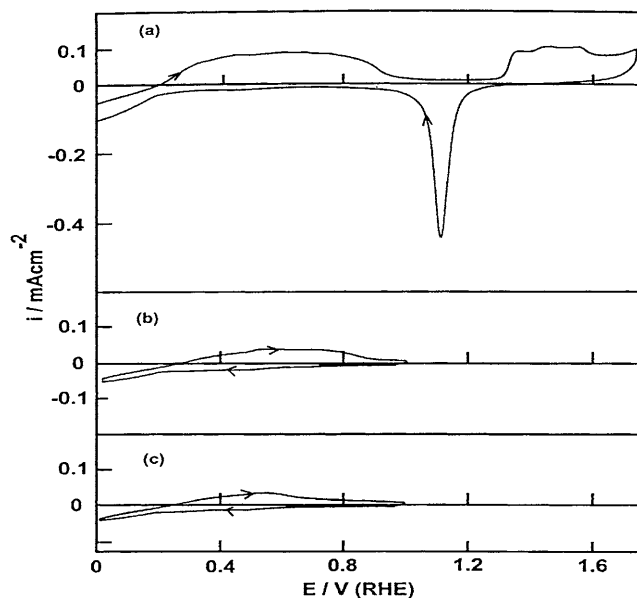


Fig. 5 Cyclic voltammograms (50 mV s^{-1}) for a gold wire electrode in $1.0 \text{ mol dm}^{-3} \text{ H}_2\text{SO}_4$ at 25°C ; this electrode was subjected to extensive cathodic polarization and repetitive cycling followed by a rest period in air of 60 h: **a** first sweep (0.00–1.80 V), **b** 15th sweep (0.00–1.00 V) and **c** 40th sweep (0.00–1.00 V)

allowed to rest in air for ca. 60 h. A large envelope of anodic charge was observed over the potential range 0.26–1.00 V; this premonolayer charge in Fig. 5a was substantially greater than that associated with monolayer oxide formation. On the subsequent negative sweep the monolayer oxide was reduced at ca. 1.16 V and this was followed by the normal double layer region until at ca. 0.30 V an increase in cathodic current was observed. The anodic charge in the positive sweep decreased slowly with repetitive cycling; the effect is illustrated in Fig. 5b and c, where scans are shown for a reduced upper limit of 1.00 V. The response was persistent; it was still evident after 40 cycles between the reduced limits. Extensive repetitive cycling was required to completely eliminate this response (0.00–1.00 V at 50 mV s^{-1} for 30 min).

The cathodic response below ca. 0.30 V was usually recorded in the present work following cathodic prepolarization. However, this feature was also observed when the electrode was not prepolarized. Responses are shown in Fig. 6 for sweeps carried out in succession with the same electrode, with no intermediate surface treatment, in which the upper limit of the sweep was increased in a series of steps from 0.90 to 1.80 V. With low upper limit values (0.90–1.20 V) the behaviour was almost ideal, i.e. quite close to that shown in the double layer region in Fig. 1. However, when the upper limit was raised above that corresponding to the onset of monolayer oxide formation at ca. 1.36 V, cathodic currents appeared in the region below ca. 0.30 V. There was even an indication of the anodic peak at ca. 0.50 V (see the arrow in Fig. 6d) in the positive sweep. The solutions used in these experiments were continuously purged with pure N_2 gas to remove

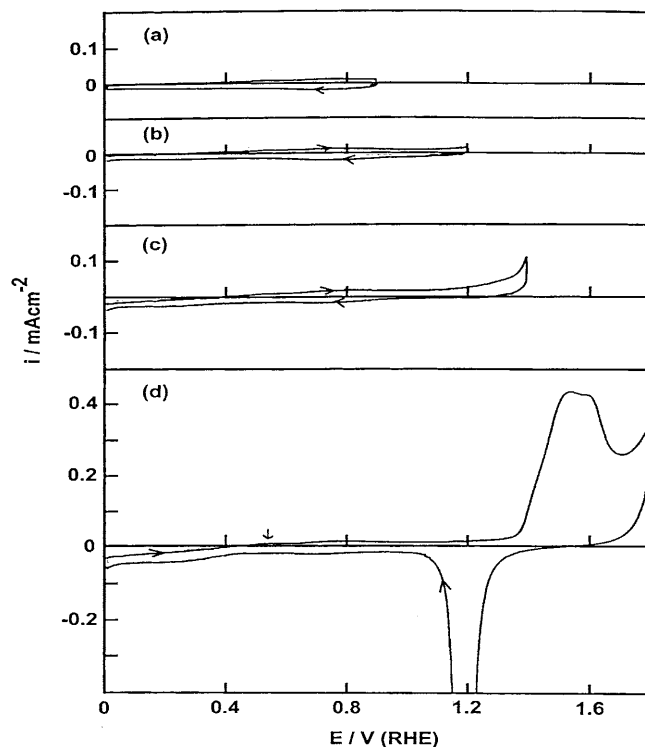


Fig. 6 Cyclic voltammograms (50 mV s^{-1}) recorded for a non-activated gold wire electrode in $1.0 \text{ mol dm}^{-3} \text{ H}_2\text{SO}_4$ at 25°C : **a** 0.00–0.90 V, **b** 0.00–1.20 V, **c** 0.00–1.40 V and **d** 0.00–1.80 V

dissolved oxygen (the reduction of the latter also results in a cathodic response at low potentials). The results outlined in Fig. 6 demonstrate that the cathodic currents below 0.30 V, as observed here also in other experiments, are unlikely to be due to some type of reducible impurity deposited on the gold surface under cathodic conditions, i.e. such responses appear without precathodization and seem to be an intrinsic part of gold electrochemistry.

Effect of cell solution temperature

The unusual effects reported here for gold electrodes precathodized in acid solution were significantly enhanced by raising the solution temperature (Fig. 7). In each case the electrode was cycled initially (0.00–0.80 V at 50 mV s^{-1} for ca. 30 min) until the conventional response (Fig. 1) was observed. Then the electrode was polarized for 15 min at -0.40 V with the solution at the appropriate temperature and the voltammograms were recorded with the electrode in the same (deoxygenated) solutions. Notable features of the results shown in Fig. 7 are the following, viz.

1. The cathodic currents below ca. 0.50 V were significantly enhanced, as were (less dramatically) the anodic currents above 0.50 V in the double layer region of the positive sweep. The anodic peak in the latter at ca. 0.50 V was usually observed; it increased markedly on going from 25 to 50°C but was surprisingly small at 75°C .

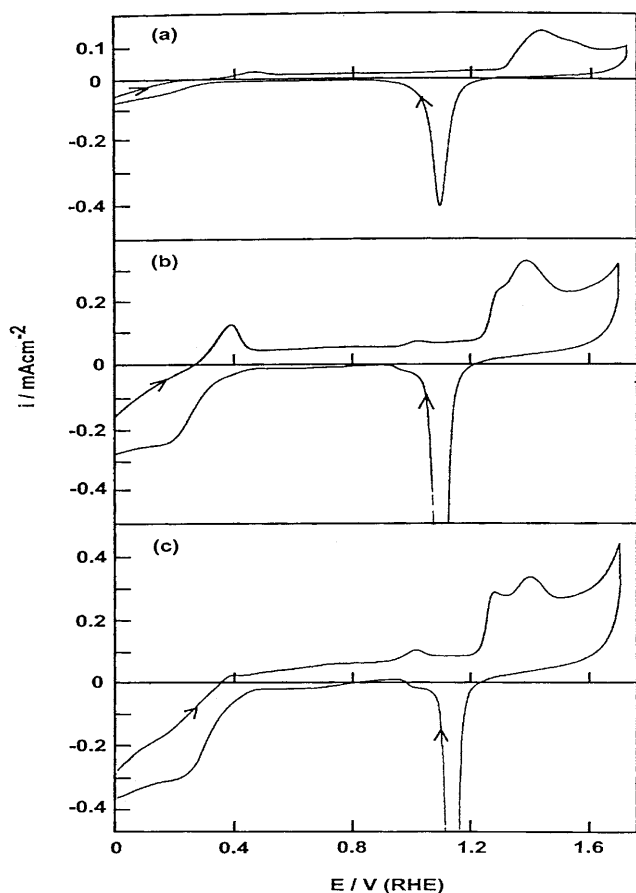


Fig. 7 Effect of solution temperature on cyclic voltammograms (0.00–1.80 V, 50 mV s^{-1}) recorded for a gold wire electrode, prepolarized at -0.50 V for 15 min in $1.0 \text{ mol dm}^{-3} \text{ H}_2\text{SO}_4$ at **a** 25°C , **b** 50°C and **c** 75°C

2. New features emerged on raising the operating temperature, e.g. a small anodic peak on the positive sweep just above 1.00 V , plus a decrease in cathodic current in the same region in the negative sweep. Also, the current increase at the start of the monolayer oxide formation process was much sharper at the higher temperatures; a poorly resolved anodic peak emerged progressively in this region as the solution temperature was increased.
3. The charge for monolayer oxide formation above ca. 1.30 V increased with increasing temperature and the subsequent oxide reduction peak at ca. 1.20 V was sharper. There was a significant difference in charge values in this region (most obvious here in Fig. 7a); the anodic charge in the positive sweep (at $E > 1.00 \text{ V}$) exceeded the cathodic charge over the region 1.2 to 0.9 V in the subsequent negative sweep.

Responses for a cathodically polarized gold RDE in acid solution

Examples of cyclic voltammograms recorded for the rotating disc electrode (RDE) in acid solution after extended polarization of the electrode surface at various

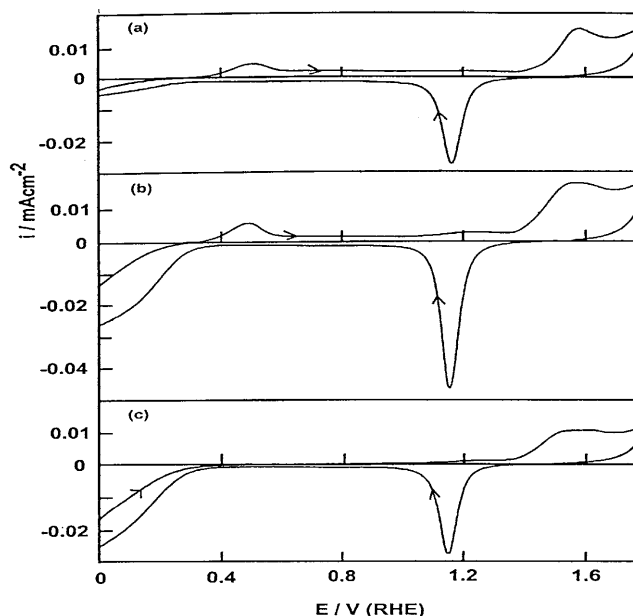


Fig. 8 Cyclic voltammograms (0.00–1.80 V, 50 mV s^{-1}) for a gold RDE (500 rpm), prepolarized at **a** -0.20 V , **b** -0.40 V and **c** -0.50 V for 30 min, in $1.0 \text{ mol dm}^{-3} \text{ H}_2\text{SO}_4$ at 25°C

potentials are shown in Fig. 8. In all cases, significant cathodic current was observed over the range 0.00 – 0.30 V in both the positive and negative sweeps after the electrode had been prepolarized within the range -0.20 to -0.50 V . The anodic peak at ca. 0.50 V was observed in most cases, as was the premonolayer oxidation response at ca. 1.1 V . The magnitude of the cathodic response below ca. 0.30 V usually increased, but not dramatically, as the prepolarization potential was decreased over the range -0.20 to -0.50 V . Usually this cathodic response increased significantly for prepolarization periods of up to 10 or more minutes. It should be noted that attaining this maximum or constant response was much more facile with gold wire in that polarization periods of only 10 min were required compared to 30 min periods for a similar maximum response in the case of the RDE.

Responses recorded subsequent to prepolarizing the RDE at potentials within the range 0.00 to -0.10 V (Fig. 9) were also rather unusual. The time used for activation in these experiments, 1.0 h, was rather long. The magnitude of the cathodic current below ca. 0.30 V was rather low and the peak at ca. 0.50 V in the positive sweep (see Fig. 8) was not observed. However, there was a substantial increase in anodic current (most obvious in Fig. 9b where a maximum is evident at ca. 1.00 V) in the positive sweep. Furthermore, the large increase in anodic current at the onset of the monolayer oxide formation, which is usually observed at ca. 1.36 V (see Fig. 1), occurred in Fig. 9 only above ca. 1.46 V . The charges associated with monolayer oxide formation and reduction in Fig. 9a were significantly lower than those in Fig. 9b; the values for reduction were ca. 0.021 and 0.045 mC cm^{-2} , respectively.

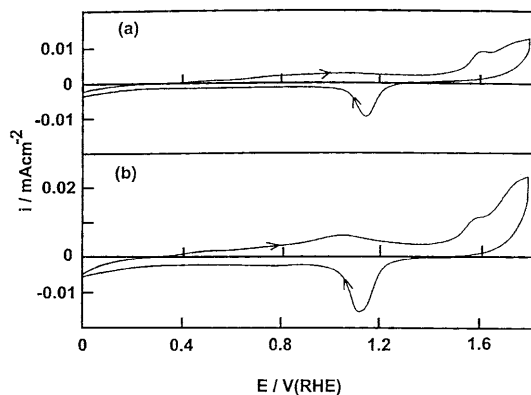


Fig. 9 Cyclic voltammograms (0.00–1.80 V, 50 mV s^{-1}) for a gold RDE (500 rpm), prepolarized at **a** 0.00 V and **b** -0.10 V for 60 min, in $1.0 \text{ mol dm}^{-3} \text{ H}_2\text{SO}_4$ at 25°C

Responses for thermally pretreated gold wire electrodes in acid solution

Severe thermal pretreatment, followed by rapid cooling, is a very effective technique [4] for generating and freezing-in highly active states of metal surfaces. The present work in this area is preliminary; it is included here to demonstrate that the unusual response in the double layer region is not confined to precathodized samples.

The first example of the effect of thermal pretreatment is shown in Fig. 10a. This was recorded for a freshly sealed electrode which was not precathodized; the surface was activated inadvertently in the course of heat sealing the gold wire into the end of the soda glass tube or electrode holder. Note the anodic peak in the positive sweep at ca. 0.32 V and the shoulder at ca. 0.50 V; similar behaviour in this region is shown in Fig. 3a; the charge values and peak ratios involved are different. Appreciable cathodic currents are also evident at low potentials in both the positive and negative sweep, despite the absence in this case of precathodization (or hydrogen) pretreatment.

The effect of a more intensive thermal pretreatment of the gold (in this case the wire was heated to its melting point and the resulting gold bead, still attached to the holder, was allowed to cool rapidly in air) is shown in Fig. 10b. Anodic peaks are still evident at ca. 0.36 and 0.54 V in the positive sweep, along with cathodic currents below 0.20 V. However, the anodic response over most of the positive sweep was unusually large, as was the cathodic response below 0.70 V on the negative sweep. The maxima of the ill-defined peaks in the double layer region in Fig. 10b occurred at ca. 0.36, 0.54, 0.70 and 1.10 V (positive sweep) and at ca. 0.66, 0.48 and 0.15 V (negative sweep). A more complete investigation of thermally pretreated gold is currently close to completion and the results will be reported shortly.

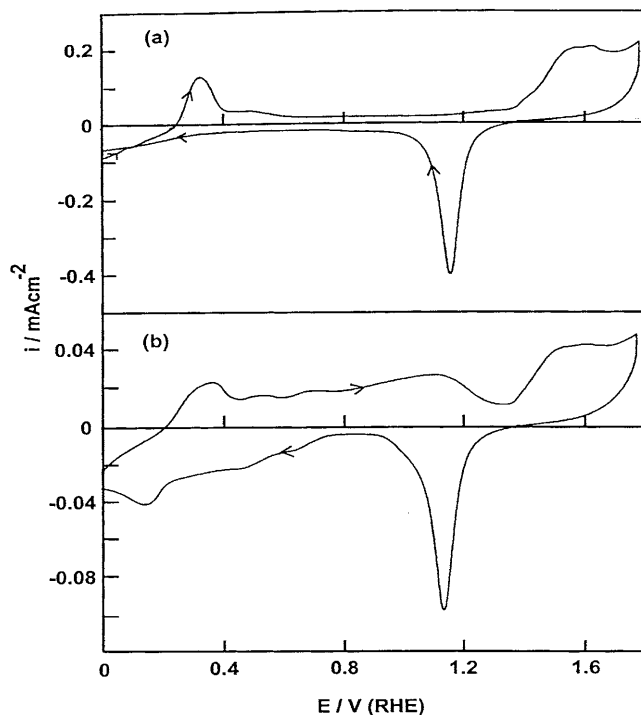


Fig. 10 Cyclic voltammograms (0.00–1.80 V, 50 mV s^{-1}) of gold in $1.0 \text{ mol dm}^{-3} \text{ H}_2\text{SO}_4$ at 25°C : **a** a freshly sealed wire electrode and **b** the exposed gold wire was melted in a natural gas/oxygen flame and the resulting bead electrode allowed to cool rapidly in air

Some electrocatalytic processes on gold in acid solution

Gold in acid (as compared to base) solution is not a very active electrode system from an electrocatalytic viewpoint [12, 13]. This is borne out here by the responses shown for gold in acid solution containing either dissolved oxygen (Fig. 11a) or hydrogen peroxide (Fig. 11b). In both cases the electrode was not preactivated and the cathodic currents observed below ca. 0.50 V are assumed to be due largely to the reduction of the dissolved oxidants. In both cases the rate of reduction was sluggish; the anodic peak in the positive sweep at ca. 0.50 V, which is quite distinct in Fig. 11a, is totally absent in Fig. 11b. In the case of oxygen (Fig. 11a), there was a minor peak or shoulder in the negative sweep at ca. 0.30 V; the rate of oxygen gas reduction increased significantly as the potential was decreased in the region below the latter value.

The only other unusual feature in Fig. 11 is the anodic response due to peroxide oxidation above ca. 1.00 V. In the region just above 1.36 V (positive sweep) there is a slight change of slope and then a maximum at ca. 1.50 V; the monolayer oxide obviously inhibited the peroxide oxidation process. There is an indication of a peroxide oxidation response in the negative sweep at potentials just below the monolayer oxide reduction region.

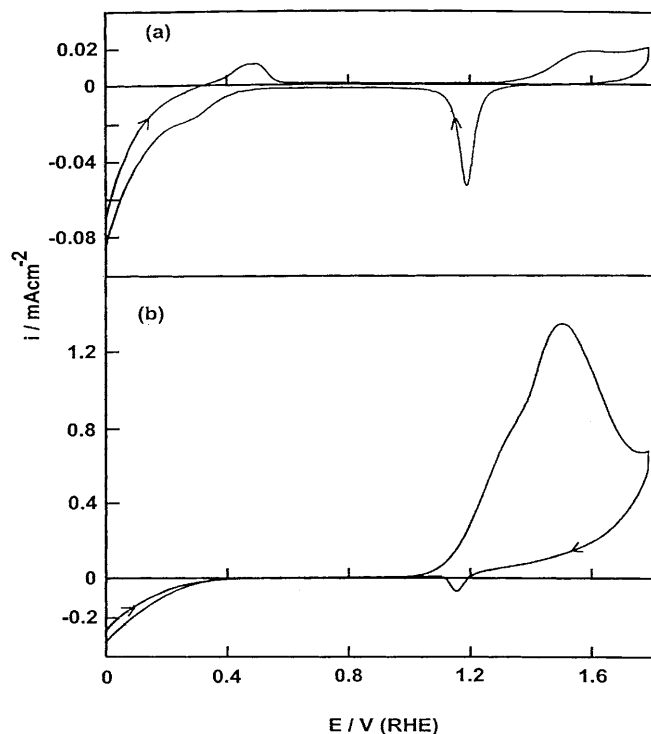


Fig. 11 Cyclic voltammograms (0.00–1.80 V) for a gold wire electrode in **a** $1.0 \text{ mol dm}^{-3} \text{ H}_2\text{SO}_4$ saturated with oxygen gas ($p = 1.0 \text{ atm}$) recorded at 20 mV s^{-1} , and **b** in $1.0 \text{ mol dm}^{-3} \text{ H}_2\text{SO}_4 + 0.01 \text{ mol dm}^{-3} \text{ H}_2\text{O}_2$ recorded at 50 mV s^{-1} , $T = 25 \text{ }^\circ\text{C}$

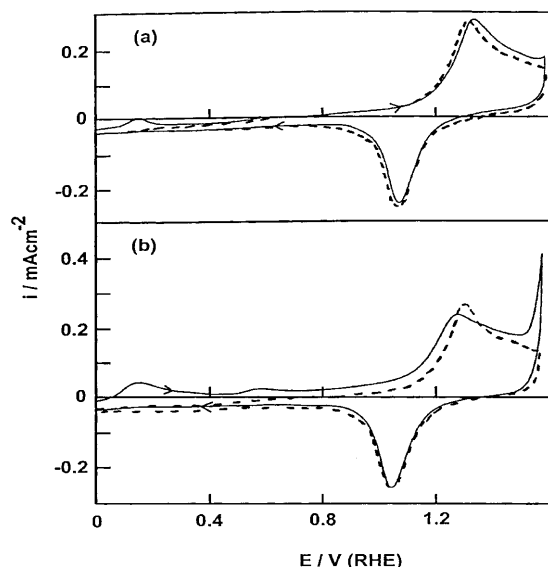


Fig. 12 Cyclic voltammograms (0.00–1.60 V, 50 mV s^{-1}) for a gold wire electrode in $1.0 \text{ mol dm}^{-3} \text{ NaOH}$ at $25 \text{ }^\circ\text{C}$: the electrode was pre-polarized at **a** 0.00 V for 5 min and at **b** -0.40 V for 30 min; the *dashed lines* indicate the second cycle

Activation of gold in aqueous base

Some typical results obtained with gold in base are outlined in Fig. 12. In the first case (Fig. 12a), the electrode was pre-polarized at 0.00 V for 5 min and the subsequent

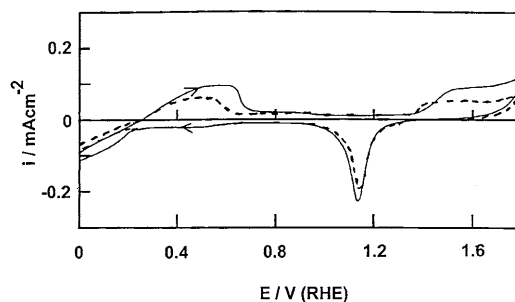


Fig. 13 Cyclic voltammograms (0.00–1.80 V, 50 mV s^{-1} , $1.0 \text{ mol dm}^{-3} \text{ H}_2\text{SO}_4$ at $25 \text{ }^\circ\text{C}$) for a gold wire electrode pre-polarized in $1.0 \text{ mol dm}^{-3} \text{ NaOH}$ at -0.40 V for 30 min; the *dashed line* is the response recorded after 20 min of repetitive cycling (0.00–1.80 V, 50 mV s^{-1}) in acid solution

voltammogram (full line) showed a minor anodic peak at ca. 0.15 V (positive sweep) and a current increase at ca. 0.60 V . The subsequent negative sweep and even the positive sweep in the second cycle (dashed line) were virtually featureless in the double layer region, but the current in the positive sweep remained cathodic until the potential reached 0.80 V . When more severe precathodization conditions were employed (Fig. 12b), the anodic peaks in the first positive sweep (full line) were enhanced (maxima were observed at ca. 0.18 , 0.61 and possibly at ca. 0.36 V ; the peak at the latter value was not very distinct) and substantial anodic current was observed at the upper limit of the sweep; this unusual feature was reported earlier for gold in base [19]. The response for the second sweep (dashed line in Fig. 12b) was rather similar to that shown for the corresponding sweep in Fig. 12a.

Superficially it appeared from these experiments that precathodization of gold in base has little effect on the metal surface. However, that this was not quite the case was demonstrated by transferring the gold electrode, which had been pre-polarized in base, to acid solution. With no pretreatment in the latter solution, major responses were observed (full line in Fig. 13) at low potentials. These were rather similar to those observed earlier for gold electrodes precathodized in acid solution, and the effect was rather persistent; it was still evident (dashed line in Fig. 13) after 20 min of continuous cycling.

Results for experiments in which an electrode was pre-polarized in acid but scanned in base are shown in Fig. 14. Cathodic currents were observed at low potentials in the positive sweep but the magnitude was quite low. Appreciable premonolayer oxidation responses at (and above) ca. 0.60 V are a well-known feature of cyclic voltammograms recorded for conventional gold in base [12, 20].

Discussion

Cathodic activation of the gold surface

Prolonged cathodic polarization of metals is assumed to induce activation of the outer layers via hydrogen

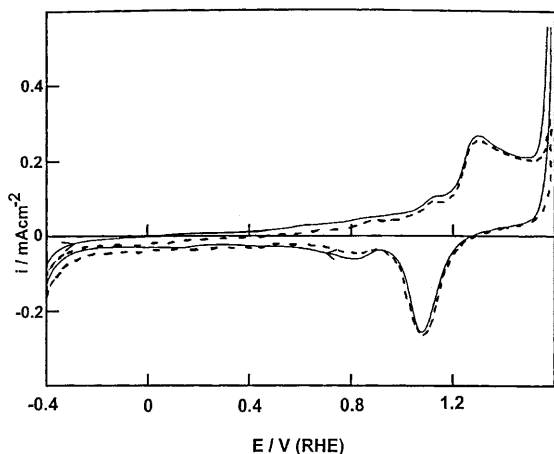


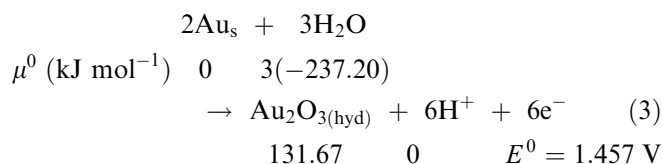
Fig. 14 Cyclic voltammograms (-0.40 – 1.60 V, 50 mV s^{-1}) for a gold wire electrode in 1.0 mol dm^{-3} NaOH at 25 $^{\circ}\text{C}$; the electrode was prepolarized in acid solution at -0.60 V for 30 min (full line) and -0.30 V for 15 min (dashed line)

embrittlement. In a survey of the latter topic, Louthan [21] pointed out that such embrittlement is a complex phenomenon and many aspects of such behaviour are not understood. An adequate model to explain the type of behaviour observed here was outlined recently by Cobden and co-workers [22] who postulated, on the basis of field emission microscopy data, that the entry of hydrogen into a metal (in their case palladium) generated strain in the lattice which resulted in the expulsion of metal atoms from the bulk to the surface. While gold does not readily adsorb or absorb hydrogen, it is assumed that the primary discharge product, atomic hydrogen (which is produced at the interface during cathodization at appreciable overpotential and high activity), is forced into various types of defects in the outer layers of the lattice where the resulting strain induces (as in the case of Pd) transfer of gold atoms from the bulk to the surface to form overlayer species. Essentially what is involved here is that some of the electrical energy inserted into the system is retained by the metal surface where gold atoms are transformed gradually from a high to a low lattice co-ordination state, i.e. from a state of low to high energy. This is the essence of metal surface activation; the same principle is involved in the case of thermal pretreatment (Fig. 10), where again some of the inserted energy is retained by the sample in the form of a metastable surface state (the lattice stabilization energy of the surface metal atoms, in both cases, is decreased in the course of activation).

The type of changes involved are illustrated, in terms of the change in redox response, by the results shown in Fig. 9. The cathodization conditions in this case were relatively mild and the alterations are not very dramatic. However, after 1 h at 0.00 V (Fig. 9a) there is an appreciable flow of anodic current in the positive sweep from ca. 0.60 to 1.20 V which is assumed to reflect the presence of gold atoms in a state of intermediate activity. The response in question was

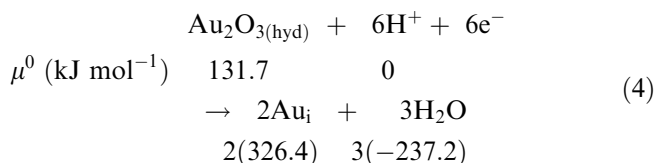
enhanced (as may be expected, Fig. 9b) when the hydrogen overpotential used in the pretreatment was increased. The other interesting point in Fig. 9 is the increase in the charge in the monolayer oxide reduction region, which is usually regarded [6] as a measure of the true surface area of the electrode. It is assumed that, in the second case, more of the gold atoms at the surface were activated, i.e. converted to overlayer species which undergo oxidation at premonolayer potentials. The removal of these gold atoms (or clusters of same) on activation creates pits and hollows in the original surface which, consequently, has a larger true surface area, hence the increased monolayer oxide response in Fig. 9b. The rather high value for the onset potential (ca. 1.46 V) for monolayer oxide formation in Fig. 9 may be due to the fact that the gold atoms that are activated on cathodization are already somewhat active, these being the species (possibly present as small clusters) that normally undergo oxidation just above 1.36 V. Basically, with polycrystalline gold, surface reactivity (both with regard to promotion to the active state and monolayer oxide formation) is influenced by particle or grain size (especially when the latter is extremely small), as already demonstrated by Henglein [23] for silver.

Increasing the cathodization overpotential (Fig. 8) appeared to have two effects: the upper region of the cyclic voltammogram (above ca. 0.80 V) returned to the normal response for polycrystalline gold, but the lower region became quite abnormal (a pronounced version of this abnormal response at low potentials is shown by the full line in Fig. 2). It appears that, as suggested here earlier, there are two distinct, virtually independent, types of electrochemical processes involved, one relating to conventional gold as described by Eq. 1 and the other to active gold as described in Eq. 2. The relevant thermodynamic data for these processes are summarized below in Eqs. 3 and 4.



The two processes in question are not totally independent; interchange is possible between the highly active and less active surface gold atom states, i.e. activation/deactivation processes are possible, as are the intervention of states of intermediate activity. The really surprising feature is the persistence (or retention) of the active gold atoms which are assumed to exist as an overlayer, i.e. virtually outside the lattice.

An estimate of the reversible potential required to convert hydrous gold oxide to isolated gold atoms (Au_i) may be made on the basis of the assumption that, in the extreme case, low co-ordination surface gold atoms are equivalent to gaseous gold (Au_g), i.e. $\mu^0(\text{Au}_g) = 326.4$ kJ mol^{-1} [24] = $\mu^0(\text{Au}_i)$ at 298 K. For the process



(the remaining thermodynamic data here are from Pourbaix [10]) the change in chemical potential ($\Delta\mu^0$) is $-190.5 \text{ kJ mol}^{-1} = -6FE^0$, i.e. $E^0 = 0.33 \text{ V}$. While there are uncertainties involved in this calculation (relating mainly to the state of the oxide and its chemical potential value), there can be little doubt that the gold atoms which give rise to the large anodic response at ca. 0.42 V in the cyclic voltammogram shown in Fig. 2 are extremely reactive species. It is assumed that these are mobile gold surface atoms; such species inevitably have an unusually low lattice co-ordination number and hence a high activity. Occasionally (as shown by the full line in Fig. 2) the charge for premonolayer oxidation was comparable with (if not in excess of) that for monolayer oxidation. It may well be that the active gold atoms are present at the interface as metastable microparticles (as observed recently for hydrogen treated Pd [22]), the latter being the main source of mobile surface atoms.

The nature of the premonolayer redox reaction

It is evident from the sweep rate data (Fig. 4) that the active gold atoms undergo oxidation in the positive sweep quite rapidly. The fact that the peak potential does not vary with sweep rate while at the same time the peak current density increases almost linearly with sweep rate is indicative [25] of a rapid quasi-reversible reaction. However, there are some deviations, e.g. the net charge involved shows a slight drop, while the increase in peak current is not quite linear, with increasing sweep rate. Evidently there is some minor source of inhibition involved in the oxidation process; possibly some of the active gold atoms are not sufficiently accessible, e.g. those at the centre of microparticles, to undergo rapid reaction in the peak region at the faster sweep rates.

One of the most intriguing features of the results is the reluctance of the β oxide species to undergo reduction. In contrast to the anodic peak at ca. 0.42 V in the positive sweep (Fig. 2), there is rarely a cathodic peak in the negative sweep in this region (the exceptions here are Fig. 10b and Fig. 11a). Usually cathodic currents were observed to increase significantly in the negative sweep below ca. 0.40 V, but the reaction involved was quite sluggish and was invariably incomplete prior to the onset of hydrogen gas evolution. The other very surprising feature was the presence of quite significant cathodic currents in many instances, e.g. Fig. 2 and Fig. 8b, at the beginning of the positive sweep (0.00–0.30 V) after the electrode had been subjected to prolonged, severe cathodization.

One of the problems of dealing with premonolayer oxidation phenomena is that none of the potential values involved are of thermodynamic significance. Even the anodic peak at ca. 0.40–0.50 V in the positive sweep is assumed to relate to a highly active, unstable state of the metal which (apart from work on nanocluster systems [23]) has received very little attention and is very poorly understood. It is possible that the species responsible for the cathodic current at the initial stages of the positive sweep in Fig. 2 is not a pure oxide. There is evidence for an anion (HSO_4^- or SO_4^{2-}) involvement in the case of the corresponding type of deposits formed on platinum in acid solutions [7]. The incorporation of electrolyte anions into the ligand co-ordination sphere may favour or promote the oxidation of the very active gold atoms at low potentials in the course of prepolarization. The nature of hydrous oxide films formed on noble metals is currently not well understood; however, for both gold [8] and platinum [26] at least three distinct components (and there may be more) appear to be involved. In the case of platinum the hydrous oxide component containing the sulfate, $\text{Pt}(\text{HO}2)$, is assumed [7] to undergo reduction at a significantly lower potential than its sulfate-free equivalent, $\text{Pt}(\text{HO}1)$.

The sluggish nature of the hydrous oxide reduction response below 0.40 V (negative sweep) is thus attributed to a combination of three effects: (1) the species that undergo reduction are assumed to be anionic [7, 8] and hydrated; they probably undergo reduction via an outer-sphere mechanism, the gold atoms produced being in a highly reactive state (hence the low potential); (2) contact between the metal and the rather dispersed (low density) β material may also not improve as the reduction progresses (the assumption here is that the reaction commences at the gold/hydrous oxide junction); (3) sulfate ions are assumed to be incorporated into the deposit as the latter is formed, thereby increasing the difficulty in reducing the β material.

The possible role of impurities

Earlier reports of Faradaic currents in the double layer region of gold were attributed by Woods (see p. 119 of [6]) to the presence of some type of impurity in the system. There is certainly some similarity between the type of response outlined here, for instance in the full line in Fig. 2, and that frequently observed in anodic stripping voltammetry (ASV) [27]. According to this view, an impurity in the solution, e.g. a metal ion such as Cu^{2+} (present at a very low concentration), is discharged at the gold surface during cathodic polarization and the resulting deposit of metallic copper is anodically removed (hence the peak at ca. 0.40 V) in the subsequent positive sweep.

This interpretation is rejected here for the following reasons, viz.

1. Large responses in the double layer region, including an anodic peak at ca. 0.40 V, were observed with

a thermally pretreated gold electrode (Fig. 10), i.e. with gold surfaces which had not been precathodized. In such experiments (the results of which were confirmed using electrically heated gold wire specimens, in the same manner as described recently for platinum [4]), active gold surfaces were produced by allowing the intensively heated wire to cool rapidly in air. As already pointed out, both activation procedures yielded active gold surfaces giving rather similar, unusual responses at low potentials.

2. The cathodic currents in both the positive and negative sweep (and to some extent the anodic response at ca. 0.50 V) could also be generated by extending the upper limit of the sweep (Fig. 6) into the monolayer oxide region. In this case the behaviour for low upper limit values was close to ideal; the deviation in question was apparently associated with a process occurring above 1.40 V. It is assumed that some of the oxide formed in these experiments (the electrode involved had been used in some of the earlier work involved here; it was probably not in a totally relaxed state) was largely an α -type deposit, with traces of highly dispersed β material also present; the latter only undergo slow reduction below ca. 0.30 V.

3. The behaviour shown by gold should not be viewed in isolation. Similar techniques as used here for gold were employed also to activate platinum [4] and the subsequent voltammetric behaviour is rather similar (a very sharp anodic peak at ca. 0.25 V in the positive sweep followed by a sluggish cathodic response commencing at about the same value on the subsequent negative sweep). The fact that the shape and potential value for the peaks are significantly different suggests that these unusual responses are characteristic of the metal rather than an impurity (the cell and electrolyte solution involved were similar for both metals). Hydrogen activation of metal surfaces was postulated independently earlier [18] in the case of iron electrodes in base.

4. The presence of low-level premonolayer responses within the double layer region for conventional polycrystalline gold, especially in base, has been discussed in several earlier publications [12, 19, 28] from this laboratory. The fact that such responses correlate quite well with the onset of electrocatalytic processes [13] – further examples of such correlations are given here later – support the view that active gold atoms, rather than impurities, are involved.

5. Unusual redox responses in the double layer region for gold in aqueous acid media are observed quite frequently in work involving gold single-crystal plane electrode surfaces [29–31]. In many cases a sharp anodic peak (positive sweep) is followed by a rather ill-defined cathodic feature, i.e. a sluggish response, in the negative sweep. The potential for the small anodic peak (for Au(100) in acid solution [31]) is ca. 0.30 V (SCE), i.e. ca. 0.60 V (RHE); there was also an anodic prepeak at ca. 0.40 V (RHE). Such behaviour in the positive sweep for the single-crystal electrode is not very different from that

shown here, for instance in Fig. 3a. Usually these features for single-crystal work are attributed to surface reconstruction effects; however, since point defects, such as adatoms, are very difficult to detect at metal surfaces [4], one cannot rule out the presence of a low coverage of adatoms (Au*) on single-crystal surfaces, or the fact that the premonolayer responses observed are of Faradaic character (this was also pointed out earlier by Conway and co-workers [32] for gold single-crystal electrodes in aqueous acid solution). It is also worth noting that the single-crystal gold surfaces are frequently annealed in a Bunsen flame prior to investigation. Such pretreatment is likely to cause random movement of gold atoms, especially at the surface, and it seems very improbable that all the displaced atoms will find a suitable vacancy in the surface lattice as the sample cools. This aspect of single-crystal electrochemistry was discussed recently for platinum [4]; it appears that premonolayer responses are a highly sensitive measure of the degree of imperfection of the outer layer of the surface, e.g. the number or coverage of active atoms present.

The effect of cell temperature

Raising the operating temperature from 25 to 50 °C (Fig. 7) greatly enhances the unusual responses observed at low potential. It appears that the species formed on prepolarization is largely a hydrous oxide or a mixture of oxide plus active metal. In the positive sweep, some of the oxide is reduced rather slowly below 0.30 V to the active metal. The latter may either remain on the surface, giving rise to the anodic peak at ca. 0.50 V (Fig. 7b) or, at a higher temperature (70 °C), decay to a more stable state (note the relatively small size of the anodic peak at ca. 0.50 V in Fig. 7c).

While the oxidation of the active gold atoms and the reverse process, the reduction of the product, are assumed to be related, it is clear from the responses shown in Fig. 7 that there are complications. The cathodic response below 0.30 V, especially at elevated temperature, is much larger in magnitude than the anodic response at ca. 0.50 V. Such behaviour is attributed to considerable loss in activity in the gold atoms formed during the sluggish reduction process. The anodic currents in the positive sweeps, and especially at the start of the monolayer oxide region, are particularly large in Fig. 7b and c. It is assumed that the gold atoms reacting in these regions are of intermediate activity, i.e. they were produced by reduction of the hydrous species below ca. 0.30 V but then decayed in activity to an intermediate level during or after the reduction process.

The data shown in Fig. 5 seem to represent an interesting case of intermediate surface atom activity. This type of response was frequently observed after an electrode, which had been extensively cycled, was allowed to rest for an extended period of time. It is assumed that stress relief in the disturbed (or active) outer layers of the lattice resulted in the expulsion of highly active gold

atoms to the surface where some of them were oxidized (note the presence of the cathodic currents at the start of the positive sweep). It appears that an unusual level of active gold atoms, with a rather broad range of activity values, exist at the interface; the retention of the active state in this case may be favoured by the presence of some β oxide (the active metal may, to some extent, be encapsulated in a thin layer of hydrous oxide).

The electrocatalytic behaviour of gold in acid at low potentials

The electrocatalytic behaviour of gold in aqueous media was surveyed recently by one of the present authors [12, 13]. The metal is a much better electrocatalyst for oxidation processes in base than in acid, and of those compounds that are oxidizable on gold in acid the majority commence reaction in the positive sweep at ca. 1.05 V (see the behaviour of peroxide in this respect in Fig. 11b and the values quoted for many of the alcohols and amino acids in [13]). In many of the voltammograms reported here there was a significant increase in anodic current in the positive sweep, e.g. Fig. 2, commencing at ca. 1.05 V. Particular attention is directed to Fig. 7, where the voltammograms recorded at the higher temperatures show a small, but reasonably reversible, redox transition at ca. 1.05 V. As discussed earlier [12], the process involved here is assumed to be the oxidation of slightly active surface gold atoms, the reactive oxide product in turn mediating the oxidation of dissolved oxidizable species such as alcohols [13] or hydrogen peroxide (Fig. 11b). This interpretation of electrocatalysis, involving mediation by oxy species generated within the double layer region of the gold/solution interface, was postulated also by Conway and co-workers [32].

It was pointed out recently in the case of platinum in acid solution [4] that surface metal atoms may exhibit different levels of activity, i.e. they may exhibit active metal atom/hydrous oxide transitions at different potential values. This is scarcely surprising as the lattice coordination number and lattice stabilization energy of a surface metal atom is variable. For gold in acid there is a second critical potential value at ca. 0.85 V where highly reactive species commence oxidation (positive sweep, as in the case of hydrazine [33], ethylene glycol [34], propargyl alcohol [35] and glycol aldehyde [34]) or reduction (negative sweep, as in the case of dichromate [5] – at least a major change in current for the reduction of this compound occurs at the latter value). It may be noted that there is a slight increase in anodic current in the positive sweep at ca. 0.85 V in Fig. 10b. Also, in the negative sweep in Fig. 7c there is a slight flow of anodic current below 1.00 V which ceases at ca. 0.85 V (this minor flow of anodic current in the negative sweep is quite unusual; it evidently reflects an unusually high level of activity of surface gold atoms at the interface in this particular case). In general, however, it seems that

dramatic responses at ca. 0.85 V for this electrode system are not very common.

In the review in question [13], there were a few processes whose behaviour was difficult to understand. Some substances, e.g. glucose and carbon monoxide, commenced oxidation (positive sweep) on gold in acid at ca. 0.45 V while a number of others, e.g. adsorbed acetylene, nitrotriazole, nitrobenzene, oxygen and hydrogen peroxide, commenced reduction (or showed significant increases in cathodic current) in the negative sweep at this potential value. At the time there was little direct evidence for a redox transition for gold in acid at ca. 0.45 V, but it is now evident, e.g. from Fig. 3b, that an interfacial transition, involving very active gold atoms, does occur at this value. This correlation with electrocatalytic behaviour, involving data from many laboratories, is significant as it supports the claim made here earlier that the unusual redox response for gold in acid at ca. 0.50 V is an intrinsic property of this electrode and not due to an impurity in the system used in the present investigation.

It appears, therefore, that gold in acid solution, like platinum under similar conditions [4], exhibits at least three distinct active metal/incipient hydrous oxide transitions and each of the three can provide mediators, as outlined elsewhere [13, 28], for the electrocatalytic oxidation or reduction of different groups of solution species. It is worth noting that thick multilayer hydrous oxide films produced on gold in acid solution by potential cycling [8] also contain three components which, in a slow negative sweep, only undergo reduction at potentials well below the monolayer oxide reduction region (this type of correlation between multilayer oxide and low-coverage, mediating oxide systems was highlighted again recently [2] for copper in base). It was pointed out here earlier that the transition at ca. 0.50 V is not very reversible as the oxide reduction step was slow. This may explain the sluggish response for both oxygen and hydrogen peroxide reduction (Fig. 11) at low potentials, at gold in acid solution; in terms of the interfacial mediator view of noble metal electrocatalysis [13] a prime requirement of a highly effective mediating couple is a very rapid, reversible redox transition (a condition that is not fulfilled in the case of the interfacial reaction commencing at ca. 0.5 V).

Another interesting correlation with earlier work arises from results reported for dichromate reduction on gold in acid solution [5]. A limiting, diffusion-limited current was observed for this reaction at $E < 0.80$ V. However, a small but significant increase in current was observed in the negative sweep, which was reversed in the positive sweep, over the range 0.40 to 0.00 V (see Fig. 1 in [5]). At the time, such behaviour was inexplicable; the effective area of the electrode apparently changes in a reversible manner with potential below 0.40 V. The latter view is evidently correct; below ca. 0.40 V, recalcitrant oxide species (obviously present at low coverage) undergo reduction and the area of

exposed gold surface is increased in the negative sweep; the reverse behaviour occurs during the positive sweep.

Activation of gold in base

It is evident from the data shown in Fig. 13 that, despite the lack of dramatic responses for precathodized gold electrodes in base (Fig. 12), hydrogen activation of the metal surface occurs in alkaline solution. The product of activation is assumed to be a hydrous oxide whose reduction at low potentials is quite sluggish. A lowering of the potential for hydrous gold oxide film reduction on changing the solution from acid to base is well established [8], but the degree of stabilization (or reluctance of the oxide to undergo reduction) in the present case is dramatic. It is assumed here that this unusual behaviour in base involves a combination of three effects: (1) the gold atoms produced initially are in a very active state; (2) the hydrous oxide complexes (as discussed earlier [8]) are much more stable, or the deposit is more inert, in solutions of high hydroxide ion activity; (3) the presence of hydrogen at the interface (at $E < 0.00$ V, Fig. 14) has an unusual inhibiting effect (the latter was demonstrated earlier in the case of hydrous oxide film reduction on platinum in base [36]; the effect seems to be due to an increased level of activity of the reduced form of the couple, i.e. the gold atoms, in the presence of adsorbed hydrogen). The presence of minor peaks in the double layer region for gold in base (full line Fig. 12b) and high anodic currents at the upper region of the sweep (Fig. 14) were discussed in some detail in earlier publications from this laboratory [19, 28].

Overview of electrochemistry of active gold surfaces

The most interesting features of the present work are (1) the appearance of redox responses at quite low potentials in the double layer region in cyclic voltammograms recorded for activated gold electrodes in acid solution, (2) the ability to activate gold surfaces by two independent techniques (cathodization and thermal pretreatment) and (3) the role of these active states in electrocatalytic processes.

There is independent evidence for the appearance of the anodic peak at ca. 0.50 V; indeed, Ling and co-workers [37] published an appendix to their paper dealing specifically with this feature in which for gold in dilute H_2SO_4 solution it was stated (in the last sentence of the paper) that “the possibility of contamination of the Au electrode or [the presence] of solution impurity effects is excluded”. They also demonstrated (see their fig. A-5) that mild cathodic prepolarization (which they described as “cathodic cleaning”) not only enhanced the charge associated with this peak but also resulted in the appearance of an overlapping prepeak (similar behaviour is shown here in Fig. 3a). They

claimed that there was no corresponding cathodic peak on the negative sweep; however, in some of their diagrams, e.g. figs. A-4 and A-5, there was a significant increase in cathodic current in the negative sweep commencing at a potential corresponding to that of the end of the anodic peak. Furthermore, the currents in the region below the anodic peak region were generally cathodic (figs. A-3 to A-5) in both the forward and reverse sweeps. These authors attributed the anodic peak at 0.50 V to the “electrochemisorption of oxygen” and pointed out that the effect was very sensitive to the condition of the gold surface.

There are also numerous reports by Arvia and co-workers [38–40] of anodic responses at quite low potentials in the positive sweep for polycrystalline gold electrodes in aqueous acid solution. These authors pointed out that, depending upon electrode pretreatment, it is possible to produce two different types of gold surfaces which yield different types of voltammetric behaviour in the double layer region. The first type (non-activated gold) exhibits the conventional response whereas activated gold exhibits a net flow of anodic current over the range 0.10–0.40 V (their mode of activation, repetitive potentiodynamic perturbation, differs from that used in the present work). The current or charge in question was attributed to oxidation of adsorbed hydrogen (a similar view was expressed earlier by Chao and Costa [41]).

The salient point in these earlier works quoted here is that with gold electrodes in acid solution, especially when the metal surface is activated by appropriate pretreatment (the latter may be inadvertent), anodic reactions occur at quite low potentials in the positive sweep which are not always easily reversed in the subsequent negative sweep. Since in some cases (see the full line here in Fig. 2) the anodic charge is comparable to that involved in monolayer oxide formation, it seems that the currents involved are of a Faradaic, rather than capacitive, character. Since the charge involved is quite substantial, the process involved cannot be regarded simply as OH^- ion adsorption (the latter reaction being non-Faradaic), and OH^- radicals are unlikely to be generated [12] at 0.50 V. The most likely species to undergo oxidation at low potentials are highly active gold atoms, the resulting cations then coordinating OH^- and other anionic species to form some type of interfacial oxy complex. There is obviously considerable scope in this area for the use of spectroscopic techniques to investigate the nature of the anodic deposit. Support for the view expressed in the present work concerning the unexpected reluctance of the oxide formed on gold at low potentials to undergo reduction even at 0.00 V has already been produced by Hutton and Williams [42]. They claimed, on the basis of scanning laser microscopy data, that incipient, premonolayer oxide species were “exceptionally stable” (obviously for kinetic reasons); to remove such species “it was necessary to reduce the potential into the hydrogen evolution region”.

Conclusions

1. It was pointed out earlier for several metals [2–4], and especially platinum [5], that a complete understanding of the redox, electrochemical and electrocatalytic behaviour of these systems requires greater emphasis on two features, namely, the defect (or active) state of the metal surface and hydrous oxide electrochemistry. The importance of the defect state of metal surfaces is independently acknowledged in Somorjai's statement [43] that "rough surfaces do chemistry".

2. The behaviour of gold in acid solution was examined here using cyclic voltammetry. Electrochemical techniques have an important advantage for preliminary work in this area as they provide a simple means for varying the surface activity of the metal and surveying the consequences in terms of changes in the redox behaviour. The present work may be regarded as a basis for further research using more sophisticated techniques; however, it should be borne in mind that the level of surface activity in question here is unusually high, and the metal atoms involved may be variable both with regard to location and energy. Such species are assumed to be important with regard to the behaviour of active sites which, for conventional surfaces, are very important from a catalytic viewpoint, but of quite low coverage and very difficult to investigate, and hence poorly understood [44].

3. With polycrystalline gold in aqueous acid media it is possible to activate the surface by severe cathodic or thermal pretreatment, the product apparently being significant coverages of quite low co-ordination (apparently mobile) gold atoms at the electrode surface. Such species (and there may well be more than one type involved [28]) are assumed [4] to be very difficult to detect by conventional surface science techniques, e.g. LEED, STM or AFM, especially at room temperature. Active metal atoms are assumed to be quite important in electrocatalytic processes. Their redox behaviour is quite different from that of well-embedded surface metal atoms in that they undergo very rapid oxidation at unusually low potentials but in many instances the reduction of the product is quite sluggish. As will be reported shortly, similar behaviour to that observed here for gold was also observed with electrically preheated platinum in aqueous acid solution at elevated (ca. 75 °C) temperature.

References

- Burke LD, Casey JK, Morrissey JA (1993) *Electrochim Acta* 38: 897
- Burke LD, Collins JA, Murphy MA (1999) *J Solid State Electrochem* (in press)
- Burke LD, Nagle LC (1999) *J Electroanal Chem* 461: 52
- Burke LD, Hurley LM (1999) *Electrochim Acta* 44: 2451
- Burke LD, Nugent PF (1997) *Electrochim Acta* 42: 399
- Woods R (1976) Chemisorption at electrodes: hydrogen and oxygen on noble metals and their alloys. In: Bard AJ (ed) *Electroanalytical chemistry*, vol. 9. Dekker, New York, pp 1–162
- Burke LD, Lyons MEG (1986) Electrochemistry of hydrous oxide films. In: White RE, Bockris JO'M, Conway BE (eds) *Modern aspects of electrochemistry*, vol 18. Plenum Press, New York, pp 169–248
- Burke LD, Nugent PF (1998) *J Electroanal Chem* 444: 19
- Belanger G, Vijn AK (1977) Anodic oxides on noble metals. In: Vijn AK (ed) *Oxides and oxide films*, vol 5. Dekker, New York, pp 1–168
- Pourbaix M (1966) In: *Atlas of electrochemical equilibria in aqueous solutions*. Pergamon Press, Oxford
- Taylor HS (1925) *Proc R Soc London Ser A* 108: 105
- Burke LD, Nugent PF (1997) *Gold Bull* 30: 43
- Burke LD, Nugent PF (1998) *Gold Bull* 31: 39
- Watanabe T, Gerisher H (1981) *J Electroanal Chem* 122: 73
- Desilvestro J, Weaver MJ (1986) *J Electroanal Chem* 209: 377
- Horanyi G, Rizmayer EM (1984) *J Electroanal Chem* 165: 279
- Gordon JS, Johnson DC (1994) *J Electroanal Chem* 365: 267
- Zakroczymski T, Kleshnya V, Flis J (1998) *J Electrochem Soc* 145: 1142
- Burke LD, Cunnane VJ, Lee BH (1992) *J Electrochem Soc* 139: 399
- Angerstein-Kozlowka H, Conway BE, Barnett B, Mozota J (1979) *J Electroanal Chem* 100: 417
- Louthan MR (1987) The effect of hydrogen on metals. In: Mansfield F (ed) *Corrosion mechanisms*. Dekker, New York, pp 329–365
- Cobden PD, Niewenhuys BE, Gorodetski VV, Parmon VN (1998) *Platinum Met Rev* 42: 141
- Henglein A (1995) *Ber Bunsenges Phys Chem* 99: 903
- Wagman DD, Evans WH, Parker VB, Halow I, Bailey SM, Schumm RH (1969) Selected values of chemical thermodynamic properties. (Technical note 270-4) National Bureau of Standards, Washington, p 39
- Srinivasan S, Gileadi E (1966) *Electrochim Acta* 11: 321
- Burke LD, Morrissey JA (1996) *J Appl Electrochem* 26: 593
- Bard AJ, Faulkner LR (1980) Bulk electrolysis methods. In: *Electrochemical methods, fundamentals and applications*. Wiley, New York, p 413
- Burke LD, O'Leary WA (1989) *J Appl Electrochem* 19: 758
- Magnussen OM, Hotlos J, Behm RJ, Batina N, Kolb DM (1993) *Surf Sci* 296: 310
- Skoluda P (1998) *J Electroanal Chem* 442: 9
- Kolb DM (1993) Surface reconstruction at metal-electrolyte interfaces. In: Lipkowski J, Ross PN (eds) *Structure of electrified interfaces*. VCH, Weinheim, pp 65–102
- Angerstein-Kozłowska H, Conway BE, Hamelin A (1996) *J Electroanal Chem* 277: 233
- Burke LD, O'Dwyer KJ (1989) *Electrochim Acta* 34: 1659
- Beden B, Cetin I, Kahyaoglu A, Takky D, Lamy C (1987) *J Catal* 104: 37
- Pastor E, Schmidt VM, Iwasita T, Arevalo MC, Gonzalez S, Arvia AJ (1993) *Electrochim Acta* 38: 1337
- Burke LD, O'Sullivan, JF (1991) *J Appl Electrochem* 21: 151
- Ling Y, Elkenbracht JC, Flanagan WF, Lichter BD (1997) *J Electrochem Soc* 21: 151
- Cordova Orellana R, Martins ME, Arvia AJ (1979) *Electrochim Acta* 24: 469
- Cordova Orellana R, Martins ME, Arvia AJ (1980) *J Electrochem Soc* 27: 2628
- Alonso C, Gonzales-Velasco J, Arvia AJ (1988) *J Electroanal Chem* 250: 183
- Chao F, Costa M (1977) *C R Acad Sci Ser C* 284: 763
- Hutton RS, Williams DE (1994) *J Am Chem Soc* 116: 3453
- Somorjai GA (1996) *Chem Rev* 96: 1223
- Wolfram T, Ellialtioglu S (1980) Concepts of surface states and chemisorption on d-band perovskites. In: Smith JR (ed) *Theory of chemisorption*. Springer, Berlin Heidelberg New York, p 150