J Solid State Electrochem (2001) 5: 319–327
DOI 10.1007/s100080000153

ORIGINAL PAPER

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Auto-inhibition of hydrogen gas evolution on gold in aqueous acid solution

Received: 4 May 2000 / Accepted: 17 May 2000 / Published online: 3 April 2001

Abstract It was demonstrated recently that dramatic changes in the redox behaviour of gold/aqueous solution interfaces may be observed following either cathodic or thermal electrode pretreatment. Further work on the cathodic pretreatment of gold in acid solution revealed that as the activity of the gold surface was increased, its performance as a substrate for hydrogen gas evolution under constant potential conditions deteriorated. The change in activity of the gold atoms at the interface, which was attributed to a hydrogen embrittlement process (the occurrence of the latter was subsequently checked by surface microscopy), was confirmed, as in earlier work, by the appearance of a substantial anodic peak at ca. 0.5 V (RHE) in a post-activation positive sweep. Changes in the catalytic activity of a metal surface reflect the fact that the structure (or topography), thermodynamic activity and electronic properties of a surface are dependent not only on pretreatment but also, in the case of the hydrogen evolution reaction, vary with time during the course of reaction. As will be reported shortly, similar (and often more dramatic) time-dependent behaviour was observed for hydrogen gas evolution on other metal electrodes.

Keywords Gold · Active states · Hydrogen evolution · Inhibition · Cathodization

Introduction

In a discussion of the selection of materials for use as catalytically active low overpotential cathodes for hydrogen gas evolution, Divisek [1] stressed the importance of two factors: electrocatalytic activity and long-term stability. Electrocatalytic activity is usually assessed in terms of the exchange current density (j_o) and Tafel slope (b), and the basic kinetic theory for hydrogen gas evolution, including the role of the electrode material, e.g. the volcano-type plot [2, 3] relating j_o to M-H bond strength in the case of single metals, is well established.

With regard to the long-term performance of the cathode, the situation is less satisfactory. Divisek [1] have demonstrated that the hydrogen overpotential for various electrocatalysts in base (mainly those based on mixtures of nickel with other metals, but also for pure Pt and pure RuO_2) increases with increasing electrolysis time. Such a deterioration in cathode activity with time has been noted also by other authors [4, 5, 6] and has been attributed [1, 4, 5] to a variety of factors, e.g. partial poisoning of the metal surface owing to the deposition of adsorbed impurities, formation of surface metal hydrides, slow dissolution of the surface of the electrocatalyst (leading to loss of either active sites or the selective loss of the more active component in the case of mixed metal cathodes), a gradual change in the reaction mechanism, etc.

In a recent publication from this laboratory [7] it was demonstrated that the activity and redox behaviour of gold surfaces in acid solution is altered dramatically during the course of hydrogen gas evolution. The effect was attributed to the generation of an unusually reactive, or superactive, localized state of the metal surface. Such a state may be generated for gold by alternative means, e.g. thermal activation [8]. The effect is important at a fundamental level as it means that the properties of the surface are not only pretreatment dependent (this is well established, e.g. from earlier work function studies [9]) but may change in an unexpected manner during the course of the hydrogen evolution reaction (HER). It was observed in the present work with gold (and, as will be reported shortly, for various other noble metal electrodes) that, at constant hydrogen

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overpotential, activation of the metal surface was accompanied by a decrease in the rate of gas evolution. The effect may be attributed to changes in the stability or coverage of the reaction intermediate (H_{ads}) as the activity of the gold atoms at the interface (and especially at active sites at the latter [10]) was increased or to the generation of inhibiting oxide species on the gold surface (the latter view is regarded as improbable for gold, but may be relevant in the case of less noble metal cathodes).

Experimental

The working electrodes 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. As outlined here later, gold anodes are not sufficiently stable for prolonged polarization work (slight anodic dissolution resulted in the transfer of gold from the anode to the cathode). Most of the work in the present project was carried out using graphite rod anodes (ca. 6 mm diameter, Johnson Matthey, Ultra "F" purity grade); however, quite similar behaviour was observed initially when gold wire electrodes were used for both the anode and cathode. The gold electrodes were usually subjected to mild abrasive pretreatment and their potentials were cycled (0.0–1.80 V at 50 mV s^{-1}) in the acid electrolyte until the conventional cyclic voltammetric responses for gold in acid solution [7] were observed.

Solutions were made up using Analar grade H_2SO_4 and triply distilled water; they were purged with oxygen-free nitrogen before, and frequently during, use. The electrochemical and microscope equipment used in this work was described earlier [7, 8]; potentials were measured, and are reported, with respect to a reversible hydrogen electrode (RHE), $p(H_2) = 1.0$ atm, in the same solution; this reference electrode was in a separate vessel which was connected to the working electrode compartment via a Luggin capillary.

Results

Typical cyclic voltammograms for polycrystalline gold in acid solution, prior to polarization, are shown for three different temperatures in Fig. 1. The main features in each case are the response due to monolayer oxide formation (positive sweep) commencing just below 1.40 V and that due to reduction of this deposit (negative sweep), i.e. the cathodic peak just below 1.20 V. For each of these temperatures the electrode was negatively polarized for 3.0 h at a constant potential and the variation of the rate of hydrogen gas evolution (or current density) was recorded as a function of time (as this rate of gas evolution at 0 °C was quite slow on polarization at –0.4 V, the response at this temperature is shown for an applied potential of –0.6 V). In all cases (only representative data are shown here; the polarization experiments were carried out over a range of cathodic overpotentials) there was a continuous decay of the hydrogen gas evolution current over the period in question (Fig. 2). At the end of the polarization period the voltammetric scans were repeated and the results are shown in Fig. 3. The most notable change, compared with the scan for the same electrode prior to polarization, was the appearance of the anodic peak in the positive sweep at ca. 0.5 V. Such a response, attributed

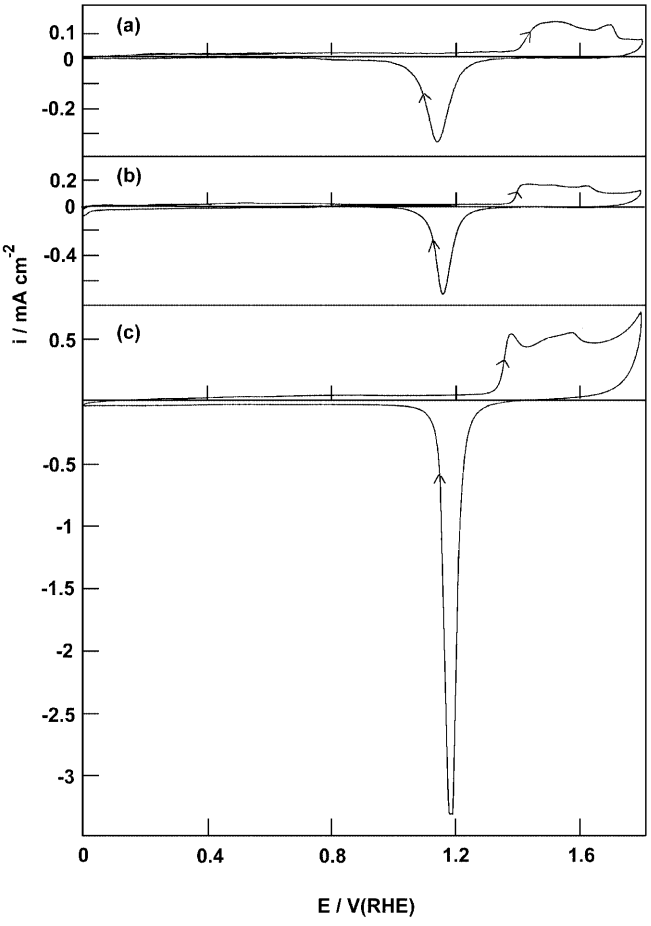


Fig. 1 Cyclic voltammograms (0.00–1.80 V, 50 mV s^{-1}) for non-activated gold wire working electrodes (carbon counter electrode) in 1.0 mol dm^{-3} H_2SO_4 at **a** 0 °C, **b** 25 °C and **c** 50 °C. These are representative data; several experiments were carried out at each temperature and the surface morphology or roughness of the gold was not the same in each case

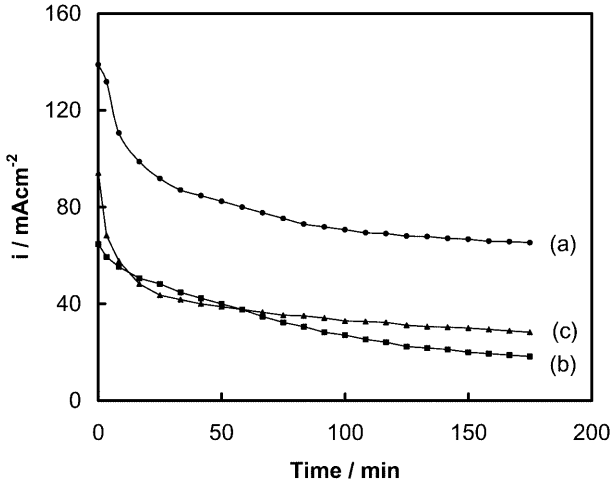


Fig. 2 Example of the decay (at constant potential) in the hydrogen gas evolution rate with time recorded immediately after the cyclic voltammograms (same electrodes and solution) shown in Fig. 1: *a* –0.6 V at 0 °C; *b* –0.4 V at 25 °C; *c* –0.4 V at 50 °C

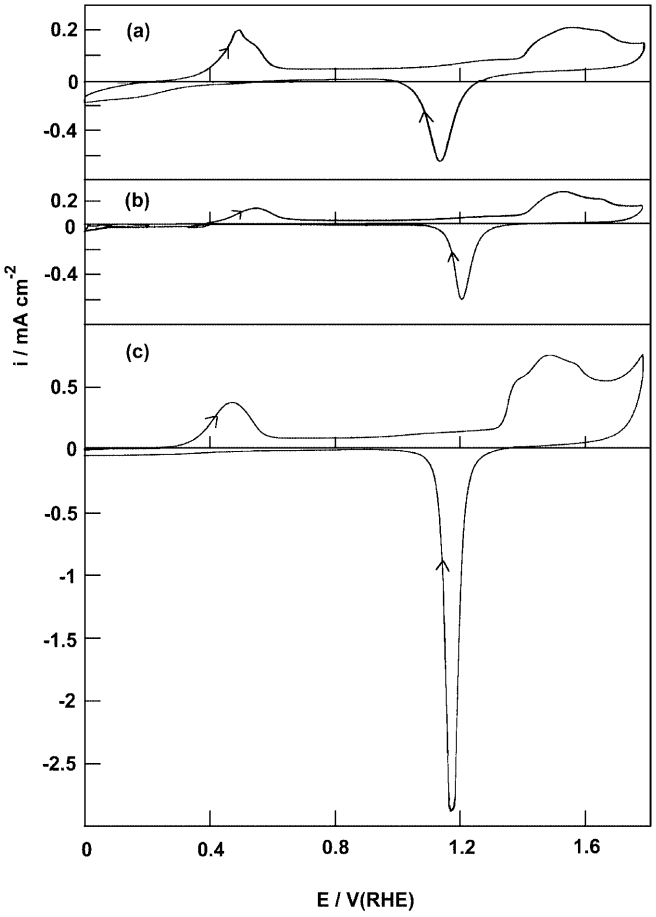


Fig. 3 Repeat of the cyclic voltammograms shown in Fig. 1; the conditions were identical except that in this case the gold electrodes were cathodically preactivated as outlined in Fig. 2

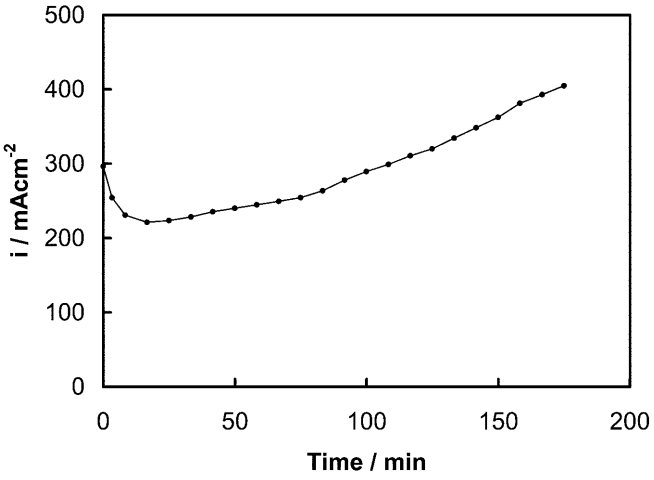


Fig. 4 Variation of the rate of hydrogen gas evolution with time; $E = -0.5$ V, 1.0 mol dm^{-3} H_2SO_4 at 35 °C; in this case, both the working and counter electrodes were gold wires

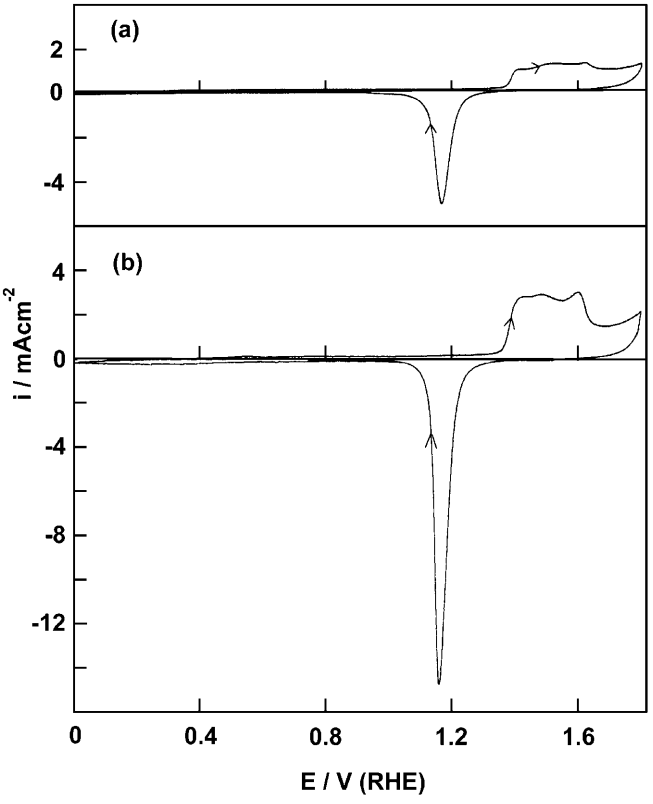


Fig. 5 Cyclic voltammograms (0.00–1.80 V, 50 mV s^{-1}) recorded prior to (**a**) and after (**b**) the polarization experiment outlined in Fig. 4

to the oxidation of highly active gold atoms, generated at the interface during the course of the hydrogen gas evolution reaction, was discussed in considerable detail recently [7]. It is assumed that there is a direct connection between the generation of this active state of the gold surface, during the course of the cathodic polarization, and the decay of the hydrogen gas evolution rate (Fig. 2) with time.

When the type of experiments summarized here in Figs. 1, 2, 3 were carried out using a gold, rather than a carbon, counter electrode, significantly different behaviour was observed. It was noted for instance that while the cathodic H_2 evolution current decayed initially (Fig. 4), it began to increase significantly after ca. 40 min of polarization. A cyclic voltammogram recorded at the end of this polarization experiment (Fig. 5b) showed only a very small anodic peak (due to the oxidation of active gold [7]) at ca. 0.5 V. However, another notable feature in this case was the increase in the monolayer oxide formation/removal charges above 1.0 V. Such an increase, which is quite obvious from a comparison of the two cyclic voltammograms shown in Fig. 5, strongly suggests that the surface area of the electrode was increased as a result of the prolonged cathodic polarization (the direct relationship between monolayer oxide charge and surface area was discussed earlier for gold by Woods [11]).

Initially the increase in surface area was attributed to a gradual rearrangement of the highly active surface gold atoms to yield a roughened surface deposit of regular gold. This would explain the increase in the rate

of hydrogen gas evolution after ca. 40 min of cathodization (Fig. 4) (the increase in the electrode area more than compensating for the inhibiting effect of the surface gold atom activation process). However, since the same trends were not observed when the anode was changed from gold to carbon (with carbon anodes there was no appreciable change in cathode area and no reversal of the hydrogen evolution current decay), this initial interpretation is deemed invalid. An alternative possibility is that the area change arose owing to slight dissolution of the gold anode. Dissolution of gold under anodic conditions in 1.0 mol dm^{-3} H_2SO_4 is normally regarded as trivial; however, formation of soluble auric species is quite possible in aqueous solutions of low pH [12] and is favoured in the present work by the high current density and the rather long electrolysis time (see Fig. 4). It is therefore assumed that the roughening of the cathode surface in the case of the experiment summarized in Figs. 4 and 5 is due to transfer of gold between the anode and cathode, i.e. electrodissolution of gold at the anode followed by its electrodeposition at the cathode, the transfer through the solution involving the movement of dissolved auric (Au^{3+}) ions, viz.:

$$Au_{anode} \xrightarrow{3e^-} Au^{3+}(aq, mobile) \xrightarrow{+3e^-} Au_{cathode} \qquad (1)$$

Such a process cannot occur using carbon anodes, i.e. with the latter it is possible to investigate the effect of the HER on the gold cathode surface without interference from the effect of the anodic dissolution of gold.

Dissolution of gold at the anode and transfer of the metal in ionic form to the cathode was subsequently confirmed by repeating the prolonged electrolysis experiment using a gold anode and platinum cathode. The cyclic voltammogram recorded for the platinum electrode at the end of the experiment (Fig. 6) clearly showed evidence for the presence of gold on the platinum surface (note the cathodic peak at ca. 1.18 V in the negative sweep). Such a procedure has interesting possibilities for producing surfaces containing different Pt/Au ratios of interest, for instance in electrocatalytic studies.

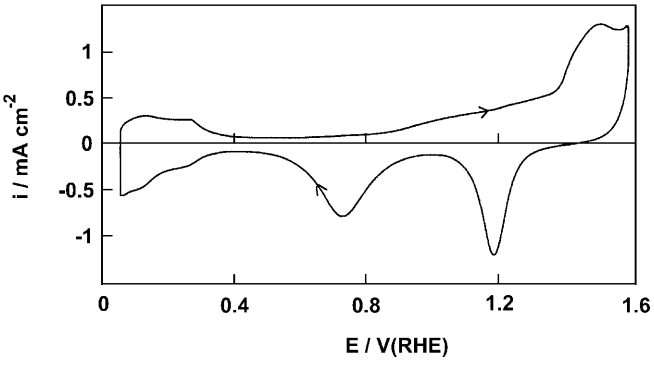


Fig. 6 Cyclic voltammogram (0.05–1.60 V, 50 mV s^{-1}) for a platinum wire electrode in 1.0 mol dm^{-3} H_2SO_4 at 25 °C; the electrode was prepolarized at –0.1 V for 3 h in the same solution using a gold counter electrode

Changes in surface topography of the gold surface induced by cathodization were investigated by SEM. Micrographs of two lengths of wire (one untreated and the other precathodized) from the same batch are shown in Fig. 7. The "activated" wire was first cathodized for 2.5 h and a cyclic voltammogram recorded to check the presence of an active state response, i.e. the presence of a significant anodic response in the positive sweep at ca. 0.5 V (Fig. 8b). It is also clear from a comparison of the two monolayer oxide reduction responses shown in Fig. 8 that the real surface area of the gold was not significantly altered as a result of the hydrogen gas evolution process. Comparison of the SEM micrographs (Fig. 7) at low magnification, (a) and (b), indicated the presence of protrusions on the cathodized surface. From the data obtained at higher magnifications, (d) and (f), it appeared that the prolonged cathodization resulted in the appearance of cracks and cavities on the gold surface. These alterations in the appearance of the cathode surface are characteristic of hydrogen embrittlement processes [13].

AFM data for unpolarized and cathodically activated gold are summarized in Fig. 9. In each case the average roughness, R_a, defined by the equation:

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

i.e. the arithmetic mean of the deviation in height from the mean height value ($\bar{Z}$), was estimated for both samples at four different regions of the surface. The average values obtained were as follows: unactivated surface, $R_a = 25.3$ nm; $\bar{Z} = 141.9$ nm; activated surface, $R_a = 33.4$ nm, $\bar{Z} = 197.5$ nm. It is evident from these data that, in agreement with the SEM results, cathodic preactivation increases the roughness and disorder at the gold surface.

In many experiments with gold electrodes in acid solution, when the metal surface was preactivated by thermal, cathodic or abrasive pretreatment, a cathodic response was observed (even with carefully deoxygenated solutions) at low potentials, e.g. 0.0–0.3 V, in both the positive and negative sweep. The effect, which was illustrated in more dramatic form earlier [7], and is evident here in both Fig. 3a and Fig. 8b, was attributed to the presence of oxy, or oxysulfate, species at the gold/solution interface which undergo reduction in a sluggish manner. To determine the amount of reducible species at the interface a gold electrode was cathodized at –0.45 V for 3 h in a 1.0 mol dm^{-3} H_2SO_4 solution which was continuously purged with a stream of nitrogen gas. At the end of this period the potential of the gold electrode was held at 0.1 V (to reduce the surface deposit and thus determine the charge associated with the latter). However, the reaction involved seemed to be particularly sluggish (Fig. 10); the cathodic current at 0.1 V remained virtually constant (indeed, it showed a slight

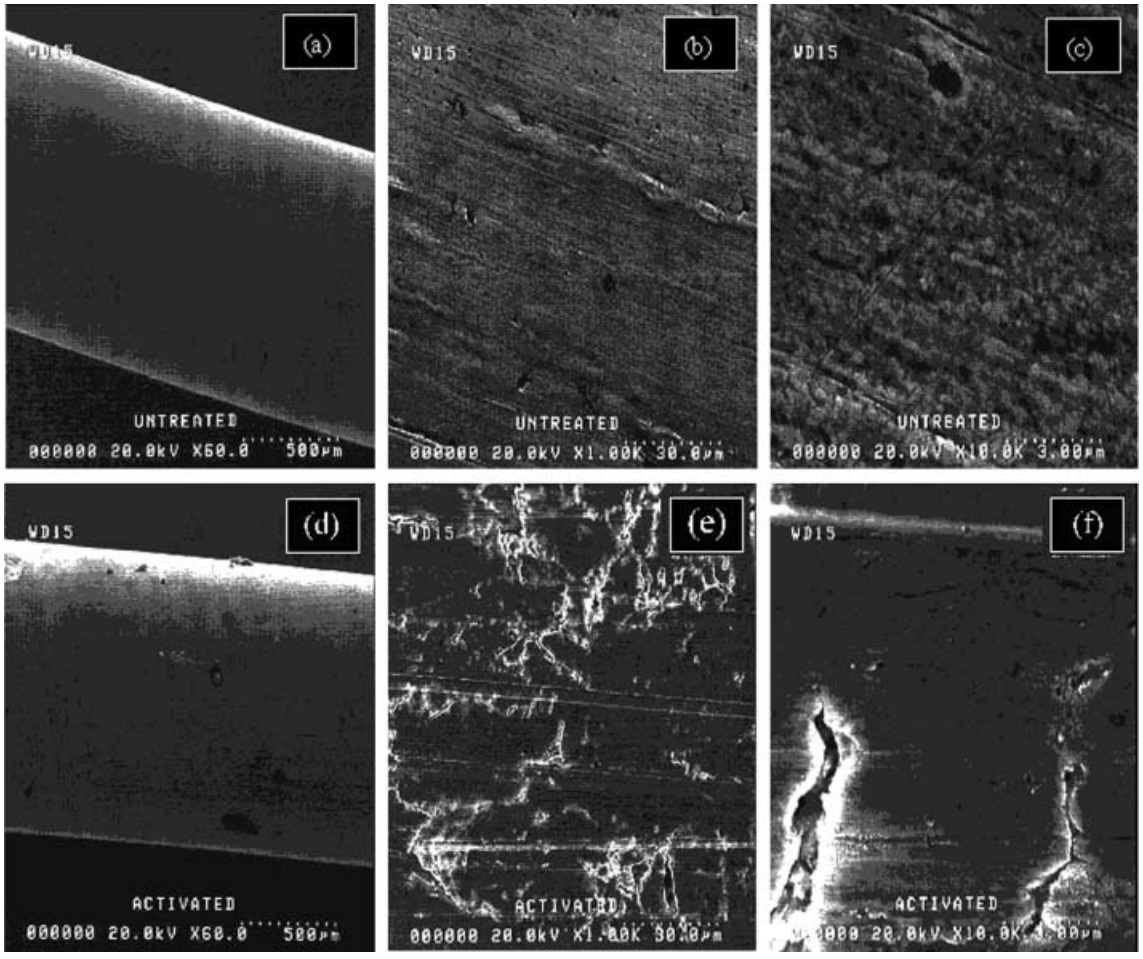


Fig. 7 Scanning electron micrographs of gold wires before (**a**–**c**) and after (**d**–**f**) cathodic pretreatment (the latter involved polarization at –0.5 V for 2.5 h in 1.0 mol dm^{-3} H_2SO_4 at 25 °C). Magnification values: **a** and **d**, ×60; **b** and **e**, $\times 10^3$; **c** and **f**, $\times 10^4$

increase with increasing polarization time over a period of 36 min) at ca. 0.008 mA cm^{-2}.

The effect of holding potential on the hydrogen evolution current decay is summarized in Fig. 11. Commencing at 0.00 V, the potential was decreased in steps of 0.05 V; the current was recorded at each potential value for a period of 10 min and the electrode was allowed to rest on open circuit for 2 min before applying the next potential. Significant current decay with time was observed for $E < -0.10$ V; this was the region where the rate of hydrogen gas evolution increased quite vigorously with increasing overpotential. It appeared that the extent of the decay increased with increasing overpotential (or increasing rate of hydrogen gas evolution).

A curious feature of the decay process was the ease with which it was reversed. For example, when a gold surface was polarized at –0.45 V in 1.0 mol dm^{-3} H_2SO_4 at 25 °C, the rate of hydrogen gas evolution decayed from ca. 141.18 mA cm^{-2} at $t = 0$ to ca. 23.53 mA cm^{-2} after a polarization period of 3.0 h. A cyclic voltammogram, 0.0–1.80 V at 50 mV s^{-1}, was recorded to monitor the change in redox behaviour of the interface. The polarization at –0.45 V was then repeated and the rate of hydrogen gas evolution again decayed from ca. 211.76 mA cm^{-2} at $t = 0$ to ca. 24.71 mA cm^{-2} after 3.0 h (note that the rate of hydrogen gas evolution was substantially greater at the beginning of the second period of electrolysis). The nature of the decay was rather similar in both cases, e.g. it was quite rapid over the first 10 min and then rather gradual for the remaining time. In such experiments this surface reactivation was observed even without recording an intermediate cyclic voltammogram; a similar effect was observed on switching off the current output of the potentiostat for a period of ca. 1.0 min after prolonged cathodic polarization; on reapplying the negative potential, high rates of hydrogen gas evolution were again observed initially.

Discussion

As discussed in earlier publications from this laboratory [7, 8, 14], active states of metal surfaces are assumed to reflect the presence at the latter of metal atoms in a state of low lattice coordination number, low lattice stabilization energy and therefore of high activity. Such atoms (or clusters of same) function as electron donors at the interface at unusually low potentials (the effect is well

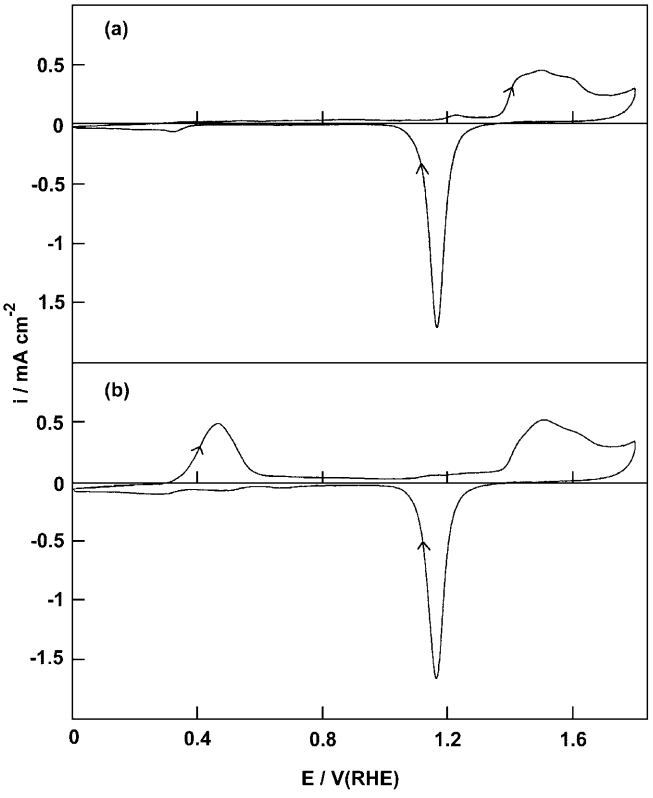


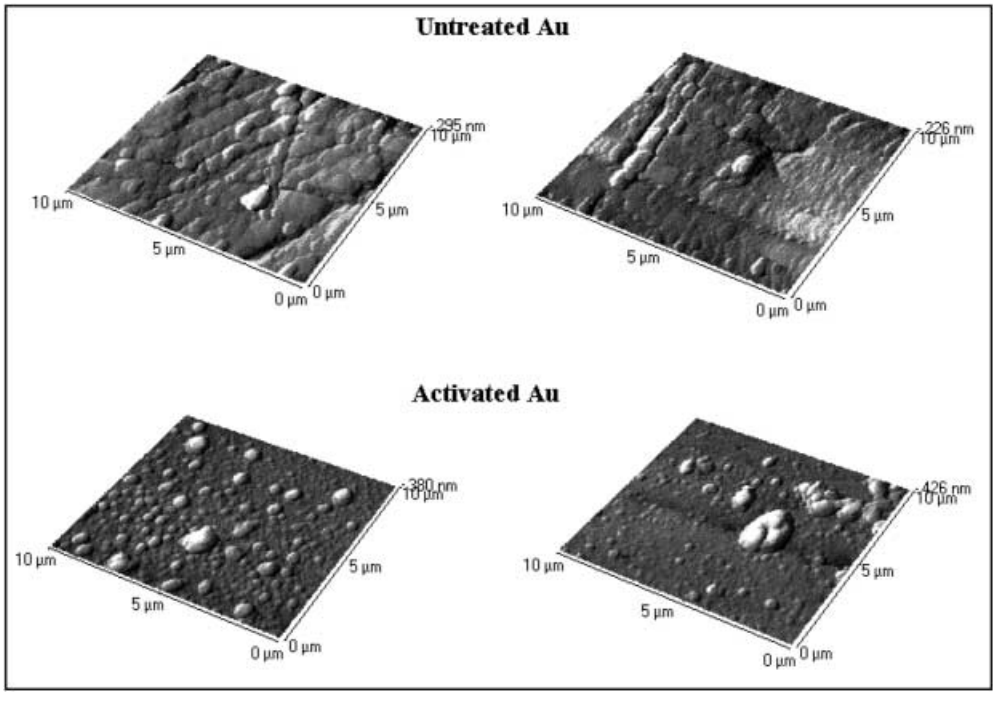
Fig. 8 Cyclic voltammograms (0.00–1.80 V, 50 mV s^{-1}) recorded for the gold electrode before (**a**) and after (**b**) cathodic pretreatment (1.0 mol dm^{-3} H_2SO_4 at 25 °C; polarized at –0.5 V for 2.5 h); this was the sample which (as outlined in the text) was later used for the SEM work, i.e. Fig. 7d–f

established for discrete metal microclusters [15] and has been demonstrated in the case of extended metal surfaces by work function measurements [9]). Cathodic pretreatment is assumed to disrupt or microroughen the gold surface in the present case and again such behaviour is well established in the hydrogen embrittlement area [13].

The anomalous, post-cathodization response in the region below 0.6 V, e.g. in Fig. 8b, may be observed after various types of surface pretreatments. Since some of these are non-electrochemical, e.g. severe thermal pretreatment [8] or abrasion (the effect of the latter will be described in more detail shortly), the presence of the anodic peak at ca. 0.5 V in the positive sweep is not due to the oxidation of some impurity deposited on the surface during the cathodic activation process. Another indication that this feature at ca. 0.5 V is specific to gold, and not some impurity, is that several electrocatalytic processes (both reductions and oxidations [8]) commence and terminate in this region for gold in aqueous acid solution. It is assumed that as the gold surface becomes more active, i.e. many of the gold atoms (probably at active sites) become more electropositive, the binding of the reaction intermediate (H_{ads}), and the coverage of same, diminish and hence the rate of hydrogen gas evolution decreases (Fig. 2).

There is, however, an alternative (although perhaps less likely in the case of gold) explanation based on the intervention of surface oxide, or oxysulfate, species. It is widely assumed [11] that gold surfaces in aqueous acid media only undergo oxidation above ca. 1.36 V. The

Fig. 9 Examples of the surface topography, as determined by AFM, of unactivated (*upper pair*) and cathodically activated (*lower pair*) gold wires (two different regions of the same sample are shown here in each case); the activation conditions were identical to those in Fig. 7



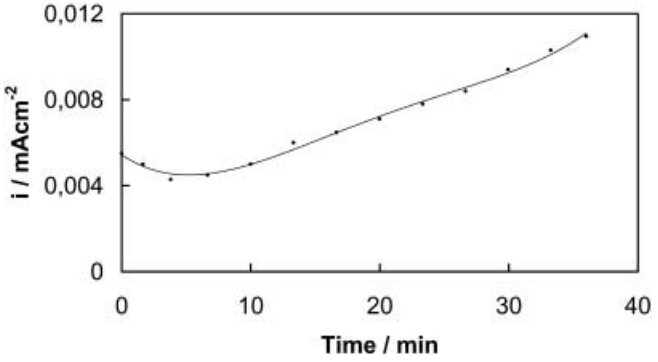


Fig. 10 Sustained cathodic current response observed on holding the potential of a freshly activated gold wire at 0.1 V in deoxygenated 1.0 mol dm^{-3} H_2SO_4 at 25 °C (note the cathodic response in the positive sweep at this potential in Fig. 8b). The electrode was precathodized at –0.45 V for 3.0 h

anodic response at ca. 0.5 V (Fig. 5b) was attributed recently [7, 8] to the oxidation of very active gold atoms at the interface; highly active metal atoms were assumed to be mobile species on an unstable, highly activated, gold surface: $E°(Au_g/Au_2O_3.nH_2O) = 0.33$ V at 25 °C [7]. The reaction involved at ca. 0.5 V is not a highly reversible process as the reverse (cathodic) step in the negative sweep is quite sluggish. Such behaviour is unusual as multilayer hydrous films (which usually undergo reduction within the double layer region) often exhibit sharp cathodic peak responses [16, 17].

The metal atoms involved in oxide growth on gold at ca. 0.5 V are quite unusual; the surface layer is very active and hence the oxide product may also be unusual, e.g. quite voluminous or extended. In general, multivalent cations such as Au^{3+} are strongly hydrated [18]. The oxidation of the active gold atoms may be viewed as a combination of oxidation, hydration and hydrolysis, viz.:

$$Au* \xrightarrow{-3e^-} Au^{3+} \xrightarrow{+(n+3)H_2O} Au^{3+}.(n+3)H_2O \xrightarrow{-3H^+} Au(OH)_3.nH_2O \quad (3)$$

followed by catenation, or oxide agglomeration, of the product. Reduction of such a material, where the product (Au) is of much lower molar volume than the reactant (the semi-rigid oxide), may result in gaps developing between the remaining oxide and the electrode surface (reduction is assumed to commence at the oxide/solution interface, the oxide involved being localized, i.e. in particulated form). Poor electrical contact at the oxide/solution interface would explain the inhibited nature of the cathodic response below ca. 0.6 V, e.g. in the negative sweep in Fig. 8b.

In the vast majority of cases, cathodic currents were observed after cathodic activation at the beginning of the first positive sweep; this is typified here by the prolonged cathodic response on holding at 0.1 V (Fig. 10). The reducible species involved, which may be an oxysulfate (for which thermodynamic data are not available), may be formed either in the course of the cathodic pretreatment

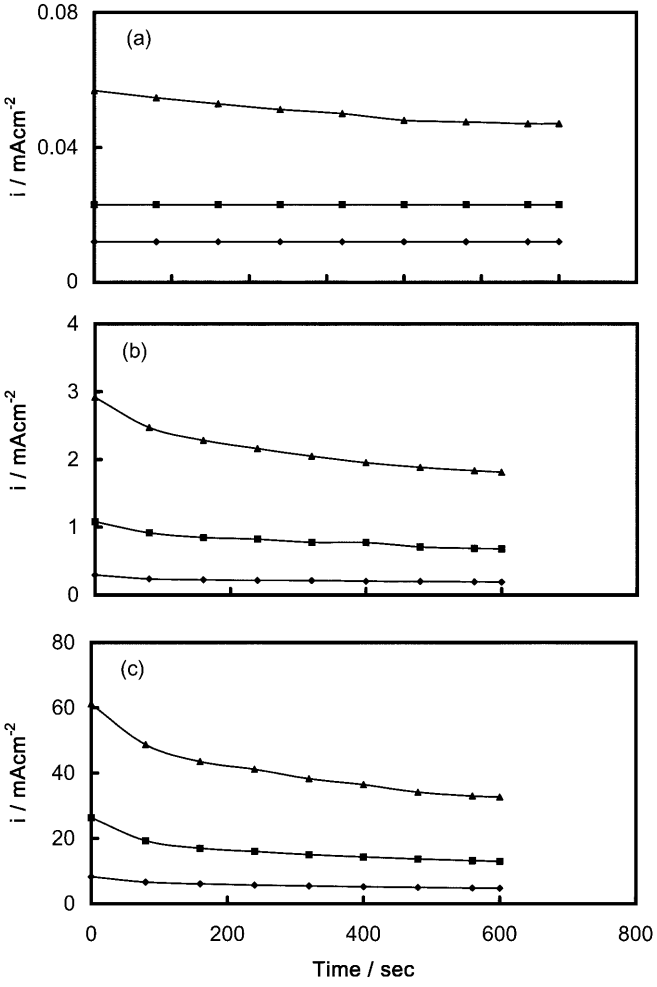


Fig. 11 Variation (usually decay) of the cathodic current density (over a period of 10 min in each case) for an initially unactivated gold wire electrode in 1.0 mol dm^{-3} H_2SO_4 at 25 °C (starting at 0.00 V and increasing the potential in steps of 0.05 V); the applied potentials were as follows: **a** ◆ 0.00 V, ■ –0.05 V, ▲ –0.10 V; **b** ◆ –0.15 V, ■ –0.20 V, ▲ –0.25 V; **c** ◆ –0.30 V, ■ –0.35 V, ▲ –0.40 V

or on switching off the cathodic current. The situation involved is complicated by the fact that the oxidation of the active state of the metal does not occur in a reversible manner; once formed, the oxidized species are quite reluctant to undergo reduction, i.e. there may be a gradual accumulation of such thermodynamically unfavourable species at the interface.

In principle, therefore, there are two possible explanations for the decay of the hydrogen gas evolution rate with time under potentiostatic conditions:

1. Activation of the surface lowers the stability and coverage of the main reaction intermediate (H_{ads}).
2. Gradual accumulation of oxy species at active sites at the interface may progressively reduce the number of such sites on the surface available for the gas evolution reaction.

The latter view may seem improbable for gold; it is given here because the same type of current decay be-

haviour will be described shortly for other metals, e.g. iridium, where even multilayer hydrous oxide films in either acid or base cannot be reduced (again contrary to behaviour expected on the basis of thermodynamic data [12]) under cathodic conditions.

The reactivation of the electrode on temporarily setting the electrode on open circuit (the response on reapplying the potential was greater than the initial hydrogen evolution rate at $t=0$) is evidently due to the rapid decay of the active state (which is assumed to promote an increase in H_{ads} coverage) at surface active sites. The enhanced hydrogen evolution observed initially after reapplying the potential may be due to changes in surface topography, e.g. an increase in real surface area or coverage of active sites. An explanation based on an oxide involvement is also possible; the retention of the oxide at active sites may be dependent on the unusually high activity of metal atoms at such sites, which in turn requires the presence of vigorous hydrogen gas evolution. Once the overpotential is removed, the hydrogen and metal atom activities decay, the inhibiting oxide undergoes reduction, and thus the sites are reactivated for subsequent hydrogen gas evolution.

At a general level, many of the observations and ideas described here are not particularly novel. Highly unusual reactivity of gold has been observed by Haruta and co-workers [19] (their work involved gold microparticles on oxide supports) and Mori and Shitara [20] (the gold surface in the latter case was activated tribologically, i.e. by scratching). The ability to disrupt a gold surface in acid solution by even mild cathodic pretreatment was noted earlier by O'Grady and coworkers [21]; similar anodic pretreatment induced far less change. As pointed out previously [7], the unusual redox response for gold in acid (Fig. 3) following cathodic pretreatment has been demonstrated independently by Ling and co-workers [22].

Hydrogen embrittlement of metals is a very well-known phenomenon; apart from causing gross changes [13], e.g. cracking, blistering and even in some cases shattering [23] in metals, it was demonstrated recently that the stresses induced by the entry of hydrogen can cause displacement of metal atoms from the bulk to the surface [24] and the formation of small agglomerates or nodules at the interface [25] (these displaced metal atoms are the ones which are assumed to be unusually reactive). Of course, gold is not a strong hydrogen absorber, but the high pressure of hydrogen at the interface under vigorous gas evolution conditions [26] probably forces some hydrogen into grain boundaries, defects and possibly some interstitial sites at the gold surface. It may be noted also that in rather similar work to the present, but concerned with hydrogen permeation through iron, Flis and coworkers [25] reported that the overpotential for the cathode in base increased (at constant current density) over an initial period of ca. 24 h, i.e. the cathode activity (as in Fig. 2 here) decayed with time. They also observed substantial topographical changes at the cathode surface and postulated (at the end of their section 4.1) the involvement of thermodynamically unstable oxide species in promoting entry of hydrogen into the metal lattice.

In our opinion, viewing an electrode surface as a uniform two-dimensional plane separating an electronic conductor from an electrolytic solution is not particularly realistic, especially from an electrocatalytic viewpoint. Defects (or active sites) are almost invariably present even at monocrystalline metal surfaces [27] and, as demonstrated here, they may be generated at the interface during the course of reaction. Atoms at such defects exhibit unusual electrochemical behaviour, quite different from that of low-energy surface or bulk metal atoms, but one that is often highly relevant to electrocatalytic behaviour [14]. Hydrogen-induced movement of metal atoms is also a possible source of Pt-activated porous anode deterioration in H_2/O_2 fuel cells.

From a practical viewpoint, two interesting points, related to counteracting the decay in cathode activity (Fig. 2), emerge from the present work. Interrupting the electrolysis for a short period of time (which allows the active state of the surface to decay) was shown to have a beneficial effect (such behaviour is already known in the case of nickel cathodes in base [6]), i.e. interrupted current may be more efficient than constant current electrolysis. Alternatively, slow deposition of metal ions from solution may maintain the cathode in a state of high activity (indeed, the activity, as in Fig. 4, may increase with time). In this case there is no need for current interruption; the dissolved metal ions required for deposition at the cathode need not necessarily require dissolution of the anode; a suitable salt may be added at a very low concentration level to the catholyte.

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