JOURNAL OF APPLIED ELECTROCHEMISTRY **14** (1984) 679–686

Hydrous oxide formation on gold in base under potential cycling conditions

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Received 3 October 1983

The formation of hydrous oxide films on gold in base under potential cycling conditions was investigated and found to be less inhibited than the same type of reaction observed when gold is strongly anodized at high potentials under d.c. conditions at high pH. The overall behaviour on cycling is quite similar to that observed with other metals, e.g. platinum. The importance of the lower limit, for instance, again appears to be related to the need under film thickening conditions to significantly reduce the compact oxide layer formed on the metal surface during the anodic sweep. It was noted that the earlier duplex model for this type of system, i.e. an inner compact and an outer dispersed oxide layer, is not always valid. Under certain conditions about six distinct peaks (suggesting six different states of gold oxide hydration, dispersion or polymerization) were observed in cathodic sweeps recorded for the reduction of thick films grown on gold under potential cycling conditions in base.

1. Introduction

The present work is a continuation of previous research on hydrous oxide formation on metal surfaces in general [1, 2] and gold in particular [3, 4] as reported from this laboratory. The earlier work with gold, in which a distinct difference in potential/pH behaviour was observed between hydrous and anhydrous oxide layers, was carried out using anodic films generated under d.c., i.e. potentiostatic, conditions. One of the problems with the d.c. technique is that only a limited thickness of hydrous material can be generated by this method in solutions of high pH [3]. We now wish to describe a potential cycling method for the production of considerably thicker hydrous oxide layers on gold in alkaline solutions.

The mechanism of hydrous oxide growth under potential cycling conditions is clear, at least at a qualitative level, from recent work with platinum [1, 2], where it was demonstrated that substantial reduction of the initial monolayer film – which is presumed to be composed of compact, largely anhydrous material – must occur at the lower limit of the sweep. However, the lower limit must be such as to avoid significant reduction of the more stable, hydrous, outer layer. The upper limit in these cycling experiments must be such as to significantly increase the oxygen-to-metal ratio at the surface above unity, i.e. some penetration of oxygen into the outer regions of the metal lattice (with appreciable disturbance of the latter and possible formation of a thin layer of a compact higher oxide) seems to be an essential feature of the hydrous oxide growth reaction. Reduction of these thin, inert, compact layers at the lower end of the sweep yields a surface covered with displaced metal atoms which on repetitive cycling are gradually converted to a dispersed, porous form of the hydrous oxide. The latter is not very protective, i.e. further oxidation of the underlying metal can occur, usually until a substantial thickness of poorly hydrated material accumulates at the inner region of the hydrous film. Direct evidence for this change in the degree of hydration across the film was obtained recently by McIntyre *et al.* [5] in the case of iridium.

In the present work the films were generated using triangular potential sweep conditions; recent work with platinum [6] suggests that square wave conditions may also be effective. The effect of the usual variables, e.g. upper and lower limit, frequency (or sweep-rate) and cycling time, was investigated. An unusual degree of complexity was

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noted in the reduction behaviour of these thick films formed on gold on cycling in base.

2. Experimental

The working and counter electrodes consisted of gold wires (1 mm diameter, *c.* 1 cm^2 exposed geometric area, 99.999% pure, Koch-Light Laboratories) sealed directly into soda glass. A 3-compartment cell was used, with a sintered glass disc separating the working and counter compartments. The potential of the working electrode was measured, and is quoted here, with respect to a hydrogen reference in the same solution; the usual type of Luggin capillary arrangement was used to minimize errors due to electrolyte IR effects. The solutions were made up using Analar grade reagents and triply distilled water; the solution in the working compartment of the cell was stirred with a flow of purified nitrogen gas.

The potentiostat used for this work (Wenking, Model FR 0.5) was controlled using a function generator (Philips, Model PM 5168). Currents were recorded as a potential drop across a standard resistor using a potentiometric chart recorder (Rikadenki, Model BW-133). Before each run the electrode surface was abraded with very fine sand paper and then washed with triply distilled water. The extent of oxide growth was determined coulometrically [3, 4] from cathodic sweeps recorded over the range 1.3–0 V, usually at a sweep-rate of 13 $mV\,s^{-1}$. It was demonstrated in preliminary experiments that, as in the case of platinum [7], the charge for reduction in the hydrous oxide region, in the case of moderately thick films grown under identical conditions on gold, did not vary significantly with sweep-rate (at least within the range 10–100 $mV\,s^{-1}$).

3. Results

Although the present project was concerned mainly with hydrous oxide growth on gold under potential cycling conditions, some experiments, mainly for the sake of comparison, were also carried out using the d.c. technique. From Fig. 1, for instance, it is clear that while increasing the anodic oxide-formation potential in the latter case over the region 2.00–2.30 V strongly favoured the oxide growth reaction, any increase above about 2.33 V did not further enhance the rate of oxidation. As pointed out earlier [3], the onset of inhibition of oxygen gas evolution at gold in base occurs in this region – the effect was attributed to increasing the formation of a less hydrated variety of the outer hydrous oxide (as an intermediate deposit between the compact and hydrous film) in this potential region. Some results for oxide growth as a function of time on gold in base at 2.3 V are shown in Fig. 2. At this potential the initial rate of net oxide growth appeared to be linear, the rate-determining step may well be the hydration of the gold oxycation, i.e. conversion of

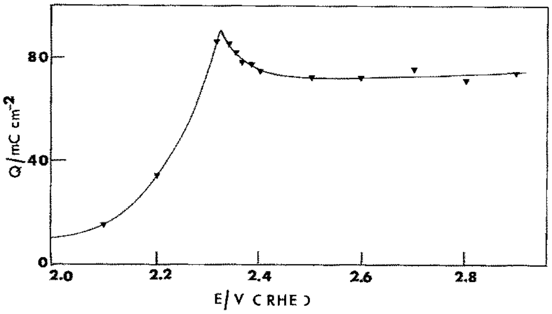

Fig. 1. Net oxide growth under potentiostatic conditions in 1.0 mol dm^{-3} NaOH at 25° C. Initially clean electrode held for 2.0 min at the specified potential. The charge capacity (Q) for the reduction of the resulting oxide layer was calculated from a potential sweep recorded over the range 1.3–0 V at 13 $mV\,s^{-1}$.

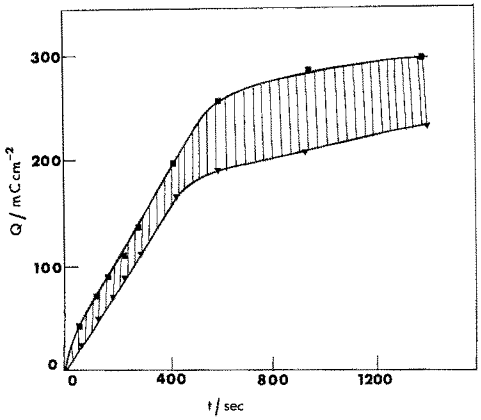

Fig. 2. Oxide formation on gold as a function of time under potentiostatic conditions in 1.0 mol dm^{-3} NaOH at 25° C, $E = 2.30$ V (RHE). The upper line (●) gives the net oxide formation while the lower (■) gives the extent of hydrous oxide formation; the shaded area in this diagram corresponds to the amount of anhydrous oxide present in the region between the metal surface and the hydrated oxide layer.

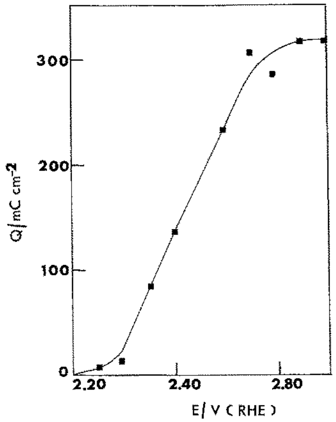

Fig. 3. Effect of the upper limit on oxide growth on gold in 1.0 mol dm^{-3} NaOH (25° C) under potential cycling conditions at 33.0 V s^{-1} for a total, in each case, of 1200 cycles; lower limit fixed at 0.75 V. Charge capacity (*Q*) measured as outlined in Fig. 1.

largely anhydrous to hydrous oxide at the outer region of the compact layer. However, after a period of about 400 s a distinct increase in compact oxide thickness occurred, water transfer to the inner regions of the hydrous film probably becoming inhibited due to the increasing thickness of the outer film. It is clear from Fig. 2 that the increase in thickness of the inner compact film coincided with the marked inhibition of the hydrous oxide growth reaction.

The effects of the upper and lower limit of the oxide growth sweep-rate are illustrated in Figs. 3 and 4, respectively. Little oxide growth was observed with the upper limit less than *c.* 2.2 V (the lower limit used in these experiments in Fig. 3 was 0.75 V, i.e. the optimum lower value, Fig. 4, for the sweep-rate in question here). Increasing the upper limit over the range 2.2–2.8 V resulted in a regular increase in film thickness; there appeared however, to be little advantage in extending the upper limit beyond this value. The optimum lower limit, for a sweep-rate of 33 V s^{-1}, upper limit 2.40 V, was found (Fig. 4) to be *c.* 0.75 V. As outlined in Fig. 5, the efficiency of the oxide growth reaction in base, using the limits 0.75–2.40 V, decreased with increasing cycling rate (especially at values above *c.* 100 V s^{-1}). However, from a practical viewpoint this is counteracted by the fact that the number of oxide growth cycles per unit time increases with increasing sweep-rate or cycling frequency. According to the second set of data shown in Fig. 5 the most effective sweep-rate for fast oxide growth on gold in base in a given period of time is *c.* 100 V s^{-1}, i.e. *c.* 30 Hz.

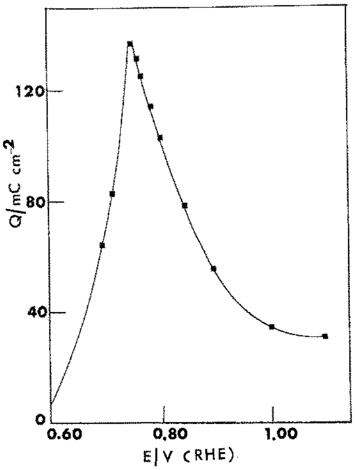

Fig. 4. Effect of the lower limit on oxide growth on gold in 1.0 mol dm^{-3} NaOH (25° C) under potential cycling conditions; upper limit fixed at 2.40 V: conditions otherwise as in Fig. 3.

The effect of extended potential cycling on the oxide growth reaction on gold in base is outlined in Fig. 6. The charge associated with the compact layer was quite significant even at the early stages of cycling but, unlike the d.c. growth (see Fig. 2), further increase in the thickness of this layer occurred only very gradually with increasing oxide-formation time. The marked increase in oxide growth under cycling conditions, as outlined in Fig. 6, is largely due (apart from the early stages) to hydrous oxide formation. The oxide coverage attainable under potential cycling conditions (Fig. 6) was significantly larger than those recorded under d.c. growth conditions (Figs. 1, 2).

As outlined earlier [3, 4] voltammetric reduction profiles for thick oxide layers grown under d.c. conditions are relatively complex, with two peaks in many cases in the compact film reduction region (*c.* 0.80–1.1 V) and – depending upon the oxide-formation potential and period of oxide growth – three overlapping peaks (approximate peak potential values: 0.7, 0.5 and 0.4 V) in the hydrous film reduction region. Similar complex behaviour was noted here (Figs. 7 and 8) for the reduction of hydrous layers grown under potential cycling conditions. In Fig. 7 the compact oxide reduction peaks above *c.* 0.8 V predominate at low upper limit potential values; however at

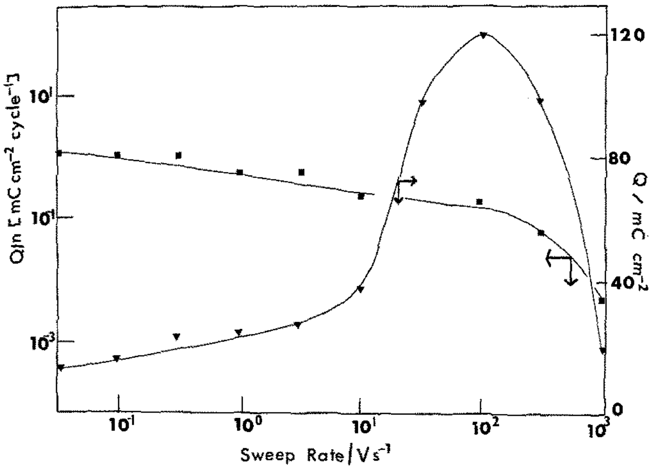

Fig. 5. Effect of sweep-rate on oxide growth on gold in 1.0 mol dm^{-3} NaOH at 25° C. Both sets of data were taken from the same experiments which involved growing the oxide on the initially clean metal on cycling between 0.75 and 2.40 V at various sweep-rates for 2 min periods, the extent of oxide formation being determined coulometrically as outlined in Fig. 1: Q (and ▼) is the total charge measured after 2 min; Q/n (and ■) is the mean charge developed per cycle over the same period.

higher values for this limit, e.g. 2.7 V, these upper, compact oxide peaks are almost negligible compared with the hydrous oxide peak at *c.* 0.6 V. On varying the lower limit, Fig. 8, the peaks for the compact oxide reduction are most clearly seen as the doublet above 0.8 V with the lower limit at 0.6 V. Reduction in this region was also observed in the case of the curves recorded for higher values of the lower limit but in many cases there was overlap with peaks for material in different stages of hydration or polymerization.

A further illustration of the complexity of the reduction process in the case of thick oxide layers on gold in base is given in Fig. 9. The sweep for the film grown under d.c. conditions at 2.4 V, i.e. the dashed line in this diagram, is similar to those reported earlier [4]. The reduction profile for the film grown for 1 min under potential cycling conditions is particularly complex, with indications of about six broad overlapping peaks. On extending the oxide-growth cycling period beyond about 5 min the most dramatic feature was the large increase in charge for the reduction peak at *c.* 0.35 V, the potential value here was virtually independent of film thickness.

4. Discussion

The present results for gold are in agreement with the general model outlined earlier for hydrous

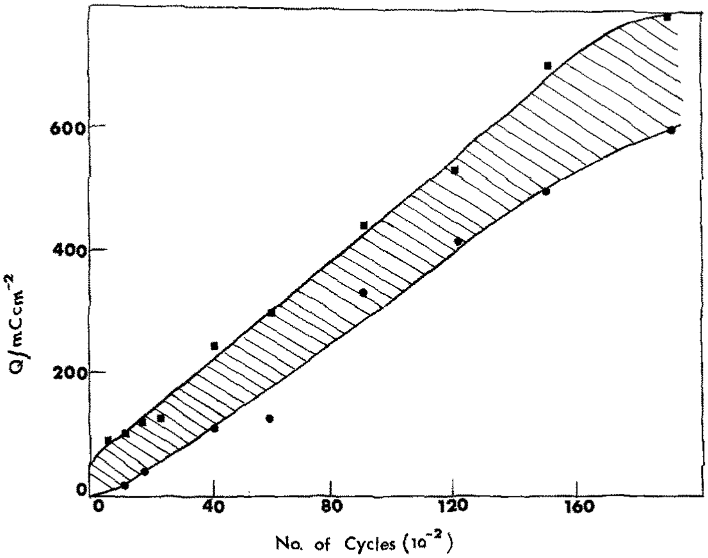

Fig. 6. Variation of the total oxide (■), hydrous oxide (●) and compact oxide (shaded region) with number of oxide growth cycles (0.75–2.40 V, 33 V s^{-1}) in the case of a gold electrode in 1.0 mol dm^{-3} NaOH at 25° C.

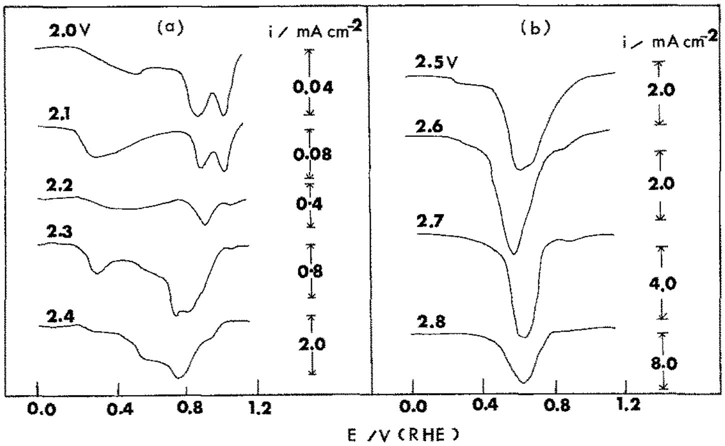

Fig. 7. Variation of the oxide reduction profile with the upper limit of the oxide growth sweep-rate in 1.0 mol dm^{-3} NaOH at 25° C. The oxide was grown in each case at 33 V s^{-1}, 1200 cycles, using a fixed lower limit of 0.75 V; it was then reduced at 13 mV s^{-1}.

oxide growth on metal surfaces. Under anodic sweep conditions surface oxidation of this metal commences at *c.* 1.36 V in acid [8]; there are indications [9] of suboxide, $Au(OH)_{ads}$, formation at lower potentials in base. Although it has been suggested [10] that monolayer oxide growth on gold, i.e. a 1 : 1 ratio of oxygen to surface metal atoms, can be produced by holding the potential of a gold electrode at 1.8 V for 100 s in 1.0 mol dm^{-3} H_2SO_4, the possible penetration of oxygen into the outer layer of the metal and also the formation of such definite oxide species as Au_2O_3 must be borne in mind. In general, however, substantial thickening of the surface layer due to formation of hydrous oxide material is observed under d.c. conditions only above *c.* 2.0 V, i.e. under conditions of rather vigorous oxygen gas evolution [3, 11]. This type of thick film d.c. growth, which is also observed with platinum [12, 13], is assumed to be due to the fact that although the initial compact film is relatively inert, with strong oxygen bridging between cations, local disturbance associated with the gas evolution reaction (for example the formation and decomposition of higher oxide intermediates) results in significant rearrangement and hydration in the outer region of the compact, virtually anhydrous, oxide layer.

Inhibition of hydrous oxide formation (and oxygen gas evolution [3]) on gold in base above *c.* 2.30 V (Fig. 2) is attributed to retardation of water transfer through the hydrous layer to the compact oxide interface. It is assumed here that the anionic gold hydroxy complexes present in the outer layer are particularly stable in base – this is in agreement with the recently proposed thermodynamic interpretation [4] of the unusual potential/pH shift for the reduction of these films.

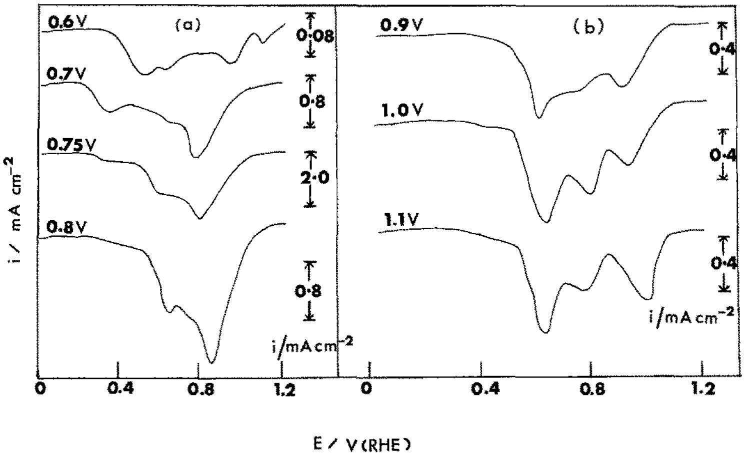

Fig. 8. Variation of the oxide reduction profile with the lower limit of the oxide growth sweep-rate in 1.0 mol dm^{-3} NaOH at 25° C. The oxide was grown in each case at 33 V s^{-1}, 1200 cycles, using a fixed upper limit of 2.4 V; it was then reduced at 13 mV s^{-1}.

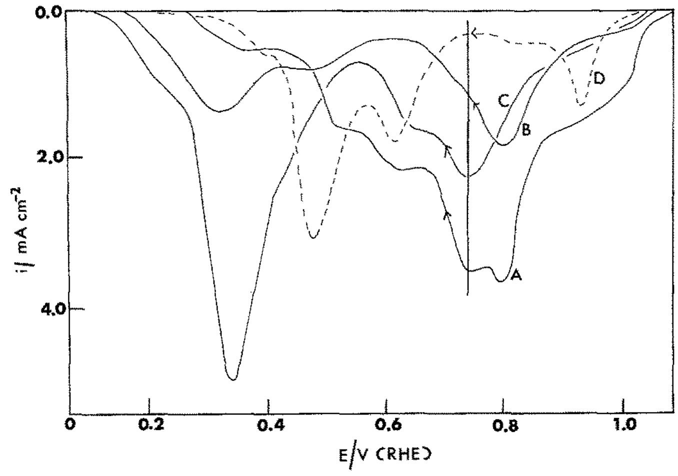

Fig. 9. Variation of the oxide reduction profile with the duration of the oxide growth sweep-rate in 1.0 mol dm^{-3} NaOH at 25° C: oxide growth (0.75–2.40 V, 33 V s^{-1}) times (A) – 1 min; (B) – 3 min; (C) – 7 min. The dashed line (D) shows the profile at the same reduction rate (13 mV s^{-1}) for a film grown under potentiostatic conditions (1 min at 2.40 V). The vertical line in this diagram illustrates the position of the optimum lower limit (0.75 V, Fig. 4) for oxide formation at a sweep-rate of 33 V s^{-1}. In the case of Curves B and C in this diagram the current density values have been divided by a factor of 2.5.

Unlike the situation in acid, where hydrous oxide growth under d.c. conditions shows little sign of retardation, the hydrous film in base appears to be unable to rearrange to a more open, crystalline (or less protective) form. Lack of water at the compact oxide/hydrous oxide interface eventually (see Fig. 2) leads to a dramatic increase in the thickness of the more anhydrous type of material. In the experiment summarized in Fig. 2 the initial compact layer is produced very rapidly and, once formed, it scarcely alters in thickness over the initial 400 s period. The main reaction at this stage is growth of the hydrous film, possibly by hydration of the outer region of the compact layer which is continuously renewed by oxidation of the base metal (another possibility, cation migration through the inner layer [11], is regarded as less likely as it would involve continuous rupture of oxygen–metal bonds in a rather inert, close-packed material). The substantial increase in compact film thickness after 400 s is assumed to be due to growth of this type of material at the compact oxide–hydrous oxide, rather than at the metal–compact oxide, interface. Hydrous oxide growth (and apparently oxygen gas evolution [3]) also becomes severely inhibited at this stage. As reported earlier [4], the inhibition of hydrous oxide formation on gold at a lower potential (2.20 V in 1.0 mol dm^{-3} NaOH) is more gradual – the reaction appeared to obey a parabolic rate law. In the present case, at 2.3 V (see Fig. 2), once the inhibition commenced it had a far more dramatic effect. The origin of this difference in behaviour (which is clearly shown also in the break in the curve just above 2.3 V in Fig. 1) is not clear at the present time; possibly the rapidly growing initial layer of hydrous material at 2.3 V rearranges or ages in an autocatalytic or catastrophic manner at a certain thickness, resulting in virtual exclusion of water molecules from, and consequently inhibition of oxygen gas evolution at, the inner regions of the surface layer.

The slow rate of hydrous oxide growth at longer times in Fig. 2 may basically be due to marked inhibition of oxygen gas evolution [3], the latter reaction being an essential step in the hydration of the compact material, especially under d.c. conditions. Oxygen evolution on gold in base may be confined largely to the compact material – the hydrous oxide, because of its dispersed character, being poorly conducting. The situation may be somewhat similar to hydrous Ir(III) films [14] which are also known to have a high resistance [15, 16]. Further work on the influence of these hydrous films on the oxygen gas evolution process at gold anodes is being carried out at the present time.

To observe hydrous oxide growth on gold in base under potential cycling conditions the upper limit must be well within the oxygen gas evolution region, a further indication of the involvement of the latter in the hydration of the oxycations in the compact layer. The potential for the sharp maximum in the case of the lower limit, *c.* 0.75 V (see Fig. 4), corresponds, according to the data shown in Fig. 9, to a quite substantial reduction of the compact inner layer. Clearly significant reduction of this inner film is essential to promote hydration at high pH. Ageing effects [17, 18] are probably important here; the initial monolayer film on gold – probably a hydroxide – rearranges rapidly to a less reactive oxide. After significant compact layer reduction a new, initially reactive, compact film is generated on each anodic sweep; this fresh material is assumed to be more readily converted to the fully hydrated form. Also apart from this ageing effect, the hydration process at the upper region of the sweep is assumed to be affected by the heterogeneous nature of the compact film, i.e. hydration will occur more slowly after the more reactive sites have been converted (however, a continuous supply of fresh, reactive, sites will be provided, at least in the early stages of hydrous film growth, by the potential cycling perturbation). While significant reduction of the compact layer is essential for oxide growth, there is a sharp limit to the beneficial effect of this process. Decreasing the lower limit below *c.* 0.75 V (see Fig. 4) retards the oxide growth process; possibly some partially hydrated material, which would eventually be incorporated in the hydrous layer, is lost from the surface due to either reduction to the metal or dissolution.

It appears from Fig. 9 that the degree of hydration of the inner layer is affected by potential cycling. With the layer formed under d.c. conditions most of the compact layer is reduced (curve D, Fig. 9, and Burke *et al.* [4]) above *c.* 0.8 V, the main peak for this process being just above 0.9 V. Even this material (nominally Au_2O_3) may be slightly hydrated as a somewhat unusual [3] potential/pH shift (*c.* 6.5 mV/pH unit with respect to hydrogen in the same solution) for this process is also observed. In the case of films grown under cycling conditions (Curves A, B and C in Fig. 9) reduction, probably of some anhydrous material, commences at *c.* 1.0 V but the main peak in this region is now at, or just below, 0.8 V. Evidently the periodic reduction of the compact layer under this type of oxide growth condition leads to a partial hydration of the compact film – and to a significant accumulation of such partially hydrated material within the surface layer. This had been suspected earlier in the case of rhodium [19] where a gradual change in the Tafel slope for oxygen gas evolution was observed with increasing oxide thickness, i.e. as the material developed on cycling it altered from an initially anhydrous, to a totally hydrated, surface layer with increasing oxide growth cycling time. On continued cycling the main feature (Curve C, Fig. 9) was the reduction peak just below 0.4 V, obviously due to the continued accumulation of fully hydrated gold oxide which, according to previous data [4], is assumed to be a hydrated, anionic, oxyhydroxide polymer, namely, $\{[Au_2O_3(OH)_3 \cdot 3H_2O]^{3-} \cdot 3M^+]\}_n$.

The data shown in Fig. 7 are quite interesting. With a low upper limit (2.0–2.1 V) two peaks are recorded in the upper region (above 0.8 V). Then with an upper limit of 2.1–2.3 V significant reduction is also observed at *c.* 0.3 V; this is attributed to the presence of fully hydrated material. At still higher upper limit values, 2.4–2.8 V, some reduction was still observed above 0.8 and below 0.4 V but the bulk of the oxide material was reduced at an intermediate value of *c.* 0.6 V. Evidently at high values for the upper limit – and this is also the region where oxygen gas evolution is inhibited [3] – the outer layer formed on cycling is not as hydrated (or possibly as open in structure) as the hydrous material produced at lower values of the upper limit. The same type of oxides appear to be involved in the experiments relating to the variation of the lower limit (Fig. 8). The peak at *c.* 0.6 V is quite pronounced under the conditions outlined in Fig. 8b; from the current scales in this diagram it is clear that overall oxide growth at lower limit values at, or above, 0.9 V is quite slow (see also Fig. 4). At the low value (0.6 V) in Fig. 8a the two peaks in the upper region are quite distinct but overall oxide growth was again quite slow. As the value was increased a major peak emerged at *c.* 0.8 V (this could be the lower peak in the upper region, the peak maximum being displaced downwards due to the large current associated with reduction of a thicker film [4]). Indications of distinct peaks may also be noted in these diagrams at *c.* 0.6 and 0.3 V.

In summary, the oxide growth on gold under cycling conditions in base is a complex process. The initial layer formed on the anodic sweep is relatively inert. On repeated cycling the outer region of this layer passes gradually through various stages of hydration/dispersion. The overall amount of oxide, and the ratio of one form to the other (according to the peaks in the reduction sweeps in Figs. 7–9, there appear to be from 4 to

6 different types of gold oxide; see, in particular, Curve A in Fig. 9) depends on too wide a variety of variables, e.g. sweep limits, cycling time and sweep-rate, to permit a simple quantitative interpretation of the overall process. A high upper limit, while favouring thick film growth, at least in the initial stages (see Fig. 3), apparently inhibits the final hydration stages of the outer layer; see the virtual absence of the 0.3 V peak in Fig. 7b as compared with Fig. 7a. Caution, however, is required in interpreting much of the data as it is evident from Fig. 9 that the oxide distribution pattern can alter significantly with cycling time. It is also clear from the latter diagram that the distinction between compact and dispersed, or anhydrous and hydrous, films is more easily made in the case of d.c. grown coating (see also Burke and McRann [3] and Burke *et al.* [4]). The inner layer seems to be significantly thicker, somewhat more hydrated (or less compact) and probably less homogeneous when thick film formation on gold is carried out under potential cycling conditions in base.

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