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Oxidation of some reducing agents used in electroless plating baths at gold anodes in aqueous media

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The oxidation of four reductants, two of direct interest in electroless plating baths, at gold electrodes in base was investigated using cyclic voltammetry and the results were interpreted in terms of the incipient hydrous oxide model of electrocatalysis. Dimethylamine borane and tert-butylamine borane reacted in a similar manner; the results were interpreted in terms of the oxidation of the hydroxytrihydroborate anion; potential/pH studies indicate that the important mediator at the interface for this reaction is a cationic, Au(I), species. Pyridine borane reacted in a significantly different manner; the mediating species in this case appeared to be an Au(III) hydrous oxide; further work is required to explain the behaviour of this system. The oxidation of hypophosphite on gold in base was quite sluggish, as was the oxidation of hypophosphorous acid at low potentials in solutions of low pH; it was assumed here that in this system there is a complication due to phosphorous atoms adsorbing at, and thus deactivating, the gold surface.

1. Introduction

In recent publications from this laboratory [1–6] attention was drawn to the fact that oxidation reactions at metal surfaces are frequently triggered, or mediated, by low coverages of incipient oxides generated at adatom sites at the interface. Such incipient oxidation, which was also reported recently by Angerstein-Kozlowska and coworkers [7] in the case of gold single crystal surfaces, is usually quite difficult to detect as it is apparently confined to high energy, low coverage, adatom sites at the metal surface [5]. Gold in base is a very useful system for fundamental investigations in electrochemistry as the virtual absence of a hydrogen adsorption region, plus a considerable resistance to oxidation, results in an extensive double region. However, previous work in this laboratory [8] – supported by an earlier investigation by Kirk and coworkers [9] – suggests that there are a number of low level redox responses, related to incipient surface oxidation, in this system at potentials prior to the onset of regular monolayer oxidation. The first peak, at ~0.1 V/RHE, was attributed to formation of an Au(I) hydrous oxide species. A minor transition at ~0.4 V/RHE was attributed to Au(III) hydrous oxide formation; the species involved in the latter apparently acts as a mediator for hydrazine oxidation [3]. A further, slightly more pronounced, transition of similar origin was observed at ~0.65 V/RHE. Finally, a peak (or doublet [8]) just prior to the onset of regular monolayer oxide formation was attributed to Au(III) hydrous oxide formation at surface metal atom sites of relatively low lattice coordination number – though these apparently are not quite adatoms.

The emphasis here is on relating the minor transitions mentioned above to the electrocatalytic behaviour of gold. Some of the reducing agents used in electroless plating baths [10] were found to exhibit quite interesting behaviour. The reaction of dimethylamine borane (DMAB), tert.-butylamine borane (TBAB), pyridine borane (PB) and hypophosphite is described here; the oxidation of formaldehyde and hydrazine on gold in base has been reported elsewhere [4, 8].

With regard to the incipient hydrous oxide approach to electrocatalysis, which was presented recently in a generalized form [5], the distinction between hydrous and anhydrous oxide is a crucial one. In bulk form the anhydrous oxides (or hydroxides) are relatively dense whereas, as pointed out recently by Farebrother and coworkers [11] in the case of platinum, the hydrous oxides are highly porous, low density, solvent-filled, polymer-like materials. The latter conclusion was drawn earlier [12] from work with iridium; hydrous iridium oxide has an open structure that facilitates the well known bulk redox (or charge storage) and electrochromic behaviour of this system (such behaviour is not observed with thermally prepared, anhydrous, IrO_2). Participation of oxygen or hydroxide, as an adsorbed species, in electrocatalytic oxidation reactions on platinum has been suggested by other authors, for example Gilman [13, 14]; however, in the latter work one of the species being oxidized, CO [13], commenced reaction only at ~1.0 V/RHE, i.e. in the region of regular (compact or anhydrous) monolayer oxide formation. With methanol or formic acid present [14] oxidation was observed as low as 0.6 V/RHE and therefore surface oxygen (or oxide) participation was considered unlikely (the surface of platinum is usually considered as being unoxidizable, in terms of OH_{ads} formation, below ~0.8 V/RHE). Gilman

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postulated "adsorbed water species" as a participant, i.e. as an oxygen donor, in such reactions. However, other species, N_2M_4, HCHO and HCOOH, oxidize readily on platinum in acid [4] at potentials less than 0.4 V/RHE – a region where direct oxygen transfer from water is most unlikely. The advantage of the incipient hydrous oxide approach is that via the concept of premonolayer oxidation it provides an interpretation of oxygen transfer at noble metal electrodes at unusually low potentials. The major difference between the activated chemisorption and incipient hydrous oxide approach to electrocatalysis is the emphasis on the latter on the redox behaviour (or chemistry) not only of surface metal atoms but also oxygroups [15, 16] at the interface.

2. Experimental details

The working and counter electrodes consisted of short lengths of gold wire (1.0 mm diam, ~0.5 cm^2 exposed area, Johnson Matthey Chemicals, Puratronic grade) sealed directly into soda glass. Before experiments the surface was cleaned by abrasion with fine emery paper followed by washing with triply distilled water. Potentials were measured with respect to a hydrogen reference electrode in the same solution; this electrode was contained in a separate vessel, a Luggin capillary was used to minimize *iR* errors. The solution in the working electrode compartment was deoxygenated with a flow of nitrogen gas; cyclic voltammograms were usually recorded both in the presence and absence of nitrogen stirring and oxidation current values generally were slightly larger with stirred solutions.

All solutions were made up using triply distilled water and Analar grade chemicals; the four reductants investigated here were dimethylamine borane, DMAB (Johnson Matthey, Alpha Products), tert-butylamine borane, TBAB, pyridine borane, PB (both from Aldrich) and sodium hypophosphite (BDH Chemicals); due to the low solubility of PB in water, a stock solution of this compound was made up using a 30% by volume mixture of acetonitrile in water as solvent: an appropriate quantity of this solution was then added to the aqueous buffer solution. Phosphate buffer solutions contained a mixture of H_3PO_4 (0.1 M) and NaH_2PO_4 (0.1 M); the pH value was adjusted as required by addition of solid NaOH. The electrochemical equipment consisted of a Thompson Electrochem software controlled potentiostat, Autostat (Type 251), plus a Yokogama (Type PL-1000) X-Y plotter.

3. Results and discussion

3.1. *Oxidation of DMAB*

DMAB is assumed to exist [17] in a partially dissociated form in aqueous media, the equilibrium involved being represented by

$$(CH_3)_2NH:BH_3 \rightleftharpoons (CH_3)_2NH + BH_3 \qquad (1)$$

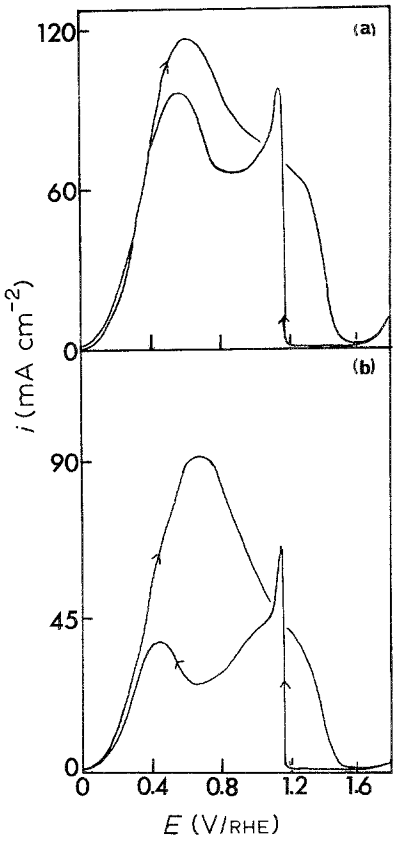

Fig. 1. Cyclic voltammograms (0.0 to 1.80 V, 50 mV s^{-1}) for gold in 1.0 M NaOH containing 0.05 M DMAB, T = 25° C: (a) N_2-stirred, (b) unstirred, solution.

However, as boranes generally are highly reactive, and borane itself (BH_3) is known only as a transitory species [18], it is probably more realistic to represent this equilibrium in the following manner;

$$(CH_3)_2NH:BH_3 + H_2O \rightleftharpoons (CH_3)_2NH_2^+ + BH_3OH^- \qquad (2)$$

The resulting hydroxytrihydroborate anion, whose formation by reaction of borane with water has been postulated earlier [19, 20], may be assumed to oxidize on gold in base according to the reaction

$$BH_3OH^- + 8OH^- = BO_3^{3-} + 6H_2O + 6e^- \qquad (3)$$

It was established in preliminary experiments that dimethylamine itself is not very active with regard to anodic oxidation on gold in base, especially at low potentials (below ~0.4 V). Some evidence in support of the scheme outlined in Equation 2 was obtained from work in acid. At low pH (<4.0) DMAB was found to be unstable, vigorous gas evolution occurred throughout the electrolyte. Loss of the hydroxide ion from BH_3OH^- due to reaction with a proton is assumed to generate the highly unstable BH_3 species at low pH. The oxidation of DMAB on gold in base was found, Figs 1 and 2, to commence just above 0 V, i.e. at the onset of the first low level, reversible transition for this system in the absence of reducible species (see Fig. 2 in [8]). It can be seen from earlier data [8] that the onset of formaldehyde oxidation on gold in base also commences in the same region. This

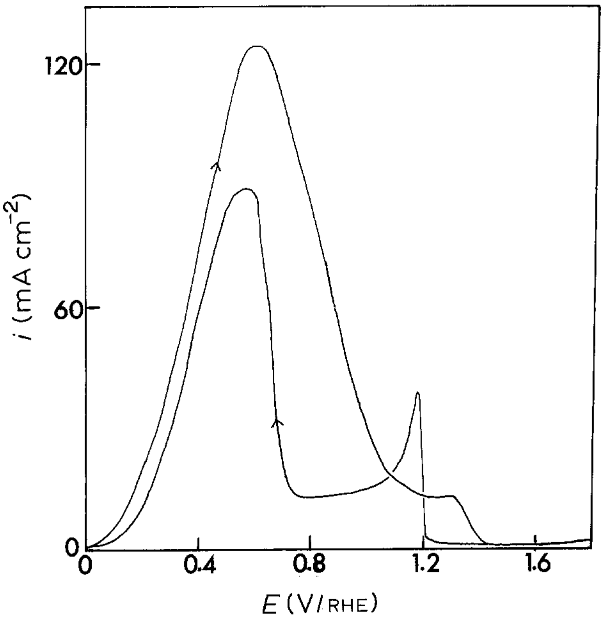

Fig. 2. Cyclic voltammogram (0.0 to 1.80 V, 5 mV s^{-1}) for gold in unstirred 1.0 M NaOH containing 0.05 M DMAB, T = 25°C.

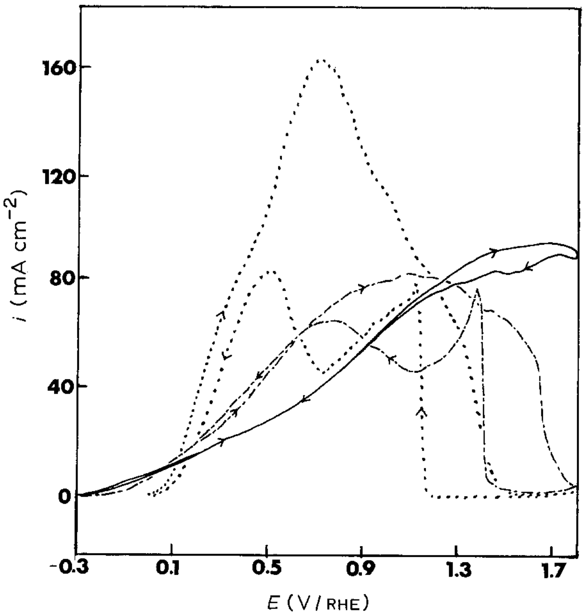

Fig. 3. Cyclic voltammograms (−0.3 to 1.80 V, 50 mV s^{-1}) for gold in unstirred phosphate buffer solutions, of different pH (T = 25°C), containing 0.05 M DMAB (····), pH 13.5; (—·—), pH 9.6; (——), pH 7.0.

is a prime requirement of the incipient hydrous oxide mediation model of electrocatalysis [2] – the onset (anodic sweep) and termination (cathodic sweep) potentials for oxidation should coincide (a condition obviously fulfilled here in the case of DMAB), and the value should be independent of the nature of the reactive solution species.

It was demonstrated earlier [21] that this lower, Au(O)/Au(I), transition for gold (and the same type of behaviour was postulated for the Group 1B metals in general) exhibits an unusual potential/pH effect. The reversible potential for the small peak in question rose with increasing solution pH (in solutions free of dissolved reducing agents) by ~59 mV/pH unit (RHE scale) – or occurred at constant potential on altering pH in terms of a pH-independent reference electrode. If the Au(I) species is the effective oxidant involved in oxidation reactions at low potentials on gold then the same type of behaviour, i.e. an increase in onset/termination potential with increasing solution pH, should be observed in electrocatalytic processes.

Some examples are given in Fig. 3 of the reaction of DMAB on gold in solutions of different pH; as already mentioned elsewhere [6] the onset/termination potential values increased with increasing solution pH, Fig. 4 (an important point in the present work is the more convincing evidence for the latter presented here later in the case of TBAB); the latter plot has a slope of ~46.5 mV/pH unit (RHE scale) – somewhat less than the expected value of 59 mV/pH unit.

It is clear from Figs 1 and 2, that the reaction of DMAB on gold is not simple. The oxidation process in base, Fig. 1, commenced at ~0.1 V, i.e. in the region where the first premonolayer oxidation peak begins to appear on gold in pure base [8]. While the simple theory for incipient hydrous oxide mediation [2] predicts that the oxidation current should then rise to a plateau value, the current on the anodic sweep in the case of Fig. 1 passed through a rather broad maximum at ~0.7 V. However, this is understandable as according to earlier data the hydrous oxide species at the interface is assumed to undergo an Au(I)/Au(III) transition in this region [1]. Because of the greater charge on the central metal ion the cation in the Au(III) state binds the OH$^-$ counterions more strongly; thus the borane species has greater difficulty in interacting directly with the gold cation – hence the decrease in oxidation rate as the potential increases above ~0.7 V. The gold surface in base became almost totally inactive with regard to DMAB oxidation above ~1.20 V as at this stage compact monolayer oxide formation commenced.

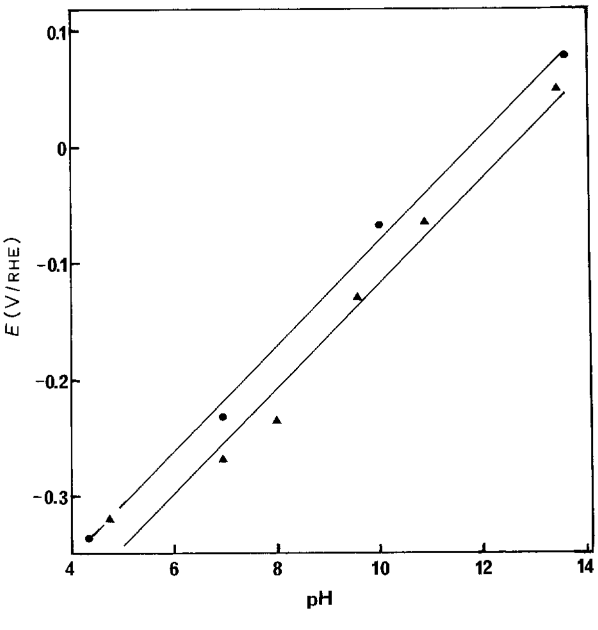

Fig. 4. Variation of the onset potential for DMAB (0.05 M, ▲) and TBAB (0.01 M, ●) oxidation (the compounds were investigated individually) on gold as a function of solution pH, T = 25°C: slope values (mV/pH unit); DMAB, 45.0; TBAB, 46.1.

It was noted also that in some cases a change in slope in the *i–E* curve recorded for the anodic sweep occurred at ~0.4 V. There is a slight indication of this in Fig. 1(b); the effect occasionally was more dramatic and it is worth noting also that in this diagram there is a maximum at this potential on the cathodic sweep. Similar behaviour was recorded earlier for formaldehyde oxidation on gold in base (see, for example, (a) and (b) in Fig. 3 of [8]). Evidently the Au(I) mediator, whose formation commences at ~0.1 V, causes the initial upsurge of current – with the latter tending to attain a limiting value at ~0.4 V. However, at the latter value a new mediating species (of quite low coverage) is generated (transition B in [8]). This may well appear initially as an Au(III) species but in the presence of the dissolved reductant it probably exists at the interface in the Au(I) state, giving rise to a further increase in DMAB oxidation current at ~0.4 V as it cycles through the Au(I)/Au* transition.

On the subsequent cathodic sweep the surface reactivated with respect to oxidation just below 1.20 V. The reduction of the monolayer oxide in this region evidently occurs via a local cell reaction, i.e. the electrons for reduction are supplied by the DMAB rather than from the external circuit. The level of activity for oxidation on removal of the deactivating monolayer was initially quite large; as formation of the compact monolayer deposit entails significant place-exchange of surface metal atoms, rapid reduction of this material leads to a high, but transient, level of gold adatoms – and hence of the mediating Au(I) oxide species. Over the range 1.1 to 0.7 V the product of adatom oxidation is assumed to be a mixture of Au(I) and Au(III) hydrous oxide. Below ~0.7 V the Au(I) product predominates – hence the increase in oxidation rate over the range 0.7 to 0.4 V on the cathodic sweep. Finally, below 0.4 V the driving force (or overpotential) for adatom oxidation decays significantly until, at ~0.1 V/RHE, the mediator (Au(I) hydrous oxide) is no longer formed and the oxidation of DMAB then ceases.

In all cyclic voltammograms recorded for DMAB oxidation on gold in base the peak current at ~0.7 V on the anodic sweep was invariably larger (by a factor of ~1.7 – this was investigated over a broad range of sweep-rates) than the corresponding peak (usually at a slightly lower potential value) on the cathodic sweep. The peak on the anodic sweep is evidently associated with a deactivation process – apparently a change in the nature of the mediator. On the anodic sweep the oxidized state of the mediator prior to the peak is predominantly Au(I) – the more inactive Au(III) state is produced only with difficulty in the presence of the reactive DMAB. However, on the cathodic sweep the mediator, at potentials above ~0.7 V, is predominantly in the less active Au(III) state which is reduced only with some difficulty; the reduction (either electrochemically or by reaction with DMAB) may exhibit some hysteresis and may well not be complete at the peak maximum. This combination of slightly lower transition potential and the presence of more of the mediator in the Au(III) form is probably the origin of the lower peak current on the cathodic sweep.

The effect of sweep-rate on the response during the cathodic sweep is also interesting. At 50 mV s^{-1}, Fig. 1b, the current density at the initial sharp peak just below 1.2 V is larger than that for the peak at ~0.4 V (~64 as compared with 39 mA cm^{-2}). The reduction of the monolayer here is assumed to yield initially Au*, or Au(I), species – hence the high level of transient activity in this region. However, at the slower sweep-rate (5 mV s^{-1}, Fig. 2) there is more time for loss of the active intermediate (Au* → Au_l or Au(I) → Au(III)). Over the region 1.0 to 0.7 V the predominant mediator at the interface at both sweep rates is the less active Au(III) hydrous oxide, hence the low rate of reaction. Below 0.7 V this mediator gradually alters to the more active Au(I) species; this causes the DMAB oxidation current to increase below 0.7 V on the cathodic sweep and as there is more time for this conversion at the slower sweep-rate the second peak on the cathodic sweep (at ~0.4 V) is much more pronounced at 5 mV s^{-1}. The larger peak current density values for stirred, Fig. 1a, as compared with unstirred, Fig. 1b, solution suggests that mass transfer, along with the interfacial reaction, has a significant influence on the rate of reaction.

The behaviour of DMAB on gold in solutions of intermediate pH (10.6 and 7.0, Fig. 3) is less clear-cut than in base. The reaction certainly started, and terminated, at lower potential but the increase in current with increasing potential on the anodic sweep was less dramatic than in base. The lower hydroxide ion concentration in the solutions of lower pH – especially for pH 7.0 – is probably the reason why passivation of the surface was less effective in the monolayer oxide region. The lower current densities at intermediate potentials may be due to a combination of two factors: (a) lower mediator coverage – the Au(I) species are not stabilized to the same degree as in base due to the lower OH^- ion concentration; (b) foreign anions, which are an intrinsic component of buffer solutions of lower pH, may act as counterions (in place of OH^-) at Au(I) centres, and exert a deactivating influence on the latter.

It is clear from Figs 3 and 4 that the onset/termination potential increases with increasing pH; this is in direct contrast to the oxidation behaviour of hydrazine on gold under similar conditions [4]. However, hydrazine oxidizes at a more anodic potential than DMAB – the mediating species for oxidation of the former compound is assumed to be an anionic Au(III) species. As pointed out previously [21] the initial product of adatom oxidation of the Group 1B metals in general is assumed to be a cationic species. Namely,

$$\mathrm{Au}^* + n\mathrm{H_2O} = [\mathrm{Au}(\mathrm{H_2O})_n]^{+1}_{\mathrm{ads}} + e^- \qquad (4)$$

That is, some form of surface-bound hydrated cation is produced which functions as a mediator for those oxidations that occur at low potentials.

According to Equation 4 there is no proton or hydroxide ion involvement in the oxidation of the adatom and – as discussed in [21] – the reversible potential for this process should be independent of pH in terms of a pH-independent reference electrode or increase by the factor 2.3 RT/F V (or 59 mV at 25° C) per unit increase in solution pH in terms of the RHE scale. The increase in the onset/termination potential for DMAB oxidation (Fig. 4) is somewhat less but the trend is certainly in the right direction. There are a number of possible explanations for the slightly low value of the slope in Fig. 4. These are:

(a) It is difficult to establish a precise value for the onset/termination potential. As is clear from Fig. 1 the current density, at low values for the latter, varies in a very gradual manner with change in potential; should one therefore take the onset/termination value as the potential at which the current rises above zero, i.e. at ~0 V, or at the start of the region of rapid increase in current, ~0.2 V? The uncertainty here is related to the fact that the peak for the adatom/hydrous oxide transition, Fig. 2 in [8], is rather broad; such peak broadening may be due to a variety of factors, for example, different types of adatom sites (or different adatom and hydrous oxide activity values), electrostatic interaction between neighbouring charged Au(I) species, etc. Clearly if the onset/termination value for base was taken as being 0.2 V the slope value in Fig. 4 would be significantly closer to 59 mV/pH unit.

(b) The nature of the product formed in the reaction shown here in Equation 4 is somewhat uncertain; in particular the manner in which this species is attached to the surface and its interaction with its counterion (which is assumed [21] to be solvent separated from the monovalent cation) – plus possible minor modifications of these factors with change in solution pH – are features that may also contribute to the unusual behaviour. Further complications may arise due to interaction of the interfacial cation with the reactant, i.e. BH_3OH^-, prior to oxidation of the latter.

All that can be stated at present is that the oxidation behaviour of DMAB on gold in aqueous media approaches that expected in terms of the Au(I) mediator mechanism of electrocatalysis. The differences in behaviour between DMAB and hydrazine apparently arise from the fact that in aqueous media hydrazine exists either in neutral form at high pH or as a cationic species (e.g. $N_2H_5^+$) at low pH. Neither of these species will interact strongly, via electrostatic forces, with the surface-bound Au^+ cation; hydrazine oxidation is mediated by hydrous oxide species associated with the Au(III) state and the onset/termination potential shows [4] the E/pH behaviour characteristic of the Au*/Au(III) hydrous oxide transition, i.e. a decrease of ~3/2(2.303 RT/F) V/pH unit (pH-independent scale). Species that interact with the Au(I) surface-bound cation are usually anionic; an example here is the reaction of formaldehyde in base where the aldehyde exists in the gem-diolate form, i.e. as $H_2CO^- \cdot OH$ [8]. The hydroxy-trihydroborate anion, BH_3OH^-, is assumed to behave in a similar manner. Evidently the electrostatic interaction between the surface-bound cation and solution anion is a major factor in the mediation of oxidation processes on gold at low potential.

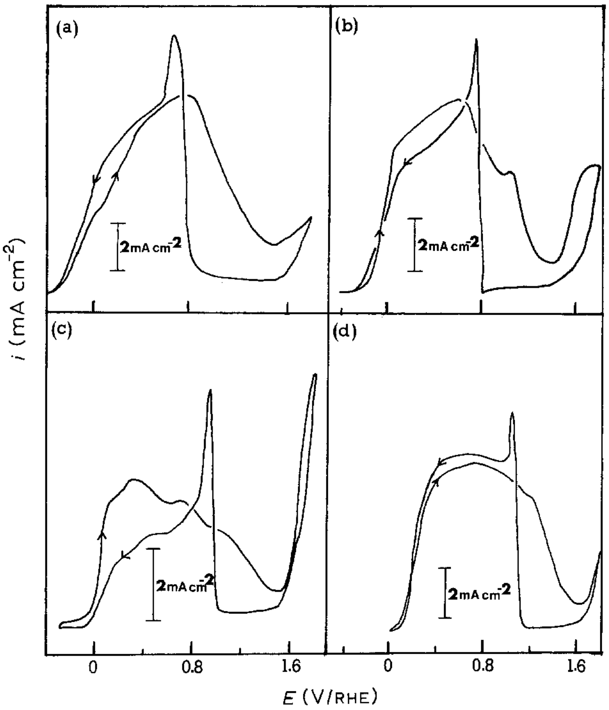

Fig. 5. Cyclic voltammograms (50 mV s^{-1}) for TBAB (0.01 M) oxidation on gold in unstirred solutions of different pH, T = 25° C: (a) –0.4 to 1.80 V, pH 4.4; (b) –0.4 to 1.80 V, pH 7.0; (c) –0.3 to 1.80 V, pH 10.0; (d) 0.0 to 1.80 V, pH 13.5 (zero current in each case was observed at the cathodic end of the sweep).

3.2. *Oxidation of TBAB*

Typical examples of cyclic voltammograms recorded for gold in the presence of TBAB are shown in Fig. 5. The behaviour in base (and in particular the onset/termination potential value) was similar to that observed in the presence of DMAB. The current increase at the onset of oxidation was much steeper in the presence of TBAB; this leads to less ambiguity with regard to both the onset/termination potential values and the fact that the latter decrease on lowering the solution pH. From the data shown in Fig. 4 it is clear that the E/pH behaviour for the onset/termination potential for DMAB and TBAB are remarkably similar.

3.3. *Oxidation of PB*

A typical cyclic voltammogram for PB oxidation on gold in base is shown in Fig. 6. No significant oxidation was observed here over the range 0 to 0.2 V; the onset/termination potential was at ~0.35 V which coincides with the value for a minor increase in current for the same system in pure base-transition B, Fig. 1, in [8]. The current rose to a plateau prior to a second increase commencing at ~0.7 V, i.e. in the region just above transition C, Fig. 1 in [8]. Inhibition occurred as the sweep entered the start of the mono-

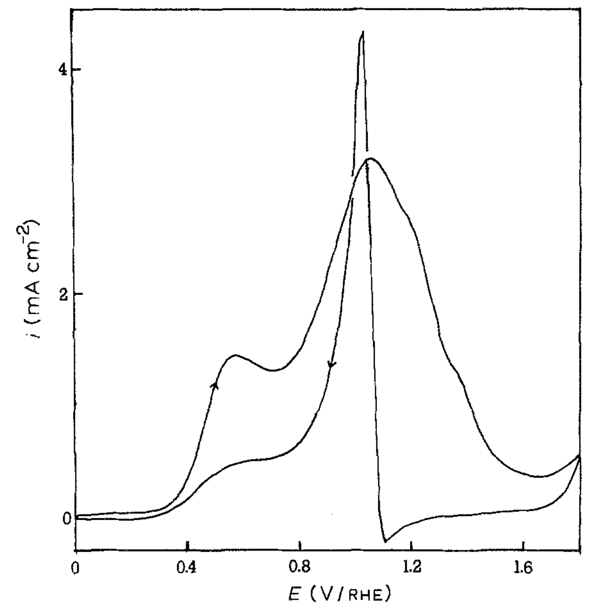

Fig. 6. Typical cyclic voltammogram (0.0 to 1.8 V, 50 mV s^{-1}) for PB (0.01 M) oxidation in unstirred 1.0 M NaOH, $T = 25°C$; the solvent in this case contained 3% (by volume) of acetonitrile in water.

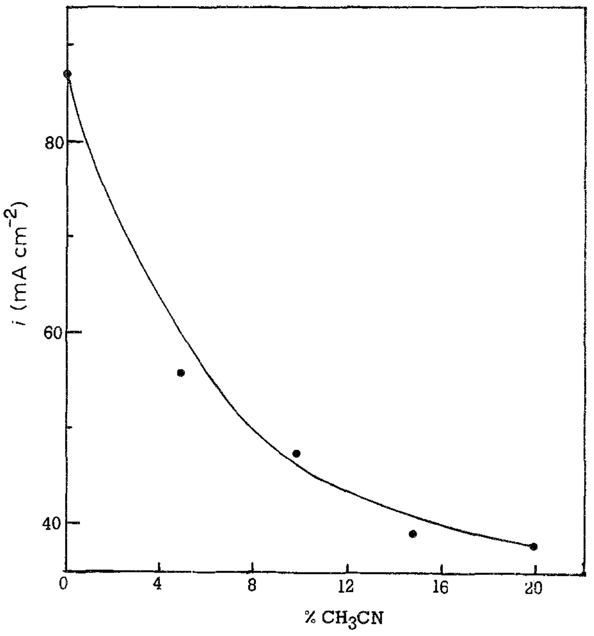

Fig. 8. Effect of the percentage by volume of acetonitrile in the liquid used to make up the cell solution on the DMAB oxidation rate at 0.4 V; conditions otherwise were as given for Fig. 7a.

layer oxide formation region; the above trends were reversed on the cathodic sweep once the monolayer oxide was removed from the surface.

It is assumed here that the borane species in the case of PB solution do not exist in the anionic form, BH_3OH^-; the latter, if present, should commence oxidation at ~0.1 V. The presence of acetonitrile in the solvent is one possible source of complication; however, it was found that the presence of substantial levels of acetonitrile did not adversely affect either formaldehyde or DMAB oxidation on gold in base (Fig. 7), these reactions maintained their onset/termination potentials at ~0.1 V. As outlined in Fig. 8 the rate of oxidation of DMAB at a potential in the active region above the onset/termination value was adversely affected by the presence of increasing levels of the organic solvent; this may reflect increasing competition for active sites on the metal surface between OH^-, OH_2, BH_3OH^- and acetonitrile species.

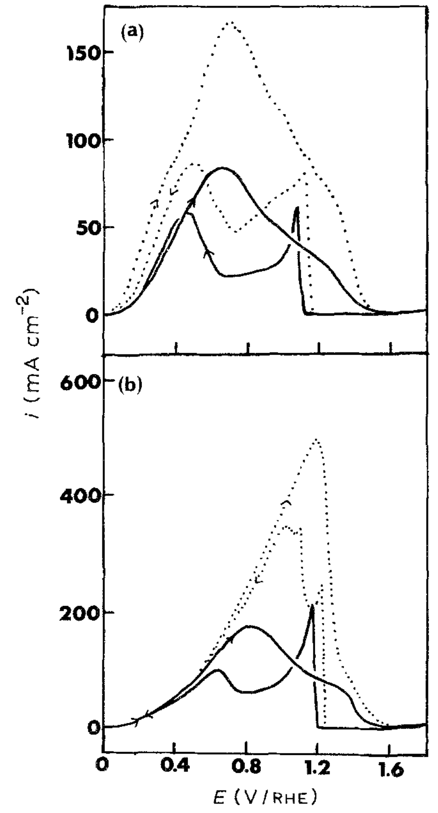

Fig. 7. Cyclic voltammograms (0.0 to 1.80 V, 50 mV s^{-1}) for gold in unstirred 1.0 M NaOH made up using pure water (····) and a 10% (by volume) mixture of acetonitrile in water (——), $T = 25°C$: (a) 0.05 M DMAB present; (b) 0.05 M HCHO present.

Since pyridine is known [1] to give a minor response at gold in base at low potentials, it is possible that the lack of oxidation of PB in the region of 0.2 V is due to inhibition of the Au*/Au(I) reaction due to the presence of the organic base. This seemed to be ruled out by the fact that addition of pyridine to the aqueous solution had little effect on the onset/termination potential (or current values above the latter) in the case of the DMAB oxidation. Further work is obviously required in the case of the PB reaction and two ancilliary techniques that should be useful in this area are (a) boron NMR which should provide information on the nature of the solution species, and (b) Surface Enhanced Raman Spectroscopy (SERS) which should give useful data on the state of species adsorbed at the interface.

3.4. *Oxidation of hypophosphorous acid and hypophosphite*

The acid in question here, $H[H_2PO_2]$ is monobasic, $pK_a = 1.2$ ($T = 25°C$), and both it and its salts are powerful reducing agents which react as follows [22, 23],

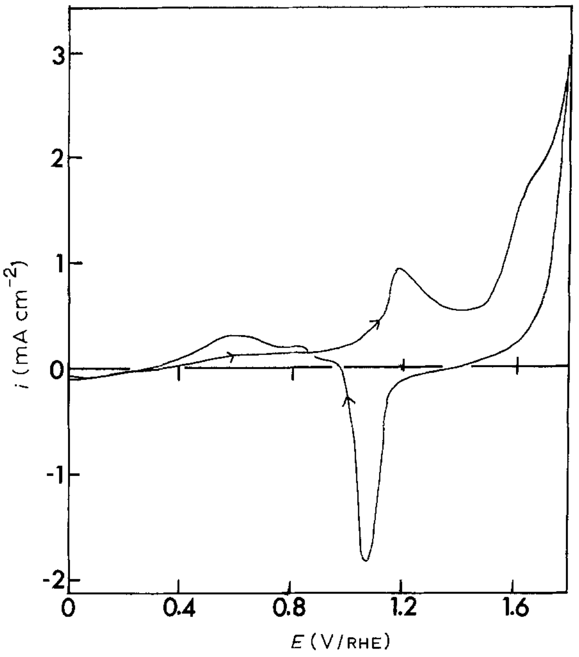

Fig. 9. Cyclic voltammogram (0.0 to 1.80 V, 50 mV s^{-1}) for hypophosphite (0.16 M) oxidation on gold in 1.0 M NaOH at 90° C.

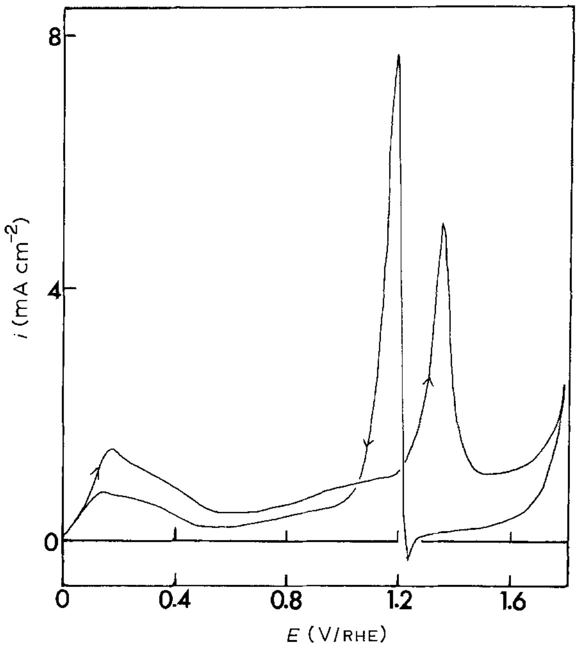

Fig. 10. Cyclic voltammogram (0.0 to 1.80 V, 50 mV s^{-1}) for hypophosphorous acid (0.16 M) oxidation on gold in 1.0 M H_2SO_4 at 90° C.

(a) alkaline media

$$H_2PO_2^- + 3OH^- = HPO_3^{2-} + 2H_2O + 2e^-, \quad E^0 = -1.57\,V/SHE \qquad (5)$$

(b) acidic media

$$H_3PO_2 + H_2O = H_3PO_3 + 2H^+ + 2e^-, \quad E^0 = -0.50\,V/SHE \qquad (6)$$

Since electroless metal plating baths based on the use of hypophosphite are frequently operated at elevated temperature [24], investigation of the oxidation of this compound on gold was carried out using a cell solution temperature of 90° C. The response in base, Fig. 9, was not very dramatic; the slow rate of reaction of hypophosphite in this case is well illustrated by the fact that the monolayer oxide formed at 1.80 V was almost totally removed by the externally applied current. Compare this type of behaviour (the cathodic peak at ~1.1 V in Fig. 9) with that, for the same region, in the presence of DMAB, Fig. 1. There was some indication of hypophosphite oxidation at lower potentials, especially on repeated cycling (the voltammograms shown in Figs 9 and 10 were both the seventh cycle, starting with a clean electrode in each case). On both the anodic and cathodic sweep the current passed through zero at ~0.2 V; this suggests the involvement of an Au(I) mediator in a rather sluggish $H_2PO_2^-$ oxidation process. Again in this case there is a tendency for the current to level off (anodic sweep) or attain a local maximum (cathodic sweep) at ~0.65 V, i.e. in the region of the Au(I)/Au(III) hydrous oxide transition. An unusual feature here, compared with earlier data for formaldehyde oxidation [8] or the response for DMAB (Fig. 1) under similar conditions, is that for most of the active range, ~0.3 to 0.9 V, the rate of oxidation during the anodic sweep was significantly lower than that for the cathodic sweep. It is possible that in this case there is inhibition due to deposition of phosphorus atoms which are produced, according to Gutzeit [25], via the following reaction,

$$H_2PO_2^- + H_{ads} = H_2O + OH^- + P_{ads} \qquad (7)$$

Other routes to phosphorus deposition have also been outlined [22]. The following reaction by Gouda and coworkers [26] involves formation, rather than consumption, of surface hydrogen,

$$2H_2PO_2^- = H_2O + HPO_3^= + \tfrac{1}{2}H_2 + P_{ads} \qquad (8)$$

The phosphorus atoms generated in these reactions at the lower end of the sweep are assumed to chemisorb and thus partially deactivate the electrode surface. These poisoning species are probably oxidatively removed at higher potential — this would explain why the oxidation currents are significantly larger over most of the cathodic sweep in the region below 0.9 V.

The response for hypophosphorous acid oxidation on gold in acid is outlined in Fig. 10. The region of high activity in this case is above 1.0 V; the peak on the anodic sweep here is at the onset of the regular monolayer oxide formation process for this system, i.e. at ~1.35 V. The high reactivity in this case is also borne out by the low electrochemical response (in the form of a minor cathodic excursion at ~1.2 V) for the monolayer oxide reduction process. Evidently a slight reduction of the monolayer species yields Au* adatoms and hence hydrous oxide species. The latter then mediate extensive oxidation of the dissolved hypophosphorous acid (which probably provides the electrons for reduction of the remaining monolayer film, via a local cell reaction mechanism) and give rise to the sharp anodic spike on the cathodic sweep at ~1.2 V.

The current decay after the anodic peak at ~ 1.2 V in this case is assumed to be due to a combination of two factors: (a) a loss of adatoms ($Au^* \rightarrow Au_l$) as the latter decay by increasing their lattice coordination number, and (b) a loss of the mediating hydrous oxide species – the peak for the reduction of this hydrous oxide film on gold in acid is at ~ 1.0 V [27]. Virtually identical trends with regard to oxidation behaviour, especially during the cathodic sweep, was reported earlier [28] for the reaction of oxalic acid on gold at low pH. One minor difference, however, is that in the case of oxalic acid the oxidation also commenced (as expected in terms of the adatom/incipient hydrous oxide mediator mechanism) on the anodic sweep at ~ 1.0 V. The absence of appreciable oxidation in this region in the case of hypophosphorous acid is possibly again due to deactivation of the gold surface (or at least the very active regions of the latter) by adsorbed phosphorus atoms generated at lower potentials according to the processes outlined in Equations 7 and 8. The deactivating atoms are assumed to be oxidatively removed from the surface above 1.2 V: in addition, hydrous oxide species may be generated at less reactive, unpoisoned sites on the surface in this region.

With regard to electroless plating the anodic reaction above 1.0 V is of little interest; the potential is clearly too anodic to induce nickel or cobalt ion discharge. However, there is a region of lower activity close to 0 V; the anodic reaction involved here, for example, in the case of nickel plating, is frequently assumed [29] to be similar to that shown in Equation 6. The current for hypophosphorous acid oxidation at low potential is quite low, presumably due to phosphorus atom deactivation of the surface. There is an important difference between the reaction of hypophosphorous acid on gold at low potentials and in an electroless plating bath. In the former case phosphorus atoms, produced for instance via Equations 7 and 8, are assumed to adsorb at, and consequently deactivate, the surface – hence the small anodic response for this reaction and the difficulty of mechanistic investigation of the nature of the process involved at low potential. In the electroless case phosphorus atoms are also involved as the product formed in such baths is generally [29] a Ni/P alloy, rather than pure nickel. An important point, however, is that as the phosphorus atoms are incorporated into the product layer, inhibition is far less marked. Indeed, as the nickel in the alloy has a lower free energy than the pure metal, the presence of the phosphorus atoms may well enhance the rate of the plating reaction. It is unfortunately impossible to determine whether or not cationic Au^+ species (which are assumed here to be produced on gold in acid solution at quite low potentials) act as mediator species for hypophosphorous acid oxidation on gold.

In conclusion, it is worth noting that the earlier proposal [21] that Group 1B metal atoms, in the adatom state, readily form M(I) hydrous oxide species, has apparently been confirmed by recent X-ray work [30] with Under Potential Deposited (UPD) copper. Copper atoms on high surface area platinum, the latter being dispersed on carbon, were found to exist in the Cu(I) state (the electron having been transferred to the platinum), i.e. as Cu^+ ions, which were associated with both platinum and oxygen, with the latter present as either OH or OH_2. The uniqueness of copper (or the other Group 1B metals) was borne out by the fact that under similar conditions the positive charge on UPD lead atoms was much less. Recent work in this laboratory [31, 32] has established that copper adatoms in base oxidize to the Cu(I) hydrous oxide state at ~ 0 V/RHE; this corresponds to premonolayer oxidation; regular monolayer oxide, Cu_2O or Cu(OH), formation on copper under the same conditions commences at ~ 0.4 V/RHE. The potential for premonolayer, adatom, oxidation of copper in acid is expected [21] to be significantly lower (in terms of the RHE scale), whereas that for monolayer oxidation is assumed to be virtually pH-independent. The behaviour of the UPD copper on platinum can be rationalized quite simply by assuming that such copper exists as adatoms which behave in the same manner as outlined in Equation 4 for gold. Thus,

$$Cu^* + nH_2O = [Cu(H_2O_n)]^{+1} + e^- \qquad (9)$$

Whereas copper atoms of high lattice coordination number at the surface of bulk copper become oxidized to form Cu_2O above about 0.4 V/RHE, UPD copper atoms at a platinum surface, which evidently behave as adatoms, become oxidized to the Cu(I) hydrous oxide state at a much lower potential; the equilibrium potential for the process shown above in Equation 9 is rather indefinite but is apparently well below 0 V/RHE in the case of acidic media. This approach outlined here for copper is assumed to be valid also for silver and gold.

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