The importance of superficial (adatom) surface oxidation in the electrocatalytic behaviour of noble metals in aqueous media

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The conventional, activated chemisorption, model of electrocatalysis is unable to explain fully the surprisingly high level of activity of gold anodes in base for certain organic electrooxidation reactions or even the ability of platinum to catalyse certain oxygen insertion reactions, e.g. methanol or formaldehyde oxidation in acid, at low potentials (in the hydrogen or double layer region) where the surface is considered usually to be oxygen-free. It was demonstrated that such behaviour can be rationalized by postulating the involvement of a quite low coverage of hydrous oxide species, generated at low potential at adatom sites, which act as mediators or catalysts in many electro-oxidation reactions. The converse situation was also shown to arise, i.e. the reduction of certain species, e.g. HNO_3 or NO_3^-, which requires the involvment of adatoms, was shown to be inhibited as long as the latter existed in the oxidized, hydrous oxide, form. An appreciation of hydrous oxide electrochemistry was shown to be very useful in interpreting electrocatalytic effects at noble metal electrodes in aqueous media.

1. Introduction

Chemisorption, especially activated chemisorption, is frequently considered as being the dominant factor in noble metal electrocatalysis. However, this view was questioned recently by one of the present authors [1]; it was pointed out that various organic compounds commence (anodic sweep) and terminate (cathodic sweep) their oxidation on gold and other substrates in aqueous media at a potential corresponding to incipient hydrous oxide formation. The nature of hydrous oxides, and the distinction between them and conventional, anhydrous oxides, has been reviewed recently [2]. With regard to electrocatalysis it is assumed [1] that hydrous oxide formation occurs at adatom sites which constitute only a small fraction of the total surface metal atoms, and that the resulting reactive species are the mediators which induce oxidation of reactive species dissolved in solution. Activated adsorption or coordination, possibly due to interaction at the same adatom or adion sites, may still be important but for most organics the oxidation apparently does not occur until the adatom is oxidized. An interfacial redox cycle, widely postulated [3] and quantitatively described [4] for oxide electrode systems, is assumed to operate in many cases.

The role of metal adions and hydrous oxides in noble metal electrocatalysis has been virtually ignored to date for various reasons. Firstly, in deriving thermodynamic data, for instant in the form of Pourbaix diagrams, differences in behaviour between hydrous and anhydrous oxides [5] have been largely ignored. For example, gold and platinum in acid solution are assumed to be resistant to oxidation up to potentials as high as approximately 1.35 and 1.00 V (RHE or SHE), respectively [6]. However, thick films of reactive hydrous oxides resist reduction to much lower values, approximately 1.0 V for Au [7] and ca. 0.2 V for Pt [8] at low pH (and to significantly lower values in base). While the formation of hydrous oxide films is an inhibited process (the lattice atom → adatom transition being slow), reversible (and hence thermodynamically significant) behaviour at these low potentials can be seen in the case of gold in base [9, 10]). The second reason why the role of hydrous oxides in electrocatalysis has been ignored is that these species are extensively hydroxylated and/or hydrated; evidently to produce them most of the metal atom coordination sites must be exposed to the solution, i.e. their formation on oxidation is restricted to only very few special sites. Essentially the voltammetric response for these species, when working with the bare metal, is so low that it is often difficult to detect, ignored or attributed to the presence of impurities (major responses for these oxide species can be obtained by pretreating the surface so as to produce thick deposits of hydrous oxide [2]). In the present work the involvement of incipient oxidation products in electrocatalytic behaviour will be outlined further with particular reference to formaldehyde oxidation on gold in base; data on a few other systems will also be presented to illustrate, among other things, that hydrous oxides in some instances can play an inhibiting role. The emphasis here is on the changes in the nature of the metal surface, not the detailed mechanism of aldehyde oxidation; the latter reaction has been the subject of a

number of earlier investigations [11–14] with one group [11] postulating the involvement of OH (or Au⁺) species and others either specifically discounting [12] or not considering [13, 14] the possibility of superficial (adatom) oxidation.

2. Experimental

The working electrode was gold (1.0 mm diam.) or platinum (0.5 mm diam.) wire sealed directly into glass; the exposed length was 1.0 cm (gold) or 2.0 cm (platinum) and the counter-electrode was of the same material as the working electrode. The platinum electrode was coated with a layer of platinum black (plated in Pb-free, 2% H_2PtCl_6 solution for 60 s at 20 mA at room temperature). The reference electrode was hydrogen in the same solution and a Luggin capillary was used to minimize iR_e drop (unless designated otherwise, all potential values refer to RHE). All solutions were made up using triply distilled water; the first distillation involved the use of $KMnO_4$ to destroy organics and the later ones were carried out using quartz glassware. All reagents used were of Analar grade but, as also noted elsewhere [13], the commercial formaldehyde solution (B.D.H. Chemicals Ltd) was stabilized by about 13% methanol (preliminary experiments showed that both methanol and formic acid, in aqueous media, were virtually inert with regard to oxidation on gold in base). Before use the gold electrode was subjected to mild abrasion followed by washing with triply distilled water. Solutions were purged between voltage scans with a flow of nitrogen gas. The electrochemical equipment consisted of a three-compartment cell, a potentiostat (Wenking, Model LT-78), a function generator (Metrohm VA Scanner, Model E612) and an X-Y recorder (Rikadenki, Model RW-21).

3. Results and discussion

3.1. The behaviour of gold at low potentials in organic-free base

A summary of the voltammetric behaviour of gold in

base is shown in Fig. 1. The main surface oxidation reaction occurs above approximately 1.2 V and the monolayer-type deposit produced at 1.5 V is apparently fully reduced at approximately 0.96 V on the subsequent cathodic sweep. However, the processes of interest here are the minor transitions, A to E, as indicated in this diagram. These lower transitions give rise to only very low and variable responses but in most cases there is independent evidence for their presence.

A: This transition can be more clearly observed on increasing the sweep-rate (Fig. 2); a reversible peak (showing some hysteresis) appears at approximately 0.1 V. Independent evidence for this transition is provided by the work of Kirk and coworkers (peak A in Fig. 2, ref. 15, is at approximately −1.0 V (SCE) which corresponds to approximately +0.05 V (RHE) for the pH in question).

B: A small increase in current may be observed at approximately 0.35 V on the anodic sweep in Fig. 1. A distinct peak in the same region has been observed by Burke and Hopkins (Figs 8 and 9 in ref. 16) during the reduction of thick hydrous gold oxide films in base: a similar peak at approximately 0.33 V was reported more recently [1] when thick gold oxide films were reduced at a slow sweep-rate in pyridine-containing base.

C: There is ample evidence by Conway [9], Gonzales-Valasco and Heitbaum [10] and earlier work in this laboratory [1] for a transition at approximately 0.65 V for gold in base.

D and E: A peak (or two peaks in some instances in the present work) was observed prior to regular monolayer oxide formation — see the dashed line for gold in ClO_4^--free base in Fig. 1 of Ref. 10 (in fact the minor peaks at approximately 0.1, 0.65 and 1.2 V for gold in NaOH are quite clear in the latter diagram). Two peaks in the upper region in question have been reported by Adzic and coworkers (Fig. 4 in Ref. 17) for Au (100) single crystals in organic-free NaOH solution.

The other, more indirect, evidence for these transitions at low potentials is the onset of electrocatalytic currents for the oxidation of dissolved organics on the
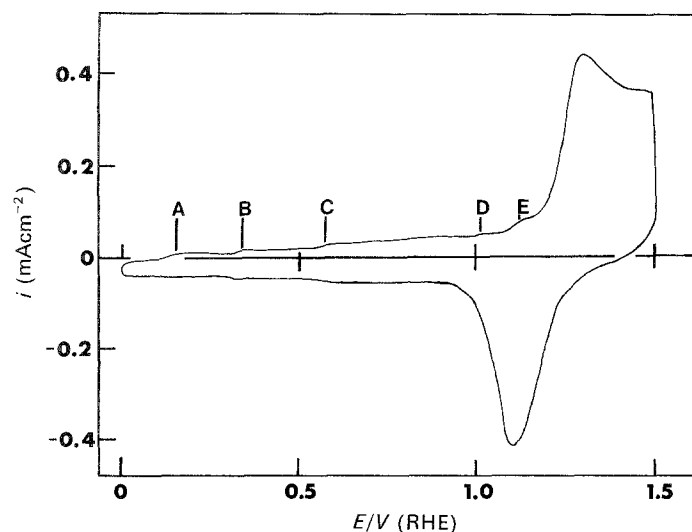

Fig. 1. Cyclic voltammogram (0.0–1.50 V, 50 mV s⁻¹) for gold in N_2-stirred 1.0 mol dm⁻³ NaOH, $T = 20°$C.
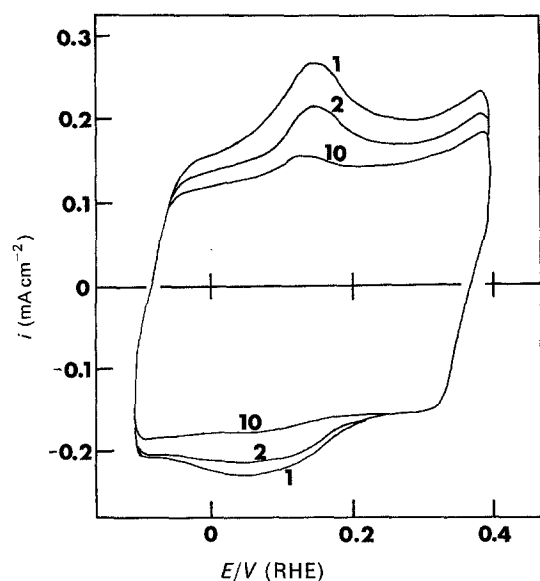
Fig. 2. Cyclic voltammograms for gold in base: some conditions as in Fig. 1 except at reduced limits (-0.1 to $+0.4$ V) and a faster sweep-rate ($500\,\mathrm{mV\,s^{-1}}$). The electrode was preanodized at 1.60 V for 5 min: the first, second and tenth cycle are shown here.

anodic sweep at the various potentials quoted above. This aspect will be discussed in more detail later for A and B but it is worth pointing out here that the earlier suggestion [1] as to the importance in the case of electrocatalysis at gold in base of the transition at C — this was assumed [1] to be Au/Au (III) hydrous oxide transition — is borne out by the more recently published data of Ocon and coworkers [18]. It is clear from Fig. 1 in their work that the onset (anodic sweep) and termination (cathodic sweep) of n-propanol oxidation of Au in base coincides (at approximately -0.8 V (MSE), i.e. approximately 0.6 V (RHE)) with the minor peak (C in Fig. 1) at the same value for Au in organic-free base. The basic questions at this stage, however, are why the magnitude of these lower peaks or current increases are so small and variable, and what reactions or processes are involved.

The answers here must at present be speculative but it is reasonable to assume firstly that special, adatom sites are involved and that at least in the case of A, and possible B, a Au/Au(I) transition occurs. At approximately 0.1 V those metal adatoms protruding from the surface, and virtually surrounded by solvent species, are assumed to ionize according to the following reaction

$$Au \cdot xH_2O = Au^{+1} \cdot OH^- \cdot (x-1)H_2O + H^+ + e^- \tag{1}$$
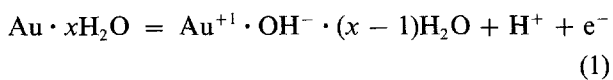
The response is low because the adatom state (Au*) is of high energy and most of the metal atoms at the interface revert readily to a high bulk lattice metal coordination state (Au$_l$). This latter reaction,

$$Au^* = Au_l \tag{2}$$

explains why on repeated cycling in the low potential region the response (Fig. 2) decreased with time or number of cycles. The process at B also gives a

low response: the same reaction, Equation 1, may be involved but a slight difference in site geometry and energy is assumed to shift the potential from approximately 0.1 to 0.35 V — the possibility of formation of an Au(III) species at the latter values cannot at present be definitely disproved. Other features to be borne in mind here — in view of recent work in this laboratory on silver [19] — are the effect of cycling to the high anodic limit (Fig. 1) which may not only roughen the surface, i.e. increase the Au adatom concentration on subsequent reduction, but introduce subsurface oxygen into the metal. Some minor dissolution of the product formed on oxidation is also possible (most of these lower anodic peaks for Au in pure base have cathodic counterparts [10] but — as the shapes differ — it is difficult to decide if the magnitudes — for formation and removal — are exactly equal). Finally, it is clear that the process represented by Equation 1 could also be considered as a form of adsorption process — accompanied by charge transfer.

Before considering the reaction of easily oxidizable species, e.g. formaldehyde, with gold in base at low potentials, it is worth considering briefly the interaction of non-oxidizing organic molecules, e.g. pyridine, in this region. Such molecules also give rise [1, 20] to a reversible peak (or peaks) at low potential (0–0.2 V). The SERS technique has been applied here [20] and this pronounced optical effect is first observed on the anodic sweep only at the potential corresponding to the first (minor) anodic peak. The authors also point out that, unlike other systems, e.g. silver, the SERS effect for pyridine on gold in base is not totally quenched at very negative potentials, i.e. the active sites on gold are retained to a significant degree. It has been suggested [21] that the reason why the SERS effect is so pronounced with the Group 1b metals (Cu, Ag and Au) is that these readily form the $1+$ state which, because of the low charge on the cation, do not strongly bind the OH^- counterion and thus permit the organic ligand to interact directly with the surface cation in the presence of a strong electric field. It is also noteworthy that Ca^{2+} ions (C $= 2 \times 10^{-5}\,\mathrm{mol\,dm^{-3}}$) in base ($0.1$ to $1.0\,\mathrm{mol\,dm^{-3}}$ NaOH) commence to adsorb [22] on gold in the region of the lower peak (A in Fig. 1). As the authors point out this cannot be direct cation adsorption (the adsorption increases with increasing positive potential — the opposite of what one would expect for cationic species). As suggested earlier [21] the gold adatoms are oxidized to the Au^+ state at one plane; outside this (and possibly solvent separated from it) are the OH^- counterions — it is into the latter region that the highly charged Ca^{2+} ions are assumed to be attracted by electrostatic forces. Also relevant here is the fact that the Ca^{2+} uptake is time dependent: the charge, or Au^{1+} concentration, at the interface apparently increases with time presumably as some surface metal atoms transform to the adatom — and then the Au(I) — state. Thus, in electrocatalysis involving such species the concentration of active sites may be both potential and time dependent.

3.2. Electrocatalytic oxidation of formaldehyde on gold in base

Some typical examples of formaldehyde oxidation on gold in base are shown in Fig. 3. At all concentrations reaction commenced (anodic sweep) and terminated (cathodic sweep) at approximately 0.1 V, i.e. in the region of the lower anodic peak. This is a prime requirement [4] of an interfacial surface redox route for electrocatalysis as obviously such a route cannot operate at a potential below which the oxidized (Au^{1+}) state cannot exist. In most cases the current, on the anodic sweep, rises to a plateau, as expected [4] in terms of either a kinetic or diffusion controlled interfacial step. However, in the region of approximately 0.4 V a further increase in current was usually observed — apparently due to the intervention of a new surface redox couple corresponding to the minor increase in current shown as B in Fig. 1. At low formaldehyde concentration this again was followed by a further plateau which extended up to the start of the regular monolayer-type oxide formation region at approximately 1.15 V. For very low formaldehyde concentration, Fig. 3a, the oxide formation peak was still evident — the recorder sensitivity was quite high in this case as the net oxidation current was low. However, as the formaldehyde concentration was increased, the main feature at high potentials on the anodic sweep was the drop in current, associated with the monolayer oxide deactivation of the gold surface, for the aldehyde oxidation reaction.

On the subsequent cathodic sweep the surface reactivated when the oxide layer was removed. It can be seen that as this occurred in Fig. 3a vigorous formaldehyde oxidation recommenced but at this low bulk concentration the supply of organic material at the interface was depleted and the current dropped and a portion of the oxide removal peak reappeared at approximately 1.0 V. At higher formaldehyde con-
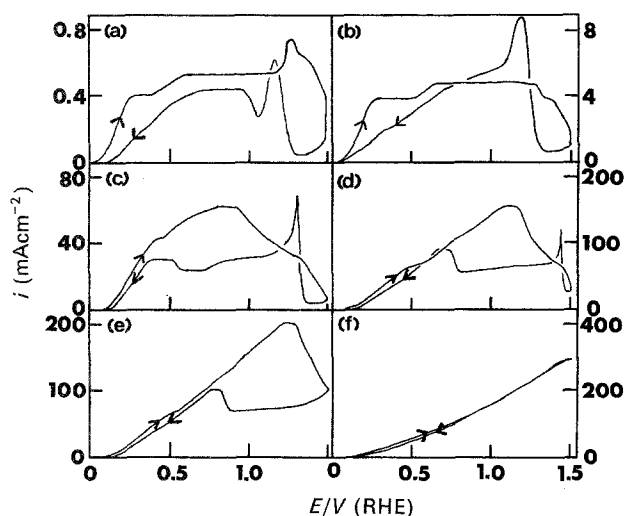
centration values no indication of this main oxide removal step was evident; under these conditions the oxide may well be removed by direct reaction with formaldehyde — although this type of reaction probably also involves an electrochemical route [23]. At intermediate formaldehyde concentrations (Fig. 3b–d) a high oxidation current was observed in the oxide layer removal region; evidently as the monolayer oxide material is reduced a high, but transient, adatom concentration or activity is generated. This is not seen in Fig. 3e and f, presumably because the aldehyde concentrations in these cases are so high that little monolayer oxide can exist even at 1.5 V — especially in Fig. 3f.
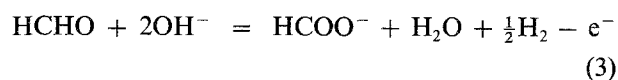
There is clear evidence also in several of the cathodic sweeps, (c) to (e), of an increase in surface activity within the region 1.0 to 0.5 V. This is probably due to reduction of some Au(III) hydrous oxide sites which occurs, C in Fig. 1, at approximately 0.65 V. The Au/Au(I) cycle is assumed to be more active than the Au/Au(III), or Au(I)/Au(III), for aldehyde oxidation because the OH^- ion is not easily displaced from the more highly charged Au(III) centres. This effect is not observed in (f) because the monolayer oxide, high adatom concentration, and Au(III) hydrous oxide — in this sequence — are not formed to a significant extent under these conditions. In (a) and (b) in Fig. 3 the oxidation currents below 0.5 V are significantly lower on the cathodic sweep; at these low formaldehyde concentration values the degree of oxidation at the upper limit (1.5 V) is extensive and there may, as in the case of Ag [19], be some penetration of oxygen into the outer layers of the metal resulting in some loss of surface activity.

As outlined in Fig. 4 the plateau currents for the anodic sweep are virtually a linear function of formaldehyde concentration, at least up to a value of the latter of approximately $0.5 \, mol \, dm^{-3}$ HCHO. The behaviour at higher concentrations is uncertain as well defined plateaux are not observed under such conditions.

The above outline of formaldehyde oxidation on gold in base confirms the work of other authors. Beltowska–Brzezinska [14] for instance has pointed out that the reaction commenced close to O V(RHE) and anodic sweeps showing two plateaux are shown in several instances [13, 14]. The work of Sibille [11] is significant also in another respect; it shows that the onset of aldehyde oxidation at Au in base is virtually independent of the nature of the aldehyde — again as required by the interfacial redox model.

3.3. The mechanism of formaldehyde oxidation

In a recent report of an investigation of this reaction on gold in base Beltowska–Brzezinska [14] assumed that formaldehyde oxidizes by either a 1-electron or 2-electron route.
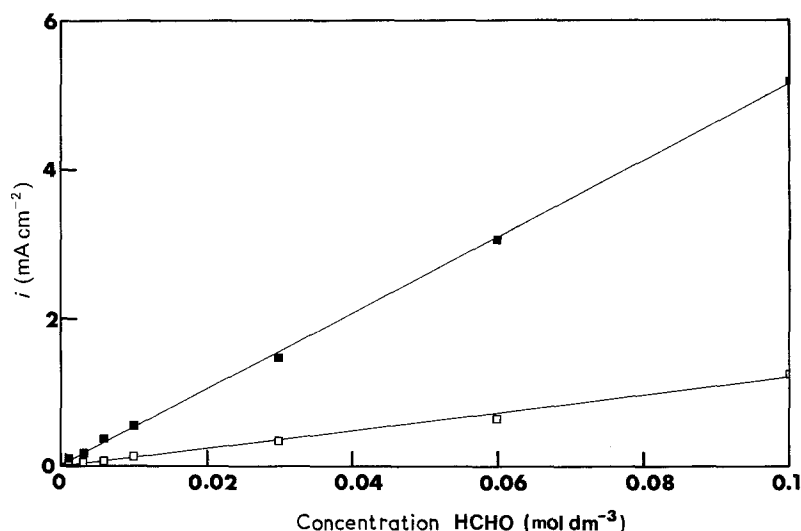
$$HCHO + 2OH^- = HCOO^- + H_2O + \tfrac{1}{2}H_2 - e^-$$
(3)

Fig. 3. Cyclic voltammograms (0 to 1.50 V, $50 \, mV \, s^{-1}$) recorded for gold in unstirred $1.0 \, mol \, dm^{-3}$ NaOH + increasing concentration of formaldehyde, $T = 20°C$: HCHO concentration ($mol \, dm^{-3}$): (a) 0.01, (b) 0.06, (c) 0.30, (d) 0.50, (e) 0.60, (f) 0.70. The data shown here refer, in each case, to the third cycle.

Fig. 4. Variation of the plateau currents (at approximately 0.3[1] and 0.8 V[2] — see Fig. 3a) with formaldehyde concentration for gold in 1.0 mol dm^{-3} NaOH at 20°C. The values were taken from voltammograms (0.0–1.50 V) recorded at 50 mV s^{-1}: ■, plateau 1; □, plateau 2.

$$HCHO + 3OH^- = HCOO^- + 2H_2O + 2e^-$$ (4)
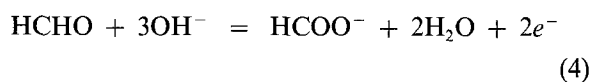
It was suggested that the two waves or current increases on the anodic sweep was due to splitting of the 2-electron process into two 1-electron stages with increasing sweep-rate. In both this and related work [13] the possibility of incipient oxidation of the gold surface was not considered. The related work [13] is important as in that case the behaviour of not only gold but also platinum and platinum/gold alloys were investigated as substrates for formaldehyde oxidation in base. These two metals have significantly different electronic properties and one would expect a much lower rate of oxidation on gold — especially in terms of the activated chemisorption model for electro-catalysis — as gold is only a weakly chemisorbing metal. However in 1.0 mol dm^{-3} NaOH the oxidation rate at -0.4 V(SCE), or approximately $+0.6$ V(RHE), is approximately 0.6 mA cm^{-2} on Pt and approximately 4 mA cm^{-2} on Au: the conditions quoted for these data (Figs 1 and 3 in Ref. 13) are not quite identical but they illustrate the unusual activity of gold which cannot be explained in terms of the conventional activated chemisorption model of electrocatalysis.
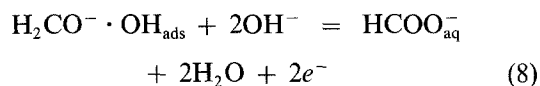
As indicated earlier [1] the high level of activity of gold at low potentials in base is not confined to formaldehyde — it is also observed with CO and gycolaldehyde (further examples are given in Refs. 11 and 12). Also, among the non-platinum metals, the Group 1b elements, i.e. Cu, Ag and Au, seem to be exceptional; in base HCHO oxidation commences at 0.5 V on Cu, approximately 0.2 V on Ag and 0.1 V on Au (the low response of Ni — which probably forms a Ni(II) species — is worth comparing [24]). As pointed out here earlier in connection with SERS phenomena the initial oxidation product formed according to Equation 1 is a strong base, the OH$^-$ ion is not strongly held at the M$^+$ site and strong interaction occurs between the latter, which is a Lewis acid, and the gem-diolate anion (a Lewis base) produced by interaction of HCHO with a hydroxide ion in bulk solution.

$$HCHO_{aq} + OH_{aq}^- = H_2CO^- \cdot OH_{aq}$$ (5)

$$H_2CO^- \cdot OH_{aq} = H_2CO^- \cdot OH_{ads}$$ (6)
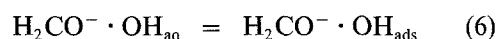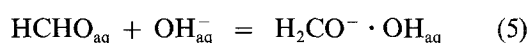
There are two routes for further reaction, one predominating at the start of the first current increase.

$$H_2CO^- \cdot OH_{ads} + OH^- = HCOO_{aq}^-$$
$$+ H_2O + \tfrac{1}{2}H_2 + e^-$$ (7)
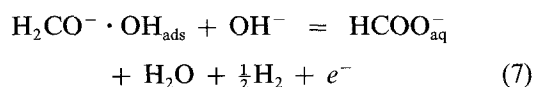
and the other at higher potentials.

$$H_2CO^- \cdot OH_{ads} + 2OH^- = HCOO_{aq}^-$$
$$+ 2H_2O + 2e^-$$ (8)

The scheme outlined here is based on that proposed by Bindra and Roldan [24]; the OH$^-$ ions are obviously solutions species but may react at an intervening stage as weakly bound surface entities. The release of gaseous hydrogen gas under anodic conditions is an interesting phenomenon (it supports the view that gold metal is not a good catalyst in the chemisorption mode); however, release of this gas is not observed beyond the end of the first wave [13, 14]. Kinetic isotope studies [12] indicate that aldehyde oxidation on gold involves cleavage of a carbon–hydrogen bond in the rate-limiting step — hence the linear variation (Fig. 4) of the plateau currents with aldehyde concentration (although diffusion control may also be important [14] at this point) This does not conflict with the idea that incipient surface oxidation is important as such cleavage is assumed to occur only at Au(I) sites, i.e. it is the generation of the latter that triggers the organic oxidation reactions.

The oxidation of formaldehyde at the gold/solution interface is quite fast — possibly in some cases diffusion controlled [14]. However, it is assumed here that only a small fraction of surface sites, i.e. adatom or Au(I) centres, are effective. If on reaching approximately 0.35 V on the anodic sweep (B in Fig. 1) a new type of Au(I) centre is generated then the second increase in current in this region observed here in many cases, even at relatively slow sweep-rate (Fig. 3), is understandable. In terms of the interfacial redox model the surprising feature in the present work was the lack of an increase in current on the anodic sweep

above approximately 0.7 V, i.e. above point C in Fig. 1 where the Au/Au(III) hydrous oxide transition is known to occur, and where other organics, e.g. pyrrolidine and piperidine [1] are known to oxidize strongly. Initially the second increase in current on the anodic sweep was assumed to be due to this transition, but the onset potential is clearly too low. In fact the strong binding of OH⁻ ions at Au(III) centres appears to have an inhibiting effect in the case of formaldehyde whose oxidation seems to occur by an inner sphere mechanism. Another factor involved in the inhibition may be the anionic character of the gem-diolate which will give rise to repulsion at the anionic hydrous gold oxide, $Au_2(OH)_9^{3-}$ [2], species at the interface (pyrrolidine and piperidine, on the other hand, are neutral bases and such repulsion is far less).

The gradual disappearance of the plateau after the first peak with increasing formaldehyde concentration (Fig. 3) is evidently due to the effect of the increasing current on the overpotential associated with the reaction giving rise to the first peak. At high values for the oxidation current (or HCHO concentration) just above the first surface transition the potential becomes so anodic (due to the increased overpotential) that as it reaches the limiting value or plateau it coincides with or exceeds the value for the start of the second plateau, i.e. both processes merge at high concentration, Fig. 3f, to give a smooth continuous current increase.

3.4. Other reactions involving adatoms

Although nitric acid and nitrate anions are strong oxidizing agents, unstable with regard to reduction at pH = 0 below approximately 1.26 V [6], their reduction, even with active cathode materials, e.g. Pt, is highly inhibited (an overpotential of 1.5 V has been mentioned [25]); the origin of the inhibition is not clear at the present time. At pH values significantly above zero the reduction may be represented [6] as

$$2NO_3^- + 12H^+ + 10e^- = N_2 + 6H_2O \quad (9)$$
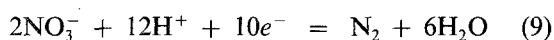
— although a range of products, including nitrous acid, ammonia and hydroxylamine [26], can be produced. It is clear from Fig. 5 that with gold in base significant nitrate reduction currents are observed only below ca. 0.15 V, i.e. below peak A in Fig. 1. It appears that nitric acid reduction occurs only at highly reactive adatom (Au*) sites which are easily deactivated by incipient oxidation according to Equation 1. NO_3^- (or HNO_3) reduction on gold at low pH is even more inhibited; as shown in Fig. 6 hydrogen evolution currents on gold become significant as approximately -0.25 V but reduction in the presence of NO_3^-/HNO_3 becomes significant at approximately -0.1 V. This increased inhibition of nitrate species reduction on lowering the solution pH is in agreement with the incipient surface oxidation model because, as demonstrated earlier [21], the potential of the Au/Au(I) transition decreases significantly on lowering the pH. In fact the inhibition at low pH is expected to be appreci-
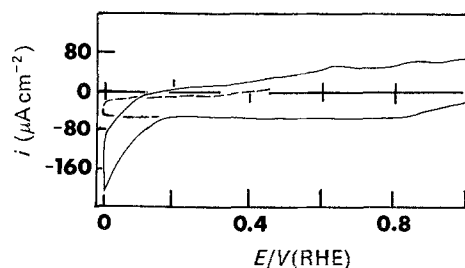

Fig. 5. Cyclic voltammogram (0–1.0 V, 100 mV s⁻¹) in N_2-stirred 1.0 mol dm⁻³ NaOH containing 1.1 mol dm⁻³ $NaNO_3$ at 20° C: the dashed line indicates the behaviour of gold in the absence of nitrate (the cathodic curent at low potential in the latter is assumed here [19] to be due to the presence of some subsurface oxygen).

ably larger than observed here but a number of factors require further investigations: (1) the current in acid, even in the presence of NO_3^-, may be predominantly hydrogen gas evolution (promoted by the presence of NO_3^-); (2) the presence of a trace of hydrogen on the surface may affect the Au/Au(I) potential; (3) the overpotential in acid is so great (due to the absence of unoxidized Au* sites) that a new route (involving, for instance, less active surface species) for NO_3^-/HNO_3 reduction may operate.

The case of platinum is particularly interesting. This metal has vacancies in the d-band and (in direct contrast to gold) is a strong chemisorber. Hydrous oxide formation on platinum can be achieved by potential cycling or vigorous anodization techniques [2] and thick films of this material reduce at approximately 0.2 V(RHE) in acid and significantly below O V(RHE) in base. The reaction involved here is assumed to be of the following type.

$$[Pt(OH)_6]^{2-} + 6H^+ + 4e^- = Pt^* + 6H_2O \quad (10)$$

$$Pt^* = Pt_l \quad (11)$$
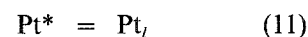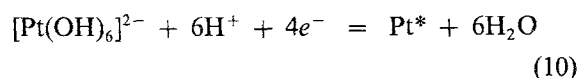
— the actual reduction potential value is somewhat sweep-rate dependent because as the sweep-rate is decreased the adatom activity drops (there is more time for relaxion — Equation 11) and, hence, the oxide reduction potential increases. Incipient surface oxi-
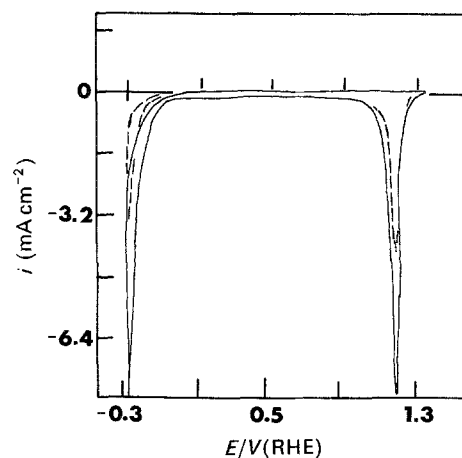

Fig. 6. Cyclic voltammogram (0–1.6 V, 100 mV s⁻¹) for gold in N_2-stirred 1.0 mol dm⁻³ H_2SO_4 (– – –) and 1.0 mol dm⁻³ H_2SO_4 + 0.1 mol dm⁻³ HNO_3 (——) at 20° C.
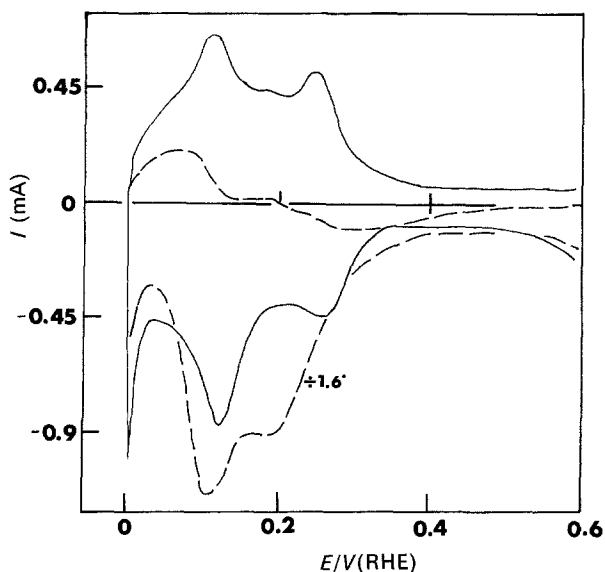
Fig. 7. Cyclic voltammograms (0–1.6 V, 10 mV s⁻¹) for a platinized Pt electrode in (a) N$_2$-stirred 1.0 mol dm⁻³ H$_2$SO$_4$ (——) and (b) N$_2$-stirred 1.0 ml dm⁻³ H$_2$SO$_4$ + 0.1 mol dm⁻³ HNO$_3$ (– – –); $T = 20°$C. Note that the true current density in the latter case is larger (by a factor of 1.6) than shown in this diagram.

Fig. 8. Cyclic voltammograms (0–1.6 V, 10 mV s⁻¹) for a platinized Pt electrode in (a) N$_2$-stirred 1.0 mol dm⁻³ NaOH (——) and (b) N$_2$-stirred 1.0 mol dm⁻³ NaOH + 1.1 mol dm⁻³ NaNO$_3$ (– – –). The true current density in the latter case is larger (by a factor of 3.3) than shown in this diagram.

dation in the region of 0.2 V is more difficult to detect with platinum because the response is quite small and it is largely masked by the hydrogen desorption reaction which extends over the region from 0 to approximately 0.35 V(RHE).

The interfacial properties of platinum is aqueous media have been surveyed recently by Conway [27]. Briefly, there are two major hydrogen peaks; for NO$_3^-$-free acid, Fig. 7, these are at approximately 0.25 V (strongly bound hydrogen) and 0.12 V (weakly bound hydrogen) — the corresponding values for NO$_3^-$-free base, Fig. 8, are at approximately 0.37 and 0.26 V. The detection of other, minor, peaks in the hydrogen region has been described by Conway; the one of specific interest here is the intermediate peak in acid at approximately 0.2 V on the anodic sweep in Fig. 7. The process responsible for this peak (the latter is designated H$_3$ by Conway) is totally different in character to any of the other reactions in the hydrogen region of platinum — see the entropy values quoted for various peak reactions [27, 28]. It is assumed here that this H$_3$ peak is due to incipient surface oxidation of platinum, i.e. the reverse of Equation 10 at platinum adatom sites which are quite limited in number — hence, as in the case of gold, the low response.

The behaviour of platinum in this region, however, is complicated by another factor, namely the fact that the potential of zero charge (pzc) for this metal also occurs in the region in question. As pointed out by Balashova and Kazarinov [29] and, more recently, by Horanyi and Rizmayer [30] cations adsorb on platinum at potentials more cathodic than approximately 0.2 V(RHE) while anions adsorb at more anodic values. The situation here is complex as Gileadi et al. [31] quote a pzc value for hydrogen-free platinum of 0.565 V(RHE) — the value being somewhat lower with hydrogen present in the metal. Two further
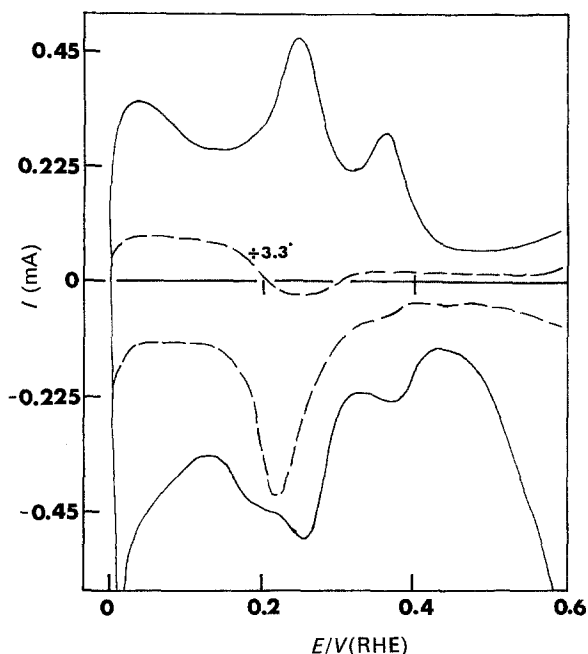
points made by these authors are (a) the pzc value for platinum (irrespective of the hydrogen content) is pH-independent on the RHE scale, and (b) this pH-independence is due to the presence of hydroxy species on the platinum. It may be pointed out also that the values quoted for the pzc for platinum in acid, approximately 0.1–0.27 V, by Frumkin et al. [32] are significantly lower — it is interesting that the latter group assume (in a detailed acount of this area) an involvement (at high pH) of hydrated surface oxide groups of acidic character — it may well be that it is the presence of this type of species, i.e. Pt(OH)$_6^{2-}$, at a low, and variable, coverage that makes the pzc value for platinum such a controversial issue.

According to the interfacial redox model of electrocatalysis the 0.2 V(RHE) region is a critical potential for platinum in acid: above this Pt(OH)$_6^{2-}$ species should exist at a low coverage and accelerate hindered anodic reactions. The effect can best be seen in formic acid oxidation on Pt(III) single crystals [33] where the oxidation of this compound commences (anodic sweep) and terminates (cathodic sweep) at this value. The initial increase is followed by a short plateau (as again expected [19] — see also Fig. 3 of the present work) but the current soon drops as the surface is deactivated by either oxides or strongly adsorbed intermediates. The case of methanol is more complex as under conventional potential sweep conditions [33] this compound commences oxidation at 0.4 V, rather than 0.2 V. However, this result does not disprove the interfacial cyclic redox model based on the intervention of incipient hydrous oxide species. The more anodic commencement potential in this case is evidently associated with surface deactivation. This was demonstrated by the work of Russian authors [34]

who found that if provision is made to minimize the effect of surface deactivation by reaction intermediates or side-products the oxidation of methanol on Pt in acid also commences at approximately 0.2 V (curve 1, Fig. 2 in Ref. 34). Evidently for all reactive organic species the onset potential for oxidation on the anodic sweep (in the absence of deactivating species) occurs at the potential corresponding to the generation of the hydrous oxide mediator at Pt adatom sites.

The reduction of nitrate ions at platinum and related metal electrodes is a reaction of considerable interest in connection with radioactive waste handling [35]. Some data for HNO_3 reduction on Pt at low pH is shown in Fig. 7. On the cathodic sweep the reduction current for this reaction commenced just below 0.4 V (this is just above the value for hydrogen adsorption which commences at approximately 0.36 V). The peak for hydrous oxide reduction at the sweep-rate in question here ($10\,mV\,s^{-1}$) was shown earlier [8] to be at approximately 0.37 V. A short plateau is seen here at approximately 0.2 V but then, following the peak for the adsorption of weakly bound hydrogen, the surface appeared to be significantly deactivated for HNO_3 reduction: this could be due either to anion (NO_3^-) repulsion by the surface at potentials below the pzc or (perhaps more likely) to the inability of the NO_3^- or $Pt(OH)_6^{2-}$ anions to compete with hydrogen (at high coverages of the latter) for adsorption sites at the interface. This deactivation continued into the start of the anodic sweep: the drop in current at approximately 0.1 V in the latter is evidently due to an upsurge of nitrate reduction at the beginning of the first hydrogen oxidation peak (the net current here is the sum of the HNO_3 reduction and H_{ads} oxidation currents). The reduction current predominates above approximately 0.25 V as at this stage most of the adsorbed hydrogen is removed. However, the HNO_3 reaction decays gradually above approximately 0.35 V where evidently various types of Pt adatom sites are converted to the hydrous oxide state. The HNO_3 reduction currents are larger during the cathodic sweep as the Pt adatom concentration at the interface is greater in this case following reduction of the oxide monolayer material.

Essentially the same behaviour for nitric acid reduction on Pt in acid as observed here has been reported by Horanyi and Rizmayer [36] who carried out a much more extensive investigation of this reaction using polarization and radiotracer technqiues. Their conclusion with regard to the importance of competitive adsorption of NO_3^- and SO_4^{2-} anions is accepted here — with the proviso that the sites being competed for are adatom centres which are gradually deactivated above 0.2 V(RHE) due to hydrous oxide formation. Behaviour very similar to the nitric acid case arises in dichromate reduction on Pt at low pH [37]; in the latter reaction the overpotential on both the anodic and cathodic sweep is unusually large. The inhibition is obviously not due to the oxide monolayer as the latter is not formed on the anodic sweep below 0.8 V while the inhibition is significant even at

0.3 V(RHE). The effective reducing agent is not H_{ads} as some reduction is still evident at potentials as high as 0.6 V(RHE). Evidently the reduction of the dichromate ions involves activation at adatom sites. However, these are only available in the reduced state at low potentials — the maximum current for dichromate reduction (according to our data which will be published shortly) occurs at approximately 0.2 V(RHE).

The behaviour for platinum in base is outlined in Fig. 8. The first point to note here is that the intermediate (H_3) peak is generally not observed on the anodic sweep: this is in agreement with the point mentioned earlier that the $Pt(OH)_6^{2-}$ species is stable (or reduced) at much lower potentials in base. There appeared to be some reduction of nitrate in the region of 0.25 V but the rate is much slower in base compared with acid. Note the much higher concentration of the oxidant in Fig. 8; with $0.1\,mol\,dm^{-3}\,NO_3^-$ in base no cathodic current was observed on the anodic sweep. Evidently only at high NO_3^- concentration can the latter species compete with OH^- — over a short potential range — for Pt adatom sites in base. Organic molecules, e.g. ethylene glycol [38], commences to oxidize on Pt in base at approximately 0.5 V(RHE); it should, according to the present model, oxidize at much lower values but the author clearly points out that inhibition by adsorbed CO-type species is again a major complication in this case.

In a recent survey of electrocatalysis Pletcher [39] has pointed out that development in this area is largely empirical with a significant gap between theory and practice. In our view this unsatisfactory situation is due largely to the lack of emphasis on the important role of incipient surface oxidation products — especially in the case of platinum and gold which are widely used in fundamental work in this area. It is clear that in many electrooxidation reactions, e.g.

$$CH_3OH + H_2O = CO_2 + 6H^+ + 6e^- \quad (12)$$

an oxygen insertion process is involved — the problem is that water at low pH is normally considered as being inactive on platinum [2] below approximately 0.85 V whereas the above reaction commences at approximately 0.4 V (or even lower if provision is made [34] to minimize deactivation effects). Some authors, e.g. Bagotzky and Vasilyev [34] in the case of platinum and Sibille et al. [11] in the case of gold, have postulated the involvement of oxy-species at low potential. The basic objection to this viewpoint, however, is that — as pointed out earlier — there is no direct evidence for the formation of such discrete species, e.g. OH_{ads}, on Pt or Au in this region. The assumption of hydrous oxide formation at special (adatom) sites is the most obvious solution to this dilemma and an appreciation of the properties of such species, especially the influence of pH on their redox properties, is quite important.

To illustrate the latter the behaviour of formaldehyde on gold in acid, as compared with base, is worth considering. At low pH this compound does not

oxidize [24] below approximately 0.8 V, i.e. at the onset of Au(III) hydrous oxide formation (the trivalent state is more active at low pH due to the low OH⁻ ion activity) while formaldehyde in acid is presumably in the neutral — rather than in the gem-diolate, anionic — form). There is no oxidation due to Au(I) species in acid because as mentioned here earlier the Au/Au(I) transition occurs well below 0 V at low pH, i.e. the HCHO is thermodynamically unable to reduce Au(I) species (if the latter do exist) at adatom sites under such conditions. An additional factor here is that while formaldehyde in base exists as the gem-diolate anion it is more likely to exist in acid in the neutral form which is less likely to interact with, and thus stabilize, any type of Au^+ species at the interface. In the case of Pt adatoms the common transition is Pt → Pt(II) or Pt → Pt(IV); the Pt(I) state is not involved in here as may be deduced also from the absence of a strong SERS effect for this metal.

4. Conclusions

Detailed investigation of the voltammetric behaviour of hydrous oxides of the noble metals is a relatively novel area and the involvement of such species in the electrocatalytic behaviour of gold was outlined earlier in terms of the Au/Au(III) hydrous oxide couple. These species are produced in such small amounts under normal anodic sweep conditions that both their formation and participation in interfacial processes is easily overlooked In the present work evidence for two additional, possibly Au(I), species in base is provided and these are used to rationalize the unexpectedly high activity of gold at high pH for the oxidation of certain organic compounds, e.g. aldehydes and CO[1], at low potential. The low coverage of such species at the interface is rationalized in terms of the requirement of a high degree of metal atom hydration at the interface before the hydrous oxide species, Au(III) or Au(I), can be generated. If, as assumed here, these species are the vital ingredients in many electrocatalytic processes, a major challenge or problem is provided in the use of either *in situ* or *ex situ* spectroscopy techniques to investigate this area due to the very low coverages in question. The connection between the present work and SERS has been briefly mentioned here and, for certain favourable systems, this technique appears to have interesting possibilities. Indeed it has already provided evidence [40] for the formation of hydroxy species on gold in base at potentials well below the onset of (and differing substantially in character from) the regular monolayer oxide product.

The case of platinum is even more controversial as here the incipient hydrous oxide formation occurs within the hydrogen desorption region, the potential for the former is sweep-rate dependent, and there is a well established alternative (the activated chemisorption model) to explain the electrocatalytic activity. It is again stressed here that the importance of activated chemisorption is not disputed; however, the fact that many species react in the $Pt/Pt(OH)_6^{2-}$ region high-

lights the importance of the hydroxy species in the electrocatalytic process. Surface oxide participation in these electroorganic oxidation reactions is also borne out by the work of Motoo and Shibata [41] who attributed the beneficial effect of certain types of adatoms, e.g. Ge, Sn and Sb, to the ability of the latter to supply oxygen species at low potentials.

An interesting question here is why, if redox transitions are so important, other couples are not good electrocatalysts. The $MnO_2/MnO \cdot OH$ system — which shows a clear transition at approximately 1.0 V on the anodic sweep in base [42] — was investigated recently in this laboratory and found to be a very poor electroorganic oxidation catalyst. Evidently the fact that both species involved in this couple are in a relatively high oxidation state (strongly binding the O or OH ligands) precludes activated chemisorption — an inner-sphere coordination mechanism is therefore not possible and high activity is not observed.

The nitric acid work outlined here demonstrates another important aspect of incipient hydrous oxide formation, namely inhibition of cathodic processes at adatom sites. If the latter are oxidized then, despite the large driving force, species such as HNO_3 or NO_3^- are unable to react as they apparently cannot displace OH⁻ or OH_2 groups at the active sites. Once such sites are reduced reaction can commence — although electrostatic repulsion [36] and competition with hydrogen for such sites are apparently a problem in the case of platinum at lower potentials. The present work also highlights once again the problem of the active site theory of catalysis and electrocatalysis. As pointed out recently by Augustine and Thompson [43] the degree of coordinative unsaturation of surface metal atoms is variable — as indeed, in the case of polycrystalline material, is the structure of the metallic phase to which such atoms are attached.

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