
The Electrochemistry of Gold:

II The Electrocatalytic Behaviour of the Metal in Aqueous Media

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Although it is the noblest and most inert of metals, and is a very weak chemisorber, gold displays a very wide range of electrocatalytic activity - especially in base. Such unexpected behaviour is rationalized here in terms of the unusual properties of nanocluster, microparticles or quantum dots. Such species, present as defects at the metal surface, undergo oxidation at unusually low potentials (significantly lower than that of bulk gold) in a process known as premonolayer oxidation. The resulting low coverage (or incipient) oxide species are assumed to be the mediators for oxidation reactions while unoxidized active gold atoms, present at lower potentials, often act as the mediators for reduction. Electrocatalysis on noble metals is quite often confined to the double layer region and only low coverage metal atoms at active sites are involved. The enhanced activity of gold in base is readily rationalized in terms of a super-Nernstian E/pH effect. The unusual properties of metal nanoclusters may also be used to rationalize the surprisingly high level of catalytic activity of oxide-supported gold microparticles as reported recently by Haruta and co-workers.

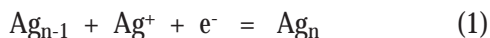
An electrocatalyst is a substance present in solution or at an electrode surface whose presence either enhances the rate (or current density) of an electrode reaction at a given overpotential, or reduces the overpotential for a given rate of reaction, without being consumed in the process. Advantages of the use of an electrocatalyst include more efficient utilization of energy in an electrolysis cell or more efficient conversion of chemical to electrical energy in a fuel cell; a more selective route for reaction, *ie* greater yield of a desired product, longer electrode service life and reduced electrode material cost are other significant advantages associated with the use of an electrocatalyst. This review deals specifically with the case where the electrode material itself, in this case polycrystalline gold, is the electrocatalyst. A synopsis of the basic electrochemistry of gold in aqueous media was given earlier (1) in Part 1 where a brief description of cyclic voltammetry is also provided.

There are two views or interpretations of the mechanism of operation of noble metal electrocatalysts (1), one based on the concept of activated chemisorption and the other on the intervention of

interfacial cyclic redox mediators (the latter is the so-called IHOAM, Incipient Hydrous Oxide/Adatom Mediator, model). In some cases elements of both reaction routes (bifunctional electrocatalysis) may be involved but activated chemisorption is a rather improbable mechanism in the case of gold as this metal is generally accepted as being a very poor chemisorber. The IHOAM approach, the basis of which arose originally from work on gold (2), is a relatively recent development and current ideas in this area will be briefly summarized here.

Surface catalysis in general is frequently assumed to occur at active sites (3), *ie* only a small percentage of the accessible surface (or surface atoms) is involved in catalysis. A major problem in this area is that the nature of these sites is not well understood (4, 5); they are generally assumed (5) to involve defects, *eg* kinks or steps, where the coordination state of a metal atom (or atoms) is low. An interesting model for active site behaviour, especially with regard to the IHOAM approach, is found in the case of nanoparticles (also known (6) as quantum dots or Q particles). Essential characteristics of the latter are that the number of

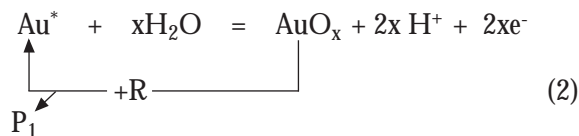
atoms (n) involved is quite small (ca 1 - 100), virtually all properties, including redox potential values, are quite different from those of the bulk metal and vary (quite dramatically at low n values) with particle size. An excellent illustration of the effect of particle size or n -value on redox behaviour is provided by the work of Henglein (7) in the case of silver nanoparticles in aqueous solution. It was observed that for the process (1), E^0 varied from +0.8 V(SHE) for $n = \infty$ to -1.9 V(SHE) for $n = 1$; i_e isolated metal atoms are far more electropositive than similar atoms in the bulk metal.



The effect may be attributed to either quantum confinement effects or the absence of lattice stabilization energy in the case of isolated metal atoms.

Low lattice stabilization energy, and low redox potential, occur not only with isolated silver atoms (or very small clusters) but also in the case of low coordination metal atoms at active sites. This is the origin of incipient oxidation of the metal in the double layer or premonolayer region of the cyclic voltammogram - as discussed earlier (1) for gold. Since the metal atom involved in such a reaction is of low lattice coordination number it is assumed that, on oxidation, it acquires a relatively large ligand coordination sphere, i.e. the product is a hydrous, rather than anhydrous (or compact), oxide species. Furthermore, since low coordination or active metal atoms protrude from the metal surface (with many of their coordination sites accessible to other solution species), they are assumed to be quite reactive from a chemical, redox and catalytic viewpoint.

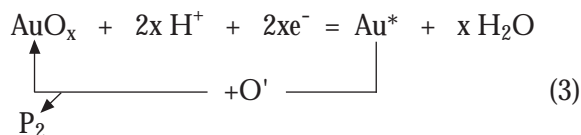
Under cyclic voltammetry conditions, with a gold electrode and a reductant present in solution whose reaction at the surface is sluggish, oxidation of active gold atoms (Au^*) at the active sites provides the oxidant or mediator (AuO_x) which triggers oxidation of the reductant (R) to eventually form the product, P_1 (multistep reactions may be involved), *viz.*



The precise nature of the mediator, represented here as AuO_x , is uncertain; it was denoted earlier (1) as $[Au_2(OH)_9]^{3-}$ - the advantage of the latter formulation is that it explains the super - Nernstian E/pH shift

observed in redox reactions involving a wide range of hydrous oxide systems.

A similar scheme may be used to explain the reduction of an oxidant (O') to product P_2 , *viz.*



While oxidation can occur, in accordance with Equation (2), only at potentials more positive than that for the Au^*/AuO_x transition (the oxide mediator cannot be generated electrochemically at lower values), reduction of O' , Equation (3), can only occur at potentials below that for the same transition - this is evident from data (Figure 2) discussed here later for the reaction of hydrazine and dichromate on gold in acid. In the case of the reduction outlined in Equation (3) the dissolved oxidant (O') oxidizes the active gold atoms (O' is simultaneously reduced to P_2 in this process) but the oxide formed at the active site, AuO_x , is almost immediately reduced back to Au^* and thus the redox cycle occurs in a repetitive manner, providing that the applied potential is negative with respect to the reversible value for the Au^*/AuO_x transition.

THE RESPONSE EXPECTED FOR SIMPLE IHOAM BEHAVIOUR

The basic features of the cyclic voltammetric responses expected, in terms of the IHOAM approach, for a gold electrode in aqueous solution are outlined in Figure 1. Among the assumptions involved here are that only one interfacial mediator system is involved, which undergoes a reversible redox transition at a discrete potential value in a solution of fixed pH - but, as explained earlier (1), exhibits a super-Nernstian E/pH shift on altering the solution pH.

Double layer charging currents are ignored in Figure 1; these are usually quite small, capacitive (non-Faradaic), currents associated with charging/discharging of the interface. The main feature in the positive sweep is the monolayer oxide formation response (M), which commences (8) at ca. 1.25 V in base and ca. 1.36 V in acid. The formation of this film frequently results in deactivation of the surface with regard to electrocatalytic processes. Oxygen gas evolution generally commences on gold at $E \approx 2.0$ V (this is not shown in Figure 1), but a transient oxygen

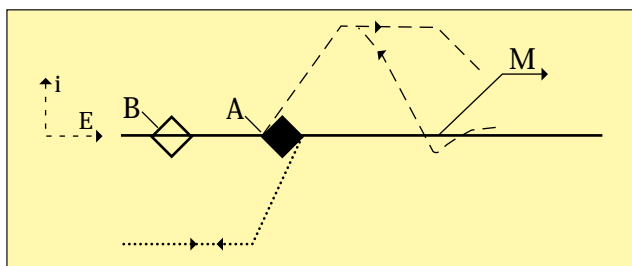


Figure 1 Schematic representation of the cyclic voltammetry (i/E) behaviour of gold in aqueous media. The full line (M) represents the monolayer oxide formation response; A and B represent the adatom/incipient hydrous oxide transition in acid and base, respectively; typical current responses observed for electrocatalytic oxidation of a reductant (---) and reduction of an oxidant (.....) in the case of gold in acid are also shown (actual recorded electrocatalytic responses are shown in Figures 2 and 3). The involvement of different interfacial mediator species is discussed in the text.

gas evolution response has been noted (9) in base at *ca* 1.8 V. The presence of minor features, associated with premonolayer oxidation of the surface in the double layer region, especially in the case of gold in base (1, 10) was outlined earlier.

On the negative sweep the monolayer oxide reduction peak usually (1) appears just below 1.2 V but with a vigorous reductant present in solution this feature is often either absent or of very low magnitude. Most of the surface oxide is reduced in such circumstances by electrons supplied by the reductant and, as these do not pass through the external circuit, the low cathodic response is understandable.

The most important features in this diagram, from the IHOAM viewpoint, are the two low level responses A (for acid solution) and B (for base). These represent the adatom/incipient hydrous oxide transitions (or mediator generation processes) at the active sites, and the potential involved is lower in base due to the super-Nernstian E/pH shift. When a reductant, *eg* hydrazine (N_2H_4), is added to the solution, oxidation commences in the positive sweep at *ca* 0.4 V in base or *ca* 0.85 V in acid, the anodic current rises rapidly, Figure 2(a), to a plateau value but may decay significantly (especially at slow sweep rates) in the monolayer oxide formation region. On the reverse sweep the anodic current remains high in the range below the monolayer oxide removal region but decreases to zero once the potential approaches the mediator (AuO_x) generation potential. It is important to note here that this behaviour is observed only with

electrocatalytic processes; it is not relevant to facile redox reactions, *eg* oxidation of Sn^{2+} - such processes do not require the participation of a mediator. Hydrazine oxidation is a useful test reaction in this area; it is a very simple, rapid process (its main disadvantage is that one of the products is gaseous - gas bubbles tend to screen some of the electrode surface). The electrocatalytic nature of the hydrazine oxidation reaction is demonstrated by the fact that the onset (positive sweep)/termination (negative sweep) potential is strongly influenced by the nature of the electrode material; for acid solution the relevant values (11, 12) are *ca* 0.85 V for Au and *ca* 0.2 V for Pt.

In the presence of an oxidant, *eg* dichromate, Figure 2(b), such behaviour is reversed. The mediator in this case is the active gold atoms (Au^*), and once these are oxidized above the Au^*/AuO_x transition potential (again at *ca*. 0.8 V for Au and *ca*. 0.2 V for Pt (12)) reduction ceases. The Faradaic current in this case is cathodic but the same onset/termination potential, and tendency to again attain a limiting current value, is quite clear. The behaviour outlined for these simple processes in Figure 2 is important as it demonstrates that (a) the conventional monolayer oxide response of gold is not very relevant to its electrocatalytic behaviour, (b) chemisorbed hydrogen, or even strong chemisorption of reactants or intermediates - at least in the case of gold, are not always the major factors in electrocatalysis, and (c) neither is poisoning by impurities, intermediates or adsorbed anions as the surface is active, for different reactions, both above and below *ca* 0.85 V. The important factor in many cases seems to be the subliminal[†] redox behaviour of active metal atoms and incipient hydrous oxide species present at very low coverages at the interface. With regard to the onset/termination potentials for N_2H_4 oxidation and $Cr_2O_7^{2-}$ reduction on Au (at *ca* 0.85 V) and Pt (at *ca* 0.2 V) in aqueous acid solution the only other processes that give responses at these potentials are multilayer hydrous oxides (11) - hence the emphasis in the IHOAM approach on the hydrous nature of the active oxide mediators.

The current/voltage plots shown for the reaction of hydrazine and dichromate on gold, Figure 2, are rather similar to polarographic responses. Indeed the limiting current or plateau value in the case of dichromate reduction is determined (12) by the rate of diffusion of $Cr_2O_7^{2-}$ ions through the boundary layer.

[†] The term *subliminal* is used here to emphasize the fact that the active species (and their responses) involved in electrocatalysis are frequently present at a level that is undetectable by many conventional techniques.

oxidation states (I and III) seem to be available to such atoms (10), and at least two different types of hydrous Au(III) oxides may be generated on oxidation of gold (1), it is not too surprising that the electrocatalytic behaviour of this metal is somewhat more complex than that discussed here earlier in terms of the scheme outlined in Figure 1. The following is a synopsis of the authors' view of the various mediator systems involved in the case of gold; it is based on earlier work reported from this laboratory (10, 18, 19), plus a survey of literature data as summarized here in tabular form, *viz.*

(i) There appears to be an Au(I) mediator (10) involved in the electrocatalytic oxidation of anionic species on gold in base; the mediator in question seems to be generated over the region of

Table 1 Alcohol oxidation on gold in aqueous acid and base

Reference	Electrolyte (mol/dm ³)	Reactant (mol/dm ³)	Onset Potential (V / RHE)
Methanol, CH₃OH 22 - 25 24	Base (0.1 → 1.0M) Acid (0.1M)	0.01 → 1.0 1.0	0.65 → 0.75 (0.69) No Reaction
Ethanol, C₂H₅OH 23, 26 23	Base (0.1 → 1.0M) Acid (0.1M)	1.7 × 10 ⁻² → 0.14 0.1	0.45 → 0.70 (0.59) 1.05
Ethylene glycol, (CH₂OH)₂ 23, 27 - 31 23	Base (0.1 → 1.0M) Acid (0.1M)	2.5 × 10 ⁻³ → 0.1 0.1	0.50 → 0.80 (0.69) 0.80
n - Propanol, C₃H₇OH 24, 32 - 34 24 33, 34	Base (0.1 → 1.0M) Acid (0.1M) Acid (0.5M)	0.01 → 0.16 2.2 10 ⁻³ → 0.5	0.53 → 0.74 (0.64) 1.10 No Reaction
2 - Propanol, CH₃CH₂(OH)CH₃ 35	Base (0.5 → 1.0M)	0.1 → 0.16	0.50 → 0.73 (0.63)
Allyl alcohol (2 - propen - 1 - ol), CH₂(OH)CH=CH₂ 36, 37 34, 38	Base (0.1 → 1.0M) Acid (0.1 → 0.5M)	0.01 → 0.1 10 ⁻³ → 0.1	0.51 → 0.65 (0.57) [also 0.25 V in (37)] 0.90 → 1.00 (0.96)
Propargyl alcohol (2 - propyn - 1 - ol), CH₂(OH)C≡CH 37 34	Base (0.5M) Acid (0.5M)	0.1 0.1	0.65 0.82
1, 2 - Propanediol, CH₂(OH)CH(OH)CH₃ 30, 39	Base (0.1M)	5 × 10 ⁻³ → 0.1	0.62 → 0.65 (0.64)
1, 3 - Propanediol, CH₂(OH)CH₂CH₂(OH) 30, 40, 41 41	Base (0.1M) Acid	5 × 10 ⁻³ → 0.1 ?	0.60 → 0.72 (0.63) No Reaction
Glycerol, CH₂(OH)CH(OH)CH₂(OH) 23, 24, 29, 42 24 23	Base (0.1M) Acid (0.1M) Acid (0.1M)	2.0 × 10 ⁻⁴ → 0.1 1.5 0.1	0.66 → 0.82 (0.72) 1.08 No Reaction
n - Butanol, C₄H₉OH 23, 30	Base (0.1M)	5 × 10 ⁻³ → 0.1	0.60 → 0.75 (0.70)
iso - Butanol, CH₂(OH)C(CH₃)₂ 23	Base (0.1M)	0.1	0.75

Reference	Electrolyte (mol/dm ³)	Reactant (mol/dm ³)	Onset Potential (V / RHE)
sec - Butanol, CH₃CH(OH)CH₂CH₃ 23	Base (0.1M)	0.1	0.75
t - Butanol, (CH₃)₃COH 23	Base (0.1M)	0.1	No Reaction
1, 2 - Butanediol, CH₂(OH)CH(OH)CH₂CH₃ 21, 30, 40	Base (0.1M)	5 × 10 ⁻³ → 0.01	0.60 (0.60)
1, 3 - Butanediol, CH₂(OH)CH₂CH(OH)CH₃ 21, 40	Base (0.1M)	0.01	0.60 (0.60)
1, 4 - Butanediol, CH₂(OH)CH₂CH₂CH₂(OH) 21, 30, 37, 40	Base (0.1M)	5 × 10 ⁻³ → 0.01	0.60 → 0.64 (0.62)
2, 3 - Butanediol, CH₃CH(OH)CH(OH)CH₃ 21, 40	Base (0.1 → 0.5M)	1 × 10 ⁻³ → 0.1	0.60 → 0.64 (0.62)
2 - Butene - 1, 4 - diol, CH₂(OH)CH=CHCH₂(OH) 30, 37	Base (0.1 → 0.5M)	5 × 10 ⁻³ → 0.01	0.50 (0.50)
2 - Butyne - 1, 4 - diol, CH₂(OH)C≡CCH₂(OH) 37	Base (0.5M)	0.01	0.65
s - Erythritol, CH₂OH(CHOH)₂CH₂OH 29	Base (0.1M)	2.5 × 10 ⁻³	0.71
D, L - Erythritol, CH₂OH(CHOH)₂CH₂OH 29	Base (0.1M)	2.5 × 10 ⁻³	0.71
1, 2 - Pentanediol, CH₂(OH)CH(OH)CH₂CH₂CH₃ 30	Base (0.1M)	5 × 10 ⁻³	0.55
1, 5 - Pentanediol, CH₂(OH)CH₂CH₂CH₂CH₂(OH) 30, 40	Base (0.1M)	5 × 10 ⁻³ → 0.01	0.50 → 0.62 (0.56)
D - Xilitol, CH₂OH(CHOH)₃CH₂OH 29	Base (0.1M)	2.5 × 10 ⁻³	0.71
Hexanol, C₆H₁₃OH 30	Base (0.1M)	5 × 10 ⁻³	0.62
Phenol, C₆H₅OH 24 24	Base (0.1M) Acid (0.1 → 1.0 M)	10 ⁻³ 0.4 × 10 ⁻³	0.74 1.07
Pyrocatechol (1, 2 - dihydroxybenzene), C₆H₄(OH)₂ 43	Acid (0.25M)	2.5 × 10 ⁻³	0.79
1, 2 - Hexanediol, CH₂(OH)CH(OH)CH₂CH₂CH₂CH₃ 30	Base (0.1M)	5 × 10 ⁻³	0.55
1, 6 - Hexanediol, CH₂(OH)CH₂CH₂CH₂CH₂CH₂(OH) 30, 40	Base (0.1M)	5 × 10 ⁻³ → 0.01	0.50 → 0.60 (0.55)
cis, trans - 1, 2 - Cyclohexanediol, C₆H₁₀(OH)₂ 21	Base (0.1M)	0.01 → 0.05	0.60
trans - 1, 2 - Cyclohexanediol, C₆H₁₀(OH)₂ 21	Base (0.1M)	0.005 → 0.05	0.60
1, 3 - Cyclohexanediol, C₆H₁₀(OH)₂ 21	Base (0.1M)	0.01	0.60
1, 4 - Cyclohexanediol, C₆H₁₀(OH)₂ 21	Base (0.1M)	0.01	0.60
D - Mannitol, CH₂OH(CHOH)₄CH₂OH 29	Base (0.1M)	2.5 × 10 ⁻³	0.71
Sorbitol, CH₂OH(CHOH)₄CH₂OH 32, 44	Base (0.1 → 0.2 M)	1.5 × 10 ⁻⁴ → 0.1	0.57 → 0.83 (0.66)
Benzyl alcohol, C₆H₅CH₂OH 24 24	Base (0.1M) Acid (0.1M)	0.4 × 10 ⁻³ 0.096	0.49 1.08
1, 7 - Heptanediol, CH₂(OH)CH₂CH₂CH₂CH₂CH₂CH₂(OH) 40	Base (0.1M)	0.01	0.50

0.1 - 0.2 V. Aldehydes (see Table 2), borohydrides, dimethylamineborane, t-butylamineborane and hypophosphite (see Table 9) all commence oxidation in the latter range. In all cases the solution species appears to be anionic, *eg* gem-diolate ($\text{RCH}(\text{OH})\text{O}^-$) in the case of aldehydes (19), which results in strong electrostatic interaction with the Au(I) mediator - the latter is assumed to be a cationic species (19), $[\text{Au}^+(\text{H}_2\text{O})_n]_{\text{ads}}$.

- (ii) Two Au(III) mediator systems seem to exist on gold in base (18), one commencing formation at 0.4 - 0.45 V and the other at 0.65 - 0.8 V (the difference may be related to the existence of the two different types of hydrous oxide, HO2 and HO1). Thus, hydrazine oxidation (Table 6) and the reduction of iodate (Table 9) commence and terminate at *ca* 0.4 V. However, most alcohols (Table 1), a few bases (Table 6) and quite a number of carbohydrates (Table 3) commence oxidation in base at *ca* 0.65 V, while chromate

Table 2 Aldehyde oxidation on gold in aqueous acid and base

Reference	Electrolyte (mol/dm ³)	Reactant (mol/dm ³)	Onset Potential (V/RHE)
Methanal (formaldehyde), HCHO 24, 28, 45 - 47	Base (0.1 → 1.0M)	0.4 × 10 ⁻³ → 0.70	0.10 → 0.37 (0.19)
24	Acid (0.05 → 0.1M)	0.1 → 0.25	0.84 → 1.06 (0.94)
Ethanal (acetaldehyde), CH ₃ CHO 47	Base (0.1M)	10 ⁻³ → 0.1	0.26 → 0.40 (0.33)
23	Acid (0.1M)	0.1	0.80
Chloral, CCl ₃ CHO 47	Base (0.1M)	10 ⁻³	0.33
Glyoxal, CHOCHO 23, 47	Base (0.1 → 1.0M)	10 ⁻³ → 0.1	0.26 → 0.40 (0.32)
23	Acid (0.1 → 0.5M)	0.05 → 0.1	0.35, 1.00 → 1.21 (0.35, 1.10)
Glycol aldehyde, CHOCH ₂ OH 23	Base (0.1 → 1.0M)	0.05 → 0.1	0.10 → 0.30 (0.20)
23	Acid (0.1M)	0.1	0.80
Propanal, CH ₃ CH ₂ CHO 47	Base (0.1 → 1.0M)	10 ⁻³	0.21 → 0.26 (0.24)
Propenal (acraldehyde), CH ₂ =CHCHO 47	Base (0.1M)	10 ⁻³	0.26
Pyruvic aldehyde, CH ₃ COCHO 47	pH = 11.7	10 ⁻³	0.26
Glutaric dialdehyde (pentanedial), CHO(CH ₂) ₃ CHO 32	Base (0.1M)	10 ⁻³	0.30
Benzaldehyde, C ₆ H ₅ CHO 24, 47, 48	Base (0.1 → 1.0M)	0.75 × 10 ⁻³ → 10 ⁻³	0.19 → 0.34 (0.26)
24	Acid (0.1M)		No Reaction
Cyclohexanecarboxaldehyde, C ₆ H ₁₁ CHO 48	Base (1.0M)	2.0 × 10 ⁻³	0.24, 0.67

Table 3 Carbohydrate oxidation on gold in aqueous acid and base

Reference	Electrolyte (mol/dm ³)	Reactant (mol/dm ³)	Onset Potential (V/RHE)
Glucose, CH ₂ OH-(CHOH) ₄ -CHO 24, 28, 32, 44, 49 - 52	Base (0.1 → 1.0M)	0.2 × 10 ⁻³ → 0.2	0.20 → 0.39, 0.60 → 0.79, (0.31, 0.68)
50, 51	pH = 6.76 → 7.4	0.01 → 0.1	0.20 → 0.40 (0.30)
53	pH = 5.85	0.025	0.40, 0.70
50	pH = 1.5	0.05	No Reaction
24, 54	(0.05 → 0.1M) H ₂ SO ₄	0.01 → 1.0	1.00 → 1.08 (1.04)
54	0.1M HClO ₄	0.01 → 0.2	0.40 → 0.50 (0.45)
54	0.1M HNO ₃	0.01	0.50
54	0.1M H ₃ PO ₄ , HCl	0.01	No Reaction
2 - Deoxy - D - glucose, CH ₂ OH-(CHOH) ₃ CH ₂ -CHO 49	Base (0.1M)	0.38 × 10 ⁻³	0.36
Fructose, CH ₂ OH-(CHOH) ₃ C(O)-CH ₂ OH 44	Base (0.1M)	1.5 × 10 ⁻⁴	0.57
51	pH = 7.4	0.01	No Reaction
Sucrose, C ₁₂ H ₂₂ O ₁₁ 44	Base (0.1 → 0.2M)	1.5 × 10 ⁻⁴ → 0.1	0.57 → 0.79 (0.65)
Maltose, C ₁₂ H ₂₂ O ₁₁ 44	Base (0.1M)	1.5 × 10 ⁻⁴	0.53
Lactose, C ₁₂ H ₂₂ O ₁₁ 55	pH = 7	10 ⁻³	0.36, 0.70

(Table 9) commences reduction at the same value. Some carbohydrates contain both aldehyde and alcohol groups and, in base, show two regions of increase in anodic current in the positive sweep, one at *ca* 0.2 V and the other at *ca* 0.65 V - typical values for the oxidation of the functional groups in question on gold at high pH. Some typical electro-oxidation responses for gold in base are shown in Figure 3.

- (iii) For gold in acid the Au(III) mediator formation potentials (and onset/termination values) seem to occur at more positive potentials - as expected in terms of the super-Nernstian shift (1). Thus the rate of hydrazine oxidation and dichromate reduction (Figure 2) undergo a dramatic change at *ca* 0.9 V; similar behaviour was observed with ethylene glycol (Table 1), some hydrocarbons (Table 5) and various aldehydes (Table 2) - the latter are easily oxidized but do not exist as anionic gem-diolates in solutions of low pH. On the other hand, most alcohols (Table 1), various acids (Table 4) and amino acids (Table 7) commence oxidation in the positive sweep at *ca* 1.05 V. Thus the critical Au(III) mediator potentials are approximately 0.4 - 0.45 V and 0.65 - 0.8 V in base and 0.8 - 0.85 V and 1.0 - 1.1 V in acid. It has also been suggested (19) that the Au*/Au(I) transition shifts to more negative potentials on decreasing the pH, and

some evidence based on borane oxidation was used to support this viewpoint.

While the interfacial cyclic redox approach provides a reasonable interpretation of the unexpectedly high electrocatalytic activity of gold, and why this activity is greater in solutions of high pH, the limitations of this approach must be borne in mind. For example:

(a) It is not relevant to all reactions on gold, *eg* hydrogen gas evolution on gold which occurs at E

< 0.0 V or simple electron transfer (non-electrocatalytic) processes. However, oxygen gas evolution (at E ≥ 2.0 V) may involve mediation by an Au(III)/Au(IV) surface oxide redox system.

(b) In some instances significant deviations from expected behaviour is evident. For example, a number of amines, such as ethylamine, ethylenediamine and propylamine (Table 6), are oxidized on gold in base only at E ≥ ca 1.0 V. It may be that an Au(I) or Au(III) amine complex, rather than an oxide species, is formed initially on oxidation of active gold atoms at the interface - the amine ligands undergoing oxidation only at more positive potentials, *ie* at ca 1.0 V.

(c) In some instances the rate of increase in oxidation current with increasing potential in the region just above the adatom/incipient oxide transition (positive sweep, *ie* above ca. 0.65 V in the case of alcohol oxidation on gold in base) appears to be quite sluggish. This is evident for instance, in the responses reported for various butanediols and cyclohexanediols by Beltowska-Brzezinska and co-workers (20, 21). Again, as suggested above in the case of some of the amines, either the organic reactant or some intermediate may impede the mediator generation step, resulting in a sluggish overall oxidation reaction - the degree of inhibition varying with the nature of the organic compound.

An alternative explanation of this slow increase in anodic current in some cases was outlined recently (12). With reactive species such as hydrazine the rate of increase in current density with increasing potential (positive sweep) is often quite rapid. Since all electrocatalytic reactions involve a release of energy, some of the latter may be trapped locally at the active site - resulting in further promotion of other metal atoms to the very active state. Hence, in the case of hydrazine, a high percentage of active site atoms are rapidly induced into the mediation process. With less active solution species, such as ethylene glycol, many gold atoms at active sites are not only not promoted to an adequate level of activity, but the active oxide possibly alters to a less reactive form - resulting, as outlined here in Figure 3(c), in a rather slow rate of increase in oxidation rate with increasing potential in the positive sweep. This approach assumes that metal atoms at active sites are not rigidly held species and that their energy is variable; a further complication is that (depending apparently on the metal atom activity) the nature of the incipient oxide or mediator formed on oxidation is also variable.

Table 4 Acid oxidation on gold in aqueous acid and base

Reference	Electrolyte (mol/dm ³)	Reactant (mol/dm ³)	Onset Potential (V/RHE)
Methanoic (formic), HCOOH			
39	pH = 13	10 ⁻³	0.55
39	pH = 13	0.1	0.95
56	pH = 6	10 ⁻³	0.58
23	Acid (0.5M)	0.01 → 1.0	0.38 → 0.41 (0.40)
18	Acid (1.0M)	0.1	0.85
Ethanoic (acetic), CH₃COOH			
23, 39	Base (0.1M)	0.075 → 0.1	No Reaction
23	Acid (0.1M)	0.1	No Reaction
Glycolic, CH₂(OH)COOH			
23	Base (0.1M)	0.1	0.55
23	Acid (0.1M)	0.1	No Reaction
Glyoxylic, CHOCOOH			
23, 47	Base (0.1 → 1.0M)	10 ⁻³ → 0.1	0.20 → 0.26, 0.66 (0.25, 0.66)
23	Acid (0.1M)	0.1	1.10
Oxalic, (COOH)₂			
23	0.1M NaOH	0.1	No Reaction
18, 23	Acid (0.1 → 1.0M)	4.0 × 10 ⁻⁴ → 0.1	0.80 → 1.10 (0.95)
Hydroxypropanoic, CH₂(OH)CH₂COOH			
39, 41	Alkaline	-	No Reaction
Pyruvic, CH₃COCOOH			
57	Base (0.1M)	1.53 × 10 ⁻³	0.88
18	Acid 0.1 → 0.5M)	7 × 10 ⁻³ → 0.01	1.00 → 1.10 (1.05)
Malonic, CH₂(COOH)₂			
58	Acid (0.5M)	9.63 × 10 ⁻⁵	No Reaction
Tartronic, HOCH(COOH)₂			
58	Acid (0.5M)	0.01	1.00
Mesooxalic, (HO)₂CH(COOH)₂			
59	Base (0.1M)	9.5 × 10 ⁻⁴ → 2.6 × 10 ⁻³	0.76 (0.76)
60	Acid (0.5 → 1.0M)	1.06 × 10 ⁻³ → 0.01	1.00 → 1.10 (1.02)
Gluconic, CH₂OH-(CHOH)-COOH			
49 - 51	Base (0.1 → 1.0M)	0.4 × 10 ⁻³ → 0.05	0.63 → 0.72 (0.68)
51	pH = 7.4	0.01	No Reaction
Glucaronic, CHO-(CHOH)-COOH			
49, 50	Base (0.1 → 1.0M)	0.45 × 10 ⁻³ → 0.05	0.30 → 0.37, 0.65 (0.32, 0.65)
Glucaric, COOH-(CHOH)-COOH			
49, 50	Base (0.1 → 1.0M)	0.33 × 10 ⁻³ → 0.05	0.65, 1.00 → 1.10 (0.65, 1.05)

SYNOPSIS OF PUBLISHED WORK ON THE ELECTROCATALYTIC BEHAVIOUR OF GOLD.

The tables are included to illustrate the scope of the work that has been carried on the electrocatalytic behaviour of gold in aqueous media. The survey is not comprehensive and, to conserve space, the list of references is curtailed (quite often the behaviour of a given compound was investigated by more than one group). The following comments are relevant, *viz.*

(i) Current density (or rate values) are not quoted. A considerable number of variables are involved, *eg* nature of the electrolyte, concentration of reactant, surface roughness, type of stirring (if any), shape of the electrode, sweep rate, etc., and the absence of agreed set conditions makes rate comparison, even at a given potential for the same compound - between different groups of authors, of little value. On the basis of the present survey, we feel that a more systematic approach would be useful and recommend the publication of reasonable guidelines for future experimental work in this area, mainly with a view to assisting comparison of results obtained in different laboratories.

(ii) The first column in each table gives the main reference from which the data was taken. The second column indicates the nature of the electrolyte (the base was usually NaOH or KOH and the acid H_2SO_4 or HClO_4) and the third gives the reactant concentration. The fourth column gives the onset potential, or onset/termination potential, for the reaction. The values, which are given here in terms of the RHE scale (1), were taken either directly (where this was stated) from the text or else estimated from a published diagram. The figure in parenthesis in this column gives the mean onset potential for cases where more than one set of published data were available. The majority of the work involved oxidation; reduction reactions are indicated by "(R)" in the final column.

(iii) In the absence of consistent rate data for electrocatalytic processes on gold, attention is focussed in the Tables mainly on onset/termination potential values, *i.e.* the potentials where electrocatalytic, or Faradaic, currents (usually in the double layer region) became significant. While no great accuracy is claimed for the listed values (in most cases the increase in current was quite gradual) it is worth noting that it is virtually impossible to explain the onset potential behaviour reported here

in terms of the conventional description of gold electrochemistry. It is clear from Figure 2, for instance, that gold in acid is active for oxidation and reduction of solution species above and below, respectively, *ca* 1.0V. It may be argued that anion, *eg* HSO_4^- , adsorption suppresses the reduction of dichromate as the potential is increased above *ca* 0.9V, but such a view cannot then explain why hydrazine oxidation increases rapidly with increasing potential above the latter value. It seems only that assumption of a subtle switch in the nature of the mediator present at low coverage active sites (a

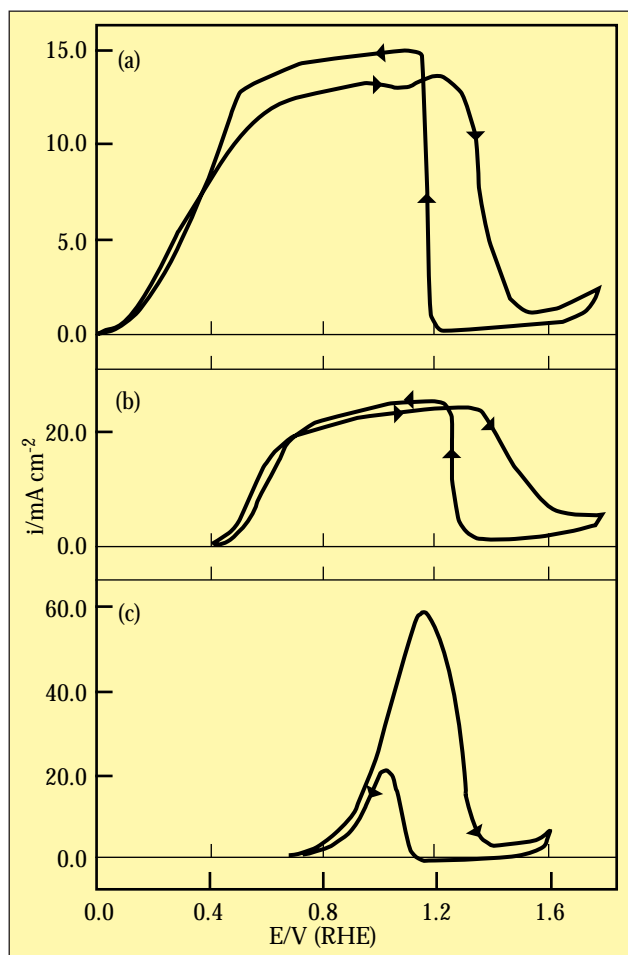


Figure 3 (a) Typical cyclic voltammogram (0 - 1.8 V, 5 mV s^{-1}) for a gold wire electrode in 1.0 mol dm^{-3} NaOH with HCHO, to a level of 0.1 mol dm^{-3} , $T = 25^\circ\text{C}$; (b) Typical cyclic voltammogram (0 - 1.8 V, 50 mV s^{-1}) for a smooth gold electrode in N_2 -stirred 1.0 mol dm^{-3} NaOH with N_2H_4 , to a level of 0.1 mol dm^{-3} , $T = 25^\circ\text{C}$; (c) Typical cyclic voltammogram (0 - 1.6 V, 50 mV s^{-1}) for a gold wire electrode in 1.0 mol dm^{-3} NaOH with 0.1 mol dm^{-3} ethylene glycol (CH_2OH)₂, $T = 25^\circ\text{C}$

Table 5 Hydrocarbon oxidation/reduction on gold in aqueous acid and base

Reference	Electrolyte (mol/dm ³)	C _{reactant} (mol/dm ³)	Onset Potential (V/RHE)
Ethane, C ₂ H ₆	23 Base (0.1M)	-	No Reaction
	23 Acid (0.1M)	-	No Reaction
Ethene (ethylene), C ₂ H ₄	61 Acid (0.05 → 1.0M)	Saturated	0.80 → 0.90 (0.86)
Ethyne (acetylene), C ₂ H ₂	61, 62 Acid (0.05 → 0.1 M)	Saturated	0.85 → 0.95 (0.90)
	63, 64 Acid (0.05 → 0.1 M)	Adsorbed	0.85 → 0.90 (0.88)
	63 Acid (0.05M)	Adsorbed	0.40 (R)
	62 Acid (0.1M)	Saturated	0.43 (R)
Propene, CH ₃ CH=CH ₂	61 Acid (0.05 → 0.1 M)	Saturated	0.85 (0.85)

process that is virtually undetectable by conventional techniques) can account for such behaviour.

Active site behaviour, as pointed out originally by Taylor (3), is complex. It seems that in the case of gold in base, Figure 3, the sites involved exhibit two different types of redox responses and this provides the basis for a limited degree of selectivity. For example, aldehydes, Figure 3(a), may be selectively oxidized, in the presence of alcohols - Figure 3(c), below *ca* 0.6V. However, the advantage of this selectivity, *eg* from an analytical viewpoint, is limited in that - as outlined in Table 2 - virtually all aldehydes are oxidized on gold in base in the latter region. Application of a gold electrode as a voltammetric detector in the analysis of mixtures of organic compounds generally entails the use of a prior separation procedure - usually based on some form of chromatography.

We believe that there is sufficient data in the Tables presented here to demonstrate some general trends and, in particular, that for virtually all of the reactions electrocatalysis occurs predominantly in the double layer region; it commences almost invariably (see Table 1) at a lower potential in base than in acid. In our experience an interesting facet of gold electrochemistry is the further investigation of those processes which show significant departure from the basic approach outlined here.

CONCLUSIONS

- (1) For a metal that is widely regarded as extremely stable and an established weak chemisorber and consequently - from an activated chemisorption viewpoint, a poor catalyst - gold is a surprisingly active electrocatalyst for a wide variety of oxidation

Table 6 Oxidation/reduction of nitrogen - containing compounds on gold in aqueous acid and base

Reference	Electrolyte (mol/dm ³)	C _{reactant} (mol/dm ³)	Onset Potential (V/RHE)
Hydrazine, H ₂ NNH ₂	24, 28, 31, 46 Base (0.1 → 1.0M)	2.0 x 10 ⁻⁴ → 1.0	0.40 → 0.48 (0.42)
	18, 31, 43 Acid (0.25 → 1.0M)	1 x 10 ⁻³ → 0.1	0.80 (0.80)
Dimethylamine, (CH ₃) ₂ NH ₂	65 Base (1.0M)	0.1	0.4, 0.6, 1.0
Ethylamine, C ₂ H ₅ NH ₂	26 Base (1.0M)	9 x 10 ⁻⁵ → 2.2 x 10 ⁻³	1.01
Ethylenediamine, H ₂ NCH ₂ CH ₂ NH ₂	24 Base (0.1M)	1.0 x 10 ⁻³	1.07
Nitrotriazole, C ₂ N ₃ H ₂ (NO ₂)	66 Acid (0.2M)	10 ⁻³	0.40 (R)
Propylamine, C ₃ H ₇ NH ₂	32 Base (0.1M)	5 x 10 ⁻⁴	0.98
Pyrrolidine, C ₄ H ₈ NH	2, 28 Base (1.0M)	0.1	0.65 → 0.70 (0.67)
3, 6 - Dihydropyridazine, C ₄ N ₂ H ₂ (OH) ₂	67 Acid (1.0M)	1 x 10 ⁻³	1.05
Piperidine, C ₅ NH ₁₁	2, 28 Base (1.0M)	0.1	0.65 → 0.70 (0.68)
Pyridine, C ₅ NH ₅	2, 68 pH = 10.15 → 11.7	0.03 → 0.1	0.20 (0.20) (R)
	69 Base (1.0M)	0.02	0.54 (R)
Phenylamine (aniline), C ₆ H ₅ NH ₂	70 Acid (0.1 → 0.5M)	0.01 → 0.10	0.95 → 1.05 (1.01)
Nitrosobenzene, C ₆ H ₅ N=O	71 pH = 6	Saturated	0.83 (R)
	71 Base (0.1M)	Saturated	0.83 (R)
Nitrobenzene, C ₆ H ₅ (NO ₂)	66, 71 Base (0.1 → 0.2M)	10 ⁻³ → 2 x 10 ⁻³	0.49 → 0.51 (0.51) (R)
	71 pH = 6	2 x 10 ⁻³	0.52 (R)
	66 Acid (0.2M)	10 ⁻³	0.37 (R)
Phenylenediamine, C ₆ H ₄ (NH ₂) ₂	72 Acid (0.5M)	0.05	0.81
Azobenzene, (C ₆ H ₅) ₂ N=N(C ₆ H ₅)	71 pH = 6	Saturated	0.48 (R)
	71 Base (0.1M)	Saturated	0.62 (R)
5 - Aminoindole, C ₆ H ₃ (NO ₂)(C ₂ NH ₃)	73 Acid (0.2M)	4 x 10 ⁻⁴	1.01

and reduction processes. The data presented here in Tables 1 - 9 represent a compilation of information from diverse sources and the interfacial mediator (IHOAM) model may be viewed as an attempt to rationalize the results obtained in this area. It is worth noting that this approach was adopted recently by Iotov and Kalcheva (93) to explain data obtained for the oxidation of phenol on platinum/gold alloy electrodes in aqueous acid solution. The mediator approach generally assumes the involvement of an

Table 7 Amino acid oxidation on gold in aqueous acid and base

Reference	Electrolyte (mol/dm ³)	Reactant (mol/dm ³)	Onset Potential (V/RHE)
Cysteine, HSCH ₂ CH(NH ₂)COOH 74 - 76	Acid (0.01 → 0.5M)	8 × 10 ⁻⁷ → 10 ⁻³	0.88 → 1.06 (0.98)
Cystine, (HOOCCH(NH ₂)CH ₂ S) ₂ 74, 76	Acid (0.01 → 0.5M)	10 ⁻³ → 5.0 × 10 ⁻³	0.87 → 1.10 (0.99)
Cysteine Sulfinic Acid, HO ₂ SCH ₂ CHNH ₂ CO ₂ H 75	Acid (0.01M)	10 ⁻⁷ → 10 ⁻⁴	1.06
Cysteic Acid, HOOCCH(NH ₂)CH ₂ SO ₃ H 74	pH = 1.7	-	No Reaction
	Acid (0.01M)	10 ⁻⁶ → 10 ⁻³	1.06
Tryptophan, C ₆ H ₄ (C ₂ NH ₂)CH ₂ CH(NH ₂)COOH 77	pH = 1.9	10 ⁻³	1.05
	pH = 5.3	10 ⁻³	1.15
	pH = 9.0	10 ⁻³	1.22
N - Acetyl Tryptophan Amide, C ₆ H ₄ (C ₂ NH ₂)CH ₂ CH(NH(C=OCH ₃))COOH 77	pH = 1.7	10 ⁻³	1.00
Methionine, CH ₃ SCH ₂ CH ₂ CH(NH ₂)COOH 74	pH = 1.7	10 ⁻³	1.10
N - Acetyl - L - Methionine, CH ₃ SCH ₂ CH ₂ CH(NH(C=OCH ₃))COOH 74	pH = 1.7	10 ⁻³	1.10
Lysine, H ₂ N(CH ₂) ₄ CH(NH ₂)COOH 78	0.05M NaOH	6.5 × 10 ⁻⁵ → 2.6 × 10 ⁻⁴	0.30, 0.50, 1.00

interfacial cyclic redox reaction and there are certain electrode processes, *eg* hydrogen gas evolution and hydrogenation of saturated organics, where this mechanism may not be relevant.

- (2) Catalytic reactions at surfaces and interfaces are generally assumed to occur at active sites and an understanding of the behaviour of the latter is crucial to the interpretation of both heterogeneous catalysis and electrocatalysis. In the present work such sites are regarded (as usual) as defects where active, low coordination gold atoms, or clusters of same, are considered as microparticles or quantum dots (6), whose properties (especially redox behaviour) are now known (7) to be quite different to those of the bulk metal. This means that the properties of either bulk gold or high coordination surface gold atoms are not particularly relevant to the catalytic behaviour of the surface.
- (3) The study of the behaviour and properties of active metal atoms at surfaces and interfaces, and gold seems to be a particularly useful metal for such work, is a very challenging area of research. Their importance stems from the fact that these active atoms, and their oxidation products, often act as the mediators for the reduction and oxidation, respectively, of dissolved solution species.

- (4) The study of the surface/interfacial mediator systems at metal surfaces is complicated by the fact that:
- very low coverages are involved,
 - the metal atoms involved are in an active, metastable state and may well increase their energy level significantly when participating in a mediated electrocatalytic process, and
 - these active atoms, and their oxidation products (incipient hydrous oxides), seem to exhibit complex chemical behaviour - and the view presented in the present article should be regarded merely as a preliminary attempt to interpret the latter.
- (5) The need to reconsider the surface behaviour of gold is clear not only from the present survey of its electrocatalytic behaviour, but also from the work of Haruta and co-workers (94) on the catalytic behaviour of the metal. The observation by the latter group that this supposedly-inert metal, in the form of microparticles on oxide supports, is active for CO gas oxidation even at -70°C is quite unexpected. Such behaviour supports the view expressed here that the properties of the bulk metal are virtually irrelevant with regard to its catalytic properties - the latter are probably dominated by the behaviour of unusually reactive surface gold atoms which are assumed to be capable of

Table 8 Oxidation/reduction of gases on gold in aqueous acid and base

Reference	Electrolyte (mol/dm ³)	Reactant (mol/dm ³)	Onset Potential (V/RHE)
Carbon Monoxide, CO			
79	Base (1.0M)	Saturated	0.00, 0.82 (0.00, 0.82)
79	Base (1.0M)	Adsorbed	0.00, 0.20 → 0.24, 0.78 (0.00, 0.22, 0.78)
80	pH = 8.8	Saturated	0.28
64, 81	Acid (0.1 → 1.0M)	Saturated	0.34 → 0.58 (0.46)
82	Acid (0.1 → 1.0M)	Saturated	0.87 → 0.93 (0.90)
83	1.0M HClO ₄	Adsorbed	0.87
84	1.0M H ₂ SO ₄	Adsorbed	0.55
Nitrous oxide, N₂O			
85	Base (1.0M)	Saturated	0.60
85	Acid (1.0M)	Saturated	No Reaction
Hydrogen, H₂			
86	0.1M HClO ₄	Saturated	0.65
86	0.5M H ₂ SO ₄	Saturated	0.36
Oxygen, O₂			
32, 44	Base (0.1M)	Dissolved	0.93 (0.93) (R)
87	Base (0.1 → 1.0M)	Saturated	0.87 → 1.05 (0.95) (R)
88	Acid (0.05 → 0.5M)	Saturated	0.45 → 0.67 (0.58) (R)
89	Acid (0.5M)	Aerated	0.58 (R)

Table 9 Oxidation/reduction of inorganic compounds on gold in aqueous acid and base

Reference	Electrolyte (mol/dm ³)	Reactant (mol/dm ³)	Onset Potential (V/RHE)
Borohydride, [BH₄]⁻ 46	pH = 12.5	0.03	0.11
Chromate, [CrO₄]⁻ 90	Base (1.0M)	0.015	0.62 (R)
Dichromate, [Cr₂O₇]²⁻ 18 12, 18	Base (1.0M) Acid (1.0M)	2 x 10 ⁻³ 2 x 10 ⁻³	0.60 (R) 0.95 → 1.05 (0.98) (R)
Dimethylamineborane, (CH₃)₂NH·BH₃ 19, 65 46	Base (1.0M) pH = 7.0	0.05 0.03	0.08 → 0.10 (0.09) 0.00
Tertbutylamineborane, ((CH₃)₃C)NH₂·BH₃ 19	Base (1.0M)	0.01	0.10
Pyridineborane, [C₅H₅N]·BH₃ 19	Base (1.0M)	0.01	0.35, 0.70
Hypophosphite, [H₂PO₂]⁻ 19 46	Base (1.0M) pH = 9	0.16 0.20	0.20 -0.23
Hypophosphorous Acid, H₃PO₂ 19	Acid (1.0M)	0.16	0.15, 1.00
Iodate, [IO₃]⁻ 18, 28, 31 18, 31	Base (1.0M) Acid (1.0M)	0.02 2 x 10 ⁻³ → 0.02	0.40 → 0.45 (0.42) (R) 0.30, 0.80 → 0.90 (0.30, 0.85)
Nitrate, [NO₃]⁻ 50	Base (1.0M)	0.02 → 0.1	0.20 (R)
Nitrite, [NO₂]⁻ 24 85 24 85	Base (0.1M) Base (1.0M) Acid (0.1M) Acid (1.0M)	0.99 x 10 ⁻³ 0.05 0.99 x 10 ⁻³ 0.05	No Reaction 0.94 (R) 1.10 0.96 (R)
Peroxide, [O₂]²⁻ 18 18 18 18	Base (1.0M) Base (1.0M) Acid (1.0M) Acid (1.0M)	0.02 0.02 0.06 0.06	0.30 (R) 0.80 0.50 (R) 1.05
Persulfate, [S₂O₈]²⁻ 18, 28, 31 91 92 18 31	Base (1.0M) 0.005M HClO ₄ 0.01M HClO ₄ 1.0M H ₂ SO ₄ 1.0M H ₂ SO ₄	0.02 1 x 10 ⁻³ 1.2 x 10 ⁻³ 0.02 0.02	0.80 → 1.07 (0.91) (R) 0.77, 1.16 (R) 1.17 (R) 0.50, 0.80 (R) 0.90 (R)

generating very low coverage surface oxide species under conditions where the bulk metal shows no affinity for oxygen.

- (6) Correlations between the behaviour of multilayer hydrous gold oxide deposits and the electrocatalytic behaviour of gold (which were the origin (2) of the IHOAM model) continue to be of interest. In a recently published account of studies in this area involving gold in acid (95) the presence of more than one type of hydrous gold oxide species, which had been postulated earlier on the

basis of electrocatalysis studies (18), was confirmed in the case of multilayer gold oxide films (the article in question (95) is reference 28 - which was indicated as unpublished in Part 1 of this review of the electrochemistry of gold (1)).

ABOUT THE AUTHORS

Lawrence Declan Burke received his BSc and MSc from University College Cork in 1959 and 1961, respectively, and a PhD in 1964 from Queen's University Belfast where he worked with FA Lewis on the palladium hydride system. He spent a year as an Alexander von Humboldt Fellow in Karlsruhe University, Germany, where he worked on solid state electrochemistry with Professor Hans Rickert. Since returning to Cork he has been involved in an extensive investigation of the electrochemistry of metals, oxides and especially hydrous oxides. This work, which is concerned largely with the unusual or non-ideal behaviour of these systems, is relevant to such areas as electrocatalysis, electrochromic systems, electroless deposition of metals, etc. Professor Burke was awarded Fellowship of the Electrochemical Society in 1995.

Patrick Francis Nugent successfully completed his PhD degree on research into the electrochemistry of gold in aqueous media in May 1998.

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