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Electrocatalysis at polycrystalline silver in base: an example of the complexity of surface active state behaviour

Abstract Four low-level redox responses, attributed to the involvement of four different types of active surface state (or site) transitions, were observed within the double layer region in the case of polycrystalline silver electrodes in base; there is now independent evidence for such premonolayer behaviour in data reported by other authors. The potentials for each of these transitions were correlated with the onset/termination potentials of different electrocatalytic processes, usually for oxidations or reductions but in some cases for both types. The data obtained are in good agreement with the IHOAM model of electrocatalysis which was outlined earlier for the other Group 11 metals, gold and copper.

Keywords Silver · Base · Active sites · Premonolayer oxidation · Electrocatalysis

Introduction

As outlined in a recent publication [1], the three Group 11 metals (Cu, Ag and Au) exhibit excellent catalytic and electrocatalytic properties, especially for oxidation reactions. One indication of the level of interest in this area is provided by a recent review of gold-catalysed oxidation of gaseous carbon monoxide [2], in which it was pointed out that this topic was the subject of at least 30 publications in 1999.

A fascinating aspect of the Group 11 metals is that they are all weak chemisorbers; for instance, they do not display significant capability to adsorb hydrogen (this is well established for gold electrodes in aqueous media [3] and, in our experience, is also valid for silver and copper

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electrodes in aqueous base). Hence, in terms of the well-known activated chemisorption model, these metals should display quite weak catalytic properties, which is not in agreement with experimental observations [1, 2].

A solution to this dilemma was provided recently [1] by the assumption of a novel, highly localized mode of chemisorption involving partial electron transfer (or polar covalent bonding) between the reactant (or solvent) molecules and high-energy surface metal atoms at active sites on the electrode surface. This view is not especially novel; the non-equilibrium character of surface active site atoms was stressed by Taylor [4] in 1925; fig. 1 in his article shows, quite explicitly, low-coordination surface Ni atoms which are essentially outside the metal lattice. Such atoms display significantly different chemical, adsorption and energetic properties, as compared with well-embedded, high-coordination-state surface metal atoms.

The interpretation of electrocatalysis used in the present work was discussed in some detail recently for gold [5] and copper [6]. The approach in question stresses the heterogeneous nature of active metal surfaces and, in particular, the importance of low-coverage, high-energy surface metal atoms. Such states, which are assumed to be almost invariably present at real metal surfaces, are regarded as vital participants in many electrocatalytic processes. A generalized scheme for such reactions, referred to as the incipient hydrous oxide/adatom mediator, or IHOAM, model of electrocatalysis, was discussed earlier [6].

The basic electrochemistry of silver in aqueous alkaline solution was described in a recent publication from this laboratory [1]. Pourbaix's $E°$ data for this system [7] may be summarized as follows: Ag/Ag_2O, 1.173 V (RHE); $Ag/AgOH$, 1.505 V; Ag_2O/AgO, 1.398 V; $AgOH/AgO$, 1.066 V; AgO/Ag_2O_3, 1.569 V (these values relate to bulk solids at 298 K; the involvement of dissolved species, e.g. Ag^+ or AgO^- ions, is ignored here). Active surface atoms, which have a reduced lattice stabilization energy, are assumed to undergo oxidation at potentials lower than the values quoted here. Such

behaviour, which results in the appearance of low-level redox transitions (or peaks) within the double layer region for this electrode system, is already well established for silver in base [8, 9, 10, 11, 12, 13, 14, 15]. The objective of the present work is to correlate these double layer redox transitions with the responses for selected electrocatalytic processes. These electrocatalytic responses are assumed to reflect an enhanced or amplified version of the active surface state behaviour which is usually of quite low magnitude and, consequently, difficult to investigate.

Experimental

The cell and cyclic voltammetry equipment used in this work was described earlier [1]. The working and counter electrodes consisted of lengths of silver wire (1.0 mm diameter, ca. 0.7 cm^2 exposed area, Johnson Matthey, Puratronic grade) sealed directly into soda glass. The working electrode was usually pretreated prior to use by brief immersion in 5:1 H$_2$O/HNO$_3$ solution, then (after drying) to mild abrasion with fine grade Emery paper followed by washing the surface with triply distilled water. The electrode was generally cycled (0.0–1.6 V at 10 mV s^{-1}) in the base electrolyte before use to ensure that it gave a conventional response for silver in alkaline solution.

The potential of the working electrode was recorded and is reported with respect to a hydrogen reference electrode [p(H$_2$) =1.0 atm], i.e. in terms of the RHE scale. Solutions, which were extensively purged with N$_2$ gas before use, were made up with triply distilled water and Analar grade sodium hydroxide. The main reagents used were as follows: acetaldehyde (Merck), benzaldehyde (Sigma), ethanol (Labscan, HPLC grade), formaldehyde (BDH, 40% w/v, Analar), glyoxylic acid monohydrate (Aldrich), hydrazine monohydrate (Aldrich), hydrogen peroxide 30% (Isoclean, Iso-electronic grade), monoperoxyphthalate (Aldrich, magnesium salt hexahydrate), nitrobenzene (BDH, Analar), 3-nitrobenzoic acid (Lancaster), 2-nitrobenzaldehyde (Sigma), 4-nitrobenzaldehyde (Sigma), nitromethane (BDH), nitrous oxide (BOC gases), oxygen (Irish Oxygen), potassium nitrate (BDH, Analar), potassium persulfate (BDH, Analar).

Results

Basic behaviour of silver in base

A typical cyclic voltammogram for silver in base is shown by the full line in Fig. 1. In the positive sweep the range from 0.0 to ca. 1.15 V appeared to be featureless, the only process involved being double layer charging. Over the range 1.15–1.5 V, three overlapping peaks (A$_1'$, A$_1''$ and A$_1'''$) appeared; as discussed earlier [1], these are attributed to an Ag(0)/Ag(I) oxide or hydroxide transition. This was followed by a further anodic peak, A$_2$, at ca. 1.63 V, which is attributed to AgO formation (this oxide is apparently more correctly formulated [16] as Ag^{I}Ag^{III}O$_2$). In the subsequent negative sweep, two cathodic peaks appeared: C$_2$ at ca. 1.35 V is attributed to an AgO/Ag$_2$O transition, while C$_1$ at ca. 1.06 V is assumed to be due to reduction of Ag$_2$O to Ag.

When such a sweep was repeated, using a higher recorder sensitivity over the range 0.0–1.0 V (dashed line in Fig. 1), some low-level, poorly defined features were observed within the double layer region. Note the small
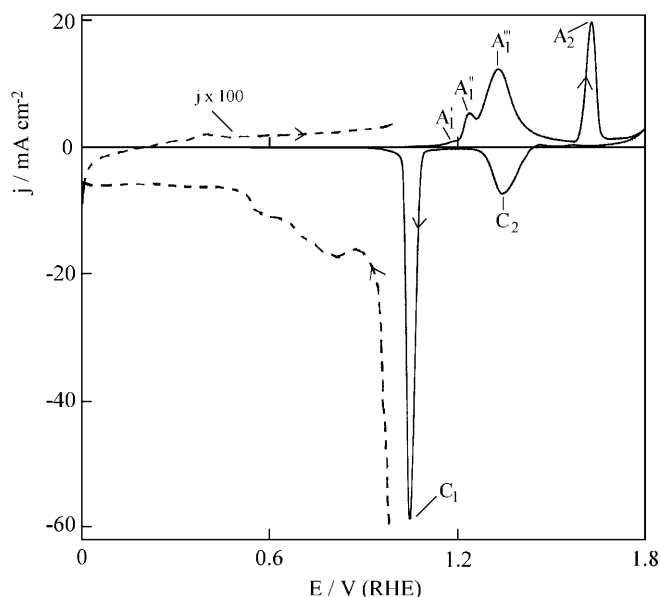

Fig. 1 Cyclic voltammogram (0.0→1.8 V at 10 mV s^{-1}) for a bright silver wire electrode in 0.5 mol dm^{-3} NaOH at 25 °C; the *dashed line* shows the response over the double layer region (0.0–1.0 V) recorded using a higher recorder sensitivity

anodic peak at ca. 0.4 V in the positive sweep, the substantial cathodic response over the region 1.0 to 0.5 V in the negative sweep and the general charge imbalance over the double layer region. This is assumed to reflect mainly the slow reduction of subsurface oxygen [10, 13].

As discussed earlier for platinum [17] and gold [5, 18], double layer responses are often a useful guide to electrocatalytic behaviour. To explore such responses in greater detail for silver in base, the upper limit of the sweep was restricted to 1.0 V, i.e. the monolayer oxide region and extensive subsurface oxide formation were avoided, and the sweep rate was increased from 10 to 100 mV s^{-1}. The double layer response for a conventional silver electrode in base under such conditions is shown in Fig. 2a. As outlined in the latter, four rather ill-defined peaks appeared in the positive sweep, and three in the negative sweep.

The resolution of these double layer peaks was significantly improved (Fig. 2b) by subjecting the electrode to cathodic pretreatment (as described recently [19, 20] for gold and other metals in aqueous media, the latter entails disruption, and hence activation, of the electrode surface via hydrogen embrittlement effects) and altering the lower limit to –0.4 V. Four active-state redox transitions, whose peak potential values (E_P) are summarized in Table 1, were observed (peak C$_{-4}$, which commenced at ca. –0.2 V in the negative sweep, over-lapped with the hydrogen gas evolution response). An interesting feature of the cathodic pretreatment was that it also resulted in a slight change in the conventional response for silver in base. Note the splitting of the monolayer oxide reduction peak in Fig. 3. The unusual feature C$_0$ (which is absent in Fig. 1) was discussed in some detail earlier [1]; its appearance was attributed to
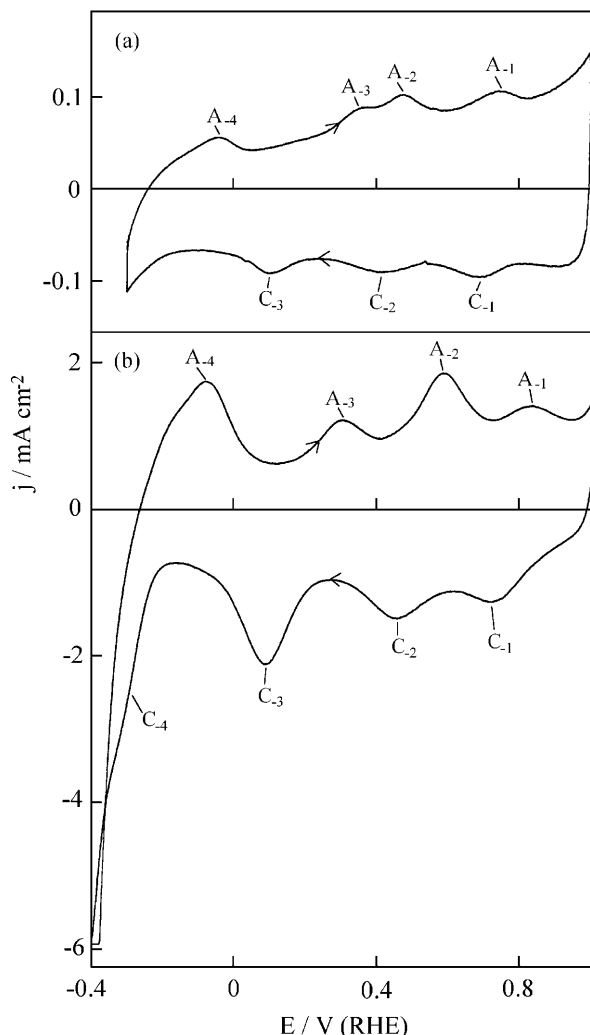
Fig. 2 Cyclic voltammograms for a silver wire electrode in 0.5 mol dm^{-3} NaOH at 25 °C: **a** no pretreatment (–0.3→1.0 V at 100 mV s^{-1}); **b** following cathodic polarization at –0.7 V for 3 h in the same solution (–0.4→1.0 V at 100 mV s^{-1})

Fig. 3 Cyclic voltammogram (–0.35→1.8 V at 10 mV s^{-1}) for a silver wire electrode in 0.5 mol dm^{-3} NaOH at 25 °C following cathodic polarization at –0.7 V for 2 h in the same solution

attributed to hydrogen embrittlement of the electrode surface during the course of cathodic pretreatment.

According to the IHOAM model of electrocatalysis [5, 6], the four low-level redox transitions outlined in Fig. 2b reflect the presence of four different types of active state (or mediator) responses for silver surfaces in base. Such behaviour is not unusual; four active-state responses have been postulated earlier for both platinum [21] and gold [18] surfaces in aqueous media. Very little definite information is known about these reaction mediators, but it is assumed [8, 9] that active metal atom (Ag*)/incipient hydrous oxide, $Ag_{ads}^{+}(H_2O)_n$, transitions are involved.

Correlating active-state responses with electrocatalytic behaviour, in terms of peak potential values and onset/termination potentials [6], is slightly complicated in the case of silver by the lack of sharpness of the peaks (Fig. 2b) and the hysteresis associated with these transitions. Another possible complication to be borne in mind is that dissolved reactants may affect the interfacial behaviour of transition metal ion species; this is the basis

the presence of a disrupted silver surface. The disruption in the earlier work [1] was due to reduction of multilayer hydrous oxide films, whereas in the present case it is
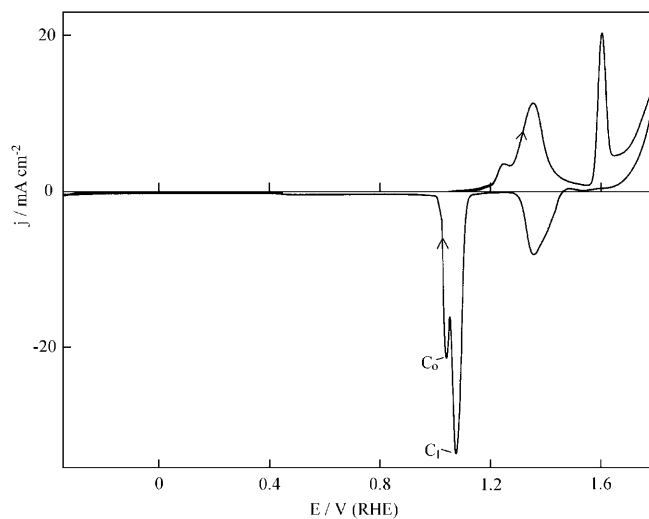
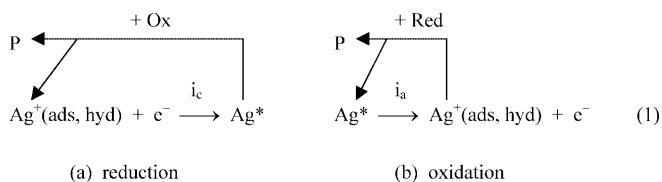| Table 1 Active-state transition potential values: peak maximum (E_P) data are taken from Fig. 2; the first set in each case, labelled (a), is from Fig. 2a, while the second, labelled (b), is from Fig. 2b. The substances listed beside each set of values are those that (as discussed in the text) show an onset/termination potential, or significant change in rate, close to the listed potential values	Active-state transition	E_P values for the anodic/cathodic responses in Fig. 2	Reactants[a] whose reduction (R) or oxidation (O) commences/terminates close to the specified E_P values
	A_{-1}/C_{-1}	(a) 0.75 V/0.70 V (b) 0.83 V/0.72 V	O_2 (R), H_2O_2 (R), $S_2O_8^{2-}$ (R)
	A_{-2}/C_{-2}	(a) 0.47 V/0.40 V (b) 0.58 V/0.44 V	N_2H_4 (O), CH_3CHO (O), $2-NO_2(C_6H_4)CHO$ (R), $4-NO_2 (C_6H_4)CHO$ (R)
	A_{-3}/C_{-3}	(a) 0.35 V/0.10 V (b) 0.29 V/0.08 V	$CHO-COO^-$ (O), HCHO (O), PhCHO (O), NO_3^- (R), N_2O (R)
	A_{-4}/C_{-4}	(a) –0.05 V/– (b) –0.09 V/–0.34 V	$CHO-COO^-$ (R), CH_3CHO (R), PhCHO (R), NO_3^- (R), $2-NO_2(C_6H_4)CHO$ (R), $4-NO_2(C_6H_4)CHO$ (R), CH_3NO_2 (R)

[a]Nitrobenzene and 3-nitrobenzoic acid are not listed here, as it was not clear in these cases whether an A_{-2}/C_{-2} or an A_{-3}/C_{-3} mediator system was involved

of operation of levellers and brighteners in metal electrodeposition reactions [22] (which also involve an $M^{z+}(H_2O)_n \rightarrow M$ transition).

Electrocatalytic behaviour of silver in base

The type of reactions of interest here are those that occur within the double-layer region and are mediated in the following manner [5] by low-coverage active-site species, viz.:

$$
\begin{array}{cc}
\xrightarrow{+Ox} & \xrightarrow{+Red} \\
P \xleftarrow{\quad} & P \xleftarrow{\quad} \\
& \\
Ag^+(ads, hyd) + e^- \xrightarrow{i_c} Ag^* & Ag^* \xrightarrow{i_a} Ag^+(ads, hyd) + e^- \quad (1) \\
\text{(a) reduction} & \text{(b) oxidation}
\end{array}
$$

In these schemes, Ox and Red represent dissolved oxidants and reductants, respectively, and P denotes reaction products. The basic objective is to assign (on the basis of reaction onset/termination potentials, as outlined earlier for gold [5]) which of the mediating couples, whose responses give rise to peaks A_{-1}/C_{-1} to A_{-4}/C_{-4} (Fig. 2b), is involved in each of the electrocatalytic processes.

Oxygen, hydrogen peroxide, persulfate and monoperoxyphthalate

A typical response for oxygen gas reduction on silver in base is shown in Fig. 4a. The rate of reaction was virtually constant at potentials below ca. 0.70 V. The region of dramatic change in rate (decrease in the positive sweep, increase in the negative sweep) was just above 0.8 V, i.e. in the region of peaks A_{-1}/C_{-1} of the cyclic voltammogram shown in Fig. 2b. Similar behaviour was observed with hydrogen peroxide (Fig. 4b). A further example of an oxidant whose reduction appears to be mediated by the couple involved in the A_{-1}/C_{-1} transition is persulfate (Fig. 5a). The potential for dramatic change ($i = 0.5i_L$, i_L being the limiting current value) in this case being at ca. 0.75 V for the positive sweep and ca. 0.85 V for the negative sweep; however, in this case, inhibition commenced in the positive sweep at ca. 0.5 V.

In the case of the monoperoxyphthalate (MPPA) anion, reduction continued at an approximately constant rate (Fig. 5b) over the range –0.30 to 1.10 V. Evidently even mildly active silver atoms seem to be capable of catalysing the reaction in this case. Reduction of the peroxy compound ceased at the onset of the monolayer oxide formation region (or peak A_1' in Fig. 1), even though the monolayer oxide coverage of the silver surface at this stage is extremely small. It may be of significance in this case that the potential for major inhibition, ca. 1.15 V (Fig. 5b), is positive with respect to the onset of peak C_1 (Fig. 1), i.e. severe inhibition

coincides in this case with the onset potential of the monolayer oxide film; the latter (as shown by the hysteresis behaviour in Fig. 1) is not readily reduced.

Hydrazine

A typical response for hydrazine oxidation is shown in Fig. 6. The reaction commenced and terminated in this case at ca. 0.5 V, the region of rapid change being at ca. 0.65 V, i.e. the mediating couple involved seemed to be that giving rise to the A_{-2}/C_{-2} response in Fig. 2b. A surprising feature here is that the monolayer oxide formation/reduction reaction (the responses for which are clearly evident in this case above 1.0 V) had virtually no effect on the rate of hydrazine oxidation. This result supports Taylor's assumption [4] that only a very low percentage of surface metal atoms, i.e. those present at active sites, are involved in surface catalysis. The data shown in Fig. 6 indicate that the electrocatalytic reaction at low-coverage active-site atoms proceeds in a manner that is independent of the state of the vast majority of the remaining surface metal atoms; the latter in this case may be in the reduced or oxidized form, i.e. their state is essentially irrelevant with regard to the electrocatalytic oxidation of hydrazine.
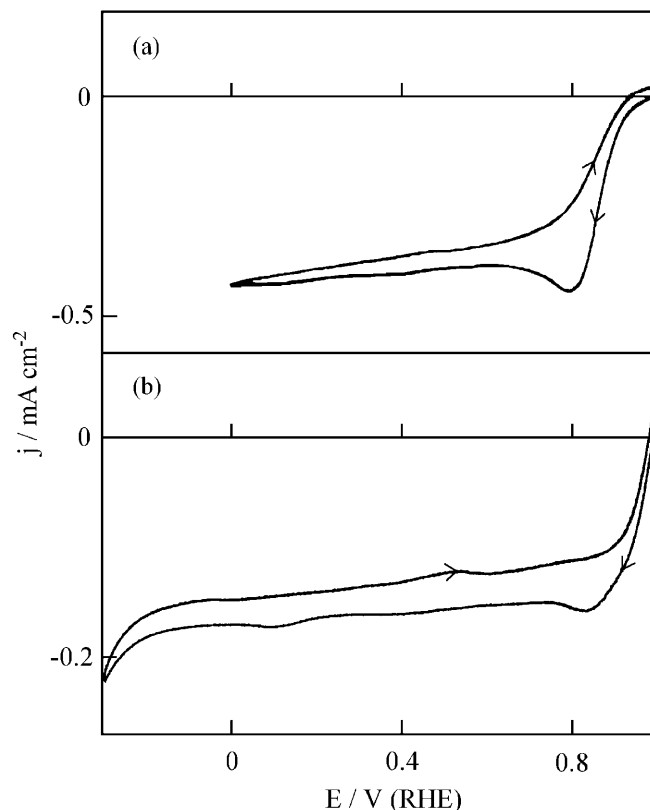

Fig. 4 Cyclic voltammograms for a silver wire electrode in 0.5 mol dm^{-3} NaOH at 25 °C: **a** 0.0→1.0 V, 10 mV s^{-1}, solution saturated with oxygen gas (p = 1.0 atm) and **b** –0.3→1.0 V, 10 mV s^{-1}, 0.01 mol dm^{-3} hydrogen peroxide present in solution
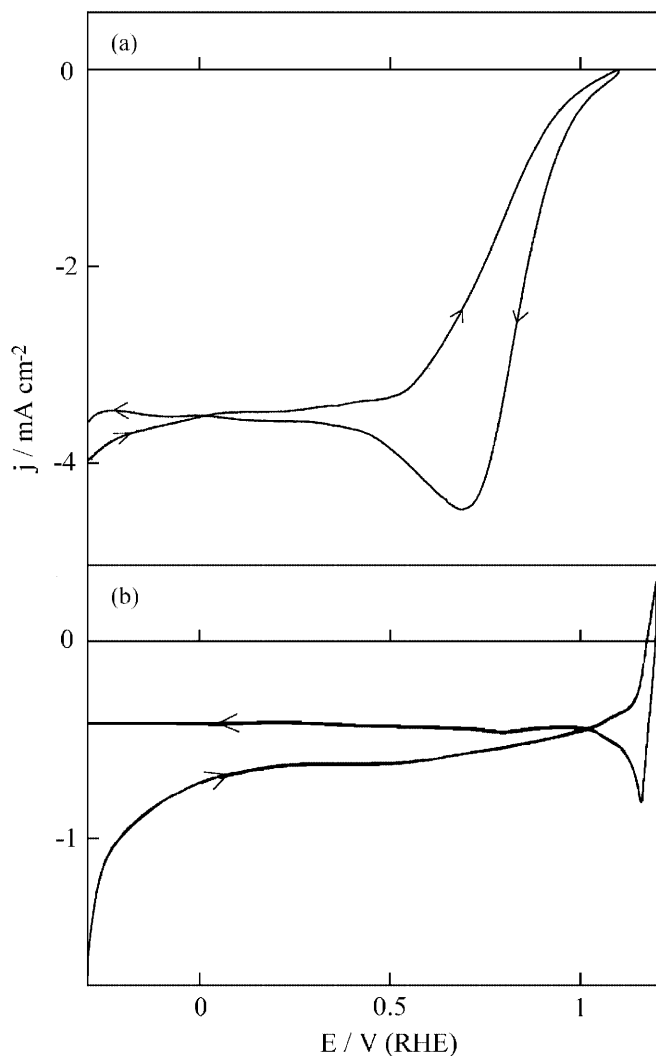
Fig. 5 Cyclic voltammograms for a silver wire electrode in 0.5 mol dm^{-3} NaOH at 25 °C containing (**a**) 0.045 mol dm^{-3} potassium persulfate ($-0.3{\to}1.1$ V at 10 mV s^{-1}) and (**b**) 0.01 mol dm^{-3} monoperoxyphthalate ($-0.3{\to}1.2$ V at 10 mV s^{-1})

Aldehydes

Responses for glyoxylate anions (an aldehyde which may undergo both oxidation, to an acid, and reduction, to an alcohol [6]) at silver in base are shown in Fig. 7. At the conventional silver surface, oxidation commenced in the positive sweep at ca. 0.14 V (Fig. 7a), but the major increase in anodic current occurred at ca. 0.3 V, i.e. in the region of peak A$_{-3}$ in Fig. 2b. At more positive potentials (above 0.4 V) the current reached a plateau value; however, there was a slight increase in rate at ca. 0.74 V, i.e. in the region of peak A$_{-1}$ in Fig. 2b. Although it is not shown here, the aldehyde oxidation response (as in the case of hydrazine, Fig. 6) was independent of the monolayer oxide formation/removal reaction. Subjecting the electrode to precathodization, prior to adding the glyoxylate (Fig. 7b), resulted in a lowering of the potential value for both the onset of oxidation (to ca. 0.08 V) and the region of rapid increase
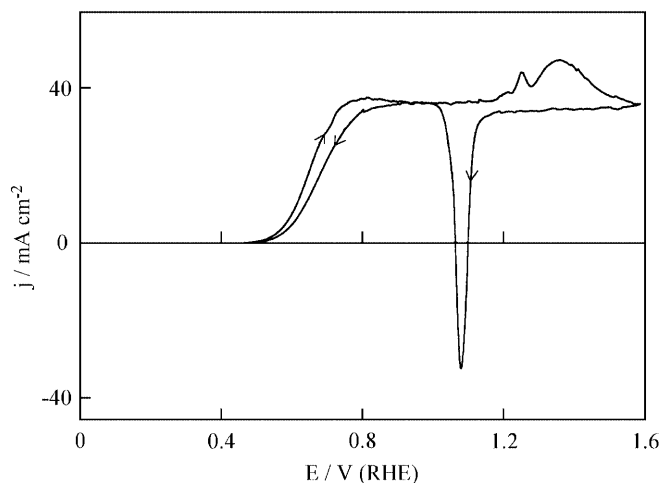

Fig. 6 Cyclic voltammogram ($0.0{\to}1.6$ V at 10 mV s^{-1}) for a silver wire electrode in 0.5 mol dm^{-3} NaOH + 0.05 mol dm^{-3} hydrazine at 25 °C
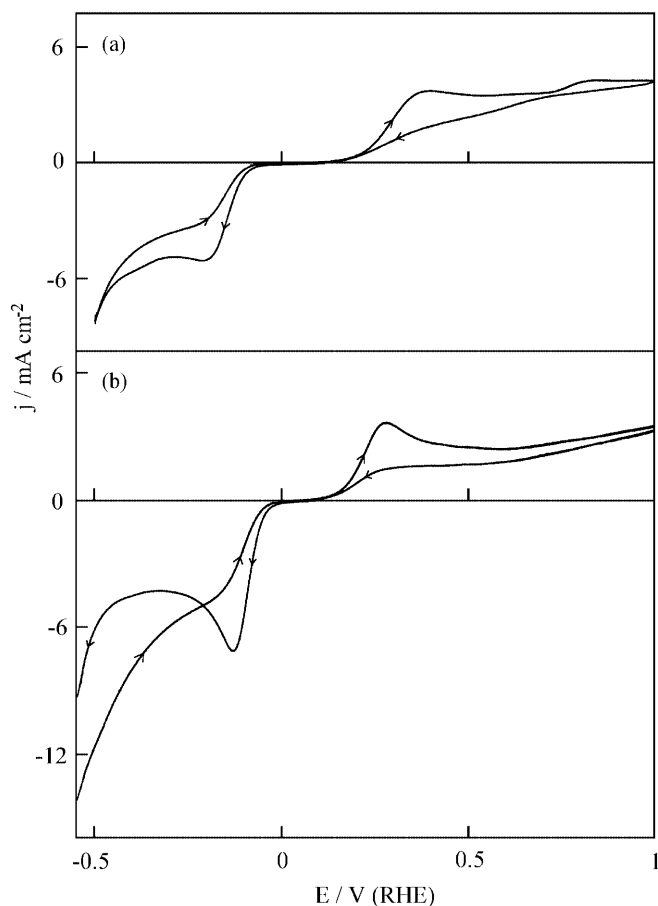

Fig. 7 Cyclic voltammograms ($-0.55{\to}1.0$ V at 50 mV s^{-1}) in 0.5 mol dm^{-3} NaOH + 0.05 mol dm^{-3} glyoxylate at 25 °C at (**a**) a fresh silver electrode and (**b**) a silver electrode which had been cathodically prepolarized at -0.7 V for 2 h

in anodic current (to ca. 0.2 V). This result again supports the assumption that the mediator involved in aldehyde oxidation on silver in base is that involved in the A$_{-3}$, rather than A$_{-2}$, transition (Fig. 2b).

The reduction of glyoxylate on silver in base occurred in the region below ca. –0.1 V, the slight maximum (Fig. 7a) in this region being at ca. –0.2 V. The corresponding values for the precathodized electrode (Fig. 7b) were slightly less negative, at ca. –0.05 and –0.15 V, respectively.

Typical responses for other aldehydes on silver in base are shown in Fig. 8. In the case of formaldehyde (Fig. 8a), there was very little cathodic response (apart from a very minor feature below ca. –0.3 V). Oxidation commenced and terminated at ca. 0.2 V, but the region of rapid change occurred at 0.4 V; complications, possibly associated with the release of hydrogen gas bubbles in this reaction [23], were observed at $E > 0.5$ V.

The oxidation of acetaldehyde on silver in base (Fig. 8b) was rather sluggish. This is evident from the low anodic current response and the rather high potential, ca. 0.5 V, required for the rapid increase in rate
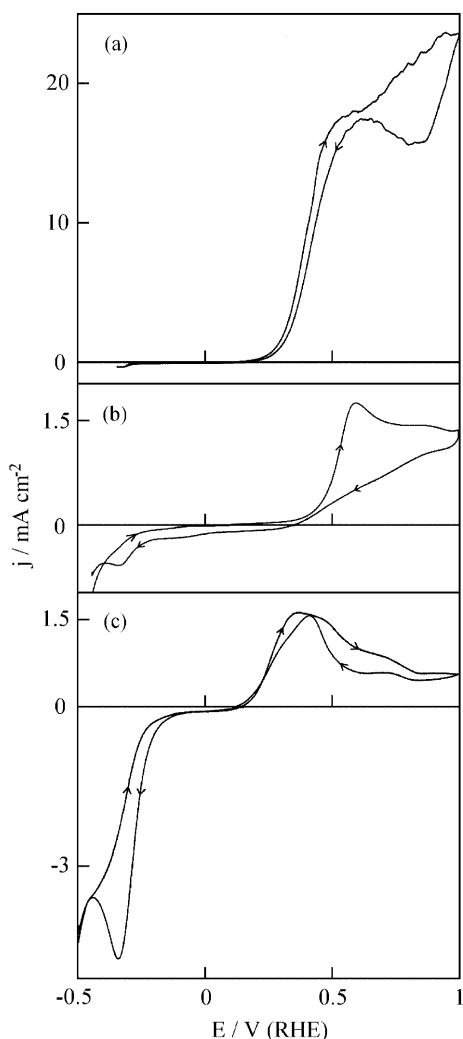
(positive sweep). Some reduction occurred at low potentials in the negative sweep, but the extent of the increase in rate, below ca. –0.2 V, was also not dramatic. It is well known [24] that the behaviour of aldehydes in base is complicated by the Cannizzaro and aldol condensation reactions; these processes may be quite marked with acetaldehyde and thus account for the sluggish behaviour of this compound at silver in base.

The response for benzaldehyde on silver in base is shown in Fig. 8c. Since this compound is not very soluble in aqueous media, the solvent used in this case contained 20% (by volume) of water in ethanol. Oxidation commenced and terminated at ca. 0.15 V, the region of rapid change in the rate being ca. 0.25 V. A complication in the case of benzaldehyde is that the rate of the oxidation reaction decreased rather steeply with increasing potential, especially above 0.5 V (positive sweep). Note that there is a further decrease in rate at ca. 0.75 V and that these decreases tend to be reversed at approximately the same values in the subsequent negative sweep. In this case a relatively high level of activity for benzaldehyde reduction was observed in the region below ca. –0.25 V.

Nitrate

The reduction behaviour of nitrate ion on silver in base (Fig. 9) was found to be highly dependent on the state (or level of activity) of metal atoms at the interface. With a conventional silver surface the reaction commenced and terminated at ca. 0.3 V, but the most dramatic change in reduction response occurred at ca. –0.2 V (Fig. 9a). However, when the surface of the same electrode was activated, by formation and reduction of an anodic oxide film, a sharp change in cathodic current was observed just below 0.3 V (Fig. 9b), and the rate of reaction remained at a limiting or plateau value from 0.0 V down to the onset of hydrogen gas evolution.

Activation of the surface by precathodization at –0.7 V resulted in a surface state of unusual character. On the negative sweep (Fig. 9c) there was a relatively sharp increase in reduction current just below 0.3 V, the limiting rate of reaction in this region being similar to those in (a) and (b) in this diagram. A significantly larger reduction current response commenced at ca. –0.2 V and the same type of behaviour is evident in the positive sweep. It is not clear in this case whether the double increase in reduction current corresponds to the same reaction at different types of surface sites (or mediators) or whether a change in the reaction route, e.g. a more extensive reduction of the NO_3^- ion in the case of the response at $E < –0.2$ V, is involved. As demonstrated in Fig. 10, the behaviour of the cathodically activated silver surface remained quite consistent; the magnitudes of the current responses were a linear function of the NO_3^- ion concentration, and the height of the plateau at ca. –0.45 V remained approximately four times that of the plateau at ca. –0.1 V.

Fig. 8 Cyclic voltammograms (–0.5→1.0 V at 50 mV s^{-1}) for a silver wire electrode in 0.5 mol dm^{-3} NaOH at 25 °C containing (**a**) 0.1 mol dm^{-3} formaldehyde, (**b**) 0.1 mol dm^{-3} acetaldehyde and (**c**) 0.04 mol dm^{-3} benzaldehyde (in the latter case the solvent used was a 4:1, v/v, water/ethanol mixture)

Fig. 10 Variation of the limiting cathodic current density values (taken at ca. –0.1 V, plateau 1, and at ca. –0.47 V, plateau 2) with nitrate concentration for a cathodically pretreated silver wire electrode; the activation and cyclic voltammetry conditions were identical to those outlined for Fig. 9c; the precathodization was not repeated between the different sweeps

Fig. 9 Cyclic voltammograms (–0.5→1.0 V at 10 mV s⁻¹, second sweeps) in 0.5 mol dm⁻³ NaOH + 0.05 mol dm⁻³ KNO₃ at 25 °C: (**a**) a fresh silver wire electrode, (**b**) the same electrode which was activated by formation and reduction of an anodic oxide film (polarized at 1.6 V for 5 min, followed by reduction, 1.0→ –0.5 V at 10 mV s⁻¹) and (**c**) a silver wire electrode which had been polarized at –0.7 V for 3.75 h (in the latter case the NO_3^- ion concentration was 0.07 mol dm⁻³)

Nitrous oxide

Reduction of nitrous oxide, $N_2O_{(g)}$ (Fig. 11a), on silver in base commenced in the negative sweep at ca. 0.5 V, but a rapid rate of reaction was only observed below ca. 0.3 V. The cathodic current rose to a plateau value just below 0.0 V and the responses for the positive and negative sweep virtually overlapped.

Organic nitro compounds

The response for nitrobenzene reduction on silver in base is shown in Fig. 11b. As with nitrous oxide, reduction commenced on the negative sweep at ca. 0.5 V, but the rate of increase in cathodic current with decreasing
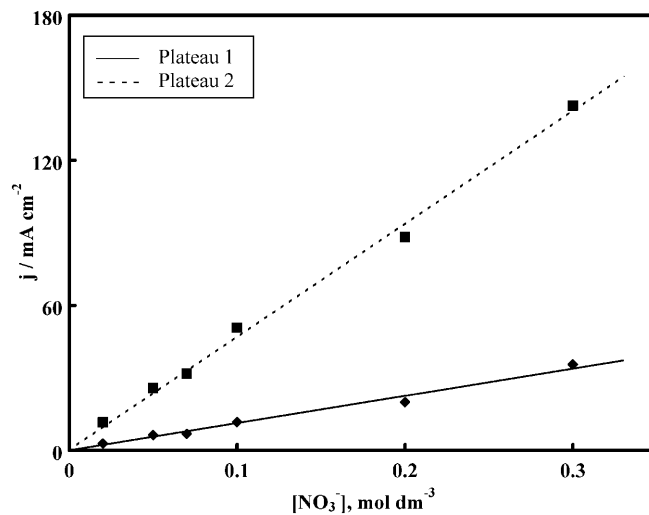
potential in this case was more dramatic. Several other nitro compounds, e.g. 3-nitrobenzoic acid (Fig. 12a), 2-nitrobenzaldehyde (Fig. 12b) and 4-nitrobenzaldehyde (Fig. 12c), exhibited this rapid change in reduction response (usually as the main feature in the cyclic voltammogram) at ca. 0.45 V. In at least one case, 4-nitrobenzaldehyde (Fig. 12c), there was a significant anodic response in the positive sweep at $E > 0.4$ V; however, this appeared to be of a transient character, e.g. it was totally absent in the negative sweep. In a number of cases, e.g. 2-nitrobenzaldehyde and 4-nitrobenzaldehyde, there were appreciable increases in the reduction rate at $E < 0.0$ V. This is typified by the steady-state response shown for 2-nitrobenzaldehyde reduction in Fig. 13a; note the second increase in reduction rate as E dropped below ca. –0.1 V. A rather extreme version of such behaviour was observed with nitromethane (Fig. 13b), where the increase in reduction current in the negative sweep at $E \approx 0.35$ V was much smaller than that at $E \approx$ –0.15 V. An interesting point here is that this increase in reduction rate at $E < 0.0$ V occurred in the absence of an aldehyde group; the absence of aldehyde, e.g. as an impurity in the nitromethane, is demonstrated by the lack of an oxidation response at any stage (but especially above 0.4 V) in the negative sweep.

Discussion

Premonolayer oxidation of silver in base

The conventional response for polycrystalline silver in base, shown here by the full line in Fig. 1, demonstrates how easy it is to miss, or overlook, premonolayer oxidation behaviour. However, following the recent (and
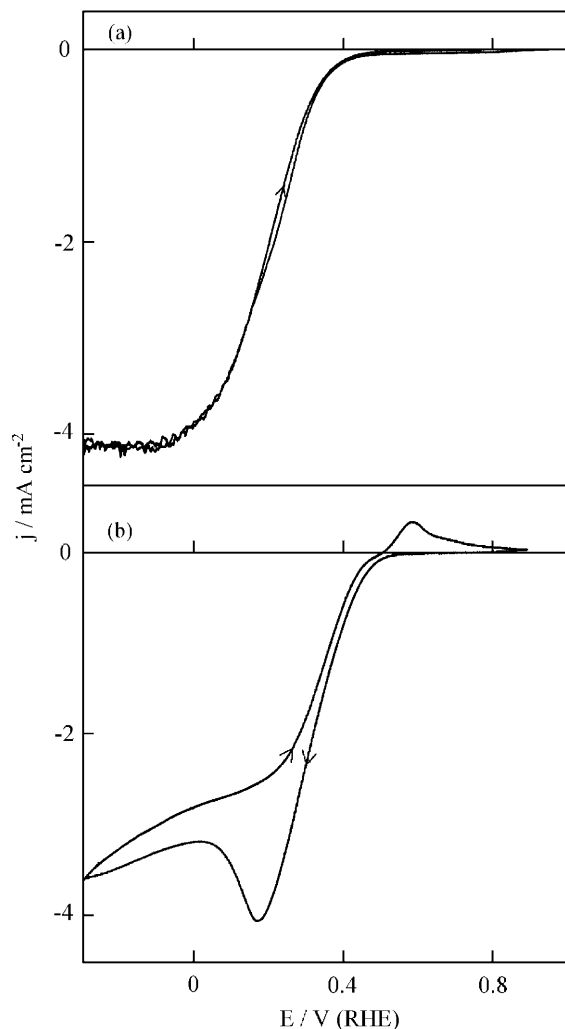
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Fig. 11 Cyclic voltammograms ($-0.3 \rightarrow 1.0$ V at 10 mV s^{-1}) for a silver wire electrode in 0.5 mol dm^{-3} NaOH at 25 °C: **a** solution saturated with N$_2$O gas ($p = 1.0$ atm); **b** nitrobenzene added (to a level of 0.01 mol dm^{-3}; solvent used was 4:1, v/v, ethanol/water mixture)

Fig. 12 Cyclic voltammograms ($-0.45 \rightarrow 1.0$ V at 10 mV s^{-1}) for a silver wire electrode in a solution (typically at 25 °C) containing (**a**) 0.003 mol dm^{-3} 3-nitrobenzoic acid in 0.5 mol dm^{-3} NaOH, (**b**) 0.015 mol dm^{-3} 2-nitrobenzaldehyde (the *dashed line* shows the response for 0.03 mol dm^{-3} 2-nitrobenzaldehyde at 40 °C) and (**c**) 0.007 mol dm^{-3} 4-nitrobenzaldehyde; both aldehydes were dissolved in a 4:1, v/v, ethanol/water base mixture

rather comprehensive) investigation of this electrode system by Doblhofer and co-workers [10, 11, 12, 13], there can be little doubt but that oxy species are generated at the interface at potentials that are well within the double layer region. According to the IHOAM approach to electrocatalysis [6], such behaviour occurs with all noble and semi-noble metals in aqueous media, and indeed such behaviour has just been reported independently by Strehblow and co-workers [25] for copper in base.

The premonolayer oxidation responses for silver in base can be seen more clearly by increasing both the sweep rate and recorder sensitivity (Fig. 2). It is evident that premonolayer oxidation is a complex process with four quasi-reversible, redox transitions involved. These peaks are rather broad and tend to overlap; however, their resolution was significantly improved by cathodic activation (Fig. 2b). However, these responses are present (Fig. 2a), even in the case
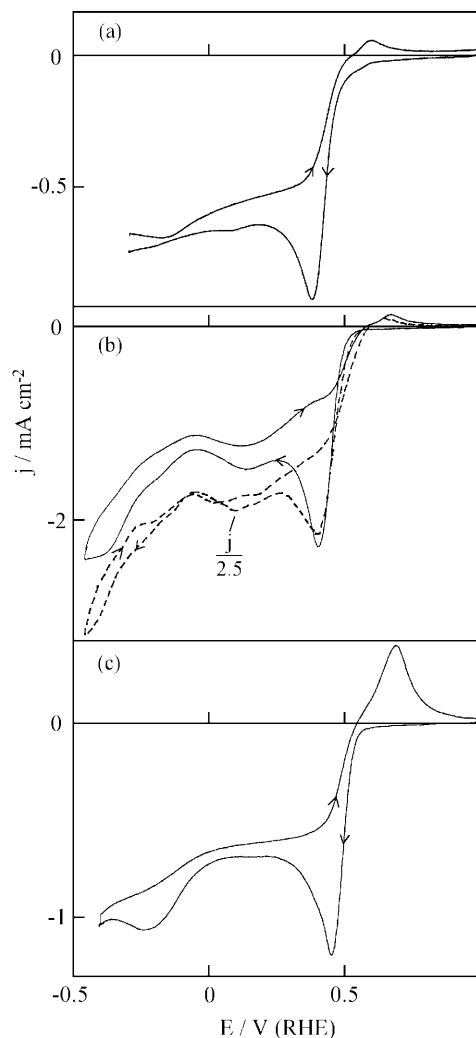
of the unactivated surface. There was an appreciable shift in some of the peak maximum values as a result of the cathodization. However, since active states are ill-defined, labile entities, such behaviour is not too surprising.

The presence of four low-level redox couples at the same interface is apparently not unusual. A similar number was suggested recently (on the basis of cyclic voltammetry data [21]) for Pt in aqueous acid solution; on the basis of impedance spectroscopy data for the same interface, Melnick and Palmore [26] also postulated the generation of a similar variety of oxy species at different potential values within the double layer region. Further work is obviously required at this stage to determine the precise nature, or the source of diversity, of these low-coverage interfacial couples and the factors affecting their transition potentials.
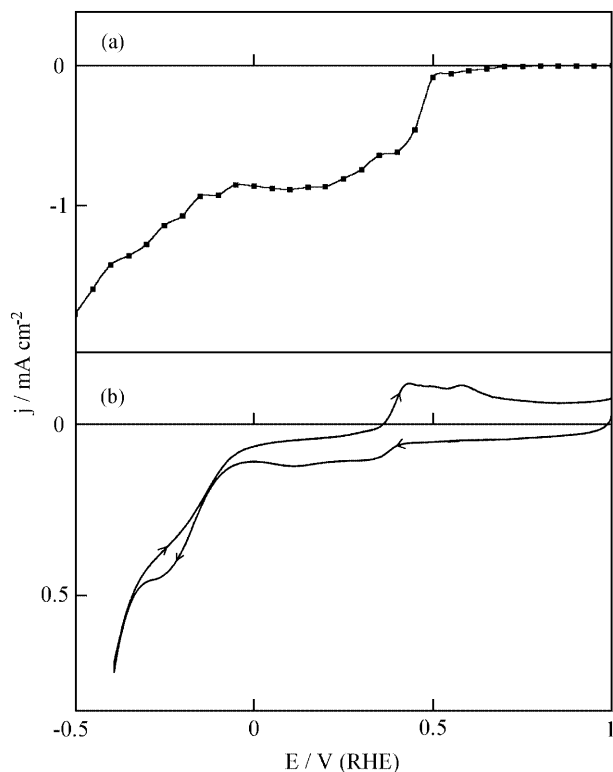
Fig. 13 a Steady-state response for 2-nitrobenzaldehyde (0.007 mol dm^{-3}) reduction at a silver electrode in 0.5 mol dm^{-3} NaOH in a 4:1, v/v, ethanol/water mixture at 25 °C; **b** cyclic voltammogram (–0.4→1.0 V at 50 mV s^{-1}) for a silver electrode in 0.5 mol dm^{-3} NaOH + 0.03 mol dm^{-3} nitromethane solution at 25 °C

Both Doblhofer and co-workers [10, 11, 12, 13] and Strehblow and co-workers [25] have discussed pre-monolayer oxidation behaviour largely in terms of radical adsorption, viz.:

$$M + OH^- \rightarrow M - OH_{ads} + e^- \qquad (2)$$
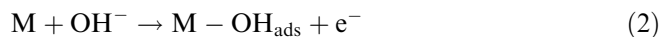
However, we consider that the process involved to be a metal hydroxide formation reaction; active metal atoms are far more likely than the OH$^-$ ions to lose electrons (the OH radical is an unusually electropositive species [27]). It appears that Doblhofer and co-workers do not discount this possibility as they attributed Raman spectroscopy bands [10] associated with premonolayer oxidation species to Ag-OH stretching and AgO-H bending vibrations.

Some of the cyclic voltammetry work by Doblhofer and co-workers is in reasonable agreement with the data shown here in Fig. 2. For example, in fig. 4 of [10], silver in 0.5 mol dm^{-3} NaOH showed three cathodic peaks in the negative sweep, at ca. –0.05, –0.55 and –0.80 V (Hg/HgO); these values correspond to ca. 0.88, 0.38 and 0.13 V (RHE) and are reasonably close to the values quoted here in Table 1 for C$_{-1}$, C$_{-2}$ and C$_{-3}$. Peak C$_{-4}$ was not observed in [10] as the negative sweep was terminated at –1.20 V (Hg/HgO), i.e. at ca. –0.27 V (RHE); according to Table 1 here, C$_{-4}$ is observed only at ca.

–0.34 V. Confirmation of the strong retention of surface OH, or AgOH, species at low potentials on silver in base is provided by the fact [10] that the loss (or quenching) of the associated Raman bands occurs (rather slowly) only at $E \approx -0.2$ V (RHE), i.e. well below the C$_{-3}$ region.

One of the major difficulties involved in dealing with the peak potential (E_P) data in Table 1 is that these values relate to active, non-equilibrium states; the redox responses may be regarded as quasi-reversible, i.e. the electrochemical steps are rapid but the species involved are thermodynamically unstable. It appears from the E_P data in Table 1 (see also Fig. 2b) that the degree of hysteresis for a given transition increases as the mean transition potential becomes more negative (or the metal atom state involved more active). Such behaviour probably reflects the greater tendency of the more active metal atoms to relax (after their generation in the negative sweep), resulting in a more marked peak separation (or hysteresis effect) in the case of sites of higher energy.

Correlation of mediator generation with electrocatalytic responses

One of the main objectives of the present work was to correlate active site (E_P) responses for silver in base with onset/termination potentials for various electrocatalytic processes that occur within the double layer region (such a correlation was demonstrated earlier with gold [5] and copper [6] electrodes). None of the electrocatalytic processes was investigated in detail as the main emphasis was on the surface-active state behaviour of the metal. It is quite clear here that the onset/termination potential, for the same basic electrode system (silver in base), varied significantly with the nature of the dissolved reactant, e.g. from ca. 0.95 V (for oxygen reduction, Fig. 4a), to ca. 0.5 V (for hydrazine oxidation, Fig. 6), ca. 0.25 V (for glyoxylate oxidation, Fig. 7) and ca. –0.1 V (for glyoxylate reduction, Fig. 7). Such diversity is attributed in terms of the IHOAM approach, to the participation of different active site mediators in the reaction of different solution species; in simple terms, the choice of mediator system is rather specific and is determined largely by the process undergoing catalysis. The last column in Table 1 represents an attempt to designate (on the basis of onset/termination potentials) which of the premonolayer couples (column 1) is involved as a mediator system for the various reactions surveyed here (Figs. 4, 5, 6, 7, 8, 9, 10, 11, 12, 13). These correlations are discussed individually later but they are somewhat complicated by (1) the width of the pre-monolayer peaks and (2) the absence in some cases of a sharp change in the electrocatalytic i/E response.

Most of the strong oxidants examined in this work (Figs. 4 and 5) underwent vigorous reduction at $E < 0.8$ V and yet, with the exception of MPPA (Fig. 5b), the rate of reaction was virtually zero at 1.0 V. Taking oxygen (Fig. 4a) as an example, the rate

of reduction in the positive sweep remained virtually constant up to ca. 0.8 V, at which stage the rate began to decrease, evidently due to the loss of the reduced form (Ag*) of the A_{-1}/C_{-1} mediator system. Note the presence of peak A_{-1} in this region in Fig. 2; the production of the reduced form of the interfacial couple (which, according to the scheme shown in Eq. 1a, is the vital mediator for O_2 reduction) becomes progressively more sluggish as the potential increases above 0.8 V; hence the rapid drop in O_2 reduction rate in this region.

It is interesting that there is no significant change in the rate of O_2 reduction at lower potentials, e.g. in the region of the A_{-2}/C_{-2} transition. Such mediator specificity has been noted with other metals, e.g. gold [5]; in electrocatalytic processes the interfacial couple operates in a dynamic (cyclic redox) mode and it is assumed that it is the interaction between the solution species and the surface couple that determines the choice of specific mediator for a given electrocatalytic process.

Among the strong oxidants, the behaviour of MPPA (Fig. 5b) is an interesting exception, as it exhibits no dramatic change in rate over the range 0.0–1.0 V. In fact the most marked change in rate in this case occurred just below 1.20 V, i.e. at the start of the monolayer oxide formation reaction. MPPA oxidation may be regarded as an electrocatalytically non-demanding reaction, i.e. its oxidation may be mediated by even mildly active silver atoms at the electrode surface. The sharp drop in rate at ca. 1.15 V in the positive sweep in Fig. 5b is somewhat surprising as the monolayer oxide coverage at this stage is minute, i.e. there are still many silver atoms exposed at the interface; evidently, even in this case, the mediating metal atoms must possess a significant amount of excess energy as compared with the high coordination surface silver atoms that undergo α-oxide formation.

The rapid decrease in peroxide reduction rate (Fig. 4b) commenced at ca. 0.9 V, i.e. at the upper end of the anodic (A_1) peak in Fig. 2b; reduction ceased in this case at $E \approx 0.98$ V, i.e. prior to the onset of α-oxide formation at ca. 1.14 V. The behaviour of persulfate (Fig. 5a) is somewhat complicated by the more gradual decay in reduction rate which extended (positive sweep) over the range 0.55 to ca. 0.95 V (slow reduction in this case was still evident even at 1.1 V). The corresponding increase in the subsequent negative sweep was sharper and the half-wave potential for this reduction response (in the negative sweep) was 0.87 V; hence it is assumed that in this case also the mediator system involved is A_{-1}/C_{-1}.

As a basis for deciding which mediator system was involved in electrocatalysis over the region 0.2–0.7 V (see Fig. 2), those reactions with an onset potential (or sharp increase in rate) above 0.4 V were assumed to be mediated by the A_{-2}/C_{-2} couple, whereas those showing similar behaviour below 0.4 V were assumed to be mediated by the A_{-3}/C_{-3} couple.

In the case of hydrazine oxidation (Fig. 6), the reaction commenced and terminated at 0.5 V and the most dramatic change in rate occurred over the range 0.6–0.7 V. This is attributed to the involvement of the A_{-2}/C_{-2} couple; the reaction involved is obviously catalytic as it depends on the nature of the metal (hydrazine oxidation on nickel in base commences in the positive sweep [28] at ca. 0.0 V). The lower onset potential of aldehyde, e.g. glyoxylate or formaldehyde, oxidation, compared with hydrazine oxidation, on copper [29] and gold [5] in base, has been noted in earlier publications from this laboratory. Aldehydes usually exist in base as anionic, *gem*-diolate species, $RCH(O^-)OH$ [5, 24] and hence their interaction with the oxidized form of the A_{-3}/C_{-3} mediator system, at ca. –0.3 V, is assumed to be assisted by electrostatic forces; the mediator in this region is assumed to be an adsorbed cationic species [8, 9], $Ag^+_{ads}(H_2O)_n$. Hydrazine exists in base as an uncharged species; there is no major electrostatic factor involved in its oxidation and hence it reacts at a more positive potential where a different, possibly more oxygenated ($AgOH^*_{ads}$), mediator may be involved. Taylor [4] has pointed out that protruding, surface metal atoms are capable of coordinating several reactant molecules, i.e. OH^- and N_2H_4 may bond to, and interact, at the same surface atom, or Ag^+_{ads}, site.

The oxidation response of benzaldehyde (Fig. 8c) is interesting. The reaction commenced in the positive sweep at ca. 0.15 V, with a major increase in rate (evidently due to mediation by the A_{-3}/C_{-3} couple) at ca. 0.25 V. However, the rate decreased again at more positive potential, firstly at ca. 0.5 V (in the region of the A_{-2}/C_{-2} couple) and secondly at ca. 0.75 V (in the region of the A_{-1}/C_{-1} couple); these decreases in rate of oxidation were reversed in the subsequent negative sweep. Such behaviour is not common; in many cases (as, for instance, hydrazine oxidation), only one mediator system seems to influence the electrocatalytic behaviour over the entire double layer region. The effect in the case of benzaldehyde may reflect significant loss of the positive charge of the Ag^+_{ads} mediator, i.e. conversion of much of the latter to an $AgOH^*_{ads}$ state at $E >$ ca. 0.5 V, with consequent loss of much of the electrostatically induced interaction effect, which is particularly effective at $E = 0.25$ V, between the *gem*-diolate and surface cationic sites.

Several species undergo reduction with an onset/termination potential below 0.0 V. The mediator system for such reactions is assumed to be the A_{-4}/C_{-4} couple. The behaviour of glyoxylate is interesting. On copper in base [6] this species undergoes oxidation and reduction above and below ca. –0.1 V, respectively, i.e. both reactions are mediated by the same interfacial (Cu^*/Cu^+_{ads}) couple. With silver (and gold) the behaviour is obviously different; as illustrated in Fig. 7, the oxidation and reduction responses commence and terminate at significantly different potentials, i.e. the mediating interfacial couples are not the same for these reactions at silver in base.

The reduction behaviour of nitrate, as summarized here in Figs. 9 and 10, is also interesting. In particular

the data in Fig. 9c provide evidence for the existence of two mediator systems, one at ca. 0.3 V and another at ca. –0.2 V; the obvious candidates for such behaviour are the A_{-3}/C_{-3} and A_{-4}/C_{-4} interfacial couples. Again, the participation of two mediators in nominally the same electrocatalytic process is unusual. It is assumed that since nitrate can undergo a variety of reduction reactions [30], the products of these two mediator-catalysed reactions are not the same, i.e. the two mediator systems in this case catalyse different reactions involving the same reactant. A further interesting factor in Fig. 9 is the extent to which the surface pretreatment influenced the nitrate reduction response.

In one respect the choice of solution reactant in some of this work may be questionable; for example, in the case of 2-nitrobenzaldehyde (Fig. 12b) there are two reducible functional groups present ($-NO_2$ and $-CHO$) and it is not obvious at this stage which undergoes reaction at a particular potential. With nitrobenzene (Fig. 11b) the reduction rate undergoes a major increase in the negative sweep just above 0.4 V. Similar behaviour (attributed to $-NO_2$ group reduction) is observed (Fig. 12b) with 2-nitrobenzaldehyde. However, in the latter case there is a further significant increase in reduction rate at $E < –0.1$ V which is typical of aldehyde behaviour. A very intriguing feature of the positive sweep in Fig. 12b is the decrease in reduction current just above 0.2 V; this is the range (Figs. 7b and 8c) where aldehydes undergo oxidation. Hence, it appears that there is a range of potential, from ca. 0.2 to at least 0.4 V, where aldehyde group oxidation (mediated by the A_{-3}/C_{-3} couple) overlaps with nitro group reduction (mediated by the A_{-2}/C_{-2} couple) in the same compound. Such unusual behaviour is currently being explored in greater detail. The use of a mixed (ethanol/water) solvent in the case of reactions involving water-insoluble aromatic reactants is assumed to have little effect on the mediator generation reactions, as in all cases there was still a very high percentage of water present in the reaction mixtures. It is interesting to note that the same trend, in the case of 2-nitrobenzaldehyde reduction, was observed under cyclic voltammetry (Fig. 12b) and steady state (Fig. 13a) conditions; such behaviour supports the conclusion that catalysis by interfacial mediators is not a transient phenomenon.

Conclusions

1. Premonolayer oxidation of silver in base [8, 9, 10, 11, 12, 13, 14, 15] now appears to be an accepted feature of the behaviour of this electrode system. The use of cyclic voltammetry as an investigative technique in this area was shown here to be particularly useful as it highlights the complexity of the premonolayer oxidation process, i.e. the involvement of four distinguishable redox, mediator generation, reactions within the double layer region.
2. With regard to the range of electrocatalytic processes surveyed here, the diversity of onset/termination potentials appears to be due to the involvement of different mediator generation or active site couples, the choice of the latter for the catalysis of a particular reaction being rather specific.
3. There is a need for further work devoted to understanding (1) the nature of these low coverage interfacial mediators, (2) the factors that distinguish one type of mediator from another (at the same surface) and (3) the detailed mechanisms of both the redox and electrocatalytic processes.
4. The active state of a metal surface is labile, the atoms involved being potentially mobile. In the course of a recent interview [31], one of the latest Nobel Prize winners, Barry Sharpless, pointed out that knowing the resting structure of a catalyst may not be particularly useful; a working catalyst (or at least its active site components) is not a very rigid system; motion of high-energy surface site species is implied here in Eq. 1.

References

1. Nagle LC, Ahern AJ, Burke LD (2001) J Solid State Electrochem DOI 10.1007/s100080100233
2. Bond GC, Thompson DT (2000) Gold Bull 33:41
3. Woods R (1976) Chemisorption at electrodes: hydrogen and oxygen on noble metals and their alloys. In: Bard AJ (ed) Electroanalytical chemistry, vol 9. Dekker, New York, pp 1–162
4. Taylor HS (1925) Proc R Soc Lond Ser A 108:105
5. Burke LD, Nugent PF (1998) Gold Bull 31:39
6. Burke LD, Collins JA, Murphy MA (1999) J Solid State Electrochem 4:34
7. Pourbaix M (1966) Atlas of electrochemical equilibria in aqueous solutions. Pergamon Press, Oxford, pp 393–398
8. Burke LD, O'Leary WA (1988) J Electrochem Soc 135:1965
9. Burke LD, Ryan TG (1990) J Appl Electrochem 20:1053
10. Savinova ER, Kraft P, Pettinger B, Doblhofer K (1997) J Electroanal Chem 430:47
11. Zemlyanov DY, Savinova E, Scheybal A, Doblhofer K, Schlögl R (1998) Surf Sci 418:441
12. Savinova ER, Zemlyanov D, Scheybal A, Schedel-Niedrig Th, Doblhofer K, Schlögl R (1999) Langmuir 15:6546
13. Savinova ER, Zemlyanov D, Pettinger B, Scheybal A, Schlögl R, Doblhofer K (2000) Electrochim Acta 46:175
14. Orozco G, Pérez MC, Rincón A, Gutiérrez C (1998) Langmuir 14:6297
15. Orozco G, Pérez MC, Rincón A, Gutiérrez C (2000) J Electroanal Chem 495:71
16. Cotton FA, Wilkinson G (1972) Advanced inorganic chemistry, 3rd edn. Wiley, New York, p 1048
17. Burke LD, Hurley LM (1999) Electrochim Acta 44:3451
18. Burke LD, Hurley LM, Lodge VE, Mooney MB (2001) J Solid State Electrochem 5:250
19. Burke LD, O'Mullane AP (2000) J Solid State Electrochem 4:285
20. Burke LD, Collins JA, Horgan MA, Hurley LM, O'Mullane AP (2000) Electrochim Acta 45:4127
21. Burke LD, Ahern AJ (2001) J Solid State Electrochem 5:553

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22. Oniciu L, Muresan L (1991) J Appl Electrochem 21:565
23. Beltowska-Brzezinska M (1985) Electrochim Acta 30:1193
24. McMurry (2000) Organic chemistry, 5th edn. Brooks/Cole, Pacific Grove, Calif
25. Strehblow H-H, Maurice V, Marcus P (2001) Electrochim Acta 46:3766
26. Melnick RE, Palmore GTR (2001) J Phys Chem B 105:1012
27. Burke LD, Nugent PF (1997) Gold Bull 30:43
28. Burke LD, Lee BH (1991) J Electrochem Soc 138:2496
29. Burke LD, O'Dwyer KJ (1991) Electrochim Acta 36:1937
30. Pourbaix M (1966) Atlas of electrochemical equilibria in aqueous solutions. Pergamon Press, Oxford, pp 493–503
31. O'Driscoll C (2001) Chem Br (11):26–29