ORIGINAL PAPER

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Some unusual features of the electrochemistry of silver in aqueous base

Abstract Multilayer oxide films were grown on silver in base by repetitive potential cycling; however, the type of oxide obtained, as assessed on the basis of its reduction behaviour, was dependent on the lower limit of the oxide growth cycles. Using limits of 1.03–2.60 V (RHE) the oxide film produced was assumed to be predominantly Ag_2O; reduction of the latter yielded a cathodic peak at ca. 0.8 V and a surface layer of silver microparticles of diameter ranging from ca. 100 to 227 nm which, although relatively stable, were prone to rapid, extensive reoxidation. Altering the oxide growth limits to 0.7–2.60 V resulted in the growth of a different type of oxide deposit which is assumed to be AgOH; reduction of the latter occurred in a negative sweep in a random manner, i.e. in the form of cathodic spikes extending to potentials as low as ca. –0.5 V. Both types of silver oxide species are assumed to be involved in premonolayer oxidation and electrocatalysis at silver in base and the nature of the former process is discussed in some detail.

Keywords Silver · Base · Oxide growth ·
Surface disruption · Premonolayer oxidation

Introduction

The catalytic properties of the Group 11 (Cu, Ag and Au) metal surfaces are interesting from both a fundamental and applied viewpoint. At the atomic level these three elements have the same outer ($d^{10} s^1$) electron configuration and in cyclic voltammetry studies their surfaces (in aqueous media) display virtually no adsorbed hydrogen response. While this suggests that their chemisorbing capability is quite weak, these three metals have very interesting catalytic properties, e.g. copper in

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the case of the water-gas shift reaction [1], silver in the dehydrogenation of methanol to formaldehyde [2] and oxide-supported gold microparticles [3] in the oxidation of CO at ambient, and even sub-ambient, temperatures.

In recent publications from this laboratory [4, 5] attention was drawn to the unusual properties of high energy, superactive, surface metal atoms, M^*; these may be regarded as adatoms, surface clusters or active site atoms. Due to their low lattice stabilisation energy such atoms are unusually electropositive; they evidently react by donating electrons to species undergoing adsorption under unusually mild conditions to yield surface dipolar species, e.g.

$$M^* + O_2 = M^{\delta+} - O_2^{\delta-} \left(+ M^* = 2M^{\delta+} - O^{\delta-} \right) \qquad (1)$$

Such a reaction provides a novel mode of highly localised chemisorption that is independent of d-band vacancies and may be used for instance to interpret the unexpectedly high catalytic activity of highly dispersed gold [3]. Two points are worth noting: (i) the high activity (from a thermodynamic viewpoint) of low coordination surface atoms was specifically discussed by Taylor [6] in his seminal active site paper (he quoted for instance abnormally high values for the adsorption energy of O_2 at low coordinated carbon atoms on charcoal) and (ii) the oxide support used in the work of Haruta and coworkers [3] seems to be of secondary importance as in the electrocatalysis area [7] high activity (in terms of catalysis and voltammetric behaviour) may be observed with gold in the absence of any oxide support (the role of the latter in the heterogeneous catalysis area may be to inhibit, in some manner that is not yet clear, the loss of the high energy surface state atoms, or agglomerates of same).

Various accounts of the active states of gold [7, 8, 9] and copper [4, 10], and their role in electrocatalysis, were published recently. The behaviour of silver is also interesting; this was the metal used in much of Henglein's work [11] on the properties of metal microclusters (he reported for instance that when a single silver atom is removed from the bulk lattice to

an aqueous phase its oxidation potential decreases by 2.6 V). Premonolayer oxidation of silver in base, which is now regarded as a manifestation of superactive surface state behaviour [4], was postulated by Burke and coworkers [12, 13] on the basis of voltammetric and electrocatalytic data. The basic assumption involved, namely that surface oxidation of the electrode commences at potentials that are well within the double layer region, was subsequently confirmed by Doblhofer and coworkers using a combination of cyclic voltammetry and SERS [14, 15]. Further extensive work by this group, involving the use of ex-situ techniques such as XPS [15, 16, 17, 18] and STM [19], led to a schematic representation or model of the premonolayer oxide-coated state of this electrode [18] (comments on this model are made here later). The anodic behaviour of silver in base has been extensively investigated also, using both electrochemical and spectroscopic techniques, by Strehblow and coworkers [20, 21, 22, 23] who confirmed [23] that there is considerable uptake of hydroxy species by the electrode surface in the double layer region of silver in base. Finally, it may be noted that silver was used in the original work that led to the discovery of Surface Enhanced Raman Spectroscopy [24]; the metal also has important applications as an industrial catalysis, e.g. in the oxidation of ethylene to ethylene oxide [25], and silver oxides are used in high energy storage, high discharge rate, battery systems [26, 27].

The present work with silver in base is divided into two sections; the first, which is presented here, is concerned with the anomalous behaviour of this electrode system (the type of approach involved is illustrated in earlier work with palladium [28], and various other metals [10]). The second section, dealing with the electrocatalytic properties of this electrode system, will be the subject of a later publication.

Experimental

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 mild abrasion with fine grade Emery paper followed by washing the surface with triply distilled water. The electrode was usually cycled (0.0→1.6 V at 10 mV s^{-1}) in the base electrolyte until the conventional cyclic voltammetric response for silver was observed.

The potential of the working electrode was recorded and is reported with respect to a reversible hydrogen electrode (RHE scale) [p(H$_2$) = 1.0 atm] in the same solution; the reference electrode was contained in a separate vessel which was connected to the working electrode compartment via a Luggin capillary. Solutions were made up using high-purity (Analar grade) chemicals and triply distilled water. The cell, including the reference electrode, was immersed in a water bath in which the temperature was controlled electronically. All solutions were purged with oxygen-free nitrogen before use. Cyclic voltammograms were obtained with the aid of a potentiostat (Wenking, model LT-78), a function generator (Metrohm, E612) and an X-Y recorder (Rikadenki, RW21). The resulting plots were subsequently transferred, with the aid of a scanner, to a computer and are reproduced directly here.

Results

Behaviour of silver in 1.0 mol dm^{-3} NaOH

A typical voltammogram for silver in 1.0 mol dm^{-3} NaOH is shown in Fig. 1. Monolayer oxide formation commenced in the positive sweep at ca. 1.2 V. There appeared to be a number of overlapping features involved, an initial current increase (A$_1$) commencing at ca. 1.14 V, an anodic peak (A$_2$) at ca. 1.27 V and a second anodic peak (A$_3$) at ca. 1.35 V (these peaks were quite broad and ill-defined). Oxygen gas evolution usually commenced in this system at ca. 1.9 V (this response is not shown here). In many cases a further anodic peak (A$_4$) appeared at ca. 1.6 V; this appeared in Fig. 1 just after the start of the negative sweep. Two cathodic peaks were observed in the subsequent negative sweep: C$_2$ at ca. 1.38 V is assumed to be the cathodic counterpart of A$_4$ (C$_2$ only appeared in the negative sweep when the upper limit of the cycle was sufficiently positive so that A$_4$ was observed at ca. 1.6 V). The second cathodic peak, C$_1$ (peak maximum at ca. 1.07 V), seemed to be the cathodic counterpart of the three features A$_1$, A$_2$ and A$_3$. It is assumed here that peaks C$_2$ and C$_1$ correspond to Ag(II)/Ag(I) and Ag(I)/Ag(0) transitions, respectively, and, as is usually observed in electrochemical oxide film formation/reduction reactions, significant hysteresis is involved. Considerably different cyclic voltammograms were recorded for silver electrodes whose surfaces had been disrupted before recording these responses (the disruption procedure, multilayer oxide growth and subsequent reduction, is described in the next section). A typical example is shown in Fig. 2; unusually large currents were observed above 1.2 V in the positive sweep and below 1.0 V in the negative sweep. Also, oxidation was incomplete at the upper limit of the scan as the flow of anodic current continued on the negative sweep until a potential of 1.2 V was attained. Peak C$_2$, at ca. 1.35 V,
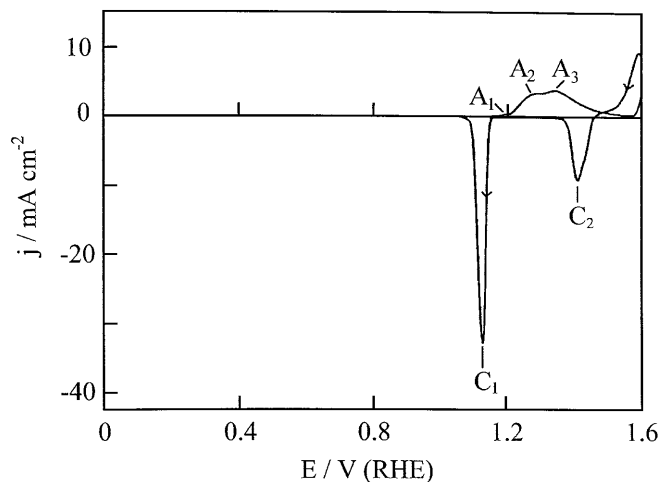

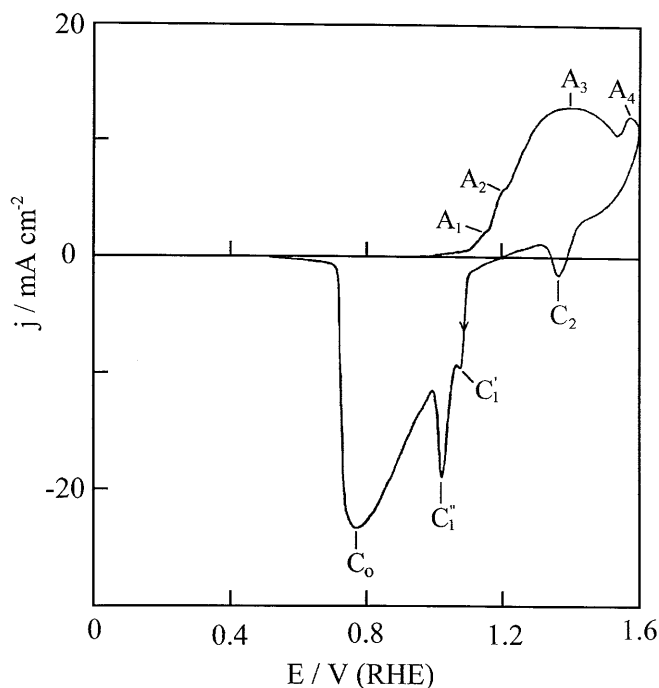**Fig. 1** Cyclic voltammogram (0.0→1.6 V at 10 mV s^{-1}) for a bright silver wire electrode in 1.0 mol dm^{-3} NaOH at 25 °C

Fig. 2 Cyclic voltammogram ($0.0 \rightarrow 1.6$ V at 10 mV s^{-1}) for a silver wire electrode in 1.0 mol dm^{-3} NaOH at 25 °C; the electrode surface in this case was extensively disrupted (it was subjected earlier to several multilayer hydrous oxide growth and reduction reactions)

Fig. 3 Cyclic voltammogram ($0.0 \rightarrow 1.6$ V at 10 mV s^{-1}) for a silver wire electrode in 1.0 mol dm^{-3} NaOH at 45 °C; the silver surface in this case was in a disrupted state (as in Fig. 2)

was quite small (as was peak A_4 on the positive sweep), C_1 seemed to split into an overlapping doublet (C'_1 and C''_1), but the major cathodic feature was a new peak, C_o, with a maximum just below ca. 0.8 V.

Rather similar behaviour was observed, Fig. 3, on raising the temperature to 45 °C; peaks A_2 and A_4 were more distinct in this case and there was no splitting of the C_1 peak. Raising the upper limit of the sweep to 1.8 V resulted in a more complex response at 25 °C, Fig. 4: note the presence of about five anodic (positive sweep) and five cathodic (negative sweep) peaks in this case. It was established at an early stage that at 25 °C peak C_o appeared only when the upper limit of the sweep exceeded 1.2 V; hence it is assumed that peak C_o is due to the reduction of an oxide produced (at a disrupted silver surface) in the region of the enhanced A_3 peak.

Multilayer oxide growth and disruption of silver in base

The disruption of the outer layers of the silver lattice in base was carried out by first growing a multilayer oxide film by potential cycling and subsequently reducing this deposit to yield a surface deposit of active silver (a similar procedure was used recently [28] to activate palladium surfaces in acid solution). Since very little multilayer oxide growth was observed at a cell temperature of 25 °C and considerable loss of silver occurred
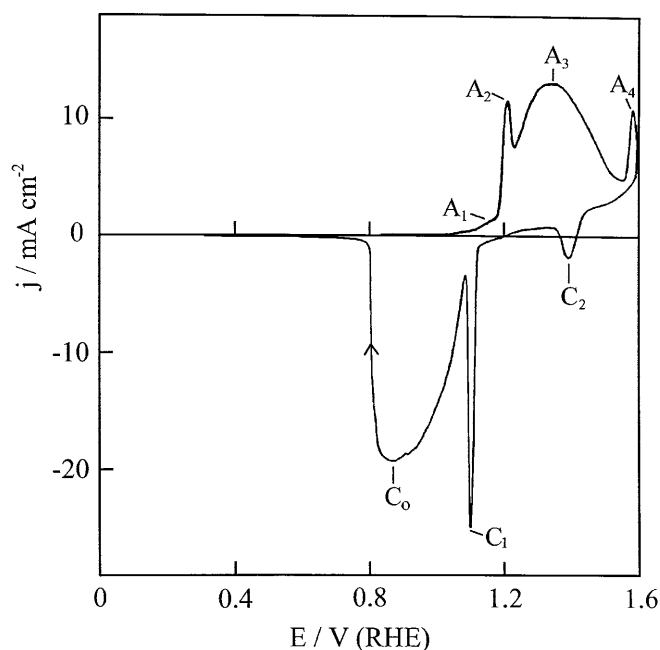

Fig. 4 Cyclic voltammogram ($0.0 \rightarrow 1.8$ V at 10 mV s^{-1}) for a silver wire electrode in 1.0 mol dm^{-3} NaOH at 25 °C; the silver surface was in a disrupted state (as in Fig. 2)

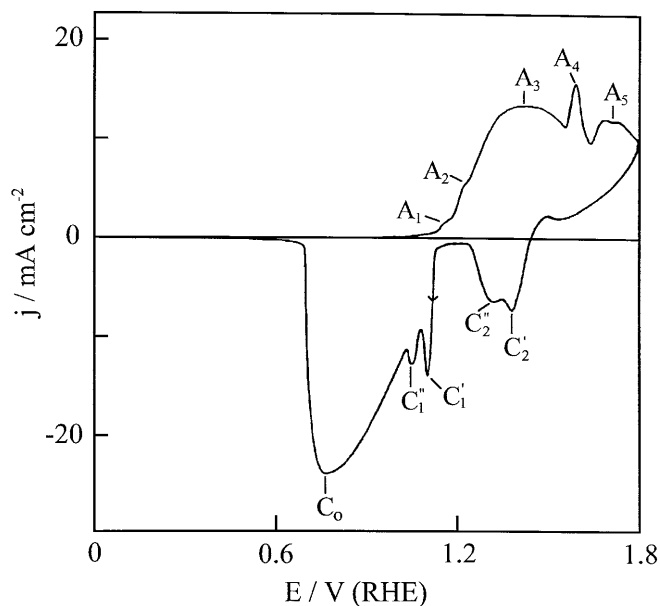on cycling at 65 °C, most of the silver activation work was carried out at 45 °C. Typical oxide growth conditions involved subjecting the electrode to 1600 cycles, at 0.5 V s^{-1}, between a lower limit of 0.7–1.1 V (Fig. 5) and an upper limit within the range 2.4–2.8 V (Fig. 6).

The effect of the lower limit of the oxide growth sweep on the subsequently recorded charges for both monolayer oxide (Q_M, peak C_1) and multilayer oxide
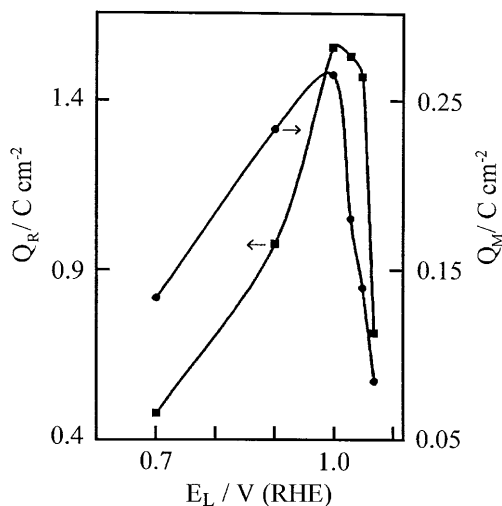
Fig. 5 Variation of charges associated with the monolayer oxide (Q_M; ●) and multilayer oxide (Q_R; ■) reduction peaks as a function of the lower potential limit (E_L) used in multilayer oxide growth (the latter involved potential cycling: $E_L \rightarrow 2.5$ V at 0.5 V s^{-1} for 2 h 30 min with silver in 1.0 mol dm^{-3} NaOH at 45 °C). The oxide reduction charges were measured from single reduction sweeps (2.0 $\rightarrow$ –0.6 V at 5 mV s^{-1}) in 1.0 mol dm^{-3} NaOH at 25 °C

Fig. 6 Variation of charges associated with monolayer oxide (Q_M; ◆) and multilayer oxide (Q_R; ■) reduction peaks as a function of the upper potential limit (E_u) used in multilayer oxide growth (1.03 V$\rightarrow E_u$ at 0.5 V s^{-1} for 2 h 30 min) on silver in 1.0 mol dm^{-3} NaOH at 45 °C. The oxide reduction charges were measured from single reduction sweeps (2.0 $\rightarrow$ –0.6 V at 5 mV s^{-1}) in 1.0 mol dm^{-3} NaOH at 25 °C

(Q_R, peak C_o) reduction is shown in Fig. 5. When the lower limit during oxide growth was raised above ca. 1.05 V the values of both Q_M and Q_R were small; evidently to enhance the growth of oxide (and extensively disrupt the surface on reducing the latter) the monolayer oxide deposit must be formed and reduced in a repetitive manner during the multicycling stage. The optimum lower limit with regard to maximising both the Q_M and Q_R values was ca. 1.0 V. It is assumed that with the latter value total reduction of the monolayer oxide but little reduction of the multilayer oxide occurs during each cycle at 0.5 V s^{-1}. The optimum value for Q_R at the E_L value of ca. 1.0 V in Fig. 5 may be due to the fact that Q_M is also at a maximum at this point. The multilayer oxide thickness, expressed by the ratio Q_R/Q_M, ranged from ca. 6.0 to 10.5 in the region of the maximum in Fig. 5. It may well be that this film thickness is not very dependent on E_L; the main reason for the maximum value for Q_R in Fig. 5 being at $E_L \approx 1.0$ V is that this is also the condition for maximum roughness (or Q_M value) for the silver surface.

The effect of the upper limit (E_u) used in potential cycling on the subsequent monolayer (Q_M) and multilayer (Q_R) charge values is illustrated in Fig. 6. Both values increased linearly, almost in parallel, over the E_u range 2.4–2.7 V; the mean value of the ratio Q_R/Q_M (which is assumed to be a measure of the multilayer oxide film thickness) for $E_u = 2.65$ V was 16.5. The steep drop in Q_R value for $E_u > 2.65$ V (Fig. 6) may well be due to the effect of the extremely vigorous oxygen gas evolution in this region; this is assumed to result in detachment of oxide particles and hence a reduction in the Q_R values at $E > 2.65$ V. It was established in preliminary experiments that very little multilayer oxide growth
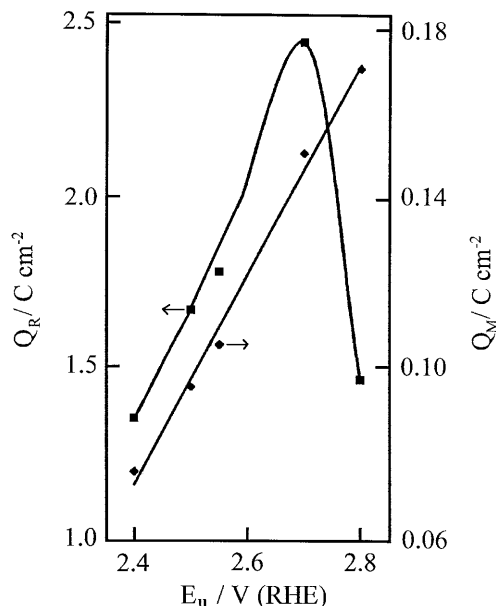
was observed with cycling sweep rates (v) < 0.3 V s^{-1} or > 6.0 V s^{-1}; the value used here, 0.5 V s^{-1}, appeared to be the optimum rate with regard to multilayer oxide growth.

Two quite unusual features of multilayer oxide growth behaviour were noted in the present work with silver in base, namely:

1. Usually when a multilayer hydrous oxide film is grown on a metal such as gold or platinum [29] the outer layers of metal formed on subsequent reduction of the oxide revert to a stable state (i.e. the thick film does not regrow on the next positive sweep), although there is usually significant roughening of the electrode surface. A minor exception was noted earlier in the case of palladium in acid [28] where a small percentage of the disrupted metal existed initially in a highly active (or superactive) state; the latter gave rise to a reversible redox transition at ca. 0.24 V, but the activity in question decayed reasonably quickly with time.
Silver behaved quite differently; once the surface layers were disrupted by multicycling and subsequent oxide reduction the disrupted zone retained its high level of activity with respect to enhanced oxidation and reduction almost indefinitely. The large peaks, A_3/C_o in Figs. 2, 3 and 4, showed little sign of decay on repeated scanning and the same type of unusual response was observed with a disrupted silver electrode after the latter had been allowed to rest for six weeks.

2. With silver in base there appeared to be a second type of Ag(I) oxide involved whose reduction behaviour below 0.8 V, i.e. after peak C_o, was most unusual. As shown in Fig. 7, the first negative sweep recorded after growing the multilayer oxide film exhibited a series of sharp cathodic current spikes which appeared in a random manner; sometimes these spikes overlapped to yield a peak but the latter rarely occurred in a regular, symmetrical manner or at a well-defined potential. In such negative sweeps there was very little indication of peak C_2 (at ca. 1.4 V, Fig. 1); this is the reason why only the more interesting region of the negative sweeps, 1.20 to –0.7 V, is shown here (note that the cathodic spikes, e.g. in Fig. 7, continued to occur even below –0.4 V). The cathodic current spikes in question here did not appear in a second negative sweep recorded after the initial multilayer oxide reduction sweep. This cathodic current spiking effect has also been observed in this laboratory, although less frequently, in similar experiments with copper in base, but not in similar experiments, using the same equipment, with platinum.

The cathodic spikes were invariably observed in the case of multilayer oxide film reduction sweeps with silver in base (sometimes these sweeps were carried out in the oxide growth solution at 45 °C; in other cases the electrode was transferred, prior to reduction, to a second cell containing fresh base at 25 °C; only a small selection of the current spike data is shown here). Usually the charge associated with peak C_o, i.e. the amount of disturbed metal present, increased over the first few activation experiments with a fresh wire electrode; however, after the third such experiment the response after activation was reasonably constant. Prolonged use of the same electrode
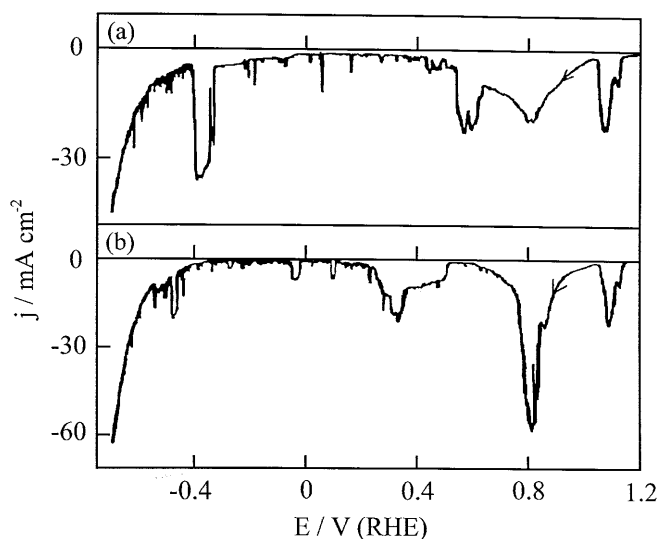
resulted in gradual loss of metal, evidently due to dissolution; eventually electrodes were discarded when the wire became rather thin.

Behaviour of silver in 5.0 mol dm^{-3} NaOH

The switch from 1.0 to 5.0 mol dm^{-3} NaOH was made following the observation that significantly thicker oxide deposits (or more extensive disruption of the outer layers of the metal lattice) could be produced more readily using the more concentrated base solution. However, the general appearance of the cyclic voltammetry responses, both for the bare unactivated metal and the activated metal (see Figs. 1 and 2 respectively) were virtually independent of the base concentration, within the limits for the latter involved here.

The most interesting feature of the work with silver in 5.0 mol dm^{-3} NaOH was the effect of the lower limit used in potential cycling, or multilayer oxide growth, pretreatment on the appearance of the cathodic peak C_o at ca. 0.8 V in the subsequent oxide reduction sweep. In the case of the reduction profiles shown in Fig. 8 the

Fig. 7a, b Reduction profiles (1.2→ –0.7 V at 5 mV s^{-1}) for multilayer oxide films on silver in 1.0 mol dm^{-3} NaOH at 25 °C; the films were grown by potential cycling at 0.5 V s^{-1} in 1.0 mol dm^{-3} NaOH at 45 °C for 2 h 30 min between the potential limits: **a** 1.0→2.6 V; **b** 1.03→2.6 V

Fig. 8a–c Reduction profiles (1.2→ –0.7 V at 5 mV s^{-1}) for multilayer oxide films on silver in 5.0 mol dm^{-3} NaOH at 25 °C; the films were grown by potential cycling (1.03→2.60 V at 0.5 V s^{-1}) in 5.0 mol dm^{-3} NaOH at 45 °C for: **a** 4 h; **b** 5 h 30 min; **c** 6 h 15 min

lower limit for oxide growth was 1.03 V. The major feature in each of the subsequent reduction sweeps was the peak at ca. 0.8 V, together with some random cathodic spikes at lower potentials. However, when the lower limit used in the oxide growth pretreatment was reduced to 0.70 V (Fig. 9) the cathodic peak at ca. 0.8 V was not observed. In such cases marked cathodic responses (in some cases, e.g. Fig. 9b, occurring in a very random manner) were noted in the region below 0.2 V. The response shown in Fig. 9c is quite unusual; the main cathodic feature was a sharp cathodic peak below –0.4 V. Some problems in this area were encountered initially due to the use of an insufficiently low oxide reduction sweep limit of –0.4 V (rather than –0.7 V); under such conditions total oxide reduction did not occur in the first negative sweep and further cathodic features appeared at low potentials on repeating the negative sweep.

SEM investigation of an activated silver surface

The changes in the nature of the silver surface as a result of multilayer oxide growth and subsequent reduction were investigated by recording SEM photographs (Fig. 10). While the original wire was relatively smooth, the oxide surface, after potential cycling, was quite dis-

rupted (Fig. 10a); discrete particles, and agglomerates of same, were clearly evident. On reduction of such a deposit in a negative sweep the surface was found to be

Fig. 10a–c SEMs of a silver wire electrode which was pretreated in the following manner: **a** $1.0 \rightarrow 2.65$ V at 1.0 V s^{-1} for 1500 cycles and then held at 2.0 V for 30 s; **b** reduced form of **a**, this electrode was subjected to two reduction sweeps $1.2 \rightarrow -0.4$ V at 5 mV s^{-1}; **c** reduced form of **a**, the electrode in this case had previously been subjected to several hydrous oxide growth and reduction experiments
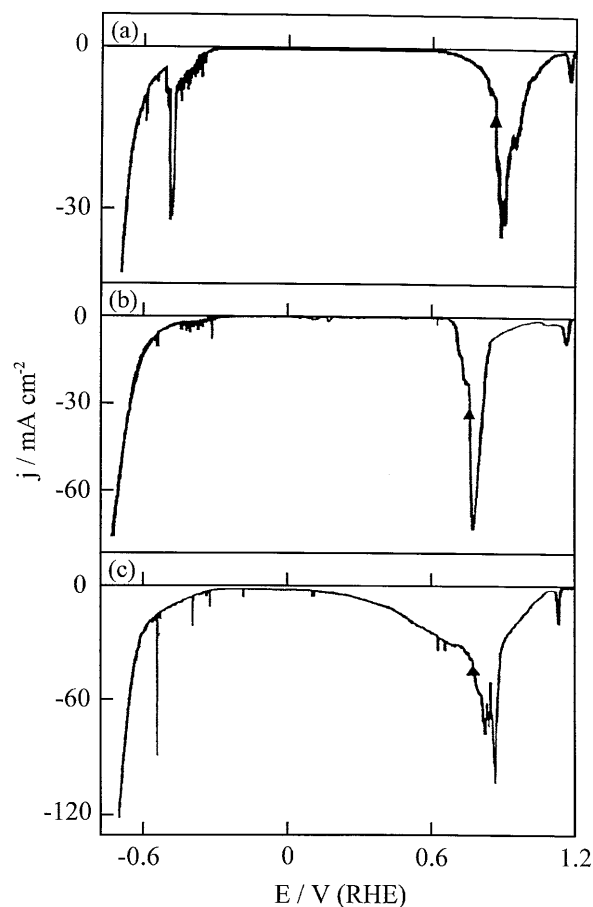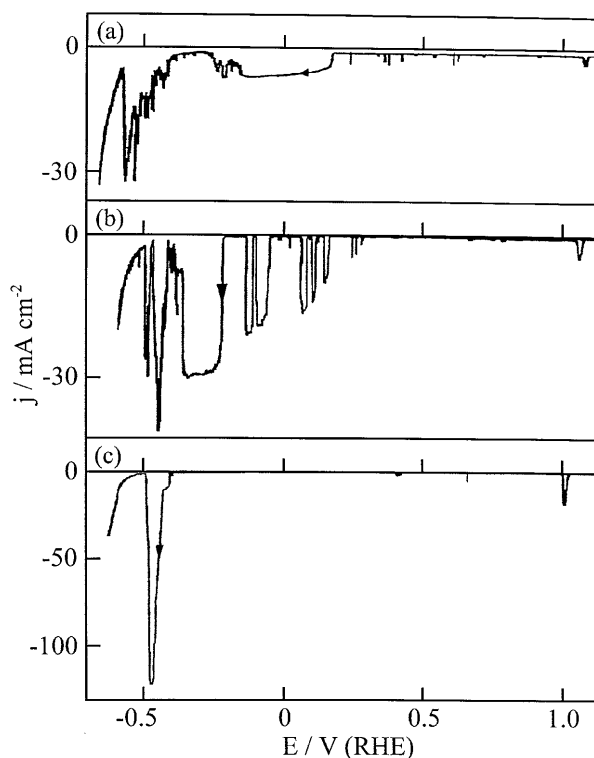

Fig. 9a–c Reduction profiles ($1.2 \rightarrow -0.7$ V at 5 mV s^{-1}) for multilayer oxide films on silver in 5.0 mol dm^{-3} NaOH at 25 °C; the films were grown by potential cycling (0.7$\rightarrow$2.60 V at 0.5 V s^{-1}) in 5.0 mol dm^{-3} NaOH at 45 °C for: **a** 2 h 10 min; **b** 2 h 30 min; **c** 2 h 45 min
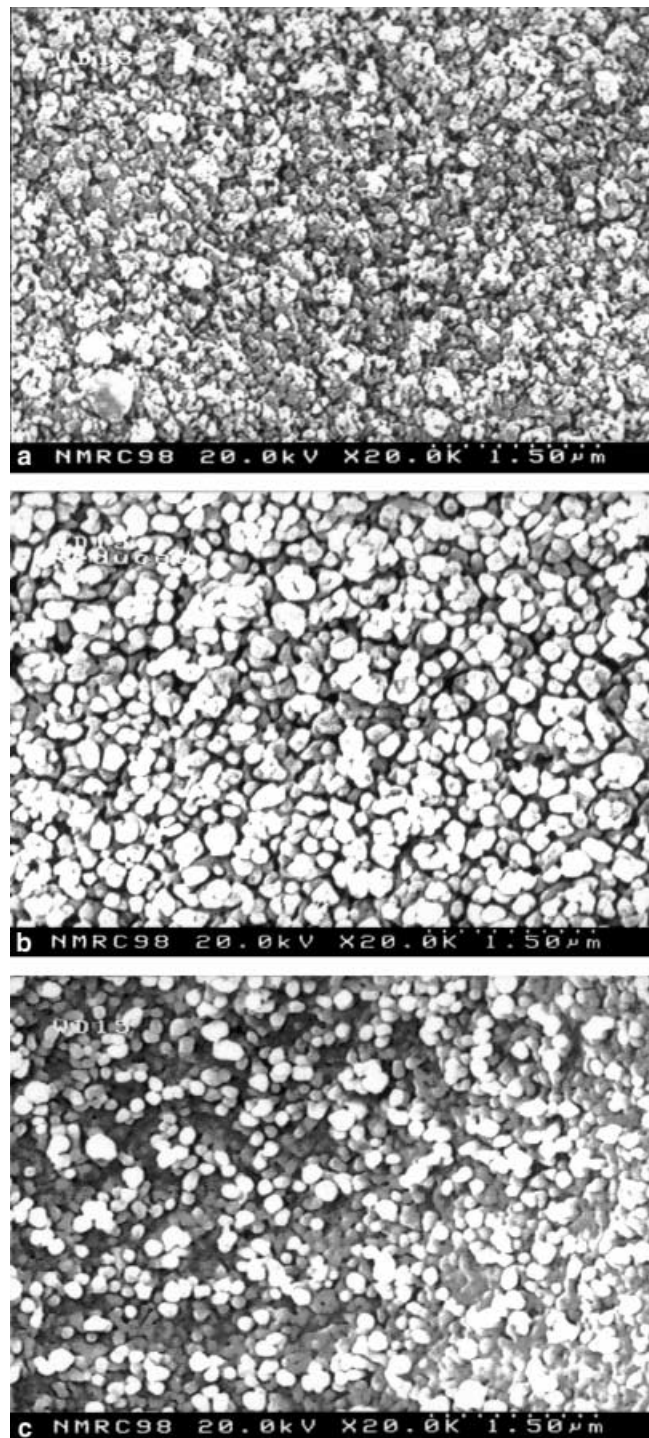
coated with a layer of silver particles (Fig. 10b). On repeating the multilayer oxide growth and reduction several times with the same electrode the layer of silver particles on the surface was still evident (Fig. 10c), but the mean particle size was considerably lower (mean diameter = 100 nm) than in the first case (mean diameter = 227 nm) (Fig. 10b). EDX analysis of these disrupted surface layers indicated the absence of any metallic contamination.

Discussion

Monolayer and premonolayer oxidation

The type of response shown in Fig. 1 for silver in base is not unusual; the first set of anodic peaks ($A_1 \rightarrow A_3$) are also evident in earlier work, e.g. by Kötz and Yeager [30], and the reaction involved may be regarded in general terms as monolayer oxide, or Ag_2O, formation (the same type of responses, apart from peak C_o, and peak notation as used here is evident in the earlier works of Droog and coworkers [31] and Arvia and coworkers [32]). The cathodic counterpart of this reaction is peak C_1. The increase in anodic current above 1.5 V (see peak A_4 in this region in the positive sweep in Fig. 2) is usually attributed to the conversion of some Ag_2O to AgO (this conversion may also be carried out photochemically [30]) and the reverse reaction gives rise to peak C_2 in the negative sweep. Stonehart [33] acknowledged the presence of three anodic peaks in the Ag(I) region but ignored the first as being a minor feature; the second (A_2) and third (A_3) peaks were attributed to formation of $AgOH$ and Ag_2O species, respectively. $AgOH$ formation was assumed to be confined to the silver surface while Ag_2O was claimed to be formed to a limited depth into the metal lattice.

Stonehart's viewpoint explains one feature of these Ag(I) anodic peaks, namely that the enhancement in charge observed after disrupting the outer layers of the electrode surface, Fig. 2, involved mainly the A_3 peak. Furthermore, in this case also (Fig. 2) there was a splitting (although the peak resolution was poor) of the subsequent cathodic Ag(I) oxide reduction peak. Usually only one sharp peak is observed for Ag(I) oxide reduction, e.g. peak C_1 in Fig. 1; however, an overlapping doublet (or a tailing of the C_1 peak) is evident in Fig. 1 of [30].

Chen and coworkers [34] also observed three anodic peaks in the Ag(I) region but their interpretation, based on ECQM data, is significantly different from that of Stonehart [33]. They attributed all three peaks $A_1 \rightarrow A_3$ in Fig. 1 to Ag_2O formation ($AgOH$ was viewed as a transient species); some dissolution was assumed to occur in the peak A_2 region prior to further formation of a porous form of Ag_2O. It is assumed here that in the peak A_2 region place-exchange commences and becomes quite significant (especially with disrupted silver surfaces, Fig. 2) within the peak A_3 region. Chen and coworkers

[34] reported an increase in surface roughness due to rapid oxide formation in the region of the A_3 peak while Stonehart [33] observed a large change in surface area of the silver after only a single potentiodynamic scan.

A factor that was widely ignored in early accounts of silver in base is premonolayer oxidation (the phenomenon in question has been referred to recently as "underpotential oxidation" [16, 35]). The surface coverage involved in such a reaction is obviously very small (which supports the view [4, 6] that it is restricted to surface active site metal atoms); the associated anomalous voltammetric responses, within the double layer region, are best observed [12, 35] using high current-recording sensitivity within the premonolayer oxide region. The recent extensive work by Doblhofer and coworkers [14, 15, 16, 17, 18, 19], which involved application of an extensive range of sophisticated analytical techniques, essentially confirms the reality of premonolayer oxidation behaviour, at least with regard to the silver/aqueous base interface. Further comments on the premonolayer oxidation reaction are given later.

Multilayer oxide growth and reduction

For most of the noble metals [29], and copper in base [36], multilayer oxide growth under potential cycling conditions is a relatively simple procedure which yields a duplex film, i.e. a thin layer of monolayer (α) oxide in contact with the metal surface and usually a much thicker hydrous (β) oxide deposit extending outwards towards the bulk solution. As demonstrated recently for copper in base [36] the reduction of the β oxide deposit often occurs, under potential sweep conditions, at a reasonably well-defined potential within the double layer region, the potential in question being of considerable relevance to electrocatalytic processes.

The behaviour of silver in base under potential cycling conditions is unusual for a number of reasons, namely:

1. In most cases reported here the main features that were enhanced following potential cycling and oxide reduction were the A_3 and C_o peaks (see Figs. 2, 3 and 4). The A_3 peak is observed in the basic monolayer oxide formation response (Fig. 1) for a conventional silver surface. Hence the enhancement of this response on disrupting the surface is attributed to the formation of an α, rather than a β, -type deposit, i.e. the oxygen enters, or is absorbed by, the outer regions of the silver lattice and the product is evidently an Ag_2O-type deposit. In the subsequent negative sweep, e.g. Fig. 3, the response for this absorbed oxygen reduction (peak C_o) occurred at a lower potential (although there is some overlap) than the α oxide reduction response (peak C_1). In our experience this major enhancement of the α oxide type response due to potential cycling is unique to silver in base.

2. Enhanced α oxide responses could be avoided by reducing the lower limit used in potential cycling to values below 0.8 V; note the absence of cathodic peak C_o in Fig. 9. Under such conditions a β oxide deposit was produced but its reduction behaviour was quite unusual; as shown for instance in Fig. 9b the reaction in question gave rise to a random series of spikes and ill-defined peaks; such behaviour is quite different to the single, sharp, cathodic peak observed in similar experiments with copper in base [36]. Attempts to grow β oxide deposits on silver in base that undergo reduction in a simple, consistent manner were not successful (despite attempts using a wide variety of sweep limits and sweep rates).

The reduction behaviour of hydrous oxide species at noble metal electrode surfaces is not always simple. For example in the case of gold in acid β oxide films grown by potential cycling [37] normally undergo reduction in a reasonably consistent manner, although there are complications with thicker deposits due to the presence of a number of slightly different components (HO1, HO2 and HO3) in the layer. However, when the same type of hydrous oxide materials are grown on gold following cathodic activation of the metal surface [8] the deposit involved was far more reluctant to undergo reduction (the same type of behaviour has been observed with thermally activated platinum [38]). The source of this unusual inhibition is not well understood but was attributed to poor contact between the β oxide material and the metal surface. The same type of inhibition may be involved in the case of silver in base. Hydrous oxide growth on silver under potential cycling conditions, with $E_u = 2.6$ V (Fig. 9), is likely to lead to some AgO and absorbed oxygen (or Ag_2O) formation at the metal surface. When such inner oxide species undergo reduction in the negative sweep there may well be partial loss of contact (due to volume changes associated with the oxide/metal transition) between the outer β oxide film and the electrode surface.

All hydrous oxide deposits tend to undergo reduction under non-reversible conditions; the effect has been attributed to the involvement, as the primary reduction product, of a low coordinated, active state of the metal [37]. Thermodynamic data [39] suggest that silver metal in base has no oxide that is stable below ca. 1.12 V (RHE), namely

$$Ag_2O + H_2O + 2e^- = 2Ag + 2OH^- \quad E = 1.173 \text{ V} \quad (2)$$
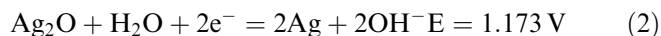
(this is in excellent agreement with the potential for the start of the α oxide formation reaction in Fig. 1). Reduction of silver β oxide deposits at much lower potentials, as in Fig. 9, is attributed here to two effects: (i) overpotential associated with the intervention, as the primary reduction product, of an active state of the metal and (ii) poor contact (giving rise to severe ohmic resistance barriers) between the β oxide species and the

silver surface. β-oxides are usually poorly ordered, low density materials; the deposit may not be very rigid, e.g. a gel-type state may be involved. Small sections or particles of the β oxide film may occasionally make good contact with the metal surface where, at low potentials, they undergo reduction. However changes in volume, as the oxide is reduced to the metal, quickly lead to poor contact, hence the appearance of random cathodic spikes and ill-defined peaks.

It is important to note that while high coverage, relatively thick silver β oxide films undergo reduction in a rather random manner, the premonolayer oxidation responses reported for silver in base are quite different. As clearly demonstrated by Burke and Ryan (see Fig. 3 in [13]) a quasi-reversible voltammetric response, which was correlated with electrocatalytic behaviour of this electrode, is observed for this electrode system at ca. 0.4 V (similar behaviour was reported subsequently by other authors [14, 35]). Such thermodynamically forbidden transitions are now regarded as a vital feature of surface active site behaviour [4, 12], the quasi-reversibility of the active metal atom/incipient hydrous oxide transition being a feature of major significance in electrocatalytic processes which involve mediators generated via interfacial cyclic redox transitions.

The disrupted state of the silver surface

It is obvious from the SEM data (Fig. 10) that the growth and subsequent reduction of multilayer oxide films resulted in marked rearrangement of the silver surface, the outer layers of metal being converted to a finely divided state. Such surface disruption, which has been noted also by previous authors [40, 41], is not confined to silver; repeated growth and reduction of β oxide films on platinum in acid has been used [42] to convert an initially bright metal surface to a platinum black-coated state. With platinum the roughening of the surface is largely a matter of increasing the surface area; there was a large increase in both the monolayer oxide reduction and adsorbed hydrogen charges but the overall shape of the voltammogram was virtually unaltered. However, in the case of silver, surface disruption led to the appearance of a new oxide reduction peak (C_o, Fig. 3) which has an anodic counterpart A_3; however, the latter appeared also (Fig. 1), in a much less dramatic manner, in the response for the initial, uncycled silver. The surface rearrangement mechanism involved was not investigated in detail but there are two possibilities: (i) dissolution/redeposition and (ii) absorption/desorption of oxygen.

Silver is not totally insoluble in base [39]; it may undergo slight dissolution, to yield AgO^- and AgO^+ species under anodic conditions and the products may be cathodically reduced to yield a more dispersed form of the metal at the lower end of each potential cycle. The alternative is that oxygen penetrates the outer layers of the metal lattice (this may also be regarded as a

thickening of the anodic oxide film), causing an expansion of the latter, at the upper end of the positive sweep. Subsequent reduction of the subsurface or absorbed oxygen at the lower end of the sweep leaves the metal atoms in an active state which then relax by rearranging to yield a more finely divided outer layer of silver. With regard to the latter mechanism it may be noted that Strehblow and coworkers [43] pointed out earlier that reduction of thin silver oxide layers (2–5 nm in thickness) caused microroughening of the electrode surface.

The appearance of the two separate peaks, C_1 and C_o, in the reduction sweep recorded after multilayer oxide growth (and in cyclic voltammograms with a disrupted silver surface, e.g. Fig. 3) is an interesting phenomenon. It is assumed that the oxide species involved, Ag_2O, are virtually identical. However, the thicker outer layer is assumed to be porous (see Fig. 10a). An inner, very thin, monolayer film of Ag_2O, which is in contact with the silver surface, undergoes reduction initially; this gives rise to peak C_1. The outer material begins to undergo reduction at the same potential but its reaction is delayed (or shifted to a more negative potential) as the product is a more active form of silver, i.e. a larger Nernstian displacement occurs in the case of peak C_o. It is well established [11] that minute metal microparticles correspond to an active state of a metal. This unusual activity of the outer layer of metal atoms is assumed to be of transitory character (the particle size probably increases as the reduction reaction takes place). Hence in the positive sweep, Fig. 3, peak A_2 preceded the enhanced peak A_3; the basic assumption here is that the particles involved in the oxidation are significantly more stable than those formed initially in the course of reduction. Peak A_3 may involve ion, e.g. Ag^+, transfer through the oxide film; hence the hysteresis involved in the formation and reduction of the thick oxide film probably involves contributions due to the non-equilibrium state of the metal and slow ion transfer.

Support for the idea that the roughness and activity of a silver surface involved in oxide formation/reduction experiments is variable (and time dependent) is provided by the work of Schumacher and coworkers [41]. They observed, using a variety of techniques, including EQCM, that not only was the surface area increased (compared with that of the original metal) when the oxide was reduced but the value subsequently decayed with time as the active surface relaxed due to reconstruction of the outer layers (in our work, which involved the repeated growth and reduction of thicker oxide films, the final disrupted, active state of the outer layers of the metal was maintained almost indefinitely).

Premonolayer oxidation

The concept of premonolayer (or underpotential) oxidation of silver in base was proposed earlier [12, 13] by one of the present authors to explain the appearance of minor, often quasi-reversible, voltammetric peaks in the double layer region, and to rationalise the electrocatalytic behaviour of this electrode system (the basic ideas involved were developed earlier [44] in work with gold). Following recent extensive work on the nature of the species formed in the premonolayer oxidation reaction of silver in base by Doblhofer and coworkers [14, 15, 16, 17, 18, 19] there can be little doubt as to the reality of premonolayer oxidation. In one of their publications Doblhofer and coworkers have given a schematic representation of the silver/aqueous base interface in the premonolayer oxide state (Fig. 5 in [18]). With regard to this model the following comments are worth considering, namely

1. Premonolayer oxidation is usually a highly localised reaction; there is obviously a voltammetric response involved but the amount of material reacting is often so small that both the process and response involved are either not readily detected or ignored (note the absence of any sign of a reversible transition in the double layer region in Fig. 1). Our assumption is that premonolayer oxidation reflects the reaction of Taylor's metastable active site metal atoms [6]; it was demonstrated recently (for several metals [10]) that the active atom coverage, and hence the premonolayer oxidation responses, may be substantially increased by appropriate electrode pretreatment.

2. In the model (or, more specifically, the diagram) in question [18] the metal surface is represented as a two-dimensional plane, i.e. surface defects are ignored. However, this does not take into account active site behaviour which, aside from Taylor's original proposal, ignores ideas expressed in more recent publications in the surface catalysis area, e.g. by Somorjai [45], Sachtler [46] and Gates [47], who stress the importance of active sites which are generally regarded as being associated with surface defects.

3. In work involving STM [19], Doblhofer and coworkers pointed out that their Ag(111) surfaces had defects in the form of steps and kinks, these being the main regions of the surface where premonolayer oxidation occurred: such behaviour is understandable as low coordinated metal atoms, e.g. at kink sites, are the most active (or electropositive) species at the interface; the involvement of such sites or defects should be stressed in any model of the interface dealing with premonolayer oxidation.

As outlined recently in the case of gold [48], hydroxy radicals are unlikely oxidation products, especially at low potentials, at a stable surface of a Group 11 metal in aqueous media. The energy of formation (or the electronegativity) of this radical is very high and silver, like gold, is usually a weak chemisorber. The hydroxy species generated at the silver/base interface, as detected by SERS [14], are assumed to be AgOH

species formed in the following type of reaction, namely

$$Ag^* \xrightarrow{-e^-} Ag^+ \xrightarrow{+OH^-} AgOH \qquad (3)$$

i.e. low coordinated, highly active silver atoms are the most likely species to undergo oxidation at low potentials (within the double layer region). According to the above reaction the interfacial hydroxy species (AgOH) is formed by OH^- ion coordination at electrogenerated Ag^+ sites, i.e. there is no need to assume an OH radical intermediate or product.

4. When protruding silver atoms undergo oxidation in aqueous media the product is assumed to be hydrated (much of this water is likely to be lost later when the electrode is transferred to high vacuum prior to XPS analysis). Hydrous oxides in general are low density, non-compact species [29] which do not hinder oxidation of further nearby or underlying active silver atoms; hence the formation of nuclei, $(AgOH)_n$. Some of these species may lose water molecules, namely

$$2AgOH \rightarrow Ag_2O + H_2O \qquad (4)$$
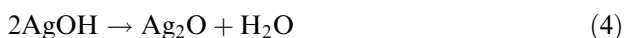
resulting in the presence of both O and OH species. The three Group 11 metals are remarkably active (despite the absence of marked chemisorbing properties) for the electrocatalysis of processes involving anionic reactants. As outlined earlier [12, 13] many of the surface-bonded, hydrated, monohydroxides are assumed to be dissociated, namely

$$AgOH(surf., hydr.) \rightleftharpoons Ag^+(surf., hydr.) + OH^-(aq.) \qquad (5)$$
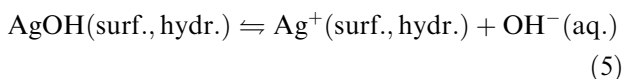
and the dissolved anionic reagents interact strongly, due to electrostatic forces, with the resulting cationic sites. According to this view surface active sites at the interface, where univalent metal ion species are involved, bear a net positive charge, balanced by an array of anions (OH^-, X^-) on the solution side. The anions are mobile and to reduce the repulsion forces in this array some cations, e.g. Na^+, will be incorporated into this region (the magnitude of the excess negative charge at the solution side of the interface will remain fixed; it is determined by the positive, Ag^+_{ads}, charge on the metal). This would explain the presence of significant quantities of Na^+ ion in premonolayer oxide deposit as observed in XPS work [18]; the tendency of the AgOH species to dissociate also explains why F^- ions can evidently replace OH^- ions in the premonolayer oxide deposit at low potentials [14].

5. The retention of localised surface order (in the form of a two-dimensional surface array [18]), under conditions where oxygen species enter the metal lattice [16], seems unlikely. Oxygen species in general are of appreciable size (the diameter of O^{2-} is ca. 0.26 nm [49]) and their entry into the silver lattice is very likely to cause considerable metal atom displacement.

Conclusions

1. It is virtually impossible to explain the marked catalytic and electrocatalytic activity of the Group 11 metals (which in conventional form are very weak chemisorbers) in general, and of silver in particular, in terms of the conventional, activated chemisorption, approach. A novel approach (referred to as the IHOAM model of electrocatalysis), outlined recently for copper in base [4], provides a satisfactory alternative approach in which the role of active, metastable surface states of the metal is stressed. Such states give rise to premonolayer (or underpotential) oxidation [12, 13] and the reality of such behaviour, in the case of silver in base is confirmed by recent independent work [14, 15, 16, 17, 18, 19].

2. The basic electrochemistry of silver in base is surprisingly complex. One illustration of this complexity demonstrated here is the ability of the metal, in disrupted form, to absorb oxygen into its outer layers (this process may also be regarded as multilayer α oxide, or Ag_2O, formation). This disrupted state was found to be quite persistent and SEM data showed that the surface in question consisted largely of a finely divided layer of silver microparticles.

3. β Oxide deposits (regarded as AgOH materials) grown by potential cycling techniques were (as usual) reluctant to undergo reduction and when they did undergo the latter the responses were generally very ill-defined. This was attributed to contact problems and was very different from the simple behaviour described recently [36] for similar work with copper in base.

4. Premonolayer oxidation of silver in base was described in earlier work from this laboratory [12, 13]; we regard it as one of the most important aspects in electrocatalysis, especially in the case of the Group 11 metals. In this area it is important to bear in mind that such a reaction is usually quite localised (as are active sites) at the interface. Both the reaction and the species involved (within the double layer region) are thermodynamically forbidden. This is not very unusual as non-equilibrium states of metals are very well established in metallurgy [50]. Our approach is in agreement with Somorjai's claim [45] that surface disorder, and in particular high energy disordered states, are vital features of effective catalysis at surfaces and interfaces. Quite subtle effects, e.g. dissociation of surface AgOH species to yield cationic mediator species, may be an important feature in some reactions of Group 11 metal/aqueous solution interfaces at low potentials.

5. The assumption of the presence of metal atoms, or small metal particles, in two different states of activity (superactive, $\mu \gg \mu°$, and conventional, $\mu \approx \mu°$) was made earlier in the case of palladium [28]. It is suggested here that the unique ability of silver to absorb

oxygen in the α oxide region is related to the unusual character of Ag₂O [51]. This material consists of two completely interpenetrating and equivalent (Ag and O) frameworks with no cross-connected primary (Ag-O) bond. Even partial retention of the open framework structure of the metal on reduction of the oxide would favour the re-entry of oxygen into the disturbed outer layers of the metal in a subsequent positive sweep.

References

1. Lloyd L, Ridler DE, Twigg MV (1989) The water-gas shift reaction. In: Twigg MV (ed) Catalysis handbook (2nd edn). Wolfe Publishing, London, pp 283–339
2. Davies P, Donald RT, Harbord NH (1989) Catalytic oxidations. In: Twigg MV (ed) Catalysis handbook (2nd edn). Wolfe Publishing, London, pp 469–518
3. Haruta M, Yamada N, Kobayashi T, Iijima S (1989) J Catal 115:301
4. Burke LD, Collins JA, Murphy MA (1999) J Solid State Electrochem 4:34
5. Burke LD, Hurley LM (1999) Electrochim Acta 44:3451
6. Taylor HS (1925) Proc R Soc Lond Ser A 108:105
7. Burke LD, Nugent PF (1998) Gold Bull 31:39
8. Burke LD, O'Mullane AP (2000) J Solid State Electrochem 4:285
9. Burke LD, Hurley LM, Lodge VE, Mooney MB (2001) J Solid State Electrochem 5:250
10. Burke LD, Collins JA, Horgan MA, Hurley LM, O'Mullane AP (2000) Electrochim Acta 45:4127
11. Henglein A (1995) Ber Bunsenges Phys Chem 99:903
12. Burke LD, O'Leary WA (1988) J Electrochem Soc 135:1965
13. Burke LD, Ryan TG (1990) J Appl Electrochem 20:1053
14. Savinova ER, Kraft P, Pettinger B, Doblhofer K (1997) J Electroanal Chem 430:47
15. Savinova ER, Zemlyanov D, Pettinger B, Scheybal A, Schlögl R, Doblhofer K (2000) Electrochim Acta 46:175
16. Zemlyanov DY, Savinova E, Scheybal A, Doblhofer K, Schlögl R (1998) Surf Sci 418:441
17. Savinova ER, Zemlyanov D, Scheybal A, Schedel-Niedrig T, Doblhofer K, Schlögl R (1999) Langmuir 15:6546
18. Savinova ER, Zemlyanov DY, Scheybal A, Schlögl R, Doblhofer K (1999) Langmuir 15:6552
19. Shaikhutdinov SK, Savinova ER, Scheybal A, Doblhofer K, Schlögl R (2001) J Electroanal Chem 500:208
20. Lützenkirchen-Hecht D, Strehblow H-H (1998) Electrochim Acta 43:2957
21. Hecht D, Strehblow H-H (1997) J Electroanal Chem 436:109
22. Hecht D, Strehblow H-H (1997) J Electroanal Chem 440:211
23. Hecht D, Frahm R, Strehblow H-H (1996) J Phys Chem 100:10,831
24. Fleishmann M, Hendra PJ, McQuillan AJ (1974) Chem Phys Lett 26:163
25. Bao X, Pettinger B, Ertl G (1993) Ber Bunsenges Phys Chem 97:322
26. Hoare JP (1968) The electrochemistry of oxygen. Wiley, New York, pp 211–238
27. Takeda K, Hattori T (2001) J Electrochem Soc 148:A44
28. Burke LD, Nagle LC (1999) J Electroanal Chem 461:52
29. Burke LD, Lyons MEG (1986) Electrochemistry of hydrous oxide films. In: White RE, Bockris JO'M, Conway BE (eds) Modern aspects of electrochemistry, no 18. Plenum Press, New York, pp 169–248
30. Kötz R, Yeager E (1980) J Electroanal Chem 111:105
31. Droog JMM, Anderliesten PT, Bootsma GA (1979) J Electroanal Chem 99:173
32. Lopez Teijelo M, Vilche JR, Arvia AJ (1982) J Electroanal Chem 131:331
33. Stonehart P (1968) Electrochim Acta 13:1789
34. Chen S, Wu B, Cha C (1996) J Electroanal Chem 416:53
35. Orozco G, Pérez MC, Rincón A, Gutiérrez C (2000) J Electroanal Chem 495:71
36. Burke LD, Murphy MA (1999) J Solid State Electrochem 5:43
37. Burke LD, Nugent PF (1998) J Electroanal Chem 444:19
38. Burke LD, Hurley LM (2000) J Solid State Electrochem 4:353
39. Pourbaix M (1966) In: Atlas of electrochemical equilibria in aqueous solutions. Pergamon Press, Oxford, pp 393–398
40. Droog JMM, Huisman F (1980) J Electroanal Chem 115:211
41. Schumacher R, Gordon JG, Melroy O (1987) J Electroanal Chem 216:127
42. Burke LD, Roche MBC (1984) J Electroanal Chem 164:315
43. Hecht D, Borthen P, Strehblow H-H (1996) Surf Sc 365:263
44. Burke LD, Cunnane VJ (1986) J Electroanal Chem 210:69
45. Somorjai GA (1996) Chem Rev 96:1223
46. Sachtler WMH (1995) Ber Bunsenges Phys Chem 99:1295
47. Gates BC (1992) Catalytic chemistry. Wiley, New York, p 352
48. Burke LD, Nugent PF (1997) Gold Bull 30:43
49. Cotton FA, Wilkinson (1972) Advanced inorganic chemistry (3rd edn). Wiley, New York, p 52
50. Suryanarayana C (1991) Rapid solidification. In: Cahn R (ed) Materials science and technology, a comprehensive treatment, vol 15. VCH Weinheim, pp 57–110
51. Wells AF (1962) Structural inorganic chemistry. Clarendon Press, Oxford, p 460