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Multilayer hydrous oxide growth on copper in base and its correlation with previously reported electrocatalytic data for this electrode system

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Abstract A repetitive potential cycling procedure was used to produce a specific multilayer hydrous oxide film on copper in base at 60 °C. Such a deposit undergoes reduction in a quasi-reversible manner at ca. -0.1 V (RHE), i.e. at a potential that is unrelated to Pourbaix data for copper but, as demonstrated previously, is of major significance with regard to the electrocatalytic behaviour of this electrode system. In accordance with the incipient hydrous oxide/adatom mediator model of electrocatalysis, an active surface state of the metal (Cu^*) is assumed to be involved both in electrocatalysis and as a primary product in the hydrous oxide reduction reaction. While the latter process occurs very rapidly at -0.1 V, it is not usually reversible as it is accompanied by subsequent rapid loss of the active state of the metal. The same general approach was used previously to explain the hydrous oxide and electrocatalytic behaviour of a range of noble metals.

Key words Copper · Hydrous oxide · Anomalous behaviour · Active state · Electrocatalysis

Introduction

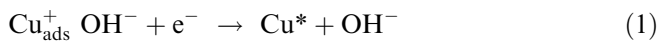
From both a catalytic and an electrocatalytic viewpoint, copper is an interesting and technologically important metal whose behaviour may be regarded as a link, from an electrochemical viewpoint, between the noble and non-noble metals. Considerable interest in copper electrochemistry is likely to follow from recent developments in the microelectronics area, where electroplated copper has recently displaced aluminium as the on-chip interconnector material [1] of choice.

Copper electrochemistry has been a subject of research in this laboratory for several years [2–6], one of the main objectives being to link the electrocatalytic behaviour of the metal (an important aspect of electrodeless plating [3]) to the fundamental properties of the electrode system. The results are interesting in that the electrocatalytic behaviour of the metal in base seems to have little in common with the conventional view of copper electrochemistry, which at the simplest level is concerned mainly with monolayer oxide formation or the $\text{Cu}/\text{Cu}_2\text{O}$, $\text{Cu}_2\text{O}/\text{CuO}$ or Cu/CuO interconversions. Usually the formation or presence of these conventional oxides results, from an electrocatalytic viewpoint, in surface deactivation [2].

As pointed out recently [2, 3], many of the electrocatalytic processes on copper in base involve two unusual species, namely, active surface copper atoms (Cu^*) and their oxidation product, incipient (or low coverage) hydrous oxide species (formulated earlier [3] as $\text{Cu}^+ \cdot n\text{H}_2\text{O}$; CuOH is regarded as a strong base, i.e. it is assumed to exist [6] largely in an adsorbed, dissociated form at the interface). The basic idea involved in this novel approach to electrocatalysis (referred to as the incipient hydrous oxide/adatom mediator, or IHOAM, model) arose initially from work with gold [7]. The crucial observation (and a similar correlation was pointed out later for platinum [8, 9]) was that the potential for the onset and termination of electrocatalysis (under cyclic voltammetry conditions) often coincided with the potential for multilayer hydrous oxide reduction (a generalised approach for such behaviour was described recently [2]). Another interesting point in this approach is that the potential in question, which is usually quite well defined experimentally, bears no relationship to the thermodynamic properties of the electrode system (as summarised by Pourbaix [10]). The assumption involved (which was discussed much earlier by Taylor [11]) is that surface and interfacial catalysis occur predominantly at active sites, i.e. at minute regions of the surface where defects act as a source of active metal atoms (represented in the present case as Cu^*).

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In the previous work with copper in base [5, 6] it was demonstrated that from an electrocatalytic viewpoint a crucial transition represented as



occurred at ca. -0.1 V (RHE), electrocatalytic oxidation of solution species (mediated by Cu_{ads}^+) taking place above this value, while reductions (mediated by Cu^*) occurred below it. According to the generalised reaction scheme outlined previously (Fig. 1 in [2]), there should be a multilayer hydrous oxide/active metal transition (line *d* in the diagram in question) in the case of copper electrodes in base. Such a response has not been reported earlier, and indeed Pourbaix data [10] for this system (which relates to bulk and not surface materials) suggest that no bulk oxide of copper is stable in base below ca. 0.47 V (RHE). However, we wish to report here that under appropriate conditions it is possible to grow substantial thicknesses of a multilayer hydrous oxide film on copper electrodes in base and that, in excellent agreement with the IHOAM viewpoint, such a deposit yields a dramatically sharp cathodic response, as it undergoes reduction at moderate sweep rates, quite close to -0.1 V (RHE).

Experimental

Repetitive potential cycling is a convenient technique for producing multilayer hydrous oxide films on various metals in aqueous solution; the basis of the technique was outlined in an earlier review

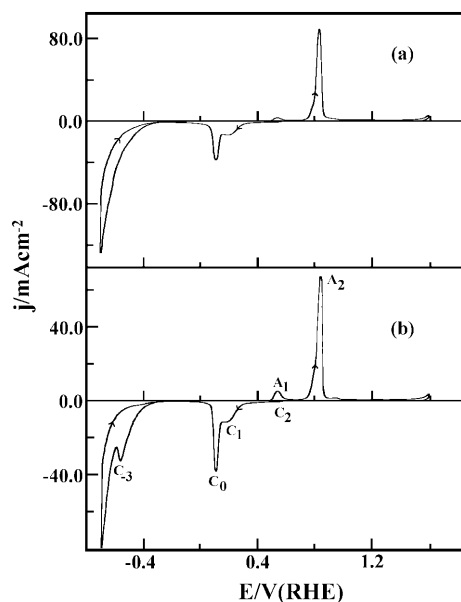


Fig. 1 Typical cyclic voltammograms (-0.7 to 1.6 V, 20 mV s^{-1}) for copper in 1.0 mol dm^{-3} NaOH at 60 $^{\circ}\text{C}$: **a** a fresh, relatively undisturbed, electrode; **b** an extensively used electrode (this voltammogram was recorded after the electrode had been used for repeated hydrous oxide growth and reduction experiments; its outer layer was disrupted or active; note the unusual, C_{-3} , peak)

[12]. Typical growth conditions for copper in 1.0 mol dm^{-3} NaOH at 60 $^{\circ}\text{C}$ were 20 triangular cycles between -0.07 and 0.86 V at 100 mV s^{-1} ; compared with the behaviour of the noble metals, the growth (as shown later in Fig. 6) was particularly rapid in the case of copper. The amount of oxide produced was determined coulometrically by applying a single analytical or oxide stripping sweep, usually from 0.4 to -0.4 V at 20 mV s^{-1} . It was established in preliminary experiments that the main hydrous oxide reduction response was a sharp cathodic peak at ca. -0.1 V, and that the process was virtually 100% efficient as there was no trace of a hydrous oxide reduction peak on repeating the oxide stripping sweep. The growth and reduction were usually carried out in the same solution.

The effect of a number of variables was investigated, e.g. the upper and lower potential limits for oxide growth, the number of oxide growth cycles and the variation with sweep rate of the various parameters recorded during the oxide stripping process. The attention here was focused on the electrochemical behaviour of the system and no attempt has been made at present to identify the nature of the unusual oxide product.

The working and counter electrodes consisted of copper wire (Goodfellow, 99.95% +, 1.0 mm diam., ca. 0.70 cm^2 exposed area) sealed directly into soda glass. To ensure a consistent starting state of the electrode surface, the working electrode was usually subjected to mild abrasion to remove any weakly adhering metal or oxide particles, followed by a brief (10 s) immersion in dilute (0.14 mol dm^{-3}) HNO_3 solution and a wash with distilled water. The state of the electrode surface was usually checked by recording a standard cyclic voltammogram (-0.7 to 1.6 V, 20 mV s^{-1}). The potential of the working electrode was recorded (and is reported) with respect to a reversible hydrogen electrode (RHE) ($P_{\text{H}_2} = 1.0$ atm) in the same solution; a Luggin capillary was used to minimise errors due to solution iR drop.

Solutions were made up using triply distilled water and were purged of oxygen with a flow of purified nitrogen. As in the previous work [3], the cell was operated at a slightly elevated temperature as this tended to give good resolution of the different oxide reduction peaks observed at ca. 0.0 V. Potential control was achieved using a Wenking (model LB95) laboratory potentiostat, programmed using a Wenking (model MVS 87) function generator. The responses were recorded using a Rikadenki (model RW-21) X-Y recorder, and those shown here may be regarded as direct traces (the originals were transferred, with the aid of a scanner, to a computer which was used to plot the diagrams).

Results

Typical cyclic voltammograms for copper in base are shown in Fig. 1. The main difference between these two experiments is that the first (a) was carried out with a fresh copper electrode whereas the second (b) was carried out with the same electrode at a later stage of the present work, i.e. after the surface had been significantly disrupted. As reported recently for platinum [9] and palladium [13], such disruption may have a considerable effect on the response observed in the double layer region; hence the appearance of peak C_{-3} , which occurs close to the onset of hydrogen gas evolution in the response for the more active copper surface. As pointed out recently [14], this unusual feature, which is not the subject of the present investigation, is apparently of particular importance in the case of the electrocatalytic reduction of carbon dioxide on copper in aqueous media.

The peak notation employed in Fig. 1b is based on earlier work [14]. In the latter, two other cathodic

peaks, C_{-1} and C_{-2} , were noted: peak C_{-1} (at ca. -0.1 V) appeared rather frequently and is the topic of main interest in the present work; peak C_{-2} (at ca. -0.4 V) appeared only infrequently. Peaks A_1/C_1 and A_2/C_2 are assumed to be due to the Cu(0)/Cu(I) and Cu(I)/Cu(II) transitions, respectively. They exhibit considerable hysteresis and peak C_2 is particularly small (indeed, it is virtually absent in the present Fig. 1) because either the CuO is insulated from the copper by the presence of an intervening layer of poorly conducting Cu_2O [6] or the main product of oxidation in the case of A_2 is a hydrated material, $\text{CuO} \cdot n\text{H}_2\text{O}$, which (as observed for many hydrated oxide deposits [12]) only undergoes reduction at very low potentials – hence, in either event, the appearance of peak C_0 at ca. 0.13 V. It is worth noting here that there is not the slightest indication of peak C_{-1} (at ca. -0.1 V [14]) in either of the negative sweeps.

Typical examples of negative sweeps recorded for copper electrodes in base, following hydrous oxide growth on the metal surface, are shown in Fig. 2. The main difference between these experiments was the value of the upper potential limit used during oxide growth. It is evident that in some cases two, rather than one, cathodic peaks were observed at ca. 0.0 V (indeed in Fig. 2b an additional shoulder is evident prior to the first peak; this is probably C_1 , see Fig. 1b; this feature, which was absent in many of the later sweeps, was ignored here). The shape and relative charges of the peaks varied with the oxide growth conditions and an example is given in Fig. 2c of a case where C_{-1} is virtually the sole feature in the negative sweep.

The conditions necessary to produce substantial quantities of the oxide giving rise to the C_{-1} response were explored by varying the oxide growth sweep limits. It was found (Fig. 3) that the oxide in question was produced only when the upper limit (E_u) used during oxide growth was greater than ca. 0.75 V, i.e. this limit had to enter, or exceed, the region corresponding to peak A_2 in Fig. 1b. The optimum upper limit for the development of the C_{-1} response was ca. 0.9 V; it was

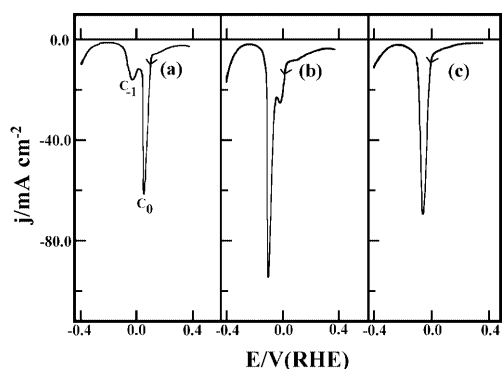


Fig. 2 Change in the oxide reduction response (0.4 to -0.4 V, 20 mV s^{-1}) on varying the upper limit (E_u) used for oxide growth (the conditions for the latter in this case were 0.15 V to E_u , 20 cycles at 100 mV s^{-1}); the E_u values here were **a** 1.4 V, **b** 0.88 V and **c** 0.86 V

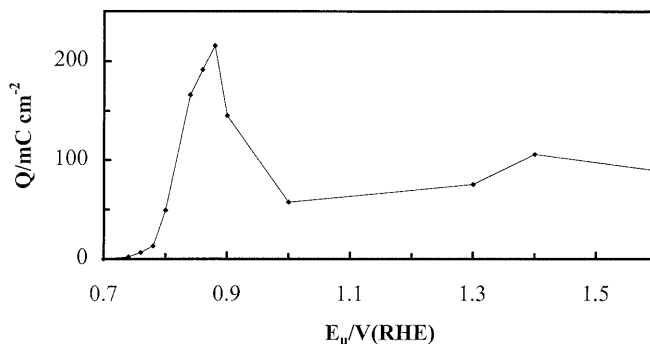


Fig. 3 Effect of the upper limit (E_u) used in oxide growth (E_L was constant at 0.05 V, 20 cycles at 100 mV s^{-1}) on the charge density associated with peak C_{-1} as observed in subsequent oxide reduction sweeps

possible to grow the oxide involved using higher upper cycling limits (Fig. 3), but the efficiency of the process dropped sharply as E_u exceeded 0.9 V.

The lower limit (E_L) used during oxide growth was even more crucial. If the value was high, e.g. 0.275 V (Fig. 4a), peak C_{-1} was quite small and there was strong overlap with peak C_0 ; evidently a mixed oxide deposit was obtained. If the value was rather low, e.g. -0.125 V (Fig. 4b), then C_0 was not observed on the subsequent reduction peak but the response for C_{-1} , and evidently the amount of hydrous oxide formed, was quite small. However, as demonstrated here in in Fig. 4c and d, substantial quantities of the oxide giving rise to peak C_{-1}

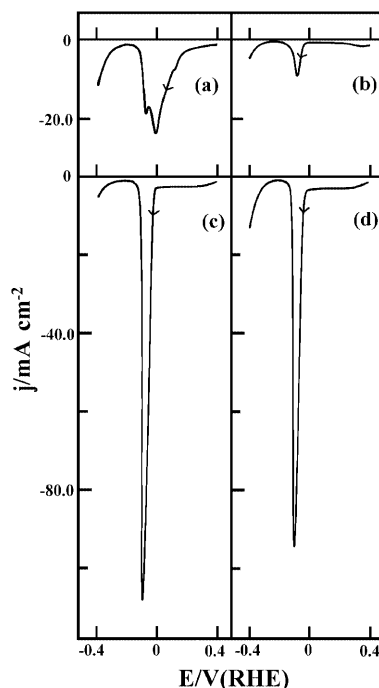


Fig. 4a-c Examples of oxide reduction responses observed after oxide growth (20 cycles at 100 mV s^{-1} , $E_u = 0.86$ V); the lower limits (E_L) during oxide growth here were **a** 0.275 V, **b** -0.125 V, **c** -0.025 V and **d** -0.09 V

could be produced using values for the lower limit that were within the range bounded by the E_L values quoted here earlier, -0.125 to 0.275 V.

The results of a more extensive investigation of the effect of the lower limit are summarised in Fig. 5. As the E_L value dropped below ca. 0.20 V the charge associated with peak C_{-1} increased almost linearly with decreasing E_L until the latter reached a value of ca. -0.07 V. Further reduction of E_L resulted in a steep decrease in the magnitude of the charge value for peak C_{-1} . Using values for the oxide growth limits close to the optimum, the amount of oxide produced at the interface (as monitored in subsequent reduction sweeps) increased almost linearly (Fig. 6) with the increasing number of oxide growth cycles (at least for the range of cycles, 0–50, investigated here).

Some of the cathodic responses shown here for the reduction of hydrous oxide deposits (see in Fig. 4c and d) are unusually sharp and symmetrical, especially for a

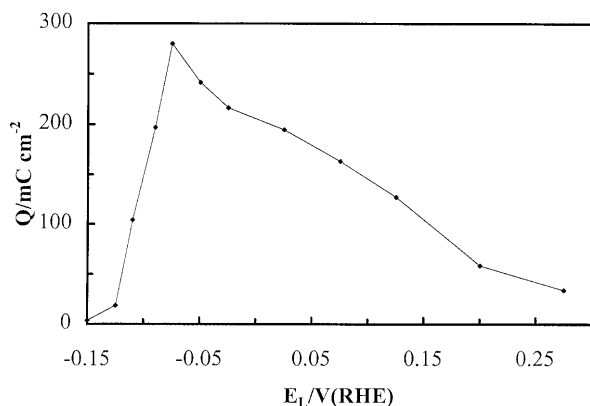


Fig. 5 Effect of the lower limit (E_L) used in oxide growth (E_u was constant at 0.86 V, 20 cycles at 100 mV s⁻¹) on the charge density associated with peak C_{-1} as observed in subsequent oxide reduction sweeps

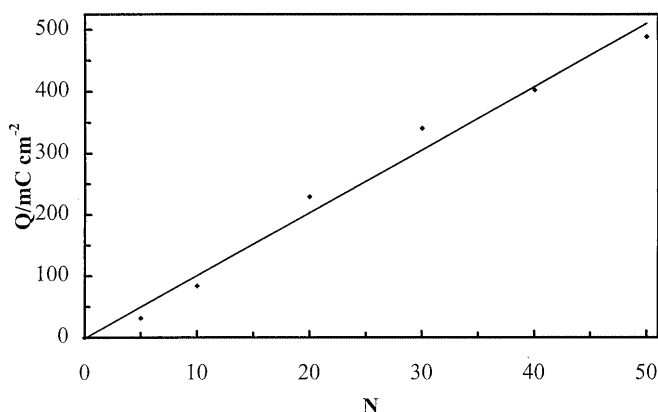


Fig. 6 Variation of the amount of hydrous oxide produced (measured in terms of the charge required, peak C_{-1} , for its reduction) as a function of the number (N) of oxide growth cycles (the growth was at 100 mV s⁻¹, -0.07 to 0.86 V); each point here entailed a separate oxide growth and reduction experiment

reaction that is clearly irreversible. The variation with sweep rate of various parameters pertaining to peak C_{-1} are shown in Fig. 7. The peak charges for the deposits, which were grown under similar conditions, were virtually independent of sweep rate (Fig. 7a). The peak current density increased quite significantly, though not linearly, with increasing sweep rate (Fig. 7b). Finally, the peak maximum potential decreased steadily with increasing sweep rate (Fig. 7c); however, the magnitude of the decay (from ca. -0.02 to -0.13 V in Fig. 7c) was not very large.

The stability of the oxide involved in peak C_{-1} was also investigated. The hydrous oxide was grown under optimum conditions and the electrode was then allowed to rest in the base solution on open-circuit for various lengths of time, up to a maximum of 15 min. No significant variation in oxide reduction charge with resting time was observed.

Discussion

The type of hydrous oxide growth and reduction behaviour outlined here for copper in base is very similar to that described earlier for many other metals, e.g. gold [15] and platinum [16], and the most surprising feature is that in virtually all cases the resulting deposits exhibit major reluctance or overpotential with regard to reduction. For example, in the case of platinum (which according to Pourbaix [10] has no bulk oxide that is stable below ca. 0.98 V) one of the major hydrous oxide components, Pt(HO₂), usually undergoes reduction in a

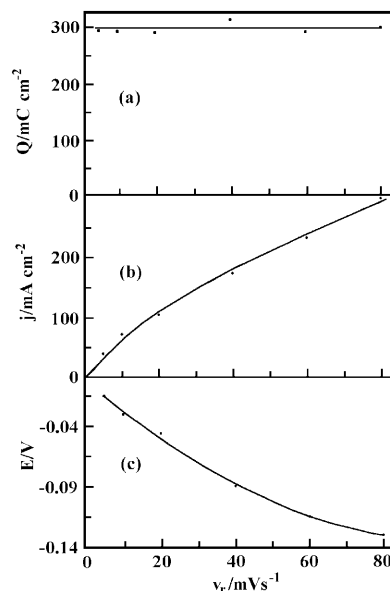


Fig. 7a–c Effect of the oxide reduction (0.4 to -0.4 V) sweep rate, v_r , on the charge density (Q), peak current density (j) and peak potential (E) observed for C_{-1} ; for each oxide reduction experiment involved here the oxide growth conditions were identical (-0.07 to 0.86 V, 100 mV s⁻¹, 20 cycles)

negative sweep only at ca. 0.20 V in acid [16] and is extremely difficult to reduce totally in base [17]. Copper in base behaves in a similar manner; it apparently has no oxide that is thermodynamically stable below ca. 0.47 V [10] and yet it is clear from Fig. 4c and d and Fig. 7c that at moderate sweep rates the potential has to drop below ca. 0.0 V before significant oxide reduction occurs. Furthermore, once the oxide begins to undergo reduction on the negative sweep the reaction occurs in an extremely facile manner, as the peaks observed (illustrated in Fig. 4c) are extremely sharp and rather symmetrical. Also, while the transition at ca. -0.1 V is not of thermodynamic significance, it is of great importance with regard to copper in base as it is also the potential value at which the low coverage electrocatalytic mediator switches from its reduced to oxidised state [3].

It is assumed, in terms of the IHOAM view [2, 3] of the type of behaviour of interest here, that the potential of -0.1 V corresponds to a redox transition of an active state of the metal. While such states have not received a great deal of attention in interfacial chemistry, they are assumed to correspond to low coordination or protruding surface metal atoms [9]. This of course is a broad, generalised explanation; two features that are far less clear are (1) what determines the value of ca. -0.1 V in the case of copper electrodes in base (or is there any way of predicting this value), and (2) what is the precise nature of the oxide deposit and to what extent does this influence the redox potential in question? These again are questions of a general nature, i.e. they are not confined to copper. The behaviour of copper in base is similar to platinum in acid in other ways: as pointed out earlier, there are at least two [16] hydrous oxides (HO1 and HO2) and two mediator systems [8] in the case of platinum. These have equivalents here, C_{-1} at ca. -0.1 V in Fig. 4 and C_{-3} at ca. -0.6 V in Fig. 1b.

Although it may appear from Fig. 7c that the multilayer hydrous oxide film grown on copper in base only undergoes reduction below ca. 0.0 V, this result should be viewed with caution. It was demonstrated earlier [18], with the corresponding films on platinum, that under constant potential conditions reduction may occur at a slow but significant rate (leading eventually to total loss of the oxide) at appreciably more positive potentials. Such loss may be explained in the case of copper by assuming the process shown in Eq. (1) is accompanied by a subsequent, significantly slower, loss of the active state of the metal, viz.



According to this interpretation the reduced form of the couple (Cu^*) is an active state of copper (this is assumed to be the main factor in determining the high reduction overpotential). Such a state is unstable; above -0.1 V it may decay gradually to form stable copper (Cu) with the result that, providing the potential is constant with time and is not too positive, all the hydrous oxide deposit should eventually be reduced even at a potential that is significantly above -0.1 V.

The interesting point that emerges from the current and earlier [2, 3] work with copper in base (and indeed other work with platinum and gold [8]) is that the interfacial (or mediator generation) process which is often of vital importance in electrocatalysis is usually totally absent both in the conventional response for the metal (note the absence of the C_{-1} peak at -0.1 V in Fig. 1) and in Pourbaix's thermodynamic data [10]. This critical response at -0.1 V (which appears also, indeed in a much more dramatic form, in hydrous oxide reduction sweeps, e.g. Fig. 4c) is attributed here to a redox transition involving two ill-defined species, the active state of the metal and its oxidation product which is regarded as a hydrous oxide species. The active state of the metal is extremely difficult to investigate as it is inherently unstable or, at best, metastable. We regard this active state as an adsorbed species, either a single copper atom (or adatom), Cu^*_{ads} , or a minute cluster, $(\text{Cu}_n^*)_{\text{ads}}$. The unusually low redox potential (or high energy) of such species, which is the essence of premonolayer oxidation and active site behaviour, has been elegantly demonstrated by Henglein [19].

The other variable is the hydrous oxide species which, usually being amorphous, is also difficult to investigate. The correlation between multilayer hydrous oxide reduction and electrocatalysis [2, 3] (the critical potential for both reactions occurs for copper in base at ca. -0.1 V) raises the question as to why the active state of the metal has such a specific value. Are "magic number" n -values, which correspond to high energy cluster states [19], or different states of the dispersed oxide, involved? While no answers to these questions are provided here, attention is drawn to the topic because the redox properties of these unusual interfacial species often seem to be the essence or vital factor in electrocatalysis at metal surfaces in general. It was suggested earlier [20] that the regular bulk metal was merely a support system for the surface active sites. It now appears that the redox behaviour of the two states, the regular surface (usually the predominant state) and the surface active sites (which may be regarded as overlayer or protruding features), are quite different and only indirectly related. Cyclic redox mediated electrocatalysis at metal electrode surfaces [2, 3] is often dominated by active site behaviour which as yet has not received great attention.

The mechanism of hydrous oxide growth on metals in general under potential cycling conditions was discussed earlier [12]. To achieve substantial growth with copper in base the upper limit (E_u) has to exceed 0.8 V (Fig. 3), i.e. it is necessary to form the Cu(II) oxy species associated with peak A_2 (Fig. 1b). The lower limit (E_L) involved in cycling is also important (Fig. 5), as the generation of a multilayer oxide deposit was quite slow with $E_L > 0.2$ V. Peak C_2 in Fig. 1b has a maximum close to the latter value and, as pointed out earlier [6], this peak corresponds to removal of the poorly conducting α (or compact) Cu_2O film on the copper surface.

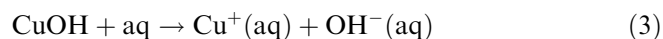
The Cu_2O deposit may be viewed as a thin barrier film which is converted at the upper limit ($E_u \geq 0.8$ V)

to a thicker, more dispersed Cu(II) deposit, probably containing a mixture of CuO and Cu(OH)₂; this layer may also be hydrated. At an early stage of the negative sweep the barrier layer of Cu₂O is restored, C₂ in Fig. 1b, but this is removed again at more negative potentials (peak C₁) and active, low-lattice coordination copper atoms are probably produced (especially in the region of peak C₀, Fig. 1) which are oxidised on the next positive sweep to form the material Cu⁺_{ads} · nH₂O, giving rise, on repetitive cycling (Fig. 6), to the thick multilayer hydrous oxide deposits. The lower limit is rather crucial; as demonstrated here in Fig. 2, it must be sufficiently low to remove the material involved in peak C₀ but greater than ca. -0.10 V (Fig. 5) as otherwise the material giving rise to peak C₋₁ will also undergo reduction.

Active states of metals are well known in connection with the unusual properties of ultrafine metal particles [19]. However, the role of such states in relation to the behaviour of solid metal surfaces has not received much attention. This situation seems to be changing. In the recent account of the replacement of aluminium by electrodeposited copper in on-chip interconnections in the microelectronics area, Andricacos [1] pointed out that fresh electroplated copper displays unusual, time-dependent behaviour for several hours after deposition. The observed changes in resistivity and stress were attributed to such factors as an increase in grain size and elimination of defects such as grain boundaries. Evidently the nascent deposit is an active form of copper, the mean lattice coordination number of the metal atoms is probably low owing to the presence of an abnormally high level of adatoms, vacancies and grain boundaries; hence the copper is initially in an active state. A similar type of high-energy surface state was reported recently for palladium [13]; it was produced by growing, and subsequently reducing, a multilayer hydrous oxide film on the electrode surface. Electron micrographs of a copper surface, taken subsequent to reduction of a hydrous oxide film in base, by Garmanov and co-workers [21] showed the presence of extensive disorder: the surface was coated with a layer of copper microglobules of mean diameter of ca. 70 nm. This group also grew their hydrous oxide deposits by potential cycling, but they only observed one unusual (and rather broad) oxide reduction peak, as opposed to the four (C₀ to C₋₃) now observed on a rather regular basis [14] in this laboratory. Changes in physicochemical properties with time in the case of fresh metal electrodeposits [1] may be regarded as relaxation effects, the metal altering spontaneously, via cold-annealing processes, from a high to the normal energy state.

The nature of the oxide deposit produced here on cycling has yet to be investigated. Hydrous oxide deposits are frequently rather amorphous, gel-type, low-density materials. It is uncertain whether the main component in these thick deposits is Cu(I) or Cu(II) species, but the potential determining reaction is assumed to involve CuOH. The latter is regarded as

equivalent to an alkali metal hydroxide [6], i.e. it is assumed to be a strong base, viz.



i.e. the component of the deposit is regarded as a virtually neutral network or agglomerate of Cu⁺ and OH⁻ ions.

The same type of trends as shown here in Fig. 7 for copper were reported earlier for gold [15], palladium [13] and platinum [22] in aqueous media. The films in the present case were of approximately equal thickness (Fig. 7a), and the fact that the reduction charge value did not alter with time (over a 15 min period as described here earlier) demonstrates that the hydrous oxide material is not particularly labile in the aqueous base. For ideally reversible surface film redox behaviour [23] the peak current density (Fig. 7b) should increase linearly with sweep rate whereas the peak potential (Fig. 7c), should be independent of sweep rate. These two conditions were not fulfilled here, but the deviations may be explained in terms of the scheme outlined earlier, Eqs. (1) and (2).

When the reduction sweep rate is increased the mean activity of the nascent copper (Cu*) is greater, and hence the potential is shifted to lower values, as there is less time for decay of the active state. Also the molar volume of the oxide and its reduction product are probably quite different and the oxide deposit may be non-uniform (it may, for instance, be composed of poorly crystallised particles or grains). Hence, contact and/or transport problems may arise (even though the sharpness of the cathodic peaks, e.g. Fig. 4c, suggests that these are not serious sources of inhibition) which restrict the maximum peak current density values (hence the non-linear increase) at higher reduction sweep rates.

The low reduction potential of the multilayer hydrous copper oxide film (ca. -0.1 V), and the large difference between this and the *E*₀ values quoted for copper in aqueous media on the basis of standard chemical potential data [10], may be regarded simply as an overpotential effect. What is more interesting, however, especially from an electrocatalysis viewpoint, is the origin of this overpotential, which is assumed here to be due to the intervention of a non-equilibrium, active state of the metal. Such states, which are rarely taken into account in surface electrochemistry, are now assumed to be of widespread occurrence and the presence of three such states (which react in a reversible manner) will be outlined shortly [24] for copper in base. In our opinion these reversible premonolayer redox responses of active metal atoms at interfaces are often the vital feature in electrocatalytic processes.

Conclusions

1. It was demonstrated that a thick multilayer hydrous oxide film of specific (though ill-defined, probably

- amorphous) character, identified in terms of its reduction behaviour, may be produced on copper in base using repetitive potential cycling techniques. The values for the upper and lower potential limits in such cycling experiments are important and the oxide growth behaviour was rationalised in terms of the conventional electrochemical behaviour of this electrode system.
2. The potential for the hydrous oxide/metal transition in a reduction sweep (ca. -0.1 V) occurs well within the double layer region for this electrode system. This reduction potential bears no relationship to the conventional thermodynamic behaviour of copper in base but exhibits an excellent correlation with the electrocatalytic properties of the system as outlined earlier [2, 3]. Such a correlation strongly supports the IHOAM view of electrocatalysis.
 3. The type of behaviour observed for copper is quite similar in general terms to that described earlier for other metals, e.g. platinum [22], palladium [13] and gold [15]. The sharp hydrous oxide reduction peak in the double layer region is attributed to the production, at a particular potential, of adsorbed, active metal atoms in a relatively high coverage, mobile state which favours loss of such adatoms (and hence rapid, total and irreversible loss of the oxide deposit) via agglomerate (M_n) formation. However, with regard to electrocatalysis, it is assumed that there are almost invariably some of these active metal atoms present at active sites or defects on the surface.

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