



Role of surface defects in the electrocatalytic behaviour of copper in base

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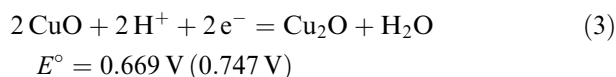
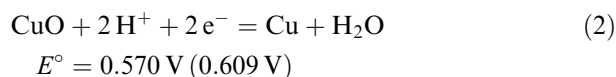
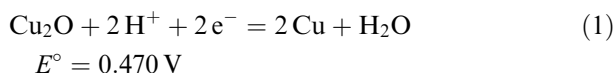
Abstract

There is increasing evidence, for example, from recently published surface enhanced Raman spectroscopy data, that copper, silver and gold electrode surfaces in base, may exist in an oxidized state at unusually low potentials. In the present work, which was carried out using electrochemical techniques, up to six oxide reduction peaks were recorded for copper in base in the region below 0.6 V vs RHE. One of these peaks, at about -0.6 V vs RHE, was particularly prominent; this occurred at a potential 1.0 V more negative than the standard potential for the Cu/Cu₂O electrode reaction in aqueous media. Such behaviour is rationalized in terms of the involvement of nonequilibrium (and hence unstable) active states of the metal surface; these states may be regarded as adatoms or minute clusters (the lowering of the redox potential being due to the unusually low lattice stabilization energy of these active metal atoms). Copper and its oxides, especially Cu₂O, are of major interest from a catalytic, electrocatalytic, photocatalytic and microelectronics fabrication viewpoint and the involvement of the active states of the metal, as a key ingredient in several of these areas, is outlined.

1. Introduction

Copper is a remarkably active metal from a catalytic and electrocatalytic viewpoint. It is widely used as a selective heterogeneous catalyst for the reduction of carbon monoxide or carbon dioxide to methanol [1] in the presence of hydrogen gas. The metal is also of increasing interest [2] in the microelectronics fabrication field and one approach used in this area is electroless plating. In the latter the electrons required for the reduction of copper ions are supplied by a dissolved reducing agents (e.g., formaldehyde [3]), which is oxidized (thereby releasing the electrons) selectively at the electrocatalytically active growing copper surface. The metal is also one of the most active electrocatalysts for the reduction of carbon dioxide to hydrocarbons [4, 5] and the recent report by Hara and coworkers [6] of the ability to split water into hydrogen and oxygen gas using visible light in the presence of a Cu₂O photocatalyst, without significant deterioration of performance of the latter, will inevitably increase the level of interest in copper and copper oxide electrochemistry.

The thermodynamic data for copper in aqueous base have been summarized by Pourbaix [7] in terms of the following equations:



The potential values are quoted here in terms of the RHE scale; those in parentheses refer to cases where the hydrated oxide, CuO·H₂O or Cu(OH)₂, rather than the anhydrous oxide, CuO, is involved; the possible involvement of soluble products (e.g., cuprite (CuO₂²⁻) or cuprate (CuO₂⁻)) is ignored here. The relevance of this type of conventional thermodynamic data, which is valid for the bulk phase material, to surface processes such as heterogeneous catalysis and electrocatalysis is debatable. Surface metal atoms, especially those present at active sites, are considerably different – especially from a thermodynamic viewpoint – from their bulk lattice equivalents as they lack much of the normal lattice stabilisation energy (they generally lack bulk phase neighbours on at least one side). Evidence for the unusual behaviour of surface atoms has been available for quite a long while. For example, in his classical account of the role of active sites in surface catalysis, Taylor [8] mentioned the work of Blench and Garner [9] who had reported that at high temperatures and low coverages the heat of adsorption of oxygen on charcoal exceeded the heat of formation of carbon dioxide by a factor of approximately 2.3. This remarkable result was

rationalized on the basis that the oxygen from the gas phase reacts initially with low coordination state (or semigaseous) carbon atoms present at the charcoal surface. The lattice energy of carbon is particularly large and its absence greatly enhances the oxidation energy of 'semigaseous' surface carbon atoms.

The concept outlined above, that some surface atoms (those of very low coordination number) are in an unusually reactive state, due to a substantial lack of lattice stabilisation energy, and, consequently, tend to undergo oxidation at unusually low potentials, is the basis of the 'incipient hydrous oxide/adatom mediator' (IHOAM) model [10, 11] of noble metal electrocatalysis. Another point made by Taylor [8], which is also embodied in the IHOAM model, is that surface atoms which are outside the normal crystal lattice are capable of coordinating several reactant species. This is the basis of the assumption (implicit in the IHOAM approach) that the processes involved in monolayer and premonolayer oxidation phenomena are somewhat different. In the former case the couple involved is $M/M(OH)_x$ or $M/MO_{x/2}$, that is, a largely anhydrous or compact oxide or hydroxide is involved, whereas in the latter the protruding metal atoms involved (M^*) are much more active and the product may contain several coordinated OH and OH_2 species, i.e. the couple in question may be represented as $M^*/M(OH)_y(H_2O)_z$. Essentially there are two types of electrochemical behaviour involved, one occurring at high coordination and the other at low coordination surface metal atoms sites. Direct evidence for two different types of hydroxy species, one generated in the premonolayer oxide region and the other at the start of the regular monolayer oxide region, has been reported, on the basis of 'surface enhanced Raman spectroscopy' (SERS) data, by Desilvestro and Weaver [12] for gold in base.

In the present project the redox and electrocatalytic behaviour of copper in base was examined in the light of the above approach. It was established that premonolayer redox processes occur with this electrode system, an unusual (and previously unreported) redox response for copper was observed, and the results obtained indicate that such behaviour provides the basis of an explanation of the electrocatalytic activity of this metal. Quite close similarities were noted between the behaviour of copper and the more noble metals, platinum and gold, in terms of unusual surface redox and related reactions in aqueous media.

2. Experimental details

Both the working and counter electrodes consisted of lengths of copper wire (1.0 mm dia., ~1.8 cm exposed length, Goodfellow, high purity (>99.99%)) sealed directly into soda glass. The working electrode was usually pretreated before use by a brief (10 s) immersion in 0.5 M HNO_3 followed by a wash with triply distilled water. The potential of the working electrode was

recorded (and is reported) with respect to a reversible hydrogen electrode ($P_{H_2} = 1.0$ atm) in the same solution; a Luggin capillary was used to minimize errors due to solution iR drop.

Solutions were made up using Analar grade chemicals and triply distilled water, and were purged of oxygen gas (and stirred) with a flow of purified nitrogen (or, where necessary, CO_2) gas; the work was carried out at a cell temperature at 60 °C. Potential control was achieved using a Wenking (model LB-95) potentiostat, programmed using a Wenking (model MVS 87) voltage scanner, and responses were recorded using a Rikadenki (model RW-21) X-Y recorder. All the voltammograms shown here are original recorder responses; these were transferred to a computer with the aid of a scanner (model Microtek ScanMaker IIXE).

3. Results

3.1. Cyclic voltammetry behaviour of copper in base

Three typical cyclic voltammograms, recorded at different sweep rates for the same copper electrode in base, are shown in Figure 1. In part (a) of this diagram the sweep rate was quite slow (2 mV s^{-1}), oxidation of the

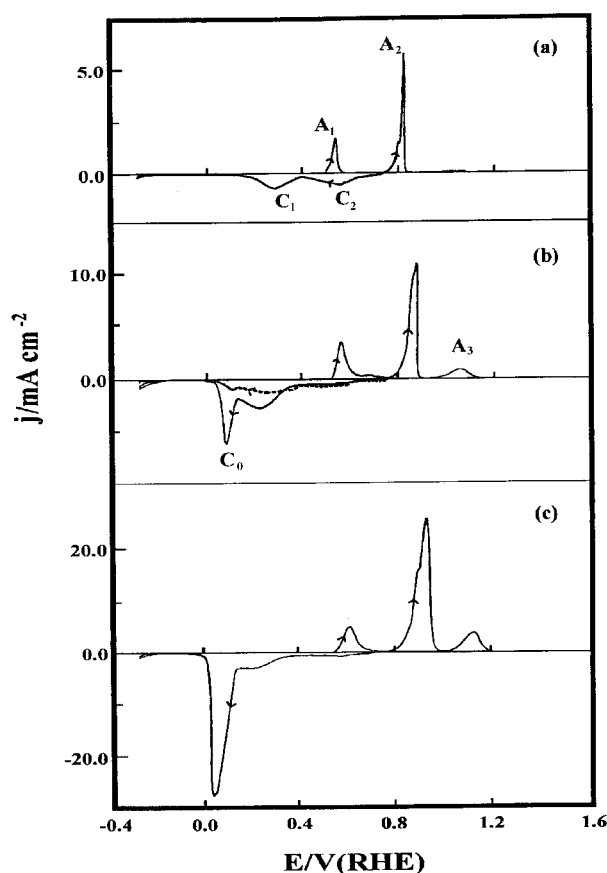


Fig. 1. Typical cyclic voltammograms (-0.3 to 1.6 V) for a polycrystalline copper electrode in 1.0 M NaOH at 60 °C: (a) 2 mV s^{-1} ; (b) 5 mV s^{-1} (only the negative sweep is shown), (—) 10 mV s^{-1} ; (c) 40 mV s^{-1} .

surface commenced at ~ 0.48 V and there was a second increase in anodic current commencing at ~ 0.72 V. The potential maxima (E_p) for the two main peaks in this case were 0.53 V for A_1 and 0.82 V for A_2 . There were shoulders on the negative side of both peaks (this is more evident in the case of A_2) and a minor flow of anodic current in the region above A_2 (from about 0.83 to 1.05 V, this response is more obvious in part (b)).

Two cathodic peaks appeared in the subsequent negative sweep, Figure 1(a), the E_p values being about 0.55 and 0.28 V, respectively. The overall behaviour observed here is relatively simple, and is rather similar to that observed with silver [13] under the same type of conditions. The two sets of peaks A_1/C_1 and A_2/C_2 correspond to formation and reduction of Cu(I) and Cu(II) oxides or hydroxides, respectively; there is (as is usual for this type of reaction) significant hysteresis and the shoulders on the positive peaks may be attributed to slight variations in the nature of the product, for example, the latter may contain a mixture of oxides and hydroxides.

A significantly more complex response for this system was observed on increasing the sweep rate, Figure 1(b). On the positive sweep two additional – but relatively minor – peaks, one at ~ 0.65 V and the other at ~ 1.03 V, may be noted. However the changes on the negative sweep were more dramatic; peak C_2 was absent, the potential maximum of C_1 (0.19 V) was considerably lower than in Figure 1(a) and a new feature, peak C_0 , $E_p \approx 0.06$ V, emerged. The dashed line in Figure 1(b) shows the behaviour (in this case only the negative sweep is shown) at an intermediate sweep rate; the cathodic charge is spread in an ill-defined manner over the range 0.6–0.0 V. Finally, at 40 mV s^{-1} , a trace of C_2 reappeared, Figure 1(c), while C_1 was only a shoulder on C_0 , the latter being the dominant feature on the negative sweep.

It appeared from Figure 1(a) that copper has a double layer region, devoid of faradaic responses over the region between hydrogen gas evolution (below about -0.3 V) and the onset of peak A_1 (at 0.48 V). However, the behaviour of a metal/solution interface (as pointed out earlier for gold [10, 11]) is rarely simple. This is demonstrated here by the cyclic voltammogram shown in Figure 2 where the appearance of a prepeak, A_0 ($E_p \approx 0.43$ V), may be noted; this feature was also observed in an earlier work [14]. Responses in the double layer were examined in greater detail by restricting the upper limit of the sweep to 0.5 V (the onset of peak A_1) and increasing the recorder sensitivity. As illustrated in the inset in Figure 2 an indication of a further set of peaks of very low magnitude ($E_p(\text{anodic}) \approx 0.22$ V; $E_p(\text{cathodic}) \approx 0.0$ V) appeared at lower potentials. A more pronounced version of these peaks in the double layer region was reported recently by Couto and Gutierrez [15]; the enhanced response was attributed by these authors to activation of the copper surface as a result of abrasive pretreatment. The anodic feature at ~ 0.4 V (peak A_0 in the main diagram) appeared in the inset in Figure 2 as a current increase

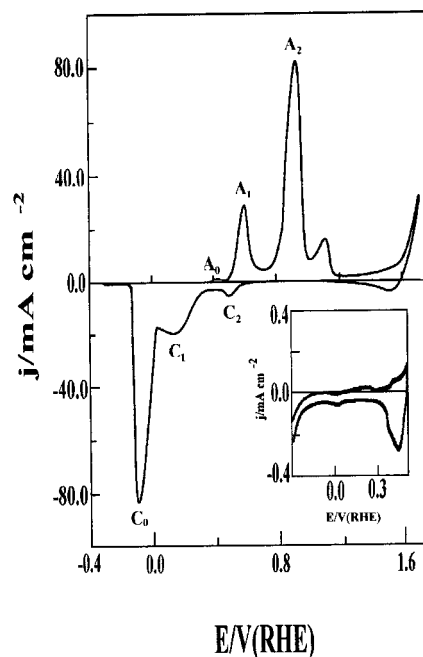


Fig. 2. Cyclic voltammogram (-0.3 to 1.6 V, 50 mV s^{-1}) for copper in 1.0 dm^{-3} NaOH; the inset shows the response for the double layer region (-0.3 to 0.5 V, 50 mV s^{-1}) with the recorder sensitivity increased by a factor of 10.

to a plateau, whereas its cathodic counterpart appeared as a relatively sharp peak.

A significantly different type of voltammetric response was observed for copper in base following activation of the metal surface. Examples of such behaviour are shown here in Figure 3; the electrode surface was activated in this case by potential cycling using a lower limit that extended well into the hydrogen gas evolution region. The responses recorded for the positive sweep were not dramatically different from those shown in Figure 1; the main changes were the increased peak currents in the case of A_2 and the appearance of a reversible response at 1.6 V, just prior to the onset of oxygen gas evolution, which is assumed to be associated with a Cu(II)/Cu(III) transition, probably in an oxide deposit on the electrode surface.

On the negative sweeps peaks C_2 , C_1 and C_0 appeared in the usual manner in the potential region below 0.6 V; in this case there was major overlap between C_1 and C_0 . However, the most unusual feature was the appearance of three cathodic peaks, C_{-1} , C_{-2} and C_{-3} at negative potentials which do not appear to have been reported earlier for this system. The observed peak maximum potentials were as follows: C_{-1} , -0.20 V (-0.27 V); C_{-2} , -0.47 V (-0.42 V); C_{-3} , -0.59 V (-0.60 V); the values in parentheses are those for the dashed line in Figure 2. These potential values are of no thermodynamic significance; the processes involved are clearly irreversible, there is no obvious anodic counterparts for peaks from C_{-1} to C_{-3} in the positive sweep. The unusual character of these three peaks was borne out by the variation of the charge values with electrode

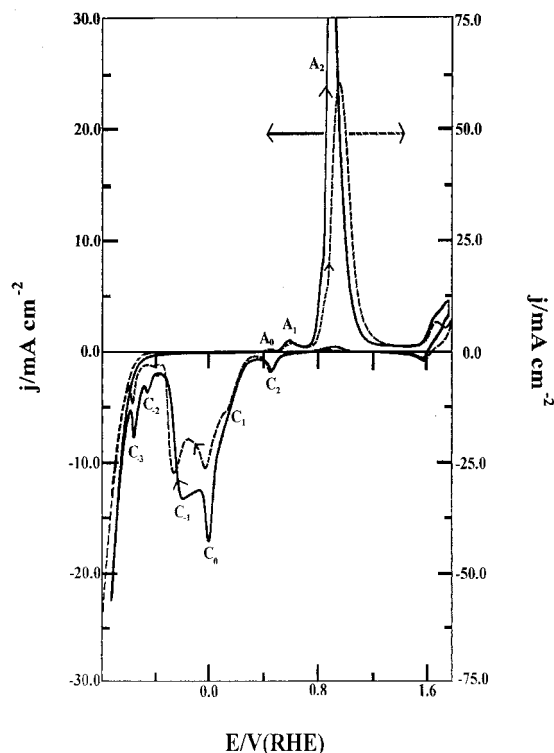


Fig. 3. Cyclic voltammograms, -0.8 to 1.75 V at 50 mV s^{-1} (---) and -0.7 to 1.75 V at 20 mV s^{-1} (—), for copper in 1.0 dm^{-3} NaOH at 60°C ; the electrode was activated by extended potential cycling (-0.7 to 1.9 V, 10 V s^{-1} , for 30 min) and the response at 50 mV s^{-1} was recorded prior to the one at 20 mV s^{-1} .

pretreatment. In the absence of cycling pretreatment all three peaks were absent in many occasions; however, the most unusual feature was the appearance of peak C_{-3} in some occasions; (as discussed later) even under conditions where peak C_0 was not observed.

3.2. Effect of surface activation on the redox response for copper in base

Oxidation–reduction cycling (sometime referred to as ORC pretreatment) is a common procedure used, for example, in surface enhanced Raman spectroscopy (SERS) [16, 17], to activate metal surfaces. The effect of such pretreatment on the nature of the oxide deposit produced at the copper/solution interface was investigated in the present case by subjecting the electrode to a brief period (2 min) of rapid (3.0 V s^{-1}) potential cycling between selected upper (E_u) and lower (E_l) potential limits, and then recording a negative sweep extending from 1.85 to -0.70 V at 50 mV s^{-1} .

In the first case E_l was maintained constant at -0.7 V and E_u was varied from 2.05 to -0.3 V. Typical examples of negative sweeps (commencing at 1.85 V) are shown in Figures 4 and 5. The main cathodic features noted were peaks C_2 , C_1 , C_0 and C_{-3} ; the responses, or the magnitude of the charge densities for these peaks, varied and a synopsis of data from a large number of experiments is given in Figure 6. The appearance of peak C_0 , Figure 6(a), was limited to

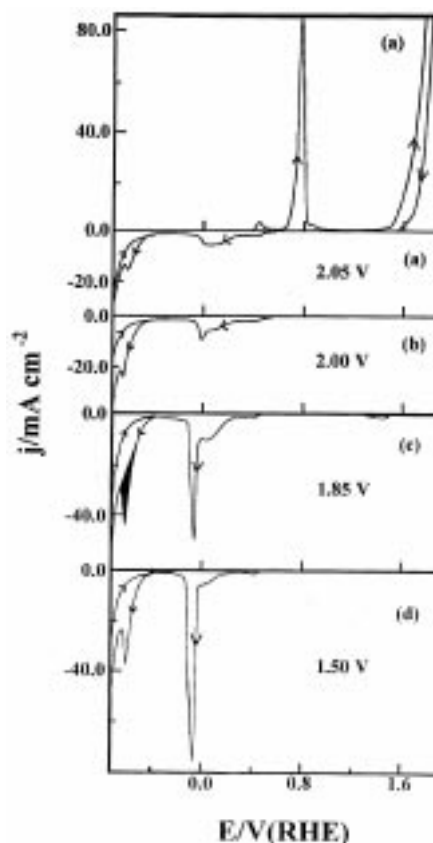


Fig. 4. Examples of negative sweeps (1.85 to -0.7 V, 50 mV s^{-1}) for copper in 1.0 M NaOH at 60°C . Prior to each sweep the electrode was activated by potential cycling (3.0 V s^{-1} for 2 min) using a fixed lower limit (E_l) of -0.7 V and various upper limits (E_u); values for E_u are given in the diagram. The subsequent positive sweep was usually also recorded, see (a); the procedure used for estimating the charge associated with C_{-3} is outlined in (c); only the darkened area was taken into account.

0.8 V $< E_u < 2.0$ V (the charge value for C_0 was virtually constant over this range). The magnitude of all peaks, with the exception of C_{-3} (which was generally quite small), decreased sharply, especially in the cases of C_0 and C_1 , at $E_u > 1.85$ V, that is, in the region associated with vigorous oxygen gas evolution. As E_u decreased below 0.9 V the magnitude of C_0 decreased while that of C_1 and, to a lesser extent, C_2 increased (the E_u value involved here corresponds approximately to that of peak A_2 , see Figure 2). The magnitude of peaks C_2 and C_1 decreased again, Figure 6(b), as E_u was reduced below 0.5 V, that is, below the region associated with peak A_1 . The minimum value for peak C_2 was observed for $E_u < -0.1$ V. Peak C_{-3} was invariably rather small especially at E_u values from 0.5 to 0.75 V. The maximum in the charge value for C_{-3} in Figure 6(b) is curious; it occurs at $E_u \approx 0.25$ V and, as pointed out here earlier in connection with the inset in Figure 2, this value coincides with the maximum an ill-defined premonolayer oxidation peak for copper in base.

Examples of the effect of the lower limit (E_l) of the activation sweep on the voltammetric reduction profile for copper in base are shown in Figure 7. Peak C_{-3} , at

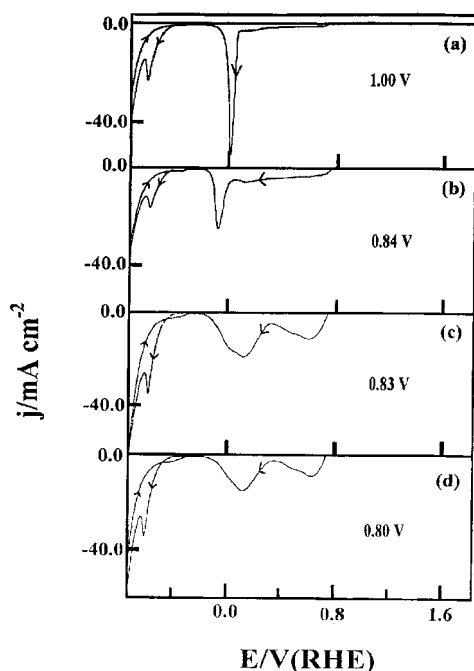


Fig. 5. Further examples of negative sweeps for activated copper electrodes (conditions similar to Figure 4) illustrating the change in response; for example, the loss of peak C_0 , as E_u was dropped below ~ 0.85 V.

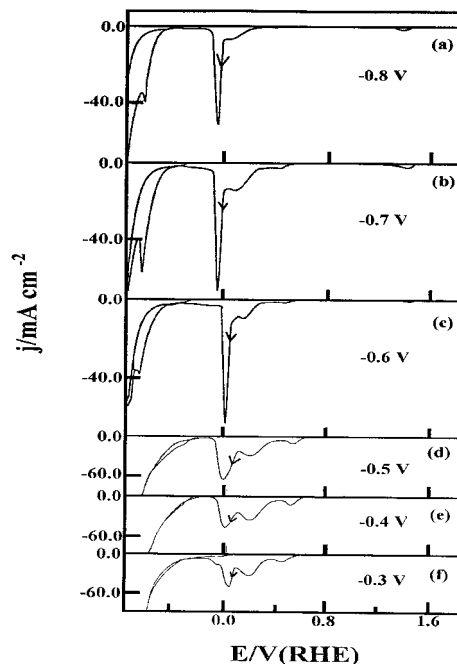


Fig. 7. Negative sweeps (1.85 to -0.7 V, 50 mV s^{-1}) for activated copper electrodes in 1.0 M NaOH at 60°C . The activation procedure involved was similar to that described in Figure 4 except that here E_u was constant at 1.85 V and E_l was varied (the E_l values are given in the diagram).

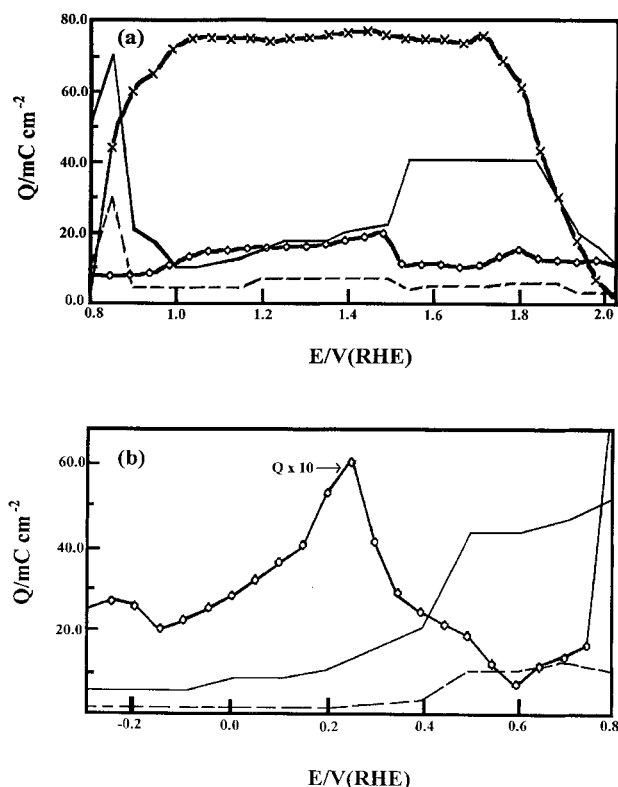


Fig. 6. Summary of the effect of the upper limit (E_u) used in the cycling pretreatment ($U_l = -0.7$ V) on the charge density values for the various reduction peaks: (\times) C_0 ; (\diamond), C_{-3} ; (—) C_1 ; (---) C_2 . Data was taken from the type of sweeps shown here in Figures 4 and 5.

about -0.6 V, only appeared with $E_l \leq -0.6$ V. Also, with $E_l > -0.6$ V the onset of hydrogen gas evolution seemed to commence in the negative sweep at more

positive potentials, while there was a change in the character of peaks $C_2 \rightarrow C_0$. For example, in Figure 7(a) C_0 was quite sharp, C_1 was quite small (and overlapped with C_0) while C_2 was not observed; however, with $E_l \geq -0.6$ V, Figure 7(c)–(f), these three peaks were clearly evident and C_0 was relatively broad.

The responses in Figures 4, 5 and 7 show not only the first negative sweep but also the lower end of the subsequent positive sweep. In several instances, for example, Figures 5(d) and 7(c), the cathodic current in the region above -0.7 V did not decrease regularly to zero with increasing positive potential (as is invariably the case with unactivated (i.e., uncycled) copper). Instead it dropped to a plateau value; the decay of the residual low level cathodic response, at about -0.2 V, was in several instances quite sharp. In virtually all cases in the negative sweeps the cathodic response for peak C_0 terminated below 0.0 V (typically at about -0.1 V). Attention is focussed here on this region of the voltammetric response for copper in base because, as outlined later, a crucial change in the electrocatalytic properties of copper in base occurs just below 0.0 V.

3.3. Evidence for enhanced premonolayer oxidation of copper in base

One of the main problems in the study of premonolayer oxidation phenomena occurring at metal/aqueous solution interfaces is that since the metal atoms involved are in a state of unusually high activity the coverage involved, and hence the voltammetric responses (usually in the double layer region), are unusually small and

frequently ill-defined. However, a procedure that yielded much larger (or enhanced) premonolayer oxidation responses was discovered, quite serendipitously, during course of the present work. If a copper electrode was subjected to repeated oxide growth and reduction work, (e.g., for one day) and then allowed to rest overnight in aqueous solution or distilled water the first voltammogram recorded on the following day, Figure 8(a), was quite unusual.

Peaks A_1 and A_2 are totally absent in this response; however, they reappeared on the second cycle, Figure 8(b). There was a slight increase in anodic current above 0.68 V in the first positive sweep, but the major feature in the latter was an anodic peak at low potentials ($E_p = -0.05$). In the subsequent negative sweep there was a small peak at ~ 0.5 V, a current plateau from 0.4 to 0.1 V and a shoulder at ~ 0.0 V. However, the main feature in this negative sweep was the cathodic peak at low potentials ($E_p = -0.1$ V). This response shown in Figure 8(a) is very unusual for several reasons: (i) the total anodic charge is much less than the total cathodic charge (this imbalance is particularly obvious in the case of the two peaks below 0.0 V); (ii) the conventional behaviour of copper (e.g., the two major features, A_1/C_1 and A_2/C_2) is strongly suppressed; (iii) although the behaviour reverted virtually to normal in the second sweep, the cathodic peak at about -0.1 V was still evident in the negative sweep.

A further example of the type of behaviour outlined in Figure 8(a) is shown in Figure 9(a). The main difference

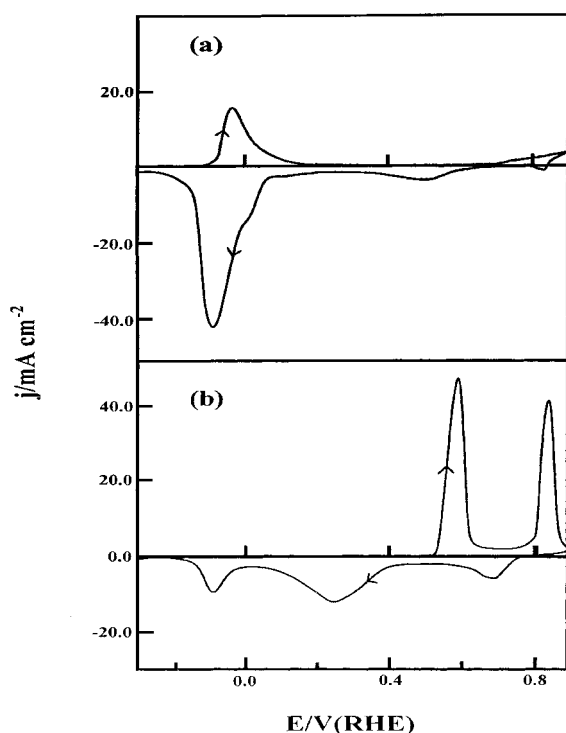


Fig. 8. First (a) and second (b) cyclic voltammograms (-0.3 to 0.9 V, 10 mV s^{-1}) for an active copper electrode in 1.0 M NaOH at 60°C . This electrode had been extensively cycled during the course of the experiments summarized here in Figures 4 and 5, and was then allowed to rest overnight in triply distilled water.

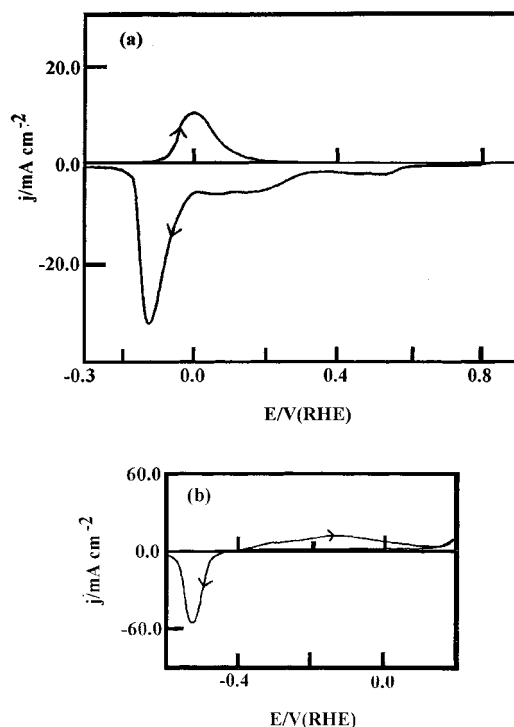


Fig. 9. (a) Cyclic voltammogram (-0.3 to 0.9 V, 2 mV s^{-1}) for a copper electrode in 1.0 M NaOH at 60°C . This electrode was first polarized in the base at 0.0 V for 3.0 h and then allowed to rest overnight in triply distilled water. (b) Cyclic voltammogram (-0.6 to 0.2 V, 2 mV s^{-1}) for copper in 1.0 M NaOH at 60°C . The electrode was activated beforehand by potential cycling (-0.7 to 1.60 V, 80 V s^{-1} for 30 min) in the same solution; no prolonged rest period was allowed in this case.

in this case was that the copper electrode was polarized at 0.0 V for 3.0 h during the previous day. After it had been allowed to rest overnight, the regular response for copper in base was totally absent in the first positive sweep, significant charge imbalance is evident, but the second cycle was virtually normal (i.e., similar to that shown in Figure 8(b)). A further example of unusual behaviour for copper in base is illustrated in Figure 9(b). In this case the surface was activated by extensive rapid potential cycling but was not allowed to rest before recording the cyclic voltammogram. The unusual feature in this case is the appearance of a cathodic peak on the negative sweep at about -0.53 V, that is, close to that for peak C_{-3} (the E_p value for the latter tended to be somewhat variable). The other interesting feature in Figure 9(b) is that the anodic and cathodic charges were virtually equivalent, the main difference being that the anodic charge in the positive sweep is spread over a wide range (from -0.4 to 0.1 V) of potential values.

3.4. Electrocatalytic behaviour of copper in base

Aldehydes are commonly used as reducing agents in electroless copper plating baths [2, 3] and generally these compounds may be oxidized or reduced to the corresponding organic acid and alcohol, respectively. The

response for a copper electrode in an alkaline solution containing a non-volatile aldehyde, glyoxylate anions ($\text{CHO}\cdot\text{COO}^-$), is shown in Figure 10(a). Two regions of activity were noted: (i) above ~ 1.0 V there was a significant increase in anodic current, apparently due to the action of a Cu(III) mediator; (ii) the region about -0.1 V was also interesting (this response at low potentials is shown more clearly in Figure 11). Above -0.1 V the aldehyde was oxidized, whereas below -0.1 V it was reduced under the conditions involved here. This behaviour at low potentials seemed to be specific to copper, that is, it reflects the electrocatalytic activity of copper in base as quite different responses were observed, Figure 10(b), for Pt and Ni electrodes under similar conditions. It may be noted that very little activity (especially in the negative sweep) was noted over the range 0.45–1.0 V, Figure 10(a); the formation of the regular Cu(I) or Cu(II) oxide coatings on copper results in deactivation of the surface.

Responses for copper in CO_2 -saturated NaOH, Figure 12(a), and NaHCO_3 , Figure 12(b), solution were also recorded. In both cases peak C_0 was clearly evident in the negative sweep (this peak was absent in the presence of glyoxylate, Figure 10(a), the aldehyde evidently reduced the oxide material involved). The cathodic responses involve at low potentials, especially in the negative sweep, were quite large, but they only became significant below ~ -0.35 V. Further work on the electrochemical behaviour of copper in CO_2 -saturated solutions is currently in progress and details will be published later.

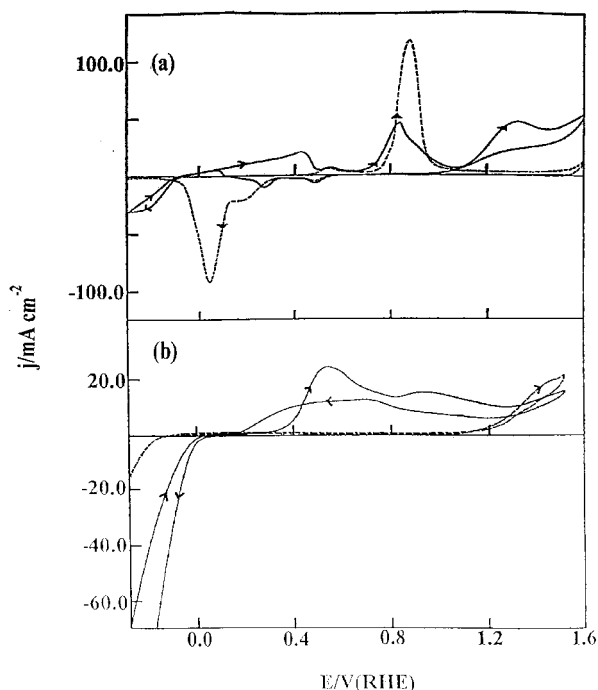


Fig. 10. (a) Typical cyclic voltammograms (-0.3 to 1.6 V, 50 mV s^{-1}) for copper in 1.0 M NaOH at 60 °C before (---) and after (—) addition of glyoxylate ($\text{CHO}\cdot\text{COO}^-$), to a final concentration of 0.2 M. (b) Cyclic voltammograms, as in (a), for platinum (—) and nickel (---) in the glyoxylate (0.2 M) containing base at 60 °C.

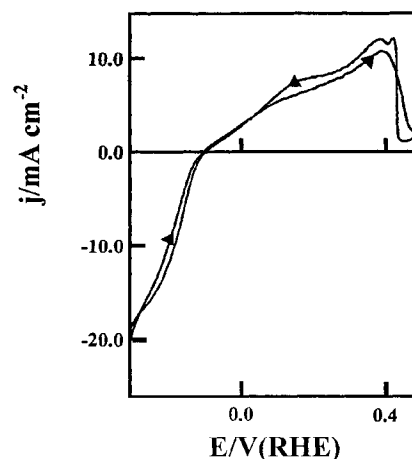


Fig. 11. Response (-0.3 to 0.5 V, 25 mV s^{-1}) for the reaction of glyoxylate on copper (conditions similar to those outlined in Figure 11). Note the switch from reduction to oxidation in the positive sweep (and vice versa on the negative sweep) at about -0.1 V.

4. Discussion

The response outlined for copper in base in Figure 1(a) was discussed earlier [14]. Peaks A_1 and C_1 were attributed to the Cu/Cu₂O couple, Equation 1, whereas peaks A_2 and C_2 are assumed to be due to a combination of the Cu/CuO and Cu₂O/CuO couples, Equations 2 and 3. The agreement between the potential regions for peaks A_1 and A_2 and the thermodynamically

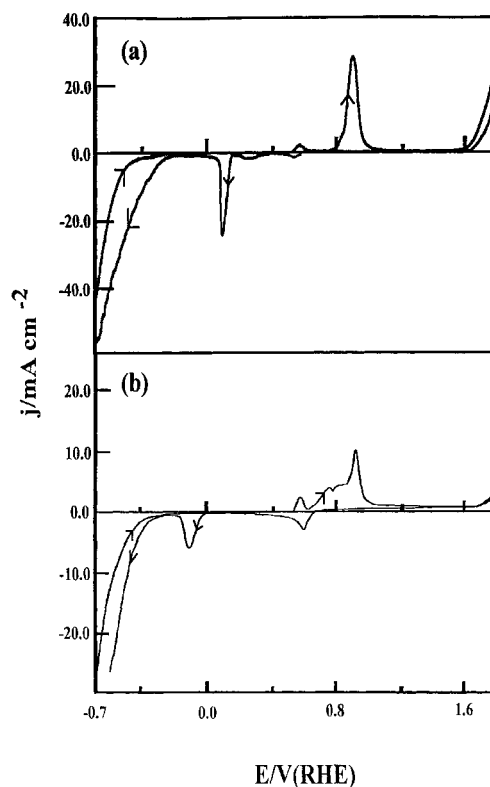


Fig. 12. Cyclic voltammograms (-0.7 to 1.85 V, 50 mV s^{-1}) for copper in CO_2 -saturated solution at 60 °C: (a) 1.0 M NaOH; (b) 1.0 M NaHCO_3 .

estimated values [7] for these transitions, which are quoted here in Equations 1–3, is reasonable. There are various complications involved; for example, Cu_2O is a poor electron conductor [14], the metal atoms involved are surface species (i.e., they are not fully lattice stabilised) and the anodic deposit may be a mixture of anhydrous and hydrated oxide, together with hydroxide.

As pointed out recently for gold [18], the participation of the hydroxy radical (an extremely energetic, high energy, species) in surface oxidation at relatively low potentials is unlikely. An alternative scheme is proposed here for Cu_2O formation (it may be extended easily to the case of CuO generation), namely,



Surface copper atoms are assumed to undergo oxidation and OH^- ions coordinate to the resulting cation sites; the product may react further to yield a polar covalently bonded oxyspecies. Repulsion between adjacent surface dipoles is assumed to induce place-exchange [19], resulting in a substantial increase in stability of the oxide deposit, and hence (as discussed for platinum [19] and other noble metals [18]) the appearance of hysteresis phenomena.

The virtual disappearance of peak C_2 and emergence of peak C_0 , with increasing sweep rate (Figure 1), was assumed earlier [14] to be due to the formation of a poorly conducting Cu_2O layer between the CuO deposit and the metal surface at an early stage of CuO reduction (peak C_2). This may still be a valid view but the presence of Cu_2O may not be the sole factor involved in the emergence of peak C_0 , Figure 1(c), as in some instances, for example, Figures 8(a) and 9(b), the peak at 0.0 V (or lower) was virtually the sole feature in the negative sweep. It appears that, as discussed recently for gold [20], cathodic peaks at unusually low potentials are a common feature of hydrous oxide film reduction processes. The effect has been attributed to the discharge of metal atoms, from these rather dispersed oxide deposits, at the interface in an initially highly active state. The oxide reacting in the C_0 regions, for example, in Figure 1(c), is assumed to be in the Cu(II) state initially. However, at the low potentials where C_0 appears there may well also be a Cu(I) involvement, possibly due to the following type of disproportionation reaction. That is,



Cu^* is assumed to be an active (or poorly lattice stabilised) surface copper atom.

The presence of the minor anodic premonolayer peak, A_0 in Figure 2, was pointed out earlier [14] and its existence was demonstrated again recently in the work of Marichev [21]. More interesting from an electrocatalytic viewpoint is the very low level response (below 0.3 V) in the inset in Figure 2. More pronounced

examples of redox peaks at these low potentials are shown here in Figures 8(a) and 9(a), and again there is independent evidence [15] for the existence of such unusual responses for copper in base. In fact evidence for premonolayer redox responses is now quite widespread, especially for the group 11 metals, and will be briefly summarized here for silver and copper (the premonolayer oxidation behaviour of gold in aqueous media was discussed in some detail recently [18]).

Direct evidence for the presence of hydroxy species on copper [16], silver [22] and gold [12] in base at low potentials has been obtained using SERS. The presence of surface hydroxide species was established by isomer shift experiments, that is, by changing the solvent from H_2O to D_2O . Using this approach with copper, Doblhofer and coworkers [16] eliminated the possible involvement of an adsorbed hydrogen species in the redox behaviour at low potentials. They also demonstrated that after ORC pretreatment the loss of the surface OH response occurred only on applying a potential more negative than -0.4 V vs RHE, that is, in the region associated with peaks C_{-2} and C_{-3} in Figure 3, or the peak on the negative sweep in Figure 9(b).

Essentially what is suggested here is that with real metal surfaces there are nonequilibrium active states which may be viewed as minute clusters that are attached to, or partially embedded in, the surface (a metal atom, or several of same, at a surface defect site may be involved; it is assumed that an important requirement for such active atoms is a state of low lattice coordination). It is difficult to control the type or occupancy of such states; the number of possible arrangements is virtually limitless and, for a polycrystalline sample, the surface state will be strongly influenced by sample history or pretreatment. The decrease in redox potential with decreasing metal cluster size is quite well established [24], but what is quite fascinating about this area is that certain premonolayer potential or energy values seem to be highly populated, e.g. with silver in base [22, 23] there is often a marked reversible response at ~ 0.3 V (such behaviour, which to date has received little attention, may reflect the unusual stability of ‘magic number’ cluster agglomeration numbers as outlined by Henglein [24]). With regard to premonolayer oxidation of copper in base it is interesting to note that Marichev [21], on the basis of ‘contact electrical resistance’ (CER) data, claimed that this reaction commenced at about -0.4 V vs RHE. Although this may appear to be an unusually low value, his conclusion is supported by the voltammetric response shown here in Figure 9(b) where the onset of anodic current in the positive sweep also commenced at about the same potential. The CER technique seems to be particularly sensitive to premonolayer oxidation phenomena because tips of protrusions are likely to contain active copper atoms, hence be most prone to exhibit premonolayer oxidation effects, and dominate the electrical resistance between the surfaces when two similar electrodes are brought into contact in CER experiments [21].

With regard to the cathodic peaks at low potentials (i.e., below the peak C_1 region, Figure 3) the appearance of C_0 and C_{-3} was quite common while C_{-1} and C_{-2} were rarely observed. The presence of these different peaks is attributed largely to the formation, in the reduction sweeps, of different states (or cluster sizes) of copper. Usually these states are unstable, the active atoms involved become incorporated into the regular surface (probably due to migration to ledge sites), so that – with a few exceptions, for example, Figure 9 – significant premonolayer oxidation peaks were not observed in the positive sweep.

The effect of rapid potential cycling on the subsequent responses for oxide film reduction on copper in base, Figures 4–7, is assumed to be due to the activation effect of such pretreatment on the metal surface. During the positive sweep, especially with a high upper limit value, the oxidation of the surface is assumed to be accompanied by place-exchange, so that on reduction on the negative sweep some metal atoms are redeposited in an active, poorly-lattice-stabilised form. Repetition of this process leads to significant accumulation of active copper on the surface. When the upper limit used in activation exceeds 0.8 V (and especially 1.0 V), Figure 6(a), a major C_0 response was observed for the subsequently grown oxide deposit. The C_0 peak is assumed to be due to reduction of a hydrous oxide deposit and the precursor of this material is assumed to be an outer layer of active copper atoms. To generate the latter the upper limit in the activation process must be such that a substantial coverage of Cu(II) oxide is produced, i.e. the process associated with peak A_2 must go virtually to completion on the positive sweep if a maximum C_0 response is to appear in the subsequent oxide reduction sweep. An interesting feature shown on the left hand side of Figure 6(a) is that the reduction in the response for C_0 is accompanied by a major increase in C_1 , and, to a lesser extent, C_2 response. This suggests that the material involved in peak C_0 is significantly different from that involved in peaks C_1 and C_2 . It is assumed that the material associated with peak C_0 is more extensively hydrated. Further complications are evident on the right hand side of Figure 6(a). The decay in the response for C_0 at $E_u > 1.7$ V and the complex nature of the C_2 response may reflect changes in the surface oxide deposit formed at high potentials due to (i) generation of Cu(III) species in the oxide layer, (ii) oxygen gas evolution (above ~ 1.6 V), and (iii) oxide dissolution (e.g., as cuprate species). The net result is that the amount of active copper (or its oxide precursor) formed on cycling (and hence the associated C_0 response) decreases dramatically when E_u is raised above 1.7 V.

Decreasing the upper limit used in activation to values below ~ 0.85 V results in a significant drop in response for C_2 , C_1 and even C_{-3} (this drop for the latter is shown on the right hand side of Figure 6(b)). A further drop, for both C_2 and C_1 , is observed, Figure 6(b), as E_u is reduced below 0.5 V, into the region where Cu_2O , or

peak A_1 , is not involved in the activation procedure. Clearly, to activate the metal with respect to oxidation, using a potential cycling procedure, it is important to ensure that the limits are such that repetitive growth and reduction of oxide deposits (but not dissolution of the latter) are involved.

The appearance of peak C_{-3} at such a low potential, about -0.6 V, was quite unexpected (this feature, to our knowledge, has not been reported earlier). Usually, it is not observed with a fresh electrode, but it appears after cycling the potential a few times with the lower limit (Figure 7) $E_l \leq -0.6$ V approximately. The upper limit seems to make little difference to the appearance of this peak, Figure 6, but it has an influence on the charge value. The potential for the maximum (~ 0.25 V) for the charge associated with C_{-3} , for low values of E_u , Figure 6(b), corresponds approximately with that for the maximum of the small anodic peak in the double layer region, inset in Figure 2, for this electrode system. Possibly repetitive redox transitions of initially rather active copper atoms promote the latter to an even more active state.

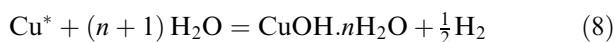
An obvious question as to the origin of peak C_{-3} is the possible role of an impurity. This is considered as unlikely as it is possible to observe C_{-3} on the very first cycle with a fresh copper electrode that received no pretreatment in solution. All that is required in this case is to melt the exposed wire, allow the resulting bead to cool rapidly in air and etch the surface to remove oxide. Rapid cooling of the hot wire evidently results in the freezing of an appropriate microstructure that results in a marked C_{-3} response in the very first voltammetric cycle (the response in question was similar to that shown in Figure 4(a)). Cathodic responses at unusually low potentials are not confined to copper; it was demonstrated recently [20] that with gold in acid an oxide reduction peak may be observed at ~ 0.6 V, even though monolayer oxide formation for the electrode system in question usually only commences at ~ 1.36 V. Again it was assumed that these unusually low reduction potential values (which are not of thermodynamic significance) were determined mainly by the unusually active, nonequilibrium, state of the initial reduction product. It appears from the effect of the lower limit of the activation cycle, Figure 7, that in order to observe peak C_{-3} the lower limit must be such that the oxidised state involved in this response must be reduced during the course of the activation cycle. Repeated oxidation and reduction of the sites involved (combined perhaps with hydrogen embrittlement effects) promotes formation of the more active copper atom state – hence enhancing the response at -0.6 V. Oxidation of the highly active surface state seems to have an inhibiting effect on the hydrogen gas evolution process at about -0.4 V (when C_{-3} is large, e.g. Figure 7(a), the hydrogen evolution response at the latter value is low; the opposite behaviour is evident in Figure 7(e)).

Rather large reversible redox responses were observed (independent of the present work) for copper in aqueous

phosphate buffer solution (pH 6.9), following severe abrasion of the electrode surface [15], at potentials, ~ 0.15 V vs RHE, that are well within the double layer region of this system. Such observations are interesting as they establish (along with the SERS and CER data mentioned here earlier) the existence of an active state of the electrode surface even when the latter is in the reduced state. This topic, nonequilibrium states of metal surfaces, was discussed by Taylor [8] as early as 1925 in relation to the behaviour of active sites which are of major importance in terms of both heterogeneous and interfacial catalysis.

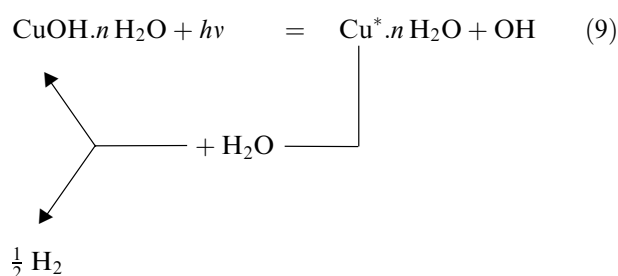
Responses similar to those of Couto and Gutierrez [15] are shown here in Figures 8(a) and 9. In some of these cases electrodes whose surfaces had been disturbed by potential cycling were allowed to rest overnight. It is assumed that the disturbed layer rearranged, resulting in loss of energy in the layer in general but accumulation of much of the residual energy in the outermost regions of the lattice. The loss of energy is easily explained; annealing of small particles (accompanied by loss of both surface area and surface energy), filling of lattice vacancies etc., would contribute to such behaviour. What is more difficult to understand (but apparently is not uncommon, the same type of effect was reported earlier for platinum [25]) is the retention of the outer layer of quite active copper. This active state response, Figure 8(a), was observed only on the first cycle; the second, Figure 8(b), resembled that of conventional copper.

The obvious discrepancy in charge values between the anodic and cathodic peaks at ~ 0.0 V in Figures 8(a) and 9(a) is very interesting. According to this result more copper oxide (of whatever form) is reduced in the negative sweep than is formed in the positive sweep. This may be explained by assuming that as the active copper layers rearranged on resting overnight very active metal atoms or clusters of same, Cu^* , were occasionally produced, which reacted with water in the following manner:



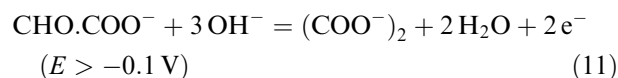
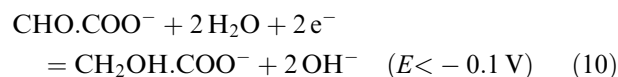
Since copper is less electropositive than hydrogen, the above reaction seems improbable. However, when present as extremely minute clusters, metal atoms tend to be extremely electropositive [24] and unusual redox behaviour is observed. Thus, in the positive sweep in Figure 8(a) the species present on the surface are probably a mixture of active copper trapped or preserved in a matrix of the hydrous oxide. The cathodic peak on the subsequent negative sweep is larger as all the surface oxide is reduced. This means that the stabilising influence of the hydrous oxide species is removed, the active state of copper decays rapidly and the second positive sweep exhibits, Figure 8(b), the usual anodic response for copper in base. Another example of an unusual response attributable to the active state of surface copper atoms is that shown in

Figure 9(b). These are difficult systems to investigate because the states involved are ill-defined and variable; however, they appear to be important in heterogeneous catalysis, electrocatalysis and photocatalysis. For example, the virtually unique ability to split water using visible light using a Cu_2O photocatalyst [6] – apparently without significant loss of performance – may involve, in the hydrogen gas generation reaction, a photodriven cyclic redox version of the process shown here in Equation 8. A possible mechanism for the repetitive photoliberation of hydrogen from water in the presence of Cu(I) oxide may be represented as follows:



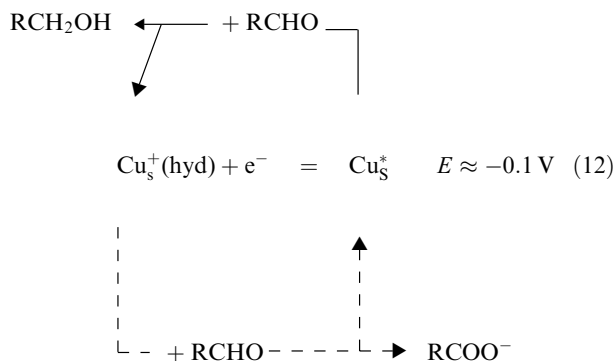
The OH radical is unlikely to be involved in this reaction as it is a very high energy species. Cu(III) and peroxy species are perhaps more likely candidates as intermediates in the oxygen gas evolution reaction under photocatalytic conditions.

With regard to the electrocatalytic behaviour of copper in base, the switch from reduction to oxidation (positive sweep) in the case of glyoxylate in base, Figure 11, may be interpreted in terms of the following reactions:



Since the responses involved here depend on the nature of the metal, Figure 10(b), they are clearly electrocatalytic in character. Furthermore, the critical potential involved, about -0.1 V, is not determined by the aldehyde as other species (e.g., nitrate and nitrite) commence reduction on copper in base at the same value (-0.1 V) on the negative sweep. The most likely interpretation of such behaviour is the involvement of an interfacial cyclic redox process based on active copper atoms (the Scheme 1 outlined here is indicative; it is not complete).

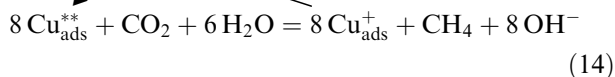
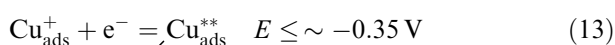
At $E < -0.1$ V the surface mediator is maintained in the reduced state (Cu^*) and the aldehyde is reduced to the alcohol (full line in Equation 12). At $E > -0.1$ V the surface mediator is maintained in the oxidised state ($\text{Cu}^+ \cdot n\text{H}_2\text{O}$) and the aldehyde is oxidized to the organic acid. The mediating species is assumed to be a low



Scheme 1

coverage, nonequilibrium, active state of copper which undergoes a rapid redox transition in the double layer region of this system. For this type of reaction the formation of the regular monolayer oxide (or Cu_2O) deposit above ~ 0.4 V results, as is commonly observed with noble metals [10, 11], in deactivation. Further aldehyde oxidation, above ~ 1.0 V (Figure 10(a)), is assumed to be associated with the intervention of a Cu(III) mediator, or a Cu(III)/Cu(II) couple; however this was not the potential region of major interest in the present work.

The presence of more than one type of mediator system, involving the same oxidation states, for the same metal was discussed earlier for both platinum [11] and gold [20]. The same type of phenomenon seems to arise here in the case of copper where different reduction peaks were observed at low potentials, Figure 3. It is assumed that whereas the mediator involved in aldehyde reduction is an active state (Cu^*) of copper, a second – even more active (Cu^{**}) – state is involved in the case of CO_2 reduction. This unusual state apparently exists in the unoxidized form only in the region below about -0.35 V and the type of redox cycle involved in CO_2 reduction may be represented as follows:



According to the approach outlined here the protruding, low coverage, highly active copper atoms are the vital centres at the interface for both reactant activation and electron transfer. It is quite significant that this unusually active state of copper is virtually unoccupied, or nonexistent, in a relaxed or conventional metal surface. It is clear also from the independent work of other authors [5, 26] that high activity for CO_2 reduction at copper cathodes is observed only below about -0.35 V vs RHE and one of the factors that may be involved in the generation of highly active copper atoms in this

region is interaction of surface metal atoms with cathodically produced atomic hydrogen.

Copper, like the other group 11 metals, does not apparently chemisorb hydrogen very strongly, e.g. there are no obvious hydrogen adsorption/desorption peaks in the cyclic voltammograms recorded for copper in base. However, all three group 11 metals display unusual catalytic and electrocatalytic activity, as demonstrated by the use of copper to reduce carbon dioxide in aqueous media to yield a variety of hydrocarbons [4, 5]. Subjecting the copper electrode to vigorous hydrogen evolution at the lower end of the metal activation sweep, Figure 7(a)–(c), activates the surface with respect to the subsequent C_{-3} response (which commences at about -0.4 V on the negative sweep). However, this surface activation apparently promotes premonolayer oxidation which in turn inhibits hydrogen gas evolution below 0.2 V (the same type of activation/deactivation behaviour by cathodically generated hydrogen was described recently for iron electrodes in base [27]).

One of the problems associated with the use of copper cathodes for CO_2 reduction is the decrease in efficiency for hydrocarbon production with time. This effect can be counteracted [5] by applying a number of rapid potential sweeps at 5 min intervals. This loss of activity was attributed recently, on the basis of SERS data [17], to the formation of a ‘cathodically generated oxide/hydroxide species’, rather than to the presence of a carbon-containing entity. What is remarkable here is that no oxide of copper is thermodynamically stable at these low potentials. The loss of activity may be due to a decrease in the coverage of the very active (Cu^{**}) state, that is, the loss of performance is not due to inhibition, but to a decrease in the coverage of the essential Cu^{**} interfacial mediator (the decay in activity of the latter is counteracted by the intermittent potential cycling). What is clear from the present work is that the electrochemistry involved in the case of copper surfaces in aqueous media at low potentials is quite complex and more attention needs to be devoted to the involvement of nonequilibrium, active, and rather transient states of metal surfaces, such states are well known in the semiconductor surface area [28].

5. Conclusions

The following remarks can now be stated:

- (i) In general terms the electrochemical behaviour of copper is similar to that of the much more noble metals, gold and platinum. Each of these has a monolayer oxide formation/reduction region which occurs at potentials that are not far removed from the values expected on the basis of conventional thermodynamic data. However, they all exhibit hydrous oxide reduction peaks that occur in the double layer region; in fact, in the case of both platinum [29] and copper (Figure 7) in base these

oxide reductions can overlap with the hydrogen gas evolution reaction. There is also increasing evidence (e.g., from SERS [12, 16, 22] and CER [21] data) that incipient oxidation of metal surfaces may commence, probably at active sites, at potentials that are much lower than the onset of the monolayer oxide reaction.

- (ii) To explain the origin of such behaviour it is necessary to assume the existence at the interface of nonequilibrium, active, and somewhat transient (or at least variable) surface species, which may be regarded as a prime component of active sites [8]. Such surface states, which are well known in the semiconductor area [28], have not received a great deal of attention in the case of metals. Yet the presence and behaviour of such species provides an excellent basis for rationalizing the electrocatalytic behaviour of metal electrodes.
- (iii) Copper in base exhibits three main regions of electrocatalytic activity: (i) above about 1.0 V where a Cu(III) mediator promotes oxidation; (ii) above and below about -0.1 V where oxidations and reductions, respectively, are mediated by a Cu/Cu(I) couple; (iii) $<$ about -0.35 V where an unusually active state of copper seems to be involved. Since the behaviour of copper and its oxides is important from a catalytic [1], electrocatalytic [4, 5] and photocatalytic [6] viewpoint, there is obviously a need for further work in this area. It is worth noting that in the commercial synthesis of methanol (from CO or CO₂ and H₂ gas) the surface of the copper catalyst is assumed [30] to be partially oxidized, i.e. the reaction at active sites is also assumed to involve Cu(O)/Cu(I) species.

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