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Redox and electrocatalytic activity of copper in base at unusually low, premonolayer potentials

Abstract The assumption involved in this work is that the formation of monolayer (α) oxide species, which occurs on copper in base at 60 °C at ca. 0.5 V (RHE), is of little relevance to the electrocatalytic behaviour of the metal at low potentials. For many processes occurring at the interface in question the critical potential is ca. −0.1 V (RHE). This is the value where several electrocatalytic oxidation and reduction processes commence or terminate under potential sweep conditions; hydrous oxide films are reduced close to this value and it is possible to produce an active (but transient) state of the metal surface which exhibits a reversible redox response in this region. The results are rationalized in terms of the incipient hydrous oxide/adatom mediator model of electrocatalysis, and the nature of the active site material at the interface is discussed.

Key words Copper · Electrocatalysis · Anomalous oxidation · Hydrous oxides · Mediation

Introduction

Much of the fundamental work in surface and interfacial science is carried out at the present time using smooth, ideally atomically flat, surfaces. However, in a recent review of this area, Somorjai [1] pointed out that the most active catalytic behaviour is observed with rough, highly defective surfaces which are extremely difficult to investigate using surface science techniques. The use of conventional electrochemical techniques in the study of rough surfaces has a number of significant advantages, e.g. they may be used to dramatically increase the roughness value (or activity) of electrode surfaces [2, 3] and monitor the resulting changes in both the redox and electrocatalytic properties in a rather simple – but highly sensitive – manner. The disadvantages of the electrochemical techniques are that they give very little direct information as to the structure, composition or state of charge of the important surface species involved in electrocatalytic processes. However, with regard to active site behaviour, these limitations are apparently not just confined to electrochemical techniques.

It has long been accepted, since the work of Taylor [4] in 1925, that catalysis at surfaces often occurs at highly localized regions of the surface known as active sites. While the nature and mode of operation of such sites is poorly understood, they are generally attributed to the presence of defects where protruding, low bulk coordination number, surface metal atoms (sometimes referred to as adatoms) exist. Taylor [4] referred to such atoms (in relation to heterogeneous catalysis) as being semi-gaseous; hence, the corresponding species in electrocatalysis may be regarded as being semi-aqueous. While the existence of metal atoms in such highly active, rather labile, states is difficult to confirm, it is worth noting that the involvement of single adatoms at active sites, is a basic assumption [5, 6] in the π-bond theory of heterogeneous catalysis.

In recent years a new interpretation of noble metal electrocatalysis was proposed in the authors' laboratory. This new approach, known as the incipient hydrous oxide/adatom mediator (IHOAM) model, is regarded as complementing, rather than displacing, the earlier activated chemisorption approach. Some of the basic assumptions in the IHOAM theory, which was discussed in some detail recently for gold, [7, 8] are as follows:

1. Electrocatalysis occurs mainly at active sites, i.e. at defects, which function as a source of high energy atoms, e.g. adatoms or clusters of same.
2. As metal clusters become extremely small their activity increases and redox potential decreases [9]; this effect is due to a combination of decreasing mean

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lattice coordination number, decreasing lattice stabilization energy and the onset of quantum confinement effects.

3. Two types of oxides are generated anodically at metal surfaces [10]. High coordination metal atoms yield the conventional (or α) monolayer oxide deposit, whose appearance is frequently accompanied by inhibition of electrocatalytic processes. Low coordination surface metal atoms appear to be oxidized in a different manner: the active atoms react at unusually low potentials in a process referred to as premonolayer oxidation and the product is assumed to be a hydrous oxide species.

4. The highly active surface metal atoms and their oxidation product, incipient hydrous oxides, act as the mediators in many reduction and oxidation reactions, respectively.

The work to date on the IHOAM model of electrocatalysis has been carried out mainly with the very noble metals, gold [7, 8] and platinum [11, 12]. The objective of the present investigation is to extend this approach to less noble metals such as copper: the latter has important applications both in heterogeneous catalysis [13] and in microelectronics [14], where copper films may be produced by electroless (or electrocatalytic) techniques.

The IHOAM model of electrocatalysis was based originally on the observation [15] that the onset/termination potentials for electrocatalytic processes (both oxidations and reductions) coincided rather closely with previously recorded potential maxima for multilayer hydrous oxide reduction processes. In fact there seems to be a general format for cyclic voltammetry responses in this area [8] which is outlined here in Fig. 1. Oxidation of 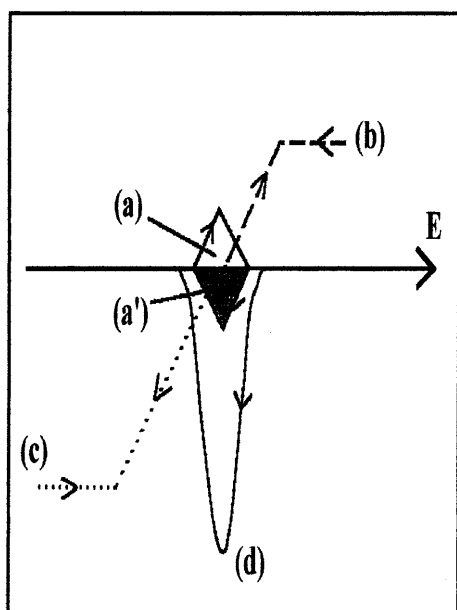low coverage active metal atoms at the interface gives rise to a small (frequently negligible) anodic response in the double layer region of the positive sweep: peak a. This response is greatly amplified, curve b, if there is a reductant present in solution which reacts vigorously with the incipient hydrous oxide mediator. The oxide mediator is reduced on the negative sweep, peak a', and the removal of the mediator leads to the loss of the anodic response for the catalytic oxidation process. However, if there is an oxidant in the solution, whose reduction is mediated by the metal adatoms, then an enhanced electrocatalytic cathodic response will be observed, curve c, at the lower end of the sweep. Peaks a and a' are often quite small and difficult to detect; however, the location of these peaks in the double layer (or in some instances in the adsorbed hydrogen) region may be identified in other ways, e.g. multilayer hydrous oxide films undergo reduction, peak d, at about the same potential [10] at which peaks a and a' appear. Furthermore, the changeover from electrocatalytic oxidation, curve b, to reduction, curve c, usually occurs in the same region. As outlined recently for platinum [12], there may be more than one type of mediator species or interfacial couple involved in the case of a particular metal.

The objective of the present investigation was to investigate the redox and electrocatalytic behaviour of copper in base and, in particular, to determine whether the results are in agreement with the IHOAM approach as summarized here in Fig. 1. It is a basic assumption in this work that polycrystalline metal surfaces are heterogeneous, and that the level of activity of surface atoms is variable. This is widely accepted in certain areas, e.g. in surface enhanced Raman spectroscopy (SERS) [17] it is usually necessary to activate metal surfaces prior to recording spectra by subjecting the electrode to some oxidation/reduction cycling, i.e. to ORC pretreatment, whose main function seems to be to perturb the metal surface by producing adatoms, etc.

Fig. 1 Diagram summarizing the essential features of the IHOAM model of electrocatalysis
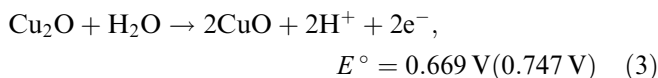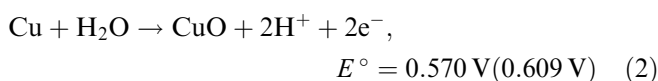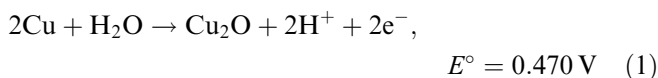
Experimental

Both the working and counter electrodes consisted of lengths of copper wire [1.0 mm diam., ca. 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 mol dm^{-3} 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; this reference electrode was in a separate compartment and 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 gas; the work was carried out at a cell temperature of 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).

Results

The conventional redox response for copper in base

A typical cyclic voltammogram for copper in base is shown in Fig. 2a. At the slow sweep rate involved in this case (2.0 mV s^{-1}), two peaks, A_1 and A_2, were observed in the positive sweep and a similar number, C_2 and C_1, in the negative sweep. The peak maximum potentials involved were ca. 0.53 V (A_1), 0.82 V (A_2), 0.55 V (C_2) and 0.28 V (C_1); there was a slight shoulder at the negative side of A_2. Pourbaix's data for copper [18], for reactions involving two solids (the $E°$ values here are in the RHE scale, and hence are pH independent), are as follows:

$$2Cu + H_2O \rightarrow Cu_2O + 2H^+ + 2e^-,$$
$$E° = 0.470\,V \quad (1)$$

$$Cu + H_2O \rightarrow CuO + 2H^+ + 2e^-,$$
$$E° = 0.570\,V (0.609\,V) \quad (2)$$

$$Cu_2O + H_2O \rightarrow 2CuO + 2H^+ + 2e^-,$$
$$E° = 0.669\,V (0.747\,V) \quad (3)$$

The values in parentheses relate to cases where the hydrated, $CuO \cdot H_2O$ or $Cu(OH)_2$, rather than anhydrous, CuO, oxide is involved. The agreement between Pourbaix's data (which refer to bulk phase material) for Eqs. 1 and 3 and the peak values for the positive sweep (which are assumed to relate mainly to high coordination surface atoms) is quite reasonable. Peak A_1 is assumed to be due to a Cu/Cu_2O reaction (Eq. 1).

Cu_2O deposit is a poor conductor [19, 20]; hence the Cu/CuO conversion is unlikely to occur until the Cu_2O layer is oxidize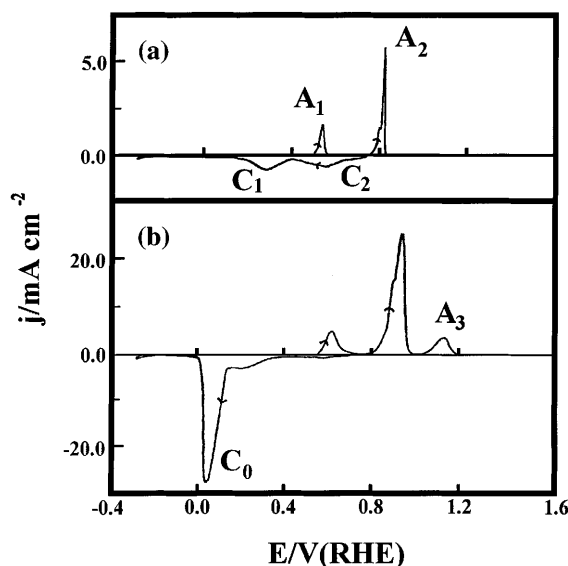d; the reaction of the monolayer Cu_2O deposit, Eq. 3, may be the origin of the prepeak or shoulder in the case of peak A_2. However, the process represented here by Eq. 2 is assumed to be the main reaction in the peak A_2 region. The two pairs of peaks, A_1/C_1 and A_2/C_2, exhibit the typical hysteresis observed for surface oxide formation/removal reactions; such behaviour has been discussed extensively by Conway [21].

Increasing the sweep rate, Fig. 2b, resulted in the appearance of additional features in the cyclic voltammogram for copper. In the positive sweep a new anodic peak, attributed to a Cu(II)/Cu(III) transition in the surface oxide layer, was observed at ca. 1.1 V. On the negative sweep the two cathodic peaks C_2 and C_1 were surprisingly small. It was suggested earlier [20] that as the reduction of the Cu(II) oxide commences at ca. 0.7 V, a layer of poorly conducting Cu_2O oxide is formed at the metal surface which inhibits further reduction of the remainder of the Cu(II) deposit. It is only when the reduction of this inner deposit of Cu_2O is close to completion that the remainder of the outer deposit of Cu(II) oxide undergoes reduction to yield peak C_0 in Fig. 2b. Evidently there was sufficient time for the CuO/Cu_2O transition to go to completion in the peak C_2 region at 2 mV s^{-1} (Fig. 2a).

Electrocatalytic behaviour of copper in base

It was demonstrated recently [22] that the glyoxylate anion, which is of potential interest as a reducing agent in electroless copper deposition baths, undergoes reduction below, and oxidation above, ca. -0.1 V at copper electrodes in base (Fig. 3). The assumption involved in this case is that there is an active state of copper (Cu*), present at very low coverage active sites, which can undergo the following type of interfacial reaction:
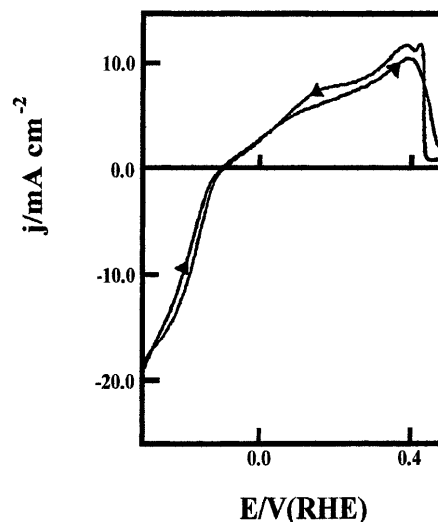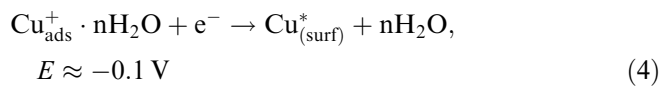

Fig. 2 Typical cyclic voltammograms (-0.3 to 1.6 V) for a polycrystalline copper electrode in 1.0 mol dm^{-3} NaOH at 60 °C: **a** 2 mV s^{-1} and **b** 40 mV s^{-1}

**Fig. 3** Response (-0.3 to 0.5 V, 25 mV s^{-1}) for the reaction of glyoxylate on copper in 1.0 mol dm^{-3} NaOH at 60 °C. Note the switch from reduction to oxidation in the positive sweep (and vice versa on the negative sweep) at -0.1 V

$$Cu^+_{ads} \cdot nH_2O + e^- \rightarrow Cu^*_{(surf)} + nH_2O,$$

$$E \approx -0.1 \text{ V} \tag{4}$$

The reduction of the aldehyde, at $E < -0.1$ V, is assumed to be mediated by Cu* according to the following scheme in which the aldehyde behaves as an oxidant:

$$2\,Cu^+_{ads}(hyd) \xrightarrow{\;i_{red}\;} 2\,Cu^*_{surf}$$

$$+RCHO + 2H_2O$$

$$RCH_2OH + 2OH^-$$
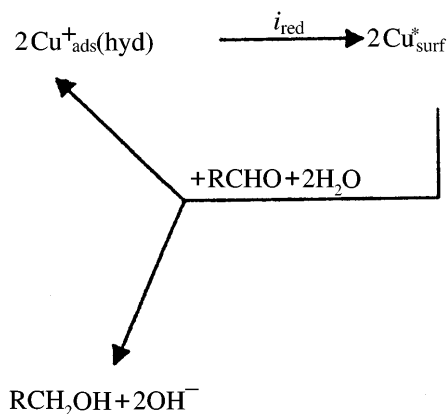
The oxidation of the aldehyde, at $E > -0.1$ V, is assumed to be mediated by Cu^+_{surf} species, the aldehyde behaving as a reductant:

$$2\,Cu^*_{surf} \xrightarrow{\;i_{oxid}\;} 2\,Cu^+_{ads}(hyd)$$

$$+RCHO + 3OH^-$$

$$RCOO^- + 2H_2O$$
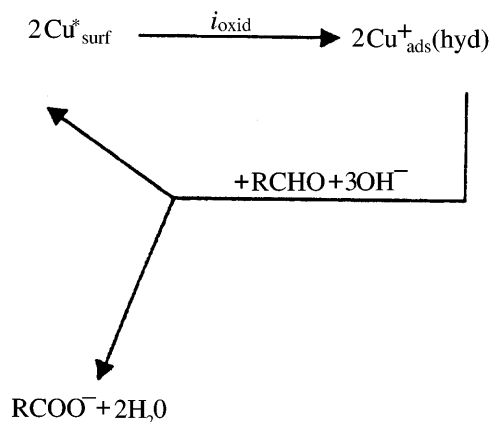
The sharp switch in redox behaviour at -0.1 V is specific to copper but not to the aldehyde [22]: other reactions, e.g. the reduction of nitrite and nitrate ions on copper in base, also undergo a dramatic change in rate at this potential. In terms of the general reaction scheme (Fig. 1), the reduction and oxidation of the aldehyde correspond to lines c and b, respectively. However, the other characteristic features shown in Fig. 1, i.e. the responses, indicated by a, a' and d, are not well known (certainly at -0.1 V) for copper in base.

One other typical feature of electrocatalytic oxidation behaviour of metals is evident in Fig. 3: the rate of reaction decreases dramatically (positive sweep) as the potential reaches ca. 0.4 V, i.e. the onset potential for monolayer oxide formation. Such behaviour was discussed recently for gold [7, 8]. It was suggested that the conventional description of the redox behaviour of metal surfaces are not very relevant with regard to electrocatalytic activity; the latter in many cases is de-

termined by the presence of active states of metal atoms at the surface, i.e. active site behaviour is often crucial in electrocatalysis and is unrelated to the conventional behaviour of the electrode surface.

Multilayer oxide reduction responses for copper in base at ca. −0.1 V

While there is usually no indication of a redox transition for copper in base at ca. −0.1 V, (see Fig. 2), a major cathodic response may be observed at this value if the copper electrode is suitably pretreated to produce a hydrous oxide deposit on the copper surface. A detailed investigation of the growth and reduction behaviour of these films is currently close to completion in this laboratory. The growth involves repetitive potential cycling to produce hydrous oxide deposits (an approach used earlier [10] in similar work involving other metals) which are then subsequently reduced in a single negative sweep.

The choice of sweep limits in such work is crucial; if the hydrous oxide is reduced (as observed at ca. −0.1 V), then the lower potential limit must be above this value, e.g. −0.075 V. The upper limit is also important; the optimum value (as will be reported in detail later) was found to be a potential close to the end of peak A_2, e.g. 0.86 V. The reduction sweep, for a film grown using these limits, is shown in Fig. 4. The main feature ob-
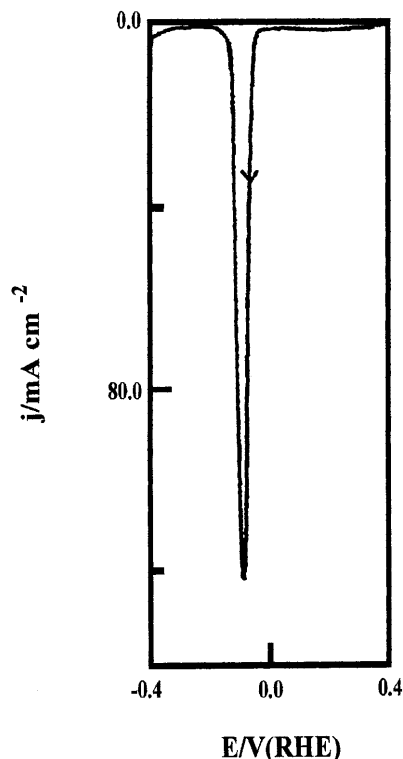

Fig. 4 Reduction sweep (0.4 to −0.4 V, 20 mV s^{-1}) for a hydrous oxide film on copper in 1.0 mol dm^{-3} NaOH at 60 °C; the oxide was produced by potential cycling (100 mV s^{-1} for 6 min) between a lower limit of −0.075 V and an upper limit of 0.86 V

served was an unusually sharp cathodic peak commencing at ca. −0.02 V and with a maximum at ca. −0.08 V (a second reduction sweep, recorded without further potential cycling, was featureless). This new peak, which has not been reported previously for copper in base, is regarded as the equivalent of peak d in Fig. 1.

Generation and redox response of the active surface state of copper

The objective here was to produce the type of redox response shown by the peaks a and a′ in Fig. 1, ideally at ca. −0.1 V, in the case of a copper electrode in base. Such a response, below 0.0 V, is clearly absent in Fig. 2 as the coverage of highly active copper atoms (or clusters of same) is evidently extremely low. What is required in this case is to perturb or activate the metal surface in some way in order to increase the occupancy (and hence the redox response) of what is regarded as a high energy, metastable state of copper atoms at the surface.

Procedures used to activated metals, and metal surfaces, to an unusual degree are already established in other areas, e.g. nanometer technology [23, 24]. A common approach is to disperse the bulk metal, e.g. by vaporization or dissolution, and then reassemble it using unusual condensation or reduction conditions so that the product is obtained in an extremely finely divided state of the metal. Basically, the active state is produced owing to the retention of some of the usually much larger amount of energy originally inserted into t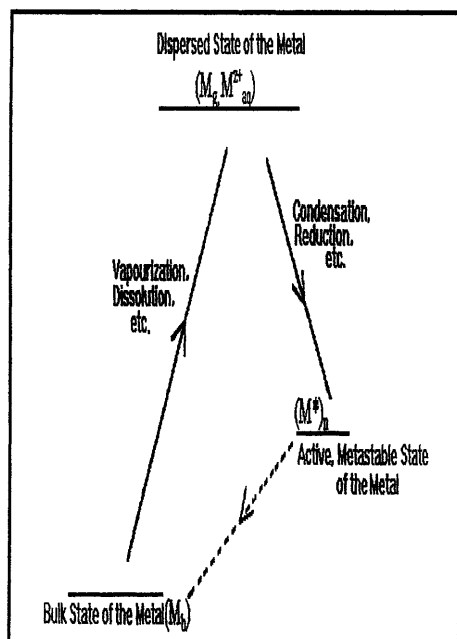he system (Fig. 5). The active form of the metal is regarded here as some type of nanoparticle, or extremely defective, state.

Techniques, which at this stage are largely empirical, for superactivating electrode surfaces have been under investigation in this laboratory for some years. The initial work was carried out with platinum [25, 26] and was extended recently to palladium [3]. The methods involved extensive potential cycling and intermittent abrasion, formation and subsequent reduction of multilayer hydrous oxide films, cathodic polarization and thermal treatment. The presence of unusual redox response at low potential in the case of copper in base, following severe abrasive pretreatment of the electrode surface, was reported recently by Couto and Gutierrez [27]; the peaks in question, at ca. 0.15 V (RHE), were not observed with a conventional copper wire electrode.

Examples of redox peaks at ca. −0.1 V observed in the present investigation are shown in Fig. 6. In the first case the copper electrode was extensively cycled (at 3 V s^{-1}) between −0.7 V and a range of upper limits (1.50–2.0 V). The surface layer was then reduced and the electrode was allowed to rest overnight in distilled water. The response shown in Fig. 6a was observed in the first
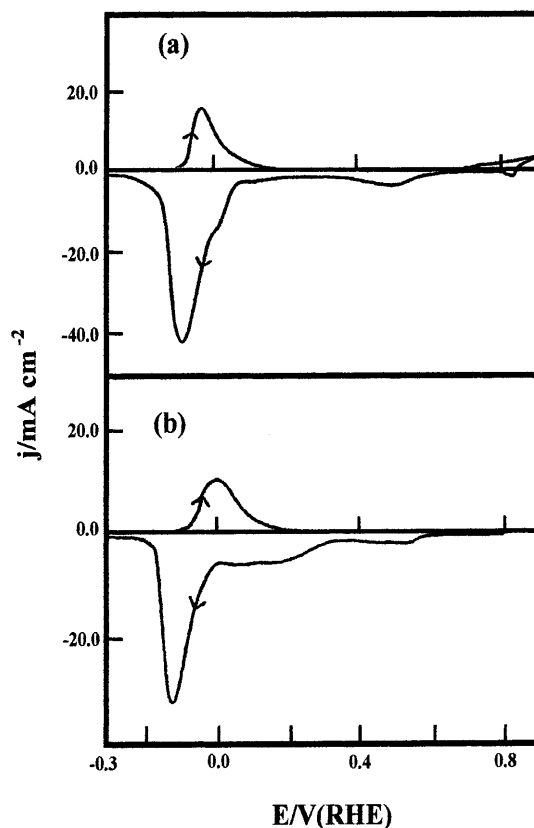

Fig. 5 General scheme for the generation of a metastable state of a metal

Fig. 6 First sweeps (−0.3 to 0.9 V, **a** 10 mV s^{-1} and **b** 2 mV s^{-1}) for activated copper electrodes in 1.0 mol dm^{-3} NaOH at 60 °C. **a** This electrode had been extensively cycled (−0.7 V to a range of upper limits, 3 V s^{-1}) and was allowed to rest overnight in triply distilled water before recording the response. **b** This electrode was activated by polarization in the base at 0.0 V for 3.0 h and then allowed to rest overnight in triply distilled water as in **a**

sweep on the following morning [a rapid return to a normal response for copper in base (Fig. 2) was observed at that stage on repeated cycling]. A similar unusual response, Fig. 6b, was observed for copper in base after the electrode was first polarized at 0.0 V for 3.0 h and then allowed to rest overnight in distilled water.

Discussion

The essential features of the IHOAM response (Fig. 1), which were deduced initially from work carried out with platinum and gold [15, 16], were confirmed here for copper in base. Obviously the present results strongly support this new interpretation of the electrocatalytic behaviour of metal surfaces and extend the range of metals to which it is applicable. The assumption of an unusually active state of the metal, M* in Fig. 5, is reinforced by the fact that such states are routinely produced and investigated in at least two other independent areas: suspended minute metal particle (or nanocolloid) systems [9] and nanometer particle or nanometer material systems [23]. Decreasing the lattice coordination number and lattice stabilization energy automatically results in a reduction in the redox potential for a surface metal atom. This is easily demonstrated by comparing the standard potential for the oxidation of bulk copper ($\mu° = 0$) with that for the same reaction for gaseous copper atoms ($\mu° \approx +298.61$ kJ mol^{-1} at 298 K [28]). The value for the oxidation potential of bulk copper to Cu$_2$O has been estimated by Pourbaix [18], and is given here as 0.470 V in Eq. 1. Using a similar approach, viz.

$$2Cu^*(g) \quad + H_2O \quad \rightarrow Cu_2O \quad + 2H^+ + 2e^-$$
$$2(298.610) \quad -237.200 \quad -146.356 \quad 0 \qquad kJmol^{-1}$$

(7)
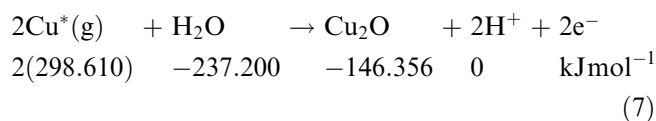
$\Delta G° = -506.376$ kJ mol^{-1} $= -nFE°$. Hence $E°$ (the standard reduction potential) for the process shown in Eq. 7 is -2.624 V. This is an unusually negative value, as is the corresponding value for an isolated silver atom according to Henglein [9]. The main point is that the potential of the active state involved in electrocatalysis, ca. -0.1 V, is far less negative than the value for the isolated copper atom; evidently the copper atoms involved at the active site are not necessarily of exceptionally low coordination number. While there is no evidence available as yet as to the precise nature of this active state, it may consist of protruding nanospheres or nanoclusters of metal atoms.

The decrease in standard redox ($E°$) potential with decreasing particle size, for extremely small values for the latter, is irregular [9]. Particles (M_n) of specific agglomeration number (n-value) exhibit unusual thermodynamic stability for certain n-values (the latter are the so-called magic numbers [29], $n = 2, 8, 20, 40, 58$ and 92; these values relate to closed shell configurations for metal clusters). While the involvement of clusters of this type could not be verified here, this approach provides an explanation of both the existence of rather well defined active states of metals, and – more importantly – the retention of these active states (particles with a magic number agglomeration value are trapped in an energy well or minimum).

A very interesting feature of the active state of copper is that it apparently does not exist, or give any significant response at -0.1 V, (Fig. 2), in the absence of easily oxidizable or reducible species in solution. It is assumed that the active nanospheres are not totally static; there may be greater contact between the particles when the surface is in the relaxed state, i.e. an extended band structure, and bulk copper behaviour predominates. However, there is always an imperceptible or subliminal amount of active material present capable of being oxidized at ca. -0.1 V and under appropriate conditions this may react with solution species in an electrocatalytic manner.

Since the electrocatalytic process involves redox cycling of the metal atoms (which also entails changes in hydration properties around the latter), plus the release of energy, other particles may be promoted to such a level that they also participate in the electrocatalytic response at ca. -0.1 V, even though the blank response in this region is virtually featureless.

There is further, independent, evidence that the anodic behaviour of copper is more complex than that suggested by the responses shown in Fig. 2. SERS data reported by Doblhofer and co-workers [30] demonstrated that, contrary to the voltammetric data [which indicated that oxidation of copper in 0.1 mol dm^{-3} NaOH commenced only at -0.5 V (SCE)], CuOH species were formed, or could exist, at this interface at -1.3 V (SCE). The loss of the CuOH response was observed only on polarizing the electrode at -1.4 V (SCE), i.e. ca. -0.4 V (RHE); the latter value virtually coincides with the onset potential for hydrogen gas evolution for the electrode system in question. Marichev [31] also claimed that formation of oxyspecies on copper in base commences at ca. -0.4 V (RHE). The technique used in the latter work, contact electrical resistance (CER), is rather novel; it is particularly sensitive to premonolayer oxidation effects, presumably because the latter occur most readily at surface protrusions, and these are also the points of contact which determine the contact resistance value. The presence of further active surface states for copper, with $E°$ values lower than -0.1 V, will be reported shortly.

The response shown in Fig. 4 for the reduction of the hydrous oxide deposit grown on copper by potential cycling is very similar in character to that reported earlier for platinum [10]. This aspect of copper behaviour is quite reproducible and is currently being investigated in greater detail. The response in Fig. 4 is assumed to be of different origin to that of peak C_0 in Fig. 2b; the latter is assumed to arise from the inhibition of the reduction of much of the Cu(II) oxide layer owing to the presence of an inner layer of poorly conducting

Cu_2O. The reaction involved at -0.1 V is assumed to involve a $Cu^*/Cu^+ \cdot nH_2O$ transition; the involvement of the latter couple in electrocatalytic processes at copper in base was discussed earlier [22].

The response shown in Fig. 6a is assumed to correspond to the redox behaviour response of the active state of the metal. It is unlikely to be due to the presence of an adsorbed impurity as it occurs close to what is clearly a critical potential for copper in base and contains both an anodic and a cathodic component (an organic impurity, totally oxidized in the positive sweep, is unlikely to be regenerated on the negative sweep). The anodic charge on the positive sweep in this case is low, relative to the cathodic charge on the negative sweep. It is assumed that after the surface was disturbed or activated by growth and reduction of oxide films (or polarization in the hydrogen region, which results in embrittlement), the disturbed layer tends to relax. The latter process probably entails movement of copper atoms on the surface. Atoms that are capable of movement are of low coordination number; hence they are active and capable of displacing hydrogen from water molecules at $E < 0.0$ V:

$$Cu^* + H_2O \rightarrow CuOH + 1/2H_2 \qquad (8)$$
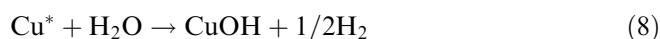
It is assumed, therefore, that the response for the active state of copper observed after the electrode had been allowed to rest overnight in distilled water is due to the formation (or preservation) of the active state of the metal in some type of metal/metal oxide matrix. This explains (1) the relatively low anodic charge in Fig. 6 (some of the active metal was already oxidized) and (2) the disappearance of this unusual response in later cycles (total oxide reduction on the first negative sweep evidently resulted in the rapid rearrangement of the copper to a less active state). It is worth noting that a similar long arrest was found to be essential also in earlier work involving the generation of an unusually active (and again rather transient) state of platinum [25] in acid solution.

Conclusions

1. It was demonstrated in the present investigation that the electrocatalytic behaviour of copper at low, premonolayer oxide, potentials, ca. -0.1 V (RHE), fulfills all of the requirements, as outlined in Fig. 1, of the IHOAM approach to electrocatalysis. The results strongly support the view that the defect state of the surface is of major importance from a catalytic and electrocatalytic viewpoint – a claim already made by Somorjai [1].

2. The absence of a detectable response at -0.1 V in some instances, e.g. Fig. 2, is attributed to the fact that the active form of the metal can relax to a slightly dormant state from which it can be reactivated due to energy transfer and other processes (redox transitions, hydration effects, etc.) associated with electrocatalytic processes.

3. The identity of the active state is a problem and – since an inherently unstable species is involved – it may well remain so for some time. It is regarded here as involving minute metallic species which are intermediate between free single metal atoms and the bulk phase metal; minute clusters or molecules of metal atoms, Cu_n (also known as quantum dots), seem to be the only state of matter that can account for the unusually low redox potential of the active site material. These unusual species are assumed to be involved, as intermediates or mediators, in such processes as hydrous oxide film reduction, premonolayer oxidation, electrocatalysis, etc. No great distinction is made between collections of discrete clusters and highly defective material consisting of agglomerates of cluster–size grains; also the bonding between the microparticles may not be very rigid.

4. The importance of activated chemisorption is not discounted, especially in the case of metals such as platinum; in some instances a bifunctional mode of electrocatalysis may be involved. Furthermore, as pointed out recently for both platinum [12] and gold [8], there may be more than one type of mediator system – or critical potential value – involved in the overall electrocatalytic behaviour of a given electrode system.

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