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ORIGINAL PAPER

Surface active state involvement in electrocatalytic reductions at copper in acid solution

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Abstract The electrocatalytic behaviour of copper in acid is dominated by a metastable state interfacial redox transition which occurs within the double layer region, at *ca.* −0.7 (±0.1) V (SMSE). The transition in question is apparently based on the presence of low coverage, redox active, copper surface clusters which function as active sites or mediators and thus facilitate electron transfer across the interface; copper in acid exhibits a remarkably high overpotential of *ca.* 1.2 V for oxygen reduction. The effect of copper plating bath additives on the electrocatalytic properties of copper was surveyed and it was demonstrated that with a compound such as thiourea, the presence in solution of a species such as nitrate, which under additive-free conditions undergoes rapid mediated reduction, exacerbates the surface deactivating effect of the additive.

Keywords Active site mediator · Bath additives · Copper in acid · Electrocatalysis · Oxygen reduction

1 Introduction

The electrochemistry of copper in acid solution is of considerable interest with regard to (a) copper electrodeposition as currently employed for interconnect fabrication in the microelectronics industry [1–5] and (b) copper electrocatalysis for the reduction of nitrate ions [6–8] and organic nitrocompounds [9–12], e.g. the conversion of nitrobenzene (NB) ($C_6H_5NO_2$) to aniline ($C_6H_5NH_2$) and *p*-aminophenol (*p*-$HOC_6H_4NH_2$) [9]. In recent publications from this laboratory [13, 14] it was suggested that these two areas of copper electrochemistry are interrelated, a surface active state of copper being both an important intermediate in copper electrodeposition and the effective mediator with regard to nitrocompound reduction at copper in acid. A brief account of the active state of electrodeposited copper, which is attributed to a partial lack of lattice stabilization energy at defect sites, was given earlier [13]; although the precise identity of the interfacial mediator system has yet to be established, isolated copper atoms are highly electropositive and hence a mediator system based on a lower energy surface magic number cluster species, $Cu_{2,ads}/Cu_2^+$, is considered as a more likely alternative [14].

Active state behaviour of metal surfaces is very difficult to investigate as the species involved are of quite low coverage and unstable (or metastable). As discussed earlier [13] the conventional cyclic voltammetry (CV) response of the copper in acid tends to be dominated by the Equilibrated Metal Surface (EMS) state which yields the normal Cu/Cu^{2+} transition (as described by Pourbaix [15]) at *ca.* −0.4 V (SMSE). However, there is a low level, Metastable Metal Surface (MMS), state transition for this electrode system [13, 14] at *ca.* −0.7 (±0.1) V whose importance with regard to nitrate ion reduction and plating bath additive behaviour was outlined earlier.

Copper (in acid) is a weak chemisorber; its CV yields no sign of an adsorbed hydrogen response [13], yet it is apparently the optimum electrocatalyst for nitrocompound reduction [9], but is active for this reaction only below *ca.* −0.7 V. The latter value is approximate; it is well within the double layer region for this electrode system and it also corresponds to the potential at which several plating bath additives, e.g. PEG+Cl^- ions or thiourea (TU), lose their inhibiting properties [13, 14]. Basically, it appears that

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there is a surface active state (or site) redox switch at *ca.* −0.7 V which may be represented as follows, viz.

$$Cu^{+}_{2,ads} + e^{-} = Cu_{2,ads}. \tag{1}$$

Only the oxidized state (on the left-hand side) combines with bath additives such as TU and thus cause plating inhibition; this cationic form disappears at *ca.* −0.7 V and is replaced by the reduced form which results in (a) loss of the plating inhibitor effect and (b) the appearance of the reduction mediator which, below −0.7 V, operates in a cyclic redox manner, viz.

$$\begin{tikzcd} nCu_{2,ads} + O_{aq} = & nCu^{+}_{2,ads} + R_{aq} \arrow[l, bend left, "i_{cath}"] \end{tikzcd} \qquad (2)$$

O_{aq} and R_{aq} are the oxidized and reduced form, respectively, of the dissolved reagent.

It will be demonstrated here that this electrocatalytic behaviour of copper in acid is not confined to nitrocompound reduction, it also operates in the case of oxygen reduction, i.e. anomalous redox responses within the double layer region are a specific (and quite important) property of metal/solution interfaces. The influence of some common plating bath additives on the electrocatalytic properties of copper in acid solution was also surveyed.

2 Experimental details

The main technique used to monitor the electrocatalytic behaviour of copper in acid solution was CV; this was carried out with a computerized electrochemical workstation (CH Instruments, model 660B). The cell electrolyte was 1.0 mol dm^{-3} H_2SO_4, and other reagents [13], e.g. thiourea, TU (Aldrich, Tanfkirchen, Germany), polyethylene glycol, PEG, mol. mass 3,350 g mol^{-1} (Sigma), bis (3-sulphopropyl) disulphide, SPS (Rashig Gmbh), diethyl saferine azo dimethyl amine, also known as Janus Green B, JGB (Sigma), Cl^{-}ions (NaCl, Merck, Hohenbrumn Germany), NO_3^{-} ions ($NaNO_3$, BDH), hydrogen peroxide (30% Merck) and nitrobenzene, NB (BDH) were added as required, usually from concentrated stock solutions (nitrate ions were added to the acid solution in the form of solid sodium nitrate).

The working electrode was a gold (exposed area *ca.* 0.2 cm^2) rotating disk (RDE) system (EG and G rotator, Model 616) whose surface was regularly cleaned and plated with copper (10 mA cm^{-2} for 5 s; this corresponds to a copper film thickness of *ca.* 18.5 nm) in 0.05 mol dm^{-3} $CuSO_4$ + 1.8 mol dm^{-3} H_2SO_4 solution. The counter electrode in the plating solution was copper and for the electrocatalytic studies was gold wire (in both cases 1.0 mm diam, Puratronic grade, Alfa Aeser, Karlsruhe, Germany) sealed directly into soda glass tubing. The reference electrode used was saturated mercury/mercury (I) sulphate (SMSE) (Radiometer Analytical) which had a standard potential of 0.641 V (SHE). It was contained in a separate vessel which was connected to the main cell (Metrohm, type EA 876-20) via a Luggin capillary; the latter was used in the usual manner to minimize iR errors due to the potential drop across the electrolytic solution. High-purity oxygen and nitrogen were flushed through the solution to saturate the electrolyte with oxygen and deoxygenate the electrolyte, respectively. The cell was usually operated at room temperature, *ca.* 18 ± 2 °C; cyclic voltammograms commenced at the upper limit and potential values are generally quoted with reference to the SMSE scale.

Since the solubility of NB in water is rather limited, 1.93 g dm^{-3} at 25 °C [16], the solvent used for this compound in the present work was a 50 vol.% isopropanol/water mixture (the use of mixed solvents for the electroreduction of nitrocompounds is quite common [9–12]). In many of the CV diagrams presented here only the negative sweeps are shown; usually the subsequent positive sweeps were not very different but they are omitted from a clarity viewpoint.

3 Results

3.1 Nitrobenzene (NB) reduction

A typical response for NB is shown in Fig. 1. The reduction commenced and terminated under CV conditions *ca.* −0.6 V. The increase in current density with decreasing potential (below −0.6 V, negative sweep) was somewhat

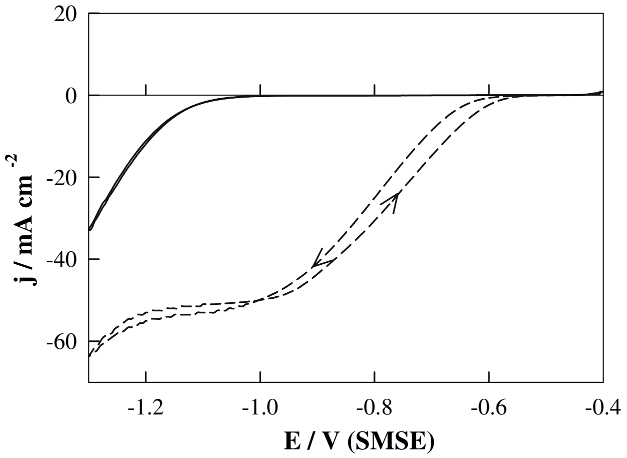

Fig. 1 CVs (−0.4 to −1.3 V, 10 mV s^{-1}) for a copper-plated RDE (500 rpm) in deoxygenated 1.0 mol dm^{-3} H_2SO_4 (in 50% water + 50% 2-propanol) without (*full line*) and with (*dashed line*) 0.1 mol dm^{-3} nitrobenzene present, T = 20 °C

sluggish, but a clear plateau is evident over the range −1.0 to −1.2 V. The limiting rate of reduction (or plateau value, j_L) was a linear function of the NB concentration, Fig. 2a, and the effect of electrode rotation rate (at a fixed NB concentration) is summarized by the Levich plot, Fig. 2b. The latter confirms that the limited current density (j_L) values are determined by the rate of diffusion of NB across the boundary layer at the solution side of the interface. The diffusion coefficient of NB in the mixed solvent was estimated in the present case to be 2.34×10^{-6} cm^2 s^{-1}; this compares with a value of 0.88×10^{-6} cm^2 s^{-1} reported by Marquez and Pletcher [9], who used an acetone/water solvent, and values of 4.4×10^{-6} [10, 12] and 5.98×10^{-6} [11] cm^2 s^{-1} reported by other authors. As pointed out earlier [13] with regard to nitrate ion reduction at copper in acid, the rate of reduction (in this case of NB) at a constant potential (−0.8 V) decreased gradually with time, e.g. from *ca.* 30 to 19 mA cm^{-2} over a period of 30 min. Such decay, which has been observed also for copper in base [17], is assumed to be due to gradual loss of coverage of the active mediator state.

The effect of adding increasing low levels of Cl^- ions and PEG on the NB reduction response is illustrated in Fig. 3a and b, respectively. The addition of PEG had only a slight inhibiting effect (see Table 1); inhibition due to the addition of Cl^- ions was more marked; the loss of NB reduction activity, at −0.8 V, is summarized (for all the additives surveyed here) as a function of additive concentration in Table 1.

The effect of adding SPS, JGB, a combination of additives, PEG+ Cl^- ions, and another well known plating bath additive, TU, is summarized in Figs. 4 and 5. In all cases significant inhibiting effects were observed, see also Table 1; this was particular true in the case of TU where the addition of 10 ppm TU displaced the onset potential for NB reduction, Fig. 5a, from *ca.* −0.6 to −0.9 V.

3.2 Reduction of dissolved oxygen

Typical responses for copper in acid solution, in the absence and presence of dissolved oxygen, are shown in

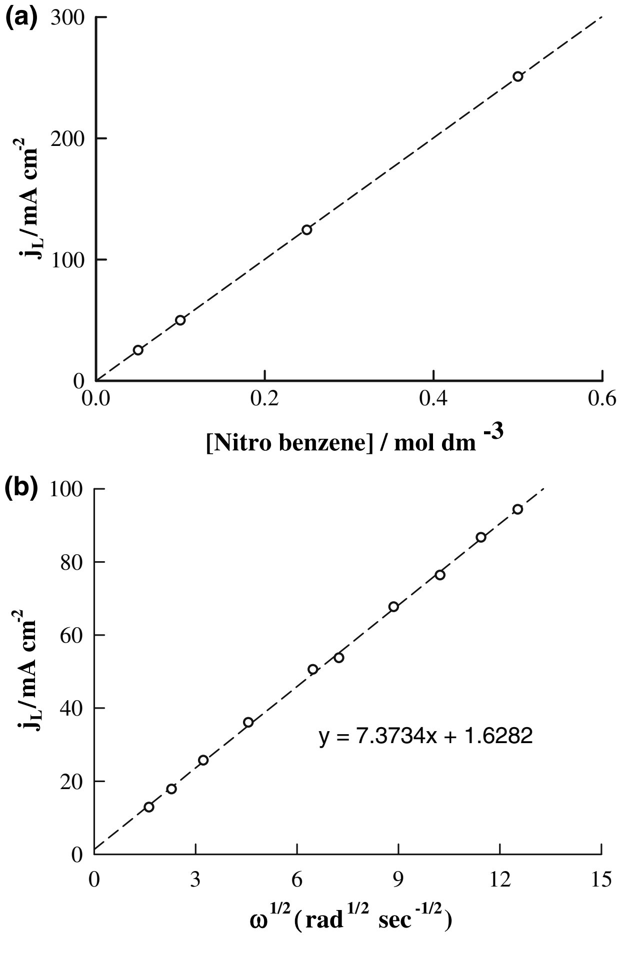

Fig. 2 (**a**) Variation of the limiting current density (j_L) for nitrobenzene (*NB*) reduction on copper as a function of the NB concentration (conditions similar to those in Fig. 1). (**b**) Levich plot for the NB reduction process; same conditions (apart from rotation rate) as in Fig. 1

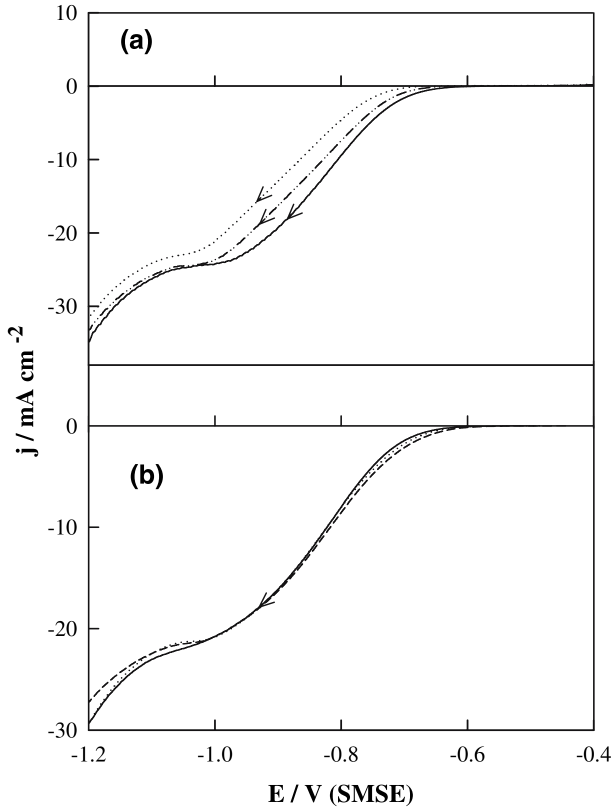

Fig. 3 (**a**) Effect of Cl^- ions on CVs recorded for NB reduction: the conditions are outlined in Fig. 1, except that [NB] = 0.05 mol dm^{-3}: [Cl^-] (ppm) = 0, (—); 30, (-···-); 120, (···). (**b**) Effect of PEG on CVs recorded for NB reduction; conditions as in (**a**) [PEG] (ppm) = 0, (—); 300, (···); 1,200, (- - -) (these responses virtually overlapped as PEG had little effect)

Table 1 Effect of addition of different levels of bath additives on the nitrobenzene reduction process; 1.0 mol dm^{-3} H_2SO_4 (in 50% water + 50% 2-propanol) + 0.05 mol dm^{-3} nitrobenzene, Cu-plated Au RDE (500 rpm); T = 20 °C; current density (j) values were taken at −0.80 V, negative sweep

[Cl$^-$] (ppm)	j/mA cm^{-2}	[PEG] (ppm)	j/mA cm^{-2}
0	9.43	0	9.51
10	8.32	100	9.41
30	7.44	300	8.97
50	5.88	600	8.50
70	4.73	900	8.67
90	4.71	1,200	8.55
[SPS] (ppm)	j/mA cm^{-2}	[JGB] (ppm)	j/mA cm^{-2}
0	9.53	0	9.53
5	4.97	5	5.21
10	3.88	10	4.47
30	3.41	30	2.73
60	2.66	60	2.45
90	2.19	90	1.93
[PEG$_{300\text{ ppm}}$ (constant) + Cl$^-$] (ppm)	j/mA cm^{-2}	[TU] (ppm)	j/mA cm^{-2}
0	9.51	0	9.53
10	4.66	10	0.43
30	3.72	30	0.034
50	2.57	50	0.033
90	1.62	70	0.062
120	1.85	90	0.068

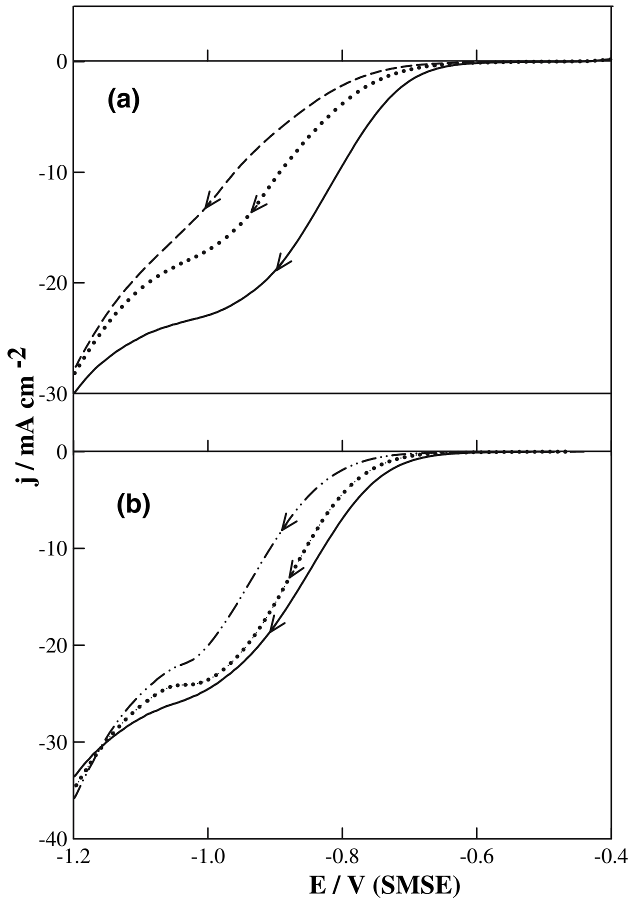

Fig. 4 (**a**) Effect of SPS on CVs recorded for NB reduction: conditions as in Fig. 3a: [SPS] (ppm) = 0, (—); 10, (···); 90, (- - -). (**b**) Effect of JGB on CVs recorded for NB reduction: conditions as in Fig. 3a: [JGB] (ppm) = 0, (—); 10, (···); 90, (-···-)

Fig. 6a. Dissolution of the metal occurred above *ca.* −0.47 V and hydrogen gas evolution below *ca.* −0.9 V. The copper dissolution and oxygen reduction responses are assumed to overlap at *ca.* −0.47 V but the cathodic response for the reduction process was quite low even at −0.6 V. The oxygen reduction current increased significantly in the negative sweep over the range −0.6 to −0.8 V, i.e. over the mediator transition range, to reach a limiting value below −0.8 V. This reduction response for oxygen is similar to that observed for NB, Fig. 1; however, the concentration of the latter used in the case of Fig. 1, and hence the limiting current density at *ca.* −1.0 V, are much higher.

There are two possible products for oxygen reduction in aqueous media (see Ref. [15], pp. 540–544), hydrogen peroxide

$$O_2 + 2H^+ + 2e^- = H_2O_2;\ E^0 = 0.68\ \text{V (SHE)} \tag{3}$$

and water

$$O_2 + 4H^+ + 4e^- = 2H_2O;\ E^0 = 1.23\ \text{V (SHE)}. \tag{4}$$

However, peroxide seems an unlikely product because, as illustrated in Fig. 6b, this compound undergoes reduction at copper in acid more readily than oxygen. The half-wave potentials (negative sweep) for H_2O_2 and O_2 reduction were *ca.* −0.67 and −0.76 V, respectively; as peroxide reduction appears to be more facile, it is assumed that oxygen reduction in this case occurs via the four-electron route, the main product being water.

The plateau current density for oxygen gas reduction at copper in acid increased significantly with increasing electrode rotation rate and a linear Levich plot was obtained, Fig. 7, with an intercept close to j = 0. Assuming a four-electron transfer reaction and an oxygen solubility value of 1.28 × 10^{-3} mol dm^{-3} [18], the diffusion coefficient of oxygen in the acid solution was estimated to be 4.73 × 10^{-6} cm^2 s^{-1}. Values reported by other authors [19–22] range from 1 × 10^{-5} to 2.7 × 10^{-5} cm^2 s^{-1}.

The effect of bath additives on the rate of oxygen reduction at −0.8 V is summarized in Table 2. Addition of chloride ions had a slight inhibiting effect whereas addition of PEG had virtually no effect on the reduction rate. SPS, JGB (as sole additives) or a combination of PEG+Cl$^-$ ion,

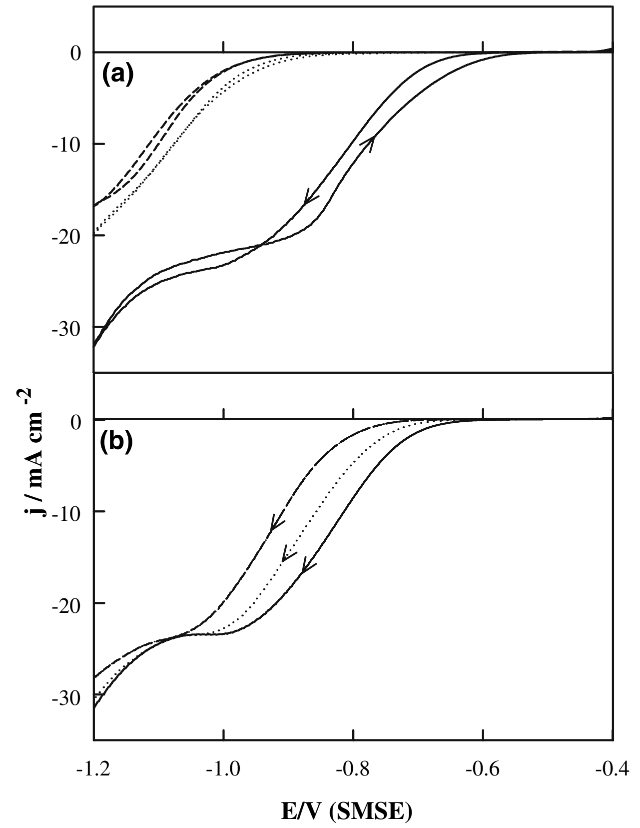

Fig. 5 (**a**) Effect of thiourea (*TU*) on CVs recorded for NB reduction: conditions as in Fig. 3a: [TU] (ppm) = 0, (—); 10, (···); 30, (- - -). (**b**) Effect of PEG (constant at 300 ppm) and Cl⁻ ion on CVs recorded for NB reduction: conditions as in Fig. 3a: [Cl⁻] (ppm) = 0, (—); 10, (···); 90, (- - -)

Fig. 8a, also had only a minor inhibiting effect; inhibition was most severe in the presence of TU, Fig. 8b.

3.3 Reduction of nitrate ions

Since this topic was discussed in some detail earlier [13, 14] only a few comments will be made here. Nitrate ion reduction at copper in acid commenced (negative sweep) and terminated (positive sweep) at *ca.* −0.6 V, see the full line in Fig. 9a. The increase in reduction rate with decreasing potential below −0.6 V was rather sluggish, but eventually a transport-limited plateau value was attained. However, as with NB, the rate of nitrate reduction in this transport limited region decreased with time, evidently due to the loss of surface active sites.

The effect of bath additives on the nitrate ion reduction reaction at −0.90 V is summarized in Table 3. PEG had very little effect; Cl⁻, PEG+ Cl⁻ and JGB were moderately inhibiting, while the sulphur containing compounds, SPS and TU (especially the latter), were sources of severe inhibition, see also Fig. 9.

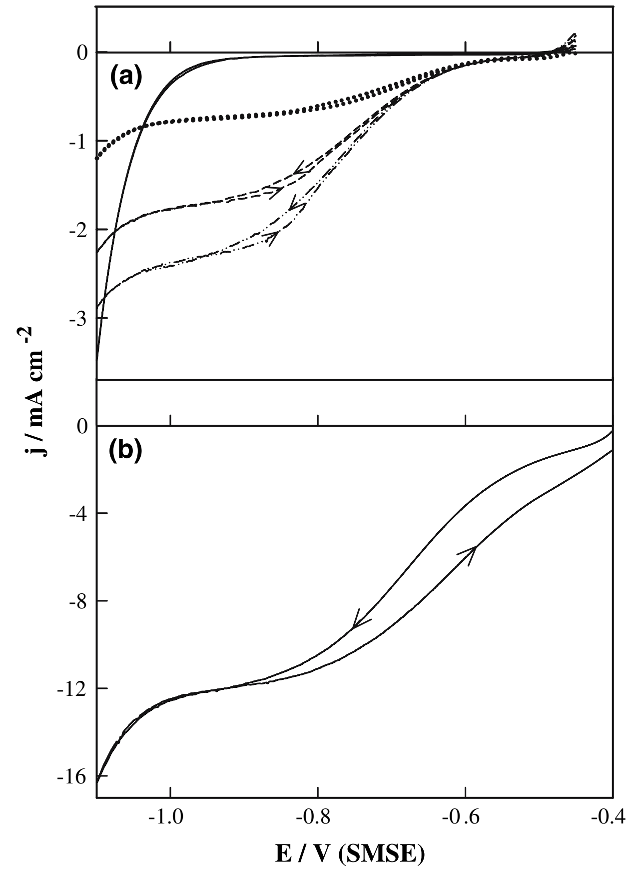

Fig. 6 CVs (10 mV s^{-1}) for a copper-plated RDE in (**a**) deoxygenated (—, 500 rpm) and oxygen-saturated (···, 50 rpm), (- - - , 500 rpm), (-···-, 1,000 rpm) 1.0 mol dm^{-3} H_2SO_4 (−0.45 to −1.10 V), and (**b**) deoxygenated 1.0 mol dm^{-3} H_2SO_4 + 0.025 mol dm^{-3} H_2O_2 (−0.40 to −1.10 V at 500 rpm)

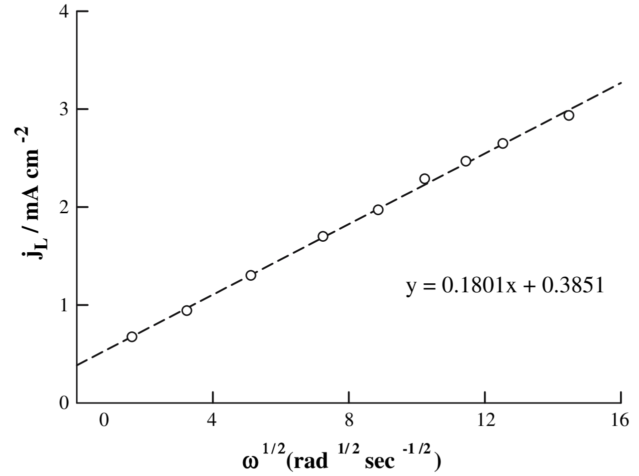

Fig. 7 Levich plot for the oxygen gas reduction at copper in acid solution; same conditions as in Fig. 6a; j_L is the limiting (or plateau) current density

Table 2 Effect of addition of different levels of bath additives on the oxygen reduction process; oxygen-saturated 1.0 mol dm^{-3} H_2SO_4, Cu-plated Au RDE (500 rpm); T = 20 °C; current density (j) values were taken at −0.80 V, negative sweep

$[Cl^-]$ (ppm)	j/mA cm^{-2}	[PEG] (ppm)	j/mA cm^{-2}
0	0.96	0	1.21
10	0.96	100	1.21
30	0.86	300	1.23
50	0.82	600	1.26
70	0.76	900	1.28
90	0.74	1,200	1.33
[SPS] (ppm)	j/mA cm^{-2}	[JGB] (ppm)	j/mA cm^{-2}
0	0.89	0	0.96
5	0.80	5	0.92
10	0.71	10	0.87
30	0.70	30	0.78
60	0.70	60	0.68
90	0.71	90	0.70
$[PEG_{300\ ppm}$ (constant) + $Cl^-]$ (ppm)	j/mA cm^{-2}	[TU] (ppm)	j/mA cm^{-2}
0	1.23	0	0.96
10	0.92	10	0.26
30	0.82	30	0.17
50	0.75	60	0.15
90	0.68	90	0.14
120	0.65		

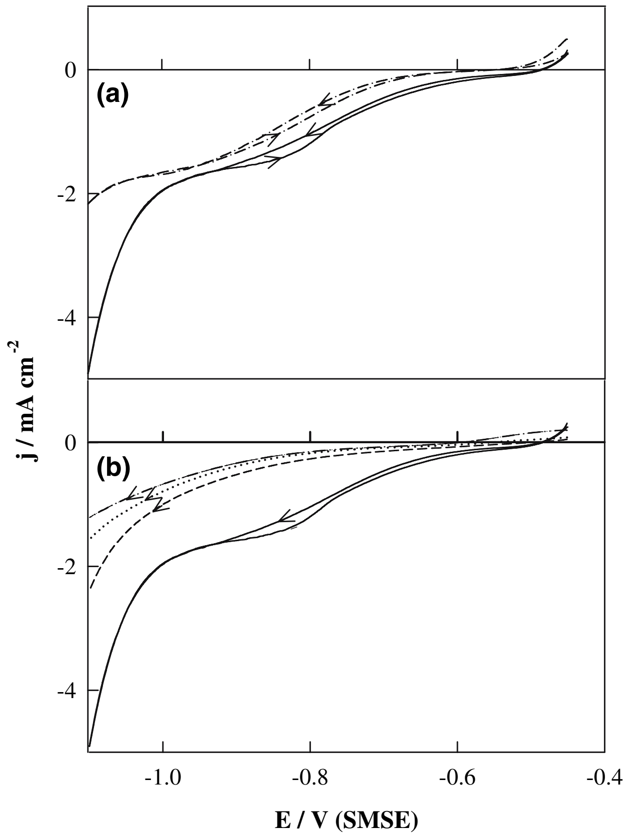

Fig. 8 (**a**) Effect of PEG (constant at 300 ppm) + Cl^- ion on CVs recorded for copper in oxygen-saturated acid solution; same conditions as in Fig. 6a: $[Cl^-]$ (ppm) = 0, (—); 120, (-··-). (**b**) Effect of TU on CVs recorded for copper in oxygen-saturated acid solution; same conditions as in Fig. 6a: [TU] (ppm) = 0, (—); 10, (- - -); 30, (···); 90, (-··-)

4 Discussion

Although active sites are the prime components in surface catalysis [23, 24], they extremely difficult to investigate and their character is not well understood. The problems in this area in general seems to be that (a) active site atom coverage is usually extremely low and in some cases the species in question may have a degree of transient character associated with surface mobility [25], (b) as discussed recently for gold [26], the chemistry of active site (MMS) atoms may well be different to that of the more stable (EMS) atoms at the same surface (this was also pointed out elsewhere by Ertl [23]). It is worth stressing here that, despite extensive worldwide investigation, the chemical behaviour of surface active sites in general is not well established and is largely a matter of speculation.

The cyclic redox, or Incipient Hydrous Oxide/Adatom Mediator (IHOAM), model of electrocatalysis was discussed in recent publications [26, 27] from this laboratory. It assumed that active site atoms undergo a rapid, quasi-reversible redox transition (in some cases, e.g. gold [26], there may be several responses of this type) within the double layer region and the species involved tend to be the mediators ($M^*_{surf}$for reduction and M^{z+}_{surf} for oxidation) for catalysis at metal/solution interfaces (for the Gp 11 metals, Cu, Ag and Au, the alternative, activated chemisorption, route for electrocatalysis [28] is regarded as being of little relevance). With copper in acid there seems to be only one metastable state transition which is active, from a mediation viewpoint, with regard to reduction but not oxidation. The effective reductant in this case, as indicated in Eq. 2, is active copper, designated here as $Cu_{2,ads}$, which (on oxidation by a dissolved oxidant) is repetively regenerated at low potentials, i.e. at $E < E^0$ ($Cu_{2,ads}/Cu^+_{2,ads}$); the mediator transition potential is crucial as above this value the reduction mediator does not exist and consequently electrocatalytic reduction (by the route outlined in Eq. 2) cannot occur. To the best of our knowledge there are no reports of electrocatalytic oxidation responses at copper in acid. This may be attributed to the fact that the oxidized form of the active site ($Cu^+_{2,ads}$) is a weak oxidant and has a short working range (the data in Fig. 6a indicates that copper dissolution in acid occurs at $E >$ *ca.* −0.45 V; the reaction involved is assumed to result in the loss of the mediator species).

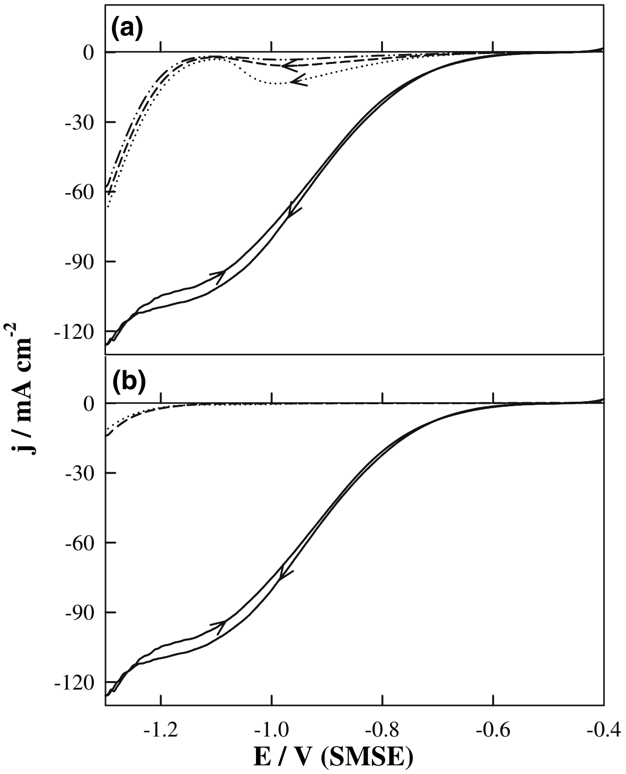

Fig. 9 (**a**) Effect of SPS on CVs recorded for nitrate (0.05 mol dm^{-3}) reduction in 1.0 mol dm^{-3} H_2SO_4; conditions similar to those in Fig. 1: [SPS] (ppm) = 0, (—); 10, (···); 30, (- - -); 90, (-···-). (**b**) Effect of TU on CVs recorded for nitrate (0.05 mol dm^{-3}) reduction in 1.0 mol dm^{-3} H_2SO_4; conditions similar to those in Fig. 1: [TU] (ppm) = 0, (—); 10, (- - -); 30, (···)

With regard to electrocatalytic reduction, the nature of the solution species seems to make little difference to the onset (negative sweep)/termination (positive sweep) potential, the latter value being determined by the surface mediator transition. For reduction to occur in an IHOAM manner certain conditions need to be fulfilled, e.g.

1. The reduction of the solution species must be capable (in thermodynamic terms) of occurring above the mediator transition potential but the reaction is slow (for kinetic reasons), i.e. the process must be electrocatalytically demanding.
2. Ideally the catalytic mediation process should occur quite rapidly; certain processes are of this type, e.g. polysulphide reduction at gold in base [26] and dichromate reduction at gold in acid [29], i.e. the surface redox transition functions like an “on/off” electrical switch, the current rising very rapidly to a transport limited value as the potential passes through the mediator generation potential; for such reactions the Tafel slope, $\delta E/\delta \log i$, is virtually zero: such behaviour was not observed here with copper in acid.

Table 3 Effect of addition of different levels of bath additives on the nitrate reduction process; 1.0 mol dm^{-3} H_2SO_4 + 0.05 mol dm^{-3} nitrate, Cu-plated Au RDE (500 rpm); T = 20 °C; current density (j) values were taken at −0.90 V, negative sweep

[Cl⁻] (ppm)	j/mA cm^{-2}	[PEG] (ppm)	j/mA cm^{-2}
0	45.1	0	48.6
10	29.6	100	48.7
30	17.8	300	48.2
60	11.6	600	47.5
90	8.41	900	48.2
[SPS] (ppm)	j/mA cm^{-2}	[JGB] (ppm)	j/mA cm^{-2}
0	44.6	0	45.1
10	9.40	10	14.7
30	4.75	30	7.28
60	2.77	60	4.04
90	2.42	90	2.81
[$PEG_{100\ ppm}$ (constant) + Cl⁻] (ppm)	j/mA cm^{-2}	[TU] (ppm)	j/mA cm^{-2}
0	48.7	0	45.1
10	24.2	10	0.12
30	11.5	30	0.06
60	4.85	60	0.05
90	2.93	90	0.04
120	1.58		

Probably the most interesting result obtained in the present investigation is the response for oxygen reduction. As pointed by Vukmirovic et al. [20] this reaction is important in corrosion chemistry where it often determines corrosion rates and damage evolution in a number of commercially important copper alloys. These authors concluded that oxygen reduction at a copper surface in aqueous media (pH range 1.5–14) occurs via a four-electron mechanism, the limiting oxygen-diffusion current density (i_L) being pH-independent. Since E^0 (H_2O/O_2) at 298 K, pH 0, is 1.23 V (SHE), Eq. 4, or *ca.* 0.6 V (SMSE), vigorous oxygen gas reduction at copper in acid, which occurs only below −0.6 V (SMSE), Fig. 6a, involves a remarkably high cathodic overpotential of *ca.* 1.2 V. As shown here in Eq. 3 the other possible product of oxygen reduction at copper in acid is hydrogen peroxide. However as illustrated in Fig. 6b, peroxide undergoes reduction in this case in a manner similar to that of oxygen. In both cases vigorous reduction occurs below −0.6 V; evidently the same interfacial mediator system is involved in these two reactions. The peroxide appears to be slightly more reactive than oxygen as significant reduction of peroxide occurs, especially in the negative sweep, Fig. 6b, above −0.6 V. This may reflect the greater kinetic reactivity of peroxide as compared with oxygen, plus the fact that there may be some background current involved above −0.5 V due to an alternative, sluggish, non-mediated route for peroxide reduction. In any event, since peroxide reduction occurs more readily than oxygen, it is not too surprising that oxygen reduction at copper in acid involves a four-electron transfer reaction [20] to yield water.

The reduction responses for both NB, Fig. 1, and nitrate ions, full line in Fig. 9a, at copper in pure acid solution are similar to that of oxygen, Fig. 6a. All three cathodic processes show an onset/termination potential at *ca.* −0.6 V which strongly supports the assumption that the same active site, cyclic redox, mediator system is involved in these three different reactions. The increase in current with decreasing potential (or increasing cathodic overpotential) below −0.6 V in all three cases was rather sluggish, e.g. in Fig. 1 the rate of NB reduction increased almost linearly with potential as the latter was decreased from about −0.6 to −1.0 V. Such behaviour may reflect the fact that the mediator transition does not occur at a discrete potential; instead, the coverage of the mediator species increases with decreasing potential, over a considerable range of the latter, below −0.6 V. Alternatively, either the mediator regeneration or the mediator/oxidant reaction step may be sluggish; this inhibition may be due to anion interaction with the oxidized form of the mediator (the process involved, giving rise to the species $Cu^{+}_{2,ads}.HSO_4^{-}$, may be regarded as a form of anion adsorption) or simply to slow electron transfer between the reduced form of the mediator and the dissolved oxidant. The Levich plots reported here for NB, Fig. 2b, and oxygen, Fig. 7, reduction (similar data for nitrate was given earlier [13]) indicate that the eventual limiting current was determined by transport of the reactant through the boundary layer. The intercept in the case of oxygen reduction, Fig. 7, was greater than zero. Similar behaviour was described recently by Hernández et al. [30] for methanol oxidation on carbon-supported gold nanoparticle electrodes in base; the effect was attributed to a mixed (diffusion and electrode kinetics) control regime. Since the surface active site (or mediator) coverage is low, some regions of the copper surface may have a low activity for oxygen gas reduction and this situation may be exacerbated by the loss of activity of copper surfaces with time [17] which was attributed recently to the spontaneous decay of metastable surface states [13]. It is assumed that Pt is a much more satisfactory substrate than copper for the determination of the diffusion coefficient of oxygen in acid solution.

The effect of the plating bath additives on the electrocatalytic properties of copper in acid are summarized in Tables 1–3; these are discussed here individually.

4.1 Cl⁻ ions

Cl^- ion is a well known catalyst for copper deposition in acid solution [31, 32]. Copper is normally deposited in the metastable state, apparently with a large excess of vacancies and other defects (such as grain boundaries) present [33]. Some of the freshly deposited copper atoms are assumed to be poorly lattice stabilized, highly active and thus present at the surface in an ionized, $Cu^{+}_{2,surf}$, form (rapid, transport-controlled, plating occurs only below −0.7 V, i.e. below the $Cu^{+}_{2,surf} \rightarrow Cu_{2,surf}$ transition). The presence of Cu_2^{+} species at the interface creates a positive electric field at the latter which repels Cu^{2+}_{aq} and thus inhibits the plating reaction. On addition of Cl^- ions, the latter become attached to surface cation sites, forming $Cu^{+}_{2,surf} - Cl^{-}$species, which reduces the positive field barrier at the interface and hence the plating rate is increased [13].

The three catalytic processes investigated here (NB, O_2 and NO_3^- ion reduction) all commence in the negative sweep at *ca.* −0.6 V, i.e. at the point where the reduction mediator begins to appear at the interface. However, for these reactions the Cl^- ion generally had a moderately inhibiting effect which is assumed to be due to interference with the active site reaction. Precise details of such inhibition are unknown, but bonding of the chloride ion to the oxidized state of the mediator may impede the regeneration of the reduced form of the latter.

4.2 PEG

The presence of PEG alone usually has little effect on either copper plating rates [34] or, in the present work, on the rates of electrocatalysis. It appears that PEG does not bind strongly to the surface or to the active sites on same.

4.3 PEG + Cl⁻ ions

The presence of this combination of additives results in severe inhibition of the copper plating above −0.7 V (see Fig. 12 [13]). Evidently below −0.4 V PEG binds strongly to a surface layer of chloride, i.e.$Cu^{+}_{2,surf} - Cl^{-}$, and the resulting deposit blocks the surface, until the surface layer begins to undergo reduction at *ca.* −0.7 V. Addition of PEG and Cl^- ions also had a severely inhibiting effect (at −0.8 V) on the electrocatalytic processes investigated here, this inhibition increasing considerably with increasing Cl^- ion concentration. In the catalytic processes the mediator system is constantly cycling between its reduced and oxidized state and the Cl^- can thus form some $Cu^{+}_{2,surf} - Cl^{-}$ species even at, or below, −0.8 V. While the adsorbed Cl⁻ species may be a source of some inhibition, as outlined here earlier in 4.1, the retardation is more marked when PEG is also present as the surface ion-pair species can now also bind PEG molecules which are more effective in blocking the active sites. Below *ca.* −0.9 V the electrocatalytic processes tend to be transport limited as the overpotential for the reduction of $Cu^{+}_{2,surf}$species is quite large in this region and thus the mediator species exists predominantly in its reduced, or active, state.

4.4 Thiourea (TU)

The effect of adding TU on the copper plating rate, Fig. 10a in [13], is similar to that observed on adding the combined additive, PEG + Cl⁻ ions. TU is a marked plating inhibitor above *ca.* −0.8 V as apparently in this region a film of blocking complexes, $Cu_2(TU)^{+}_{x,surf}$, exists at the cathode surface; the precise identity of the complex involved is unknown. Below −0.8 V, where the active copper is deposited in its reduced form, the blocking Cu(I) complex is not formed and the plating rate approaches a transport limited value. It is clear from the data shown here for NB reduction, Fig. 5a, that TU is a severe inhibitor for electrocatalytic reduction processes; this inhibition begins to decrease below *ca.* −1.0 V but does not totally disappear even at −1.2 V (the cathodic response at the latter value in the presence of TU, Fig. 5a, is appreciably below the plateau value observed for the same process in TU-free solution). Similar behaviour was observed, Fig. 9b, for nitrate ion reduction at copper in the presence and absence of TU.

TU is evidently a more persistent inhibitor under electrocatalytic, as compared with metal electrodeposition, conditions. In the plating process only the reduced form of the mediator exists at the interface below *ca.* −0.7 to −0.8 V and, hence the blocking TU complex is not readily formed in this region. However, in the electrocatalytic processes $Cu^{+}_{2,surf}$species are repetitively generated at surface active sites as the mediator system undergoes its cyclic redox transition. The latter process continues at low potentials (less than −0.8 V) as long as electrocatalysis can occur (even in an inhibited manner); all that is then required for severe inhibition is that the complex, $Cu^{+}_{2,surf}(TU)_x$, formation reaction is rapid and its subsequent reduction is slow. An interesting feature of this model is that the inhibiting complex exists at the interface, below *ca.* −0.8 V, only during the course of electrocatalysis, i.e. the presence of the inhibiting species at low potentials is induced by the catalytic mediation reaction.

4.5 SPS

When used as a sole additive in an acid copper plating bath SPS has little effect on the plating rate [35, 36]. However, it evidently interacts in some manner at the interface as SPS is known as an anti-suppressor [36], i.e. its addition (at a very low level) annuls the severe inhibiting effect of PEG + Cl⁻ ions on the plating reaction. SPS has a severe inhibiting effect on the electrocatalytic reduction reactions; this inhibition was not as marked as with TU, but in the cases of both NB, Fig. 4a, and nitrate ions, Fig. 9a, the reduction responses at −1.0 V were well below the transport limited value (especially in the case of NO_3^-). SPS is assumed to behave in a similar manner to TU with regard to its effect on electrocatalysis; its role as an anti-suppressor in plating baths is more difficult to explain, e.g. if it can counteract the inhibiting effect of PEG + Cl⁻ ions (which suggest that it interacts rather strongly with the surface) why does it not (as sole or combined additive) severely inhibit the copper plating reaction?

4.6 JGB

The addition of JGB also had an inhibiting effect on the electrocatalytic processes, see for instance Fig. 4b; however, its inhibition behaviour was less than that of SPS and especially that of TU. JGB also has a tendency to inhibit copper deposition [13, 37], but in this respect its behaviour (under CV conditions) is not simple.

5 Conclusions

1. Copper in acid solution displays a metastable surface redox transition at *ca.* −0.7 (±0.1) V (SMSE) [13] which is of major significance from both an electrocatalytic and electrodeposition viewpoint. Although the nature of this transitions is not well understood, it apparently functions as redox mediator system (in a manner similar to that observed with chemically modified [38] or redox enzyme catalysed [39] electrode systems) which dominates the electrocatalytic behaviour of this electrode system (similar proposals were made earlier for both copper in base [27] and gold in both acid and base [26]).
2. The overpotential for oxygen reduction at copper in acid was found to be remarkably large, *ca.* 1.2 V; evidently the reaction does not occur rapidly until the reduced form of the mediator systems begins to appear at the interface at *ca.* −0.6 V (SMSE). The latter potential corresponds to the early stage of the mediator, $Cu_{2,surf}$, generation process; it is obviously quite an

important value in copper electrochemistry but is not related in any way to the equilibrium behaviour (or the Pourbaix diagram [15]) of copper in aqueous media.

3. Bath additives often play a crucial role in copper electrodeposition in acid plating baths. Such additives (with the possible exception of PEG) tend to retard the electrocatalytic behaviour of copper in acid, apparently by interacting with the oxidized form of the interfacial couple. In some cases, e.g. with TU, the inhibition of the electrocatalytic behaviour, even at −1.0 V (SMSE), is quite severe as the redox cycling process at the interface ensures a supply of the oxidized state of the mediator at potentials where the state in question should not exist, i.e. the inhibition in such cases is catalysis-driven (the inhibition is attributed to localized complex formation, rather than to conventional chemisorption of the inhibitor).

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