Electrodeposition of copper from mixed sulphate–chloride acidic electrolytes at rotating disc electrode

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The effect of chloride ion on the deposition of copper from low metal concentrations in aqueous, acid sulphate solutions was investigated. The electrolytes contained 0.05 mol dm^{-3} CuSO$_4$ and 0.5 mol dm^{-3} Na$_2$SO$_4$ at pH 2 and 296 K. The chloride ion concentration was varied in a wide range from 0.03 to 2.0 mol dm^{-3}. Linear sweep voltammetry was carried out under well defined flow conditions at a smooth platinum rotating disc electrode. The progressive transition from a single, two-electron reaction for the reduction of Cu(II)→Cu(0) to two, single-electron reactions for the reduction sequence: Cu(II)→Cu(I)→Cu(0) was clearly evident as the chloride ion concentration increased. The charge transfer and mass transport characteristics of these reactions were evaluated. The formal potential for the Cu(II) reduction to Cu(I), the shift in the potential region for complete mass transport controlled reduction of Cu(I) to Cu(0) and the potential for hydrogen evolution at the deposited copper were also studied. A semi-logarithmic relationship between exchange current density and half-wave potential for Cu(II)→Cu(I) with chloride ion was achieved when the Cl$^-$/Cu(II) ratio in the electrolytes exceeded 2, due to the presence of the Cu(I) dichlorocuprous anion, CuCl$_2^-$.

List of symbols

α	Charge transfer coefficient, dimensionless
b	Tafel slope, V decade^{-1}
c_{Cl^-}	Concentration of chloride ion in the electrolyte, mol dm^{-3}
$c_{Cu^{2+}}$	Concentration of Cu(II) in the electrolyte, mol dm^{-3}
E	Electrode potential versus Ag|AgCl, V
$E_e^o\big|_{Cl^-}$	Formal potential of copper in the presence of chloride ion, V
F	Faraday constant, C mol^{-1}
j	Current density, A cm^{-2}
j_L	Limiting current density, A cm^{-2}
j_o	Exchange current density, A cm^{-2}
k	Rate constant, s^{-1}
n	Stoichiometric number in reaction (4), dimensionless
R	Molar gas constant, J K^{-1} mol^{-1}
S	Nernstian slope in equation (15), V
T	Temperature, K
z	Number of electrons involved in the electrode reaction, dimensionless

Subscripts

a	Anodic
b	Cathodic
e	Equilibrium
Cl$^-$	Chloride ions
Cu^{2+}	Cu(II) ions
L	Limited by convective diffusion mass transport

Introduction

Electrodeposition of copper is often carried out under controlled flow conditions. For laboratory investigations, rotating electrodes have been used as experimental tools for electroanalytical and mechanistic studies of electrochemical reactions. There are many types of rotating electrode geometries considered such as single electrode, roughened electrodes, bi-electrode systems and other electrodes.[1] Among these electrode geometries, the rotating disk electrode (RDE) and the rotating cylinder electrode (RCE) are the most frequently used electrodes for laboratory and industrial investigations. Such electrodes are hydrodynamic tools that use forced convection to enhance the mass transport rate to the electrode surface. The introduction of forced convection to the electrode surface results in increased current

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density and sensitivity. In practice, the hydrodynamically smooth rotating disk electrode generally operates in laminar flow, while the rotating cylinder electrode normally operates in turbulent flow.[1]

Many studies have been undertaken on the electrodeposition of copper; due to its diverse applications, e.g. electrical contacts and solder components for the electronics industry, undercoats for nickel and chromium plating and as a decorative finish. Various acidic electrolyte formulations are available, including sulphate-, fluroborate-, cyanide-, pyrophosphate- and sulfonate baths.[2,3] Pyrophosphate and cyanide solutions have been used to deposit copper at low to medium current densities whereas acid sulphate and fluroborate solutions tend to be used at higher plating rates while methanesulphonic acid electrolytes have been used at a high current density and at a high copper ion concentration.[4,5]

A wide range of additives has been investigated for the electrodeposition of copper from an acid sulphate electrolyte. In the electronics and electrical industries, additives can include suppressors, accelerators and levellers to produce desirable coatings.[6] Common examples include polypropylene glycol,[7–9] bis(3-sulphopropyl) disulphide, nitrogen containing aromatic compounds,[10,11] thiourea,[12] gelatine,[13] 3-mercapto-1-propanesulphonate[14,15] and chloride ion.[16] Such chemicals are added in small quantities and can realise an improved deposit quality involving the appearance of the plated metal (surface brightness), a modified coating structure together with physical properties (e.g. improved corrosion resistance, wear and electrical conductivity), grain refinement and suppression of dendritic growth together with improved covering and throwing power.

Chloride ion has a significant effect on the copper deposition. For example, an addition of a low chloride ion concentration, e.g. 50–200 ppm, is generally used for copper electroplating[17] and 1 to 2×10^{-3} mol dm^{-3} used in the electronics and electrical industries.[18] A higher chloride ion concentration ($0 \cdot 1$–$3 \cdot 0$ mol dm^{-3}) is used in copper electrowinning; levels up to $9 \cdot 0$ mol dm^{-3} are used for copper refining in hydrothermal systems[19] and 280 g dm^{-3} used in the leaching of copper from copper mineral chalcopyrite.[20] In most cases, chloride ion is added as a supplement to other additives to achieve combinatorial effects. For example, in the absence of other additives, Cl$^-$ will promote the reduction of copper at a more positive electrode potential.[20] In the presence of both Cl$^-$ and polyethylene glycol (PEG), however, the copper reduction may be inhibited to a more negative potential and the Cl$^-$ ion may assist in the formation of spherical PEG molecules and monolayer adsorption of PEG.[8,9,13,22–24]

The present work considers relatively dilute <50 mmol dm^{-3} copper solutions which are found in rinse waters and environmental wastes. The effect of chloride ion on copper deposition in mixed chloride–sulphate electrolytes at a constant pH of 2 is investigated using a rotating disc electrode. The presence of chloride ion is considered to form various complex formations with the copper ion, e.g. CuCl$^+$, CuCl$_2^-$, CuCl$_3^{1-}$ and CuCl$_4^{2-}$.[24,25] In most cases, the redox reaction of Cu(II) to Cu(I) is investigated.[25,27] In sulphate electrolytes, the reduction of Cu(II) to Cu(0) may involve a single, two-electron reduction step
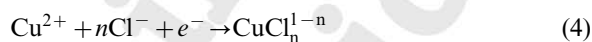
$$Cu^{2+} + 2e^- \rightarrow Cu \tag{1}$$
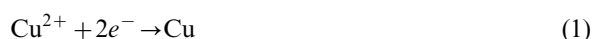
This reversible reaction has a standard potential of $0 \cdot 34$ V(SHE).

In chloride electrolytes, copper(I) is stabilised in the reduction sequence Cu(II) to Cu(I) to Cu(0);[28–30] the reduction of Cu(II) to Cu(0) may involve an intermediate step

$$Cu^{2+} + e^- \rightarrow Cu^+ \tag{2}$$

$$Cu^+ + nCl^- \rightarrow CuCl_n^{1-n} \tag{3}$$

The overall reaction becomes

$$Cu^{2+} + nCl^- + e^- \rightarrow CuCl_n^{1-n} \tag{4}$$

The second step for the reduction of Cu(I) ions to copper metal, Cu(0), may then proceed via

$$CuCl_n^{1-n} + e^- \rightarrow Cu + nCl^- \tag{5}$$

where n is the stoichiometric number for chloride ion. The formation of cuprous chloro-complexes will depend on the concentration of chloride ion in the electrolyte. The stabilisation of Cu(I) with chloride ion is evidenced by the high value of its critical stability constant (K). For Cu(I) chloro-complexes, log $K = 5 \cdot 19$ whereas for Cu(II) chloro-complexes, log $K = 0 \cdot 09$,[7] i.e. the chloride ion interacts strongly with Cu(I) but weakly with Cu(II).

Electrodeposition of copper from an electrolyte containing chloride ion has been studied at platinum[31] and gold rotating ring disc electrodes.[32] Both studies demonstrated that Cu(I) is less stable in SO$_4^{2-}$, but in the presence of Cl$^-$, the Cu(II) is stabilised and the reaction on the disc gave two separate, single electron waves. In this work, the authors have used a wide range of chloride ion to copper ion concentration ratios to investigate the progressive changes in copper reduction. Such high chloride ion levels are commonly encountered in electrowinning and the recovery of copper from aqueous effluents by electrodeposition. Linear sweep voltammetry has been carried out at a rotating disc electrode enabling the charge transfer and mass transport characteristics of copper depositions to be evaluated. The change in the limiting current density and the number of electrons involved have been investigated. The open-circuit and half-wave potentials of Cu(II) to Cu(I) were also considered. The effects of chloride ion on the exchange current density, the potential region for complete mass transport controlled reduction of Cu(I) to Cu(0) and the potential for hydrogen evolution have also been studied. An earlier paper in this journal[31] considered copper deposition from 20–50mM CuSO$_4$ + $1 \cdot 5$M NaCl at pH 2 and 293 K. The present work involves an Na$_2$SO$_4$ electrolyte to which Cl$^-$ ions are added; this study greatly extends the concentration ranges of chloride ions and dissolved copper, hence their molar ratio together with the use of simple voltammetry techniques to study the kinetics of copper deposition from chloride containing acid sulphate solutions

Experimental

Copper was deposited from an electrolyte containing $0 \cdot 05$ mol dm^{-3} copper sulphate ($99 \cdot 995\%$CuSO$_4$) and

0·5 mol dm^{-3} sodium sulphate (99·995%Na$_2$SO$_4$) at 296 K corrected to pH 2 using H$_2$SO$_4$. Various concentrations of sodium chloride (from 0·03 to 2·0 mol dm^{-3} 99·995%NaCl) were pipetted into the electrolyte prior to each experiment. All chemical reagents were analytical grade and supplied by Fischer Chemical UK Ltd. A conventional three-electrode, glass cell was used (150 cm^3 volume). The working electrode was a circular disc electrode consisting of a platinum (99·995% purity, 2 mm radius, 0·126 cm^2 nominal surface area) surrounded by a PTFE shroud (6 mm radius). The counter electrode was a platinum mesh (99·995% purity, 1 cm length × 1 cm width, 0·25 mm nominal aperture), and was placed in a glass tube compartment containing the background electrolyte of 0·5 mol dm^{-3} Na$_2$SO$_4$ corrected to pH 2 with H$_2$SO$_4$. It was separated from the main electrolyte by a Nafion (NF115/H$^+$) cation membrane. The reference electrode was silver|silver chloride electrode, Ag|AgCl in the Luggin capillary compartment, which contained an agar–agar gel of 0·5 mol dm^{-3} Na$_2$SO$_4$ corrected to pH 2 with H$_2$SO$_4$. This arrangement provided a low liquid junction potential and minimised further chloride contamination of the working electrode compartment due to leakage of the reference electrode filling solution.

The platinum disc electrode was wet-polished with 3 μm Al$_2$O$_3$ then 0·15 μm SiO$_2$ particles on a LeCloth polishing substrate. The disc surface, which was cleaned and ultrasonicated with ultrapure water to remove particulates, was freshly polished before each experiment and used immediately. The platinum RDE active surface was placed 2 mm from the tip (1 mm diameter) of the Luggin capillary and positioned centrally in the three-electrode cell. Electrolyte temperature was maintained at 296 K. A fast stream of nitrogen gas was bubbled through the electrolyte for 10 min before each experiment to remove dissolved oxygen and a nitrogen gas blanket was maintained over the surface of the electrolyte. Linear sweep voltammetry was performed using a platinum rotating disk electrode at 800 rev min^{-1}, the electrode potential was swept from + 0·9 to – 1·0 V versus Ag|AgCl at 16 mV s^{-1}. The open-circuit potential measurement was obtained at a static disc electrode after 10 min immersion time in the electrolyte. All electrochemical measurements were made with an EcoChemie Autolab potentiostat (PGSTAT20) using the General Purpose, Electrochemical Software, GPES Version 4.5.

Results and discussion

Figure 1 shows the linear sweep voltammetry for copper deposition at the platinum rotating disc electrode (a) sulphate bath and (b) to (f) mixtures of chloride and sulphate electrolytes. The platinum RDE was rotated at 800 rev min^{-1} and the electrode potential was linearly swept from + 0·9 to – 1·0 V versus Ag|AgCl at 16 mV s^{-1}. In the sulphate bath, a single limiting current density plateau was observed (plateau 1), corresponding to the two electron reduction of Cu(II) to Cu(0). In the presence of chloride ion in the electrolytes, the appearance of a second well defined wave and limiting current density can be observed. In Fig. 1*f*, plateau A represents the maximum rate for the reduction of Cu(II) to Cu(I) while plateau B results from the maximum rate of reduction of Cu(I) to Cu(0). The

Cu(I) ion is stabilised by chloride ion and the reduction of Cu(II) to Cu(I) to Cu(0) involves two, single electron steps. The starting potential for the reduction of Cu(II) to Cu(I); Cu(I) to Cu(0); hydrogen evolution on copper deposits and the limiting current density of Cu(II) to Cu(I) and Cu (0) are shifted with the chloride ion concentration in the electrolytes. Under controlled flow conditions (achieved using the rotating disc electrode), the electrode potential for the first plateau of Cu(II) to Cu(I) can be described by[33]

$$E = E_e^o\big|_{Cl^-} - b_c \log\left(\frac{j_L - j}{j}\right) \qquad (6)$$

where j_L is the limiting current density for Cu(II) to Cu(I), $E_e^o\big|_{Cl^-}$ is the formal potential for Cu(II) to Cu(I) in the presence of chloride ion, as described by reaction (4) and b_c is the Tafel slope. A plot of E against $\log\left(\frac{j_L - j}{j}\right)$ yielded a linear relationship as shown in Fig. 2*a* for the reduction of Cu(II) to Cu(I). The Tafel slope remained similar for all chloride ion concentration in the electrolytes and was estimated at approximately − 62 mV decade^{-1}. Figure 2*b* shows that the relationship between the measured open-circuit and the half-wave potentials for the reduction of Cu(II) to Cu(I) occurred at a more positive potential with an increase of chloride ion in the solution. This effect, i.e. the presence of Cl$^-$ led to an acceleration of copper ion reduction, has also been reported in the deposition of copper from a solution containing 0·3 mol dm^{-3} CuSO$_4$, 2·2 mol dm^{-3} H$_2$SO$_4$, 50 ppm (*ca.* 0·0014 mol dm^{-3}) Cl$^-$ and 1 g dm^{-3} polyethylene glycol.[13]

Figure 2*c* shows that the initial potential for the reduction of Cu(I) to Cu(0) shifted linearly with the logarithmic of chloride ion concentration and that the initial potential for hydrogen evolution on the copper deposits reached a steady state potential, approximately − 0·64 V versus Ag|AgCl at increasing chloride ion concentration in the electrolytes. The potential region for complete mass transport controlled reduction of Cu(I) to Cu(0) was also shown to vary, being approximately − 115 mV decade^{-1} of logarithmic chloride ion concentration. The deposition potential for the reduction of Cu(I) to Cu(0) shifted to more negative potentials and the mass transport control region was shortened at higher chloride ion concentrations. All the findings show that a linear dependence of deposition potential versus Cl$^-$ concentration could be obtained at a chloride ion concentration (0·1 mol dm^{-3}) approximately twice that of the copper ion concentration (0·05 mol dm^{-3}) in the electrolytes.

When the cathodic reaction is under charge transfer control, the kinetics can be approximated by the Tafel equation which shows a linear relationship between the logarithm of the current density and the overpotential[33]

$$jc = \log jo - b_c\eta \qquad (7)$$

where b_c is the cathodic Tafel slope, $b_c = -2\cdot303\alpha RT/zFT$. For a one-electron change at 296 K and a transfer coefficient of 0·5, the theoretical Tafel slope is −60 mV decade^{-1}.

Figure 3*a* shows the Tafel approximation using the reduction of Cu(II) to Cu(I) ions. The Tafel slopes remained unchanged at approximately −68 mV decade^{-1} and the exchange current density varied in the presence of chloride
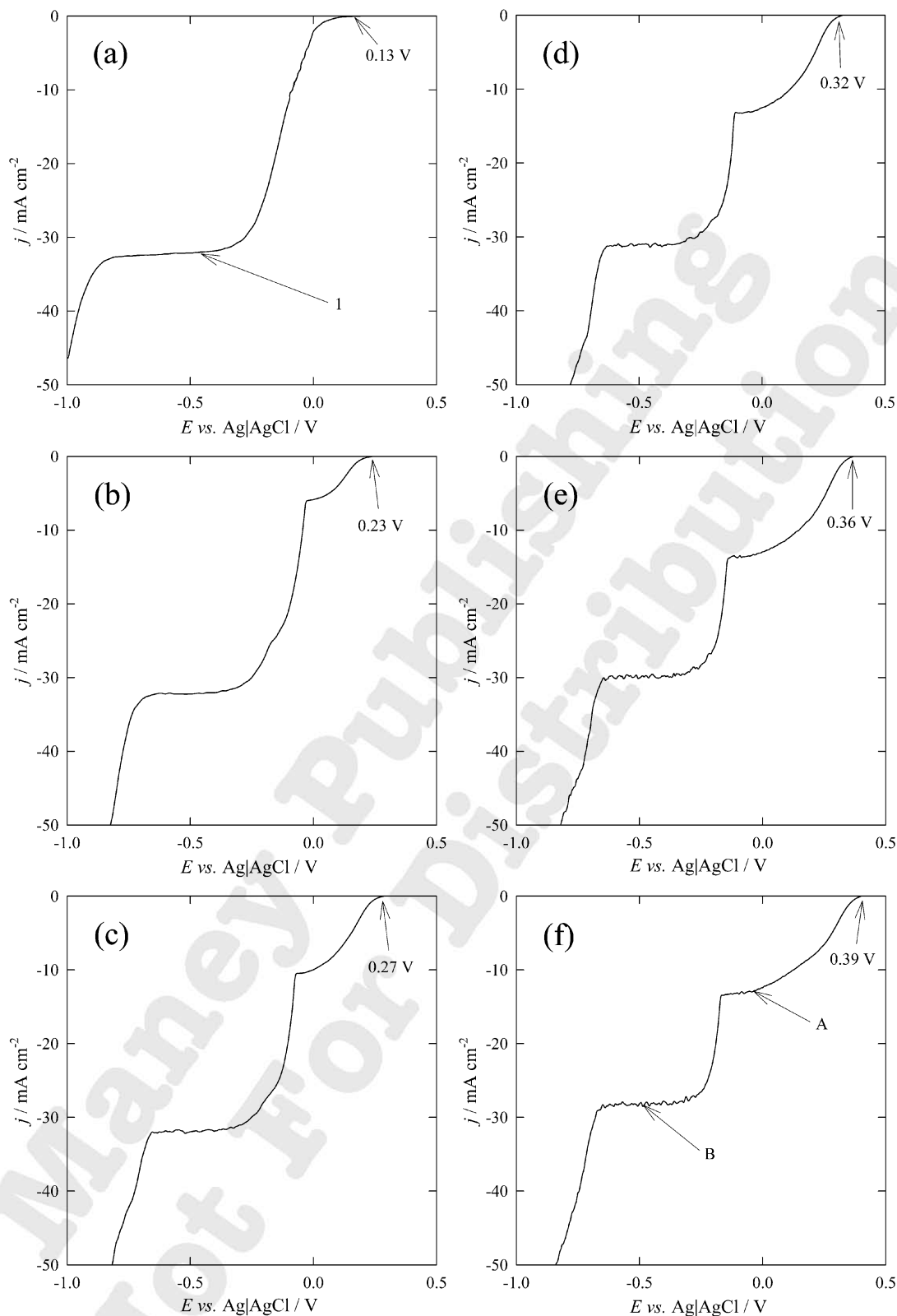
1 Linear sweep voltammetry of copper electrodeposition at controlled flow conditions: platinum RDE was rotated at 800 rev min⁻¹ and electrode potential was swept from +0·9 to –1·0 V versus Ag|AgCl at 16 mV s⁻¹; *a* sulphate media and *b–f* mixed chloride–sulphate electrolytes; *a* 0, *b* 0·12, *c* 0·32, *d* 0·69, *e* 1·29 and *f* 1·92 mol dm⁻³ NaCl; base electrolyte contained 0·05 mol dm⁻³ CuSO₄ and 0·5 mol dm⁻³ Na₂SO₄ corrected to pH 2 at 296 K; values marked on curves correspond to open-circuit electrode potentials

ion. Figure 3*b* shows the exchange current density shifted linearly with the logarithmic of chloride ion concentration, starting at chloride ion (0·1 mol dm⁻³) twice the copper ion concentration (0·05 mol dm⁻³) in the electrolyte. A

theoretical relationship between the exchange current density and chloride ion concentration can be obtained from the Butler-Volmer equation. At equilibrium, the mass balance for reaction (3) can be written in terms of a flux[29]
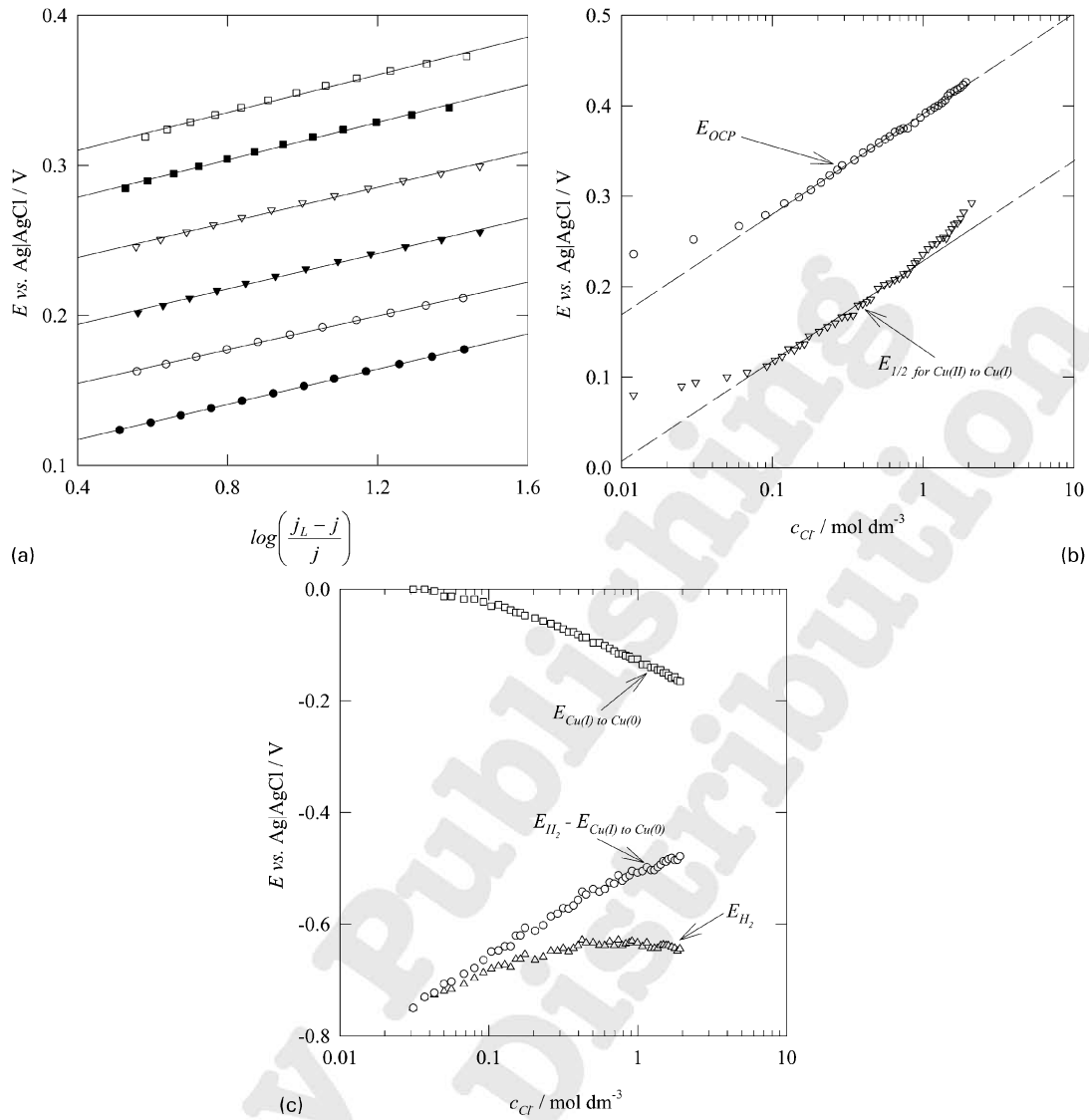
2 Electrode potential with chloride ion concentration: base electrolyte contained 0·05 mol dm^{-3} CuSO$_4$ and 0·5 mol dm^{-3} Na$_2$SO$_4$ corrected to pH 2 at 296 K: *a* expression of Nernstian plot under controlled flow conditions; platinum RDE was rotated at 800 rev min^{-1} and electrode potential was swept from +0·9 to − 1·0 V versus Ag|AgCl at 16 mV s^{-1}; ● 0·03, ○ 0·12, ▼ 0·32, ▽ 0·69, ■ 1·29 and □ 1·92 mol dm^{-3} NaCl; *b* effect of chloride ion on ○ open circuit potential and ▽ half-wave potential of Cu(II) reduction to Cu(I); *c* deposition potential with chloride ion: □ starting potential for the reduction of Cu(I) to Cu(0), △ hydrogen evolution at copper deposits and ○ potential for the reduction of Cu(I) to Cu(0) before hydrogen evolution

$$\frac{j_c}{zF} = k_c c_{Cu^{2+}} c_{Cl^-}^{\ n} \tag{8}$$

where j_c is the partial current density for cathodic reaction, z is the number of electrons involved in the electrode process, F is Faraday's constant, k_c is the cathodic reaction rate of reaction. Similarly, the anodic flux of copper ions can be described by

$$\frac{j_a}{zF} = k_a c_{CuCl_n^{1-n}} \tag{9}$$

where j_a is the partial current density for anodic reaction and k_a is the rate constant for the anodic reaction. When the electrode potential is displaced away from the equilibrium, the total current density is the difference between the partial current density of the cathodic and anodic reactions
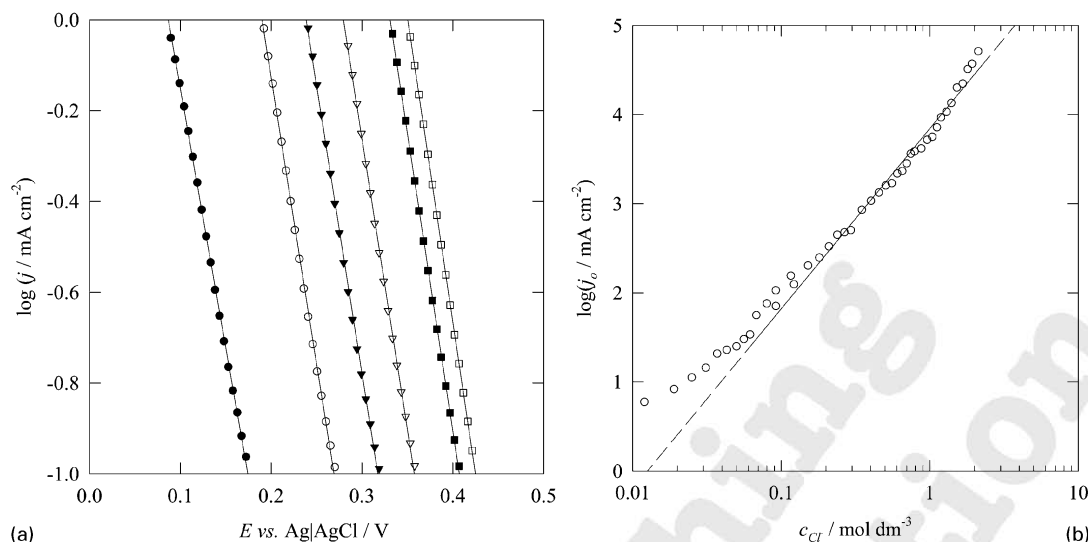
$$j = j_a - j_c \tag{10}$$

The rate of reaction can be expressed in terms of the standard rate of reaction

$$k_a = k_a^o \exp\left(\frac{\alpha_a zFE}{RT}\right) \tag{11}$$

$$k_c = k_c^o \exp\left(\frac{-\alpha_c zFE}{RT}\right) \tag{12}$$

where E is the electrode potential versus a reference electrode. Equation (12) then becomes

3 Analysis of copper ion reduction in presence of chloride ion added to sulphate media electrolyte: *a* Tafel plots of Cu(II) to Cu(I) reduction reaction ● 0·03 mol dm^{-3}, ○ 0·18 mol dm^{-3}, ▼ 0·48 mol dm^{-3}, ▽ 0·74 mol dm^{-3}, ■ 1·44 mol dm^{-3} and □ 1·86 mol dm^{-3} NaCl and *b* logarithm of exchange current density versus logarithm of chloride ion concentration

$$j = zFk_a^o \exp\left(\frac{\alpha_a zFE}{RT}\right) c_{CuCl_n^{1-n}} -$$
$$zFk_c^o \exp\left(\frac{-\alpha_c zFE}{RT}\right) c_{Cu^{2+}} c_{Cl^-}^n \qquad (13)$$

At equilibrium, the partial current density for the cathodic and anodic reactions is equal and opposite sign. The exchange current density at the equilibrium potential can be simplified to

$$j_o = zFk_a^o \exp\left(\frac{\alpha_a zFE_e}{RT}\right) c_{CuCl_n^{1-n}} =$$
$$-zFk_c^o \exp\left(\frac{\alpha_c zFE_e}{RT}\right) c_{Cu^{2+}} c_{Cl^-}^n \qquad (14)$$

where j_o is the exchange current density and E_e is the equilibrium potential. The base 10 logarithmic form of the forward, cathodic reaction in equation (14) is

$$\log j_o = S^{-1}E_e \log\left(-zFk_c^o c_{Cu^{2+}}\right) + n \log c_{Cl^-} \qquad (15)$$

where S is the Nernstian slope ($S = 2\cdot303RT/zF$ which is 58·7 mV at 296 K for a one electron reduction).

Equation (15) indicates that a plot of $\log j_o$ against $\log c_{Cl^-}$ should be linear. From Fig. 3*b*, the slope gave a stoichiometric number for the chloride ion, *n* of $2\cdot02 \approx 2$, supporting the dichlorocuprous anion, $CuCl_2^-$ as the main species complexing with Cu(I) in the electrolyte.

Figure 4*a* shows the effects of chloride ion concentration on the limiting current density for the reduction of Cu(II) to Cu(I) and Cu(I) to Cu(0). Three regions can be identified. At low chloride ion concentration,
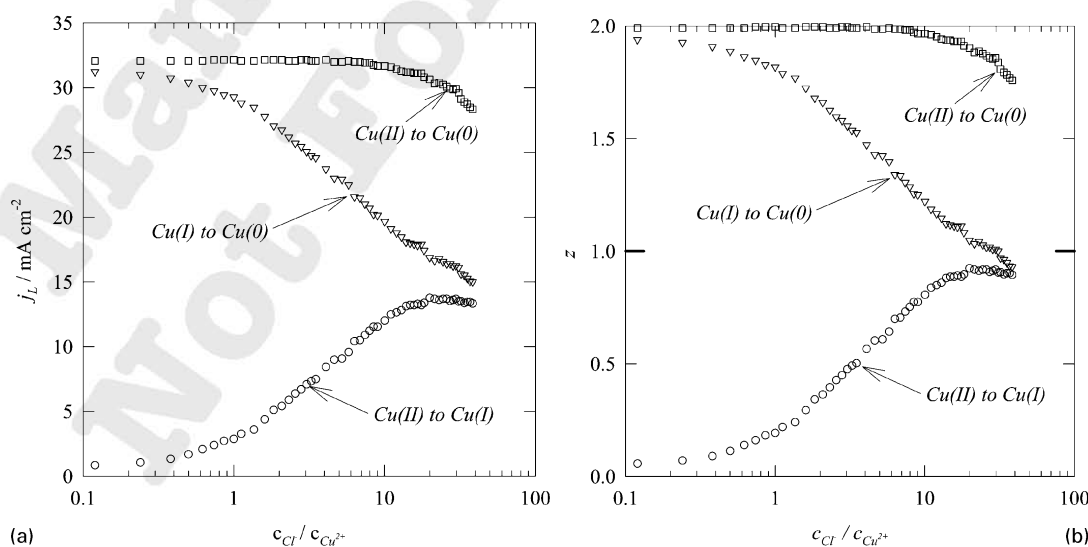
4 Influence of chloride ion concentration on *a* limiting current density for copper deposition from mixed chloride–sulphate electrolyte and *b* number of electrons involved in deposition reaction: ○ reduction of Cu(II) to Cu(I), ▽ Cu(I) to Cu(0) and □ Cu(II) to Cu(0); diffusion coefficient for Cu(II) in absence of chloride ion was $4\cdot5 \times 10^{-6}$ cm^2 s^{-1}; $4\cdot0 \times 10^{-6}$ cm^2 s^{-1} for Cu(II) in presence of chloride ion and $4\cdot5 \times 10^{-6}$ cm^2 s^{-1} for Cu(I)

$c_{Cl^-}/c_{Cu^{2+}} \leq 1$ and the limiting current density increased marginally for reduction of Cu(II) to Cu(I) then decreased slightly for the Cu(I) to Cu(0) reaction. At an intermediate concentration ratio, $1 \leq c_{Cl^-}/c_{Cu^{2+}} \leq 10$, the limiting current density further increased for Cu(II) to Cu(I) then decreased for Cu(I) reduction to Cu(0). Linear curves can be obtained in this region, where the limiting current density for the reduction of Cu(II) to Cu(I) and Cu(I) to Cu(0) was varied approximately 9.7 mA cm^{-2} per decade with respect to the chloride ion to copper ion concentration. At relatively high chloride to copper ion concentrations, $c_{Cl^-}/c_{Cu^{2+}} \geq 10$, the limiting current density for the reactions reached a steady state condition.

The limiting current density for the reduction of Cu(II) to Cu(0), e.g. 30 mA cm^{-2}, in the absence of chloride ion, was approximately twice that for the reduction of Cu(II) to Cu(I) and for Cu(I) to Cu(0), 15 mA cm^{-2}, in the presence of chloride ion. The limiting current density for Cu(II) to Cu(0) is lowered at high chloride ion compared with low chloride ion, e.g. at 0.05 mol dm^{-3} Cl$^-$, the limiting current density was approximately 32 mA cm^{-2}; at a 1.92 mol dm^{-3} Cl$^-$ ion concentration, the limiting current density was approximately 28 mA cm^{-2}. A similar observation was also reported; e.g. less copper was deposited onto a porous silica substrate from a solution containing 0.01 mol L^{-1} copper ion in trifluoromethanesulphonic acid, at an NaCl concentration >0.1 mol dm^{-3} Cl$^-$. Copper deposition was found to be progressively inhibited as the concentration of Cl$^-$ increased in the solution.[34,35] Assuming diffusion coefficients of 4.5×10^{-6} cm^2 s^{-1} for Cu(II) in the absence of chloride ion; 4.0×10^{-6} cm^2 s^{-1} for Cu(II) in the presence of chloride ion and 4.5×10^{-6} cm^2 s^{-1} for Cu(I) ions, the number of electrons involved in each reduction step can be estimated, as shown in Fig. 4b. The trends are similar to those shown in Fig. 4a. The presence of Cu(I) species during copper deposition progressively became more important as chloride addition to the sulphate electrolyte was increased.

Conclusions

1. Mixed chloride–sulphate acidic electrolytes containing 0.05 mol dm^{-3} CuSO$_4$ and 0.5 mol dm^{-3} Na$_2$SO$_4$ corrected to pH 2 with H$_2$SO$_4$ and 0.03 to 2.0 mol dm^{-3} NaCl at 296 K were investigated. Linear sweep voltammetry was used to study the influence of chloride ion on the voltammetry of copper deposition using a platinum rotating disc electrode.

2. Under controlled flow conditions at a rotating disc electrode, the reduction of Cu(II) to Cu(0) involved the simultaneous transfer of two electrons in a sulphate bath and the Cu(II) to Cu(I) to Cu(0) system showed the increasing importance of Cu(I) species when a sufficient chloride ion concentration was present.

3. Steady state, linear sweep voltammetry showed a transition from a single limiting wave in pure sulphate electrolyte to two limiting waves in mixed chloride-sulphate electrolyte. The presence of Cu(I) ions became increasingly important when sufficient chloride ion was added to the sulphate electrolyte.

4. Linear relationships between the chloride ion concentration with exchange current density, open circuit potential, half-wave potential for Cu(II) to Cu(I), start potential and potential region for complete mass transport control of Cu(I) to Cu(0), were obtained. The presence of the dichlorocuprous anion, CuCl$_2^-$ became dominant when the molar concentration ratio of chloride to copper ion exceeded 2.

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