Electrodeposition of copper from pure cupric chloride hydrochloric acid solutions

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Electrodeposition from $CuCl_2$–HCl media has been investigated to establish a clean and direct method of copper extraction from cupric chloride solutions purified by anion exchange. The major difficulties of the process – cathode corrosion, CuCl precipitation and roughness of the deposit – were taken into consideration. To prevent contamination, no chemical agents or additives were used in the electrolyte preparation. The workable range of electrolyte composition was approached from a computer aided stability study of the different aquo- and chloro-complex copper species. Experiments suggested that coordination of the fundamental electrolysis parameters can ensure acceptable copper deposits and current efficiencies. A special method of agitation proved effective in improving the conditions.

1. Introduction

Recent applications of ultrahigh purity copper [1, 2] require the elimination of impurities to reach 99.9999% or even a higher level of purity. A novel method of purification has been devised [2] based on a comprehensive anion-exchange separation in chloride media. Copper samples were produced from the purified solution by evaporation to dryness and hydrogen reduction [3], or by direct electrowinning. Due to the aggressive chemistry of this $CuCl_2$–HCl system, hardly any work has so far been reported on the practical feasibility of copper electrodeposition from pure cupric chloride media.

Electrode potentials of copper in chloride media [4, 5] suggest no obstacle to electrodeposition. Several publications [6–10], however, have reported that electrolysis of cupric chloride solutions may involve excessive corrosion of the copper cathode and/or the precipitation of CuCl.

Corrosion of the copper cathode can be essentially attributed to the reduction of Cu(II) species:

$$[CuCl_x]^{(2-x)} + Cu + (2y - x)Cl^-$$
$$= 2[CuCl_y]^{(1-y)} \quad K = 10^{3.5\sim4.1} \quad (1)$$
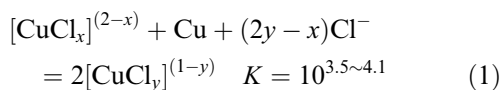
where the most likely value of x is 0, while that of y is 2 in solutions of low Cl^- concentration ($<2 \sim 3\ mol\ dm^{-3}$). Winter *et al.* [9] have pointed out that hydrochloric acid and neutral chloride salts are virtually interchangeable as sources of free chloride ions, and confirmed that even small concentrations of cupric ions in the cuprous chloride electrolyte can cause a significant decrease in the current efficiency. The rate of dissolution can be higher than that of

deposition if the cupric and chloride ion concentrations are high while the current density is low. At higher current densities, however, the copper produced is often characterized by rough, or even powdery structure [1–16]. The quality of the deposit can be improved by addition of organic levelling agents [11, 15], which should, however, be avoided when ultra high purity is the aim.

Difficulties of copper deposition from chloride solutions are further aggravated by a strong precipitating tendency of CuCl at low HCl concentrations.

The designed anion-exchange separation procedure [2, 3] ensures the production of a highly purified chloride solution, and the possible impurities of the copper cathode are only hydrogen and chlorine from the physically entrapped electrolyte or the precipitated CuCl salt. High chlorine content is undesirable because its complete removal would imply increased danger of contamination. Therefore, it is also necessary to avoid rough cathode surfaces and significant precipitation of cuprous chloride.
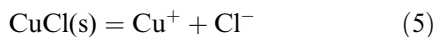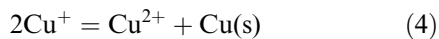
2. Chemical equilibrium in the chloride electrolyte

Stability of certain species in the Cu–Cl–H_2O system [17, 18], has not been fully clarified in earlier publications. Therefore, to elucidate chemical equilibria in the electrolyte, a detailed stability diagram was constructed referring to different total copper concentrations in the solution. Particular attention was paid to the consistency of the thermodynamic data.

The concentration of the cuprous aquo-ion, Cu^+, is strictly limited by disproportionation. According to Equation 1, however, free chloride ions can virtually reverse the process of disproportionation by forming

stable chloro-complex species. The existence of the Cu^+ (aquo) ion is also limited by the very low solubility product of CuCl. Precipitation of CuCl can be expected when the complexation and disproportionation equilibria require higher Cu^+ concentration than that permitted by the solubility product.

The concentrations of the species were estimated from the following reactions:

$$Cu^+ + xCl^- = [CuCl_x]^{(1-x)} \quad (2)$$

$$Cu^{2+} + yCl^- = [CuCl_y]^{(2-y)} \quad (3)$$

$$2Cu^+ = Cu^{2+} + Cu(s) \quad (4)$$

$$CuCl(s) = Cu^+ + Cl^- \quad (5)$$

and the selected values of the corresponding equilibrium constants [5, 17, 19] listed in Table 1. The computer simulation [2] refers to the actual case when the chloride solution is in contact with solid copper. Figure 1 shows the cumulative concentrations of the Cu(I) and Cu(II) species together with those of the Cu^+ and Cu^{2+} aquo ions, as functions of the free chloride ion concentration, in equilibrium with solid copper.

The critical conditions leading to the precipitation of CuCl are defined in Fig. 2. The precipitation dominated area shrinks as the total Cu content of the solution is reduced.

The relative stability of the various Cu(I) and Cu(II) species in the Cu–Cl–H2O system is described in Fig. 3. Precipitation of CuCl can be avoided by keeping the HCl (free Cl^-) concentration above approximately $1 \, mol \, dm^{-3}$ in the $5 \sim 20 \, g \, dm^{-3}$ copper concentration range. Much higher HCl concentrations can, however, result in a strong corrosive attack in the presence of the oxidizing cupric ions.

3. Kinetic features of the copper electrode in chloride media

Beyond the corrosion of copper cathodes and the precipitation of cuprous chloride, a further practical obstacle of copper electrodeposition from chloride solutions is the rough, dendritic morphology of the cathodes.

When free chloride ions are available, the vicinity of the copper cathode may be dominated by the Cu(I) species even if the bulk of the electrolyte contains high concentrations of the cupric ions. On the other hand, the monovalent copper species undergo elec-

trolytic and atmospheric oxidation. Therefore, the principle cathode processes are similar in the cases of initially cupric and cuprous chloride bulk electrolytes.

3.1. Mass transfer characteristics

Winter et al. [9] have determined the diffusion coefficients of Cu(I) and Cu(II) species in chloride electrolytes from the correlation of mass transfer and overvoltage. Diffusion coefficients of the $[Cu(H_2O)_6]^{2+}$ species in $1 \, M \, H_2SO_4$ solution and that of the $[CuCl]^+$ and $[CuCl_2]^0$ species in $1 \, M \, HCl$–$4 \, M$ NaCl solution are essentially equivalent ($\sim 5 \times 10^{-10} \, m^2 \, s^{-1}$). Diffusion coefficients of the Cu(I) species have been reported to decrease with the free chloride ion concentration [20].

Albert and Winand [15] have investigated the transient times on a copper cathode in a stationary HCl–NaCl–CuCl electrolyte. In good agreement with Sand's criterion for diffusion control, the products of the current densities and the square roots of the transient times were independent of the current density, but proportional to the Cu concentration.

The relatively high value of concentration polarization results in the growth of surface imperfections [21]. The macrostructural irregularities can protrude deeply into or through the diffusion layer, thereby enhancing local mass transfer and causing rougher cathode surfaces.

3.2. Charge transfer characteristics

High activation overvoltages and low exchange current densities imply high cell voltages, but also better physical quality of the deposited metal. Potential differences between the peaks and valleys and the various crystallographic orientations are reasonably suppressed.

Typical cases of different electrodes in common electrolysing cells suggest a correlation between the exchange current density and the physical characteristics of the deposited metal. At extremely high ($>1000 \, A \, m^{-2}$) exchange current densities, where activation overvoltage is low, the deposit tends to be rough, dendritic and whiskery [22]. On the other hand, high quality deposits can be easily obtained when the exchange current density is very low ($<1 \, A \, m^{-2}$) [23].

The exchange current density of about 1000 –2000 $A \, m^{-2}$ for the critical cathodic electrode reac-

Table 1. Thermodynamic data of copper chloride species at 298 K

Corresponding reactions are given as equation numbers

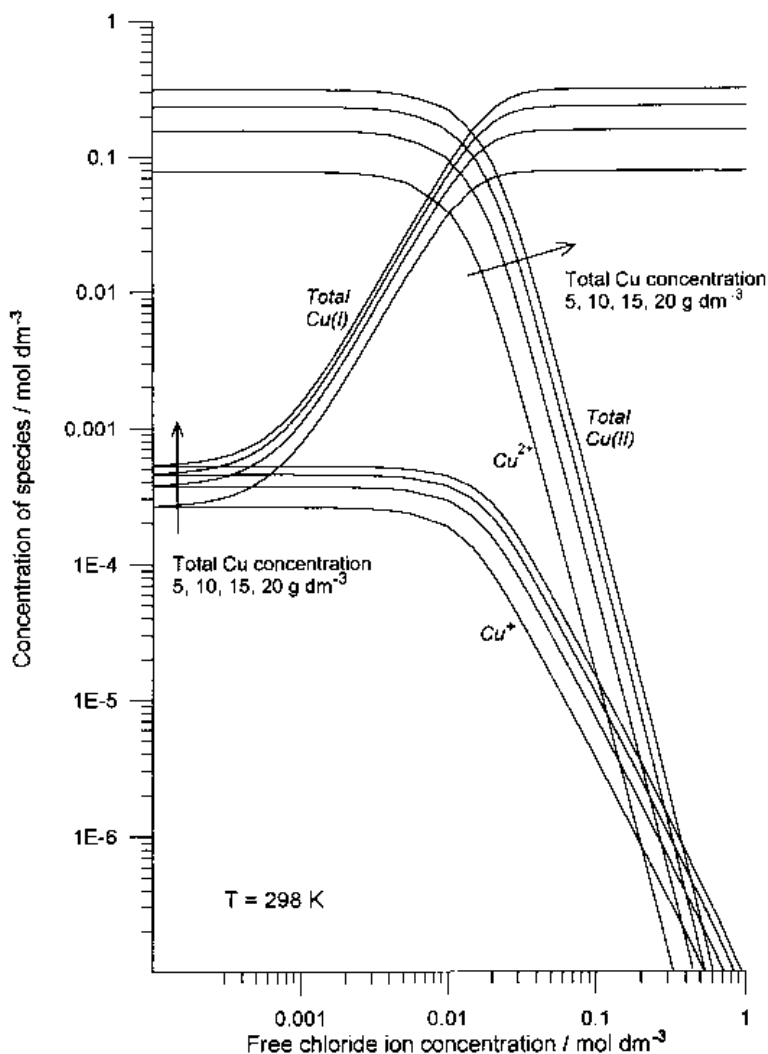| Oxidation state	Solubility product K_{so}	Cumulative stability constants				Disproportionation constant K_{disp}
		β_1	β_2	β_3	β_4	
Cu(I)	1.72×10^{-7} (5)	–	1.995×10^6 (2)	1.202×10^6 (2)	5.012×10^5 (2)	1.148×10^6 (4)
Cu(II)		1.288×10^0 (3)	2.951×10^{-1} (3)	–	–	

Fig. 1. Contribution of the aquo-ions to the cumulative concentrations of the monovalent, Cu(I), and divalent, Cu(II), species in equilibrium with solid copper.

tion in chloride solutions [15] is significantly higher than the average value of about 50–100 A m^{-2} for the corresponding electrode reaction in sulfate solutions [24]. It must also be noted, however, that reducing the concentration of copper in the electrolyte or addition of minute amounts of organic agents can significantly reduce the exchange current density [14]. The remarkably high exchange current densities of the pure chloride system suggest a quasi-reversible neutralization of the ions and a diffusion controlled process of electrodeposition, leading to the difficulty of obtaining smooth copper deposits.

3.3. Crystallization characteristics

The predominant orientations observed in electrodeposited copper crystals can be related to Fischer's classes [25, 26] of polycrystalline deposits. Copper deposits obtained from pure solutions tend to have a predominant [1 1 0] orientation [27, 28] and a 'field oriented isolation' type polycrystalline structure according to Fischer's terminology. Damjanovic [27] has proved that the overvoltage is the lowest for [1 1 0] and the highest for (1 1 1) oriented deposits.

This corresponds to a tendency of axial development. Other orientations have been observed to become significant by appropriate changes in the electrolyte composition. Addition of inhibitors in their optimum concentration range (of usually 5–10 mg dm^{-3} for thiourea or 10–50 mg dm^{-3} for polyacrylamides) stabilizes the preferred (1 0 0) or (1 1 1) structures instead of the (1 1 0) orientation [22].

Thus the fast charge transfer and the very little inhibited crystallization in pure chloride solutions can cause a strong depletion of copper ions in the vicinity of the cathode, leading to relatively high diffusion overvoltages and rapidly growing whiskers or isolated prism crystals.

4. Experimental procedures

The cell, shown in Fig. 4, was constructed from a cylindrical polyethylene (PE) tank of 9 cm inner diameter, containing approximately 300 cm^3 electrolyte. The anode discs, 3 cm in diameter, were carved out from super pure graphite sheets of 5 mm thickness, and were fixed to holders, made of polypropylene (PP) tubes. The current lead (Pt wire) and
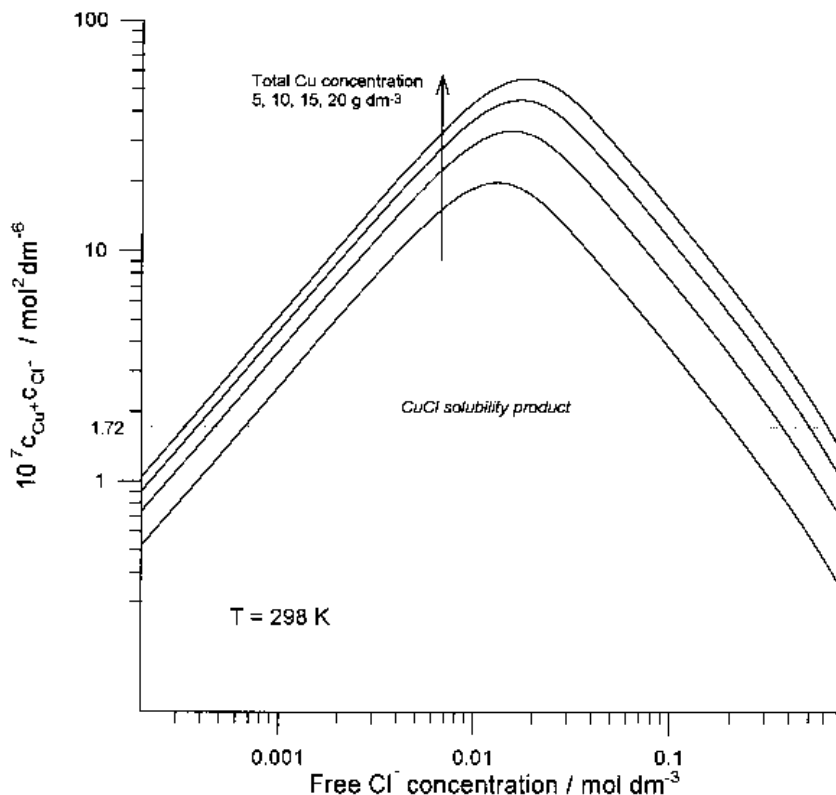
Fig. 2. Equilibrium concentration product of the Cu^+ and the Cl^- ions at different total copper concentrations.

the drain pipe was introduced through the anode holder tube. The anodes were wrapped in Kiriyama GF5 glass fibre filter material. The initially 0.5 mm thick and 5 mm wide cathodes were made of 99.9% copper. The exposed surface area was approximately 1 cm². Larger cathodes (10–20 cm²) of different geometrical shapes were also tested.

A 99.9999% Cu wire was used as the reference electrode, which was inserted into bent quartz glass tube ending in a Luggin–Haber capillary [29] of the smallest convenient diameter (~ 0.2 mm). The capillary tip was cut aslant for easier positioning of the reference point outside the diffusion layer, but very close to the body of the working electrode (~ 0.4 mm).

Fig. 3. Stability diagram of Cu(I), and Cu(II) species in chloride solutions at different total copper (ΣCu) concentrations.

Fig. 4. Schematic diagram of the electrolysis equipment.

According to the practical purpose of these experiments, the measured electrode potentials were considered only on a relative basis.

Constant copper chloride and hydrochloric acid concentration of the electrolyte could be maintained by adding calculated amounts of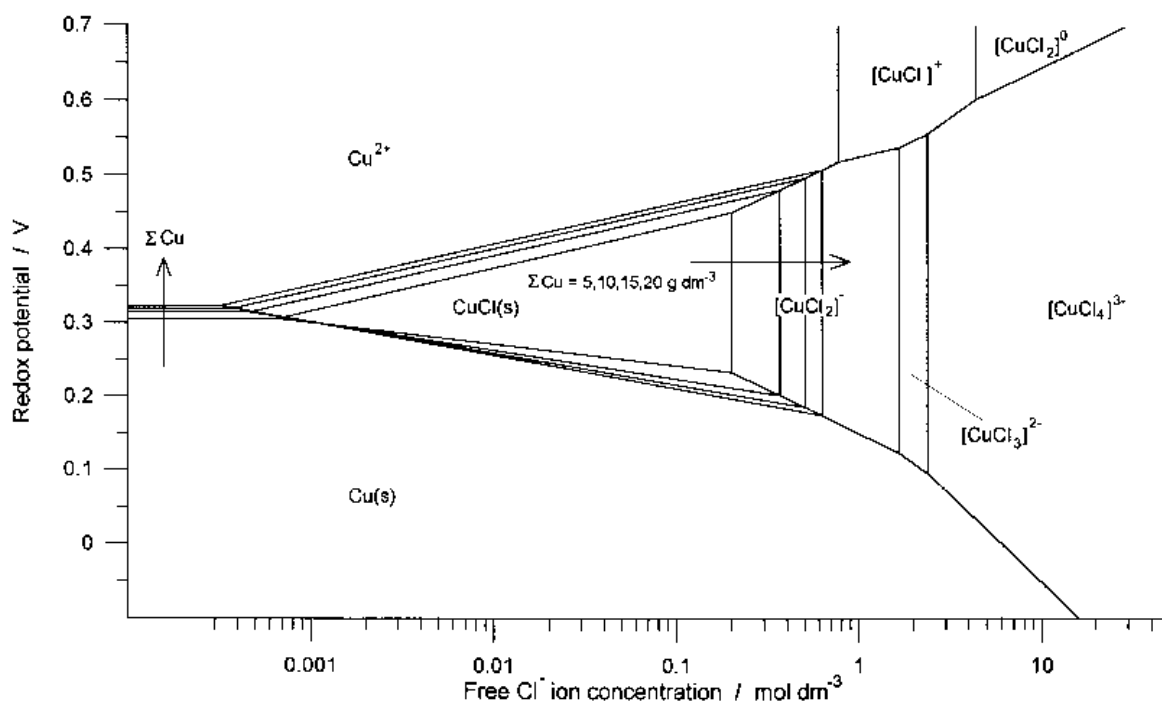 concentrated feed solution through the inlet pipe, fixed in the lid, and pumping out equal volumes of spent electrolyte from the anode compartments. Actual concentrations of copper and hydrochloric acid were checked by instant chemical analysis of the periodically taken microsamples.

The electrolytes were composed of reagent grade chemicals and deionized water of lower conductivity than $0.1 \, \mathrm{mS \, cm^{-1}}$.

5. Results and discussion

5.1. Preliminary experiments

The influence of hydrochloric acid concentration on the corrosive effect of the cupric chloride electrolyte was tested in solutions containing $20 \, \mathrm{g \, dm^{-3}}$ copper. The electrolyte was agitated vigorously, by applying a jet of nitrogen ($\sim 3 \, \mathrm{dm^3 \, min^{-1}}$, through a nozzle of internal diam. 1 mm) directed at the lower edge of a rectangular cathode plate (of $1 \, \mathrm{cm^2}$ surface area). Figure 5 shows that, under the given conditions, $3 \, \mathrm{mol \, dm^{-3}}$ HCl concentration in the electrolyte virtually prevented a net deposition of copper at even as high a current density as $2000 \, \mathrm{A \, m^{-2}}$. At lower concentrations of HCl the still severe effect of corrosion

could be partially counteracted by increased current densities, but the cathodes developed serious imperfections, especially at the corners and edges.

Further reducing the hydrochloric acid concentration to $0.5 \, \mathrm{mol \, dm^{-3}}$ resulted in the expected increase of the cathodic current efficiency, but it also caused precipitation of cuprous chloride, as predicted by the computed results of Section 2. Precipitation was observed to increase at higher current densities. This behaviour is probably attributable to the effect of vigorous electrolyte agitation, which can remove the larger CuCl crystals from the cathode surface, unless it is roughened by applying higher current densities. Furthermore, the relatively thin diffusion layer, allows the projections of the rough cathode surface, formed at higher current densities, to contact the more concentrated regions of the solution, thereby promoting precipitation of CuCl.

At the lowest examined HCl concentration ($0.01 \, \mathrm{mol \, dm^{-3}}$), chemical conditions, as predicted by the computed results of Section 2, caused a strong precipitation of cuprous chloride, and the cathode was covered with a thick layer of CuCl. This, however, only partially shields the underlying cathode surface, and does not prevent the electrode process.

Very smooth deposits and relatively high apparent current efficiencies could be obtained by appropriately adjusting the current density at low HCl ($0.01 \, \mathrm{M}$), high Cu ($42 \, \mathrm{g \, dm^{-3}}$) concentrations and high temperature ($40–60 \, ^{\circ}\mathrm{C}$) of the gently agitated electrolyte. Due to the enhanced redissolution of protruding irregularities, higher copper concentrations
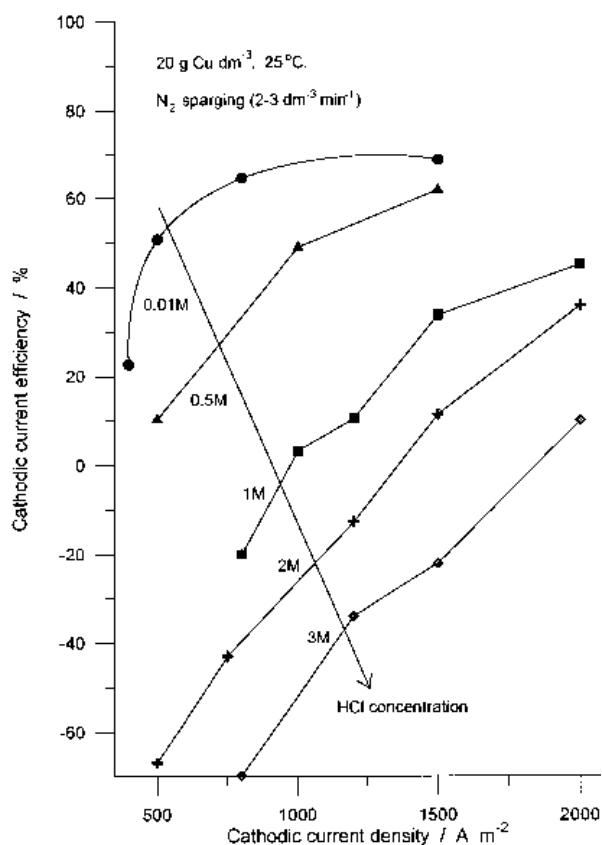
Fig. 5. Dependence of the current efficiency on the current density at different HCl concentrations in vigorously agitated cupric chloride electrolytes.

5.2. *Effects of main electrolysis parameters*

Vigorous agitation of the $CuCl_2$–HCl electrolyte proved incapable of providing practically acceptable current efficiencies and surface qualities. Therefore, the optimum conditions were approached using stagnant electrolytes. The choice of the hydrochloric acid concentration was based on the results of the chemical stability study and the preliminary experiments.

The effects of the main electrolysis parameters (geometric current density, electrolyte composition, temperature) were evaluated in terms of cathodic current efficiency and surface quality. The apparent current efficiency, in the majority of the cases, was approximately equivalent to the effective value, since no significant cuprous chloride precipitation could take place at 1 M HCl concentration. The duration of the electrolysis was usually limited to a short time (~20 min) to avoid noticeable concentration changes in the electrolyte. However, enough time was allowed for the electrode to develop a clearly recognizable surface pattern. The surface characteristics were classified according to the categories given in Table 2.

Figure 6 shows the observed dependence of the cathodic current efficiency, surface quality and cathode potential on the main electrolysis parameters. The surface quality codes are marked on the current efficiency plots. Due to the nonhomogeneous current distribution, the roughest areas were always located near the lower edges and corners. It can also be seen that the current efficiency, the cathode potential and the surface quality are generally correlated. Increasing the current density implies increased overvoltage, which is reflected in the increasing absolute value of the measured cathode potential, and the gradual roughening of the cathode deposit. The current efficiency increases as the higher rates of deposition can counteract the chemical dissolution, the rate of which is subdued by the reduced copper concentration in the cathode film. This tendency is continued until the limiting current density is approached, which is indicated by extreme deterioration of the cathode surface and finally the evolution of hydrogen, whence the copper deposit turns completely powdery. The loose and powdery structure reduces cathode polarization, through the increased specific surface area, but causes large losses in the current efficiency, due to detachment of the copper particles. The critical cur-

and temperatures were found to promote smooth surfaces. However, due to the very low HCl and high Cu concentrations, large amounts of CuCl were found to precipitate especially when the temperature was reduced. Examination of the microstructure revealed that, under the conditions of slight precipitation, CuCl is intermingled with the copper crystals, which are deposited in a densely packed field oriented texture or even an unoriented dispersed pattern, producing relatively smooth surfaces. The finely dispersed CuCl nuclei appear to act as strong inhibitors, promoting smoother deposition. At even higher rates of precipitation cuprous chloride can build up a relatively thick layer, which covers the CuCl-containing copper cathode. Conditions of CuCl precipitation, however, are undesirable for the production of superpure copper.

Table 2. Macroscopic description of cathode surface quality

| Quality code	Quality description
CC	Thick CuCl layer, covering the largest part of the working area on the cathode surface
C	Noticeable CuCl precipitation, slightly covering the surface
VF	Very fine grained smooth deposit
F	Fine grained deposit
RE	Rough edges, though the central area of the cathode is free of significant irregularities
R	Generally rough surface, possibly exhibiting relatively large projections, whiskers, dendrites or prismatic crystals
PE	Porous, powdery edges, and very rough areas on the surface
P	Porous, powdery, incoherent deposit, associated with incipient evolution of hydrogen gas
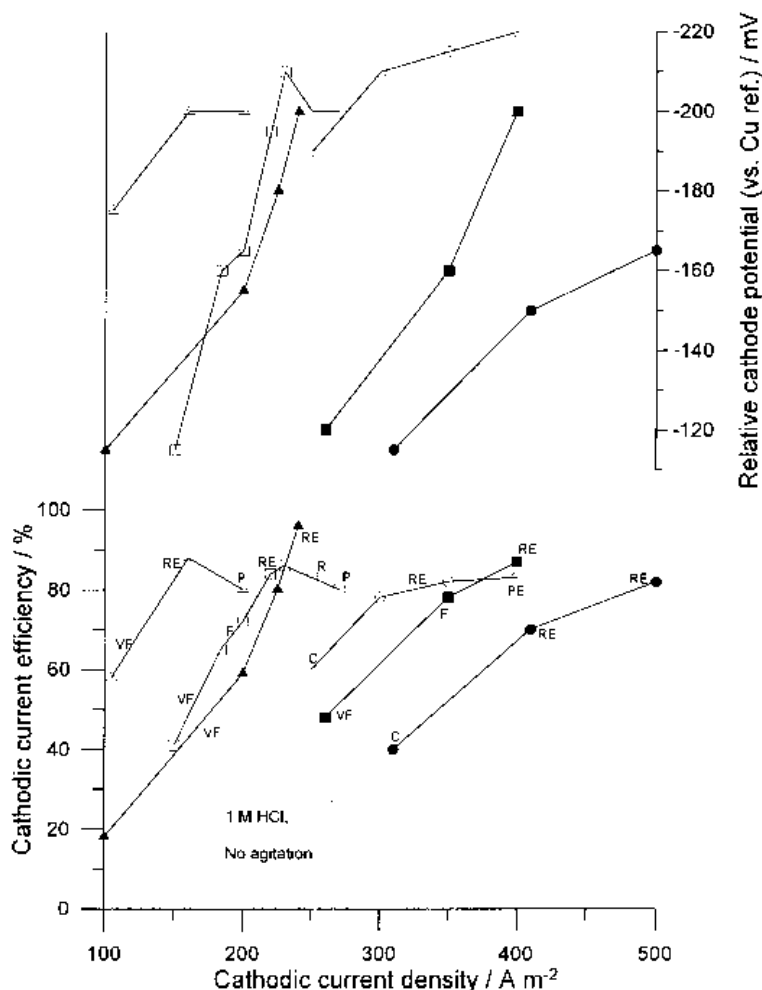
Fig. 6. Effects of the current density, copper concentration and temperature on the main characteristics of copper deposition from pure $CuCl_2$–HCl electrolytes. Surface quality code: (C) CuCl precipitation, (VF) very fine, (F) fine, (RE) rough edges, (R) rough, (PE) porous–powdery edges, (P) porous-powdery. Open symbols at 25 °C: ($\triangle$) 10, ($\square$) 15 and ($\bigcirc$) 20 g dm^{-3} Cu; filled symbols at 40 °C: ($\blacktriangle$) 10, ($\blacksquare$) 15 and ($\bullet$) 20 g dm^{-3}.

rent density was found to depend essentially on the copper concentration of the solution, and the corresponding critical value of the relative cathode potential (total overpotential) was in the range from −200 to −220 mV.

At the highest examined copper concentration (20 g dm^{-3}) lower current densities produced a slight precipitation of CuCl, which was soon followed by the roughening of the edges as the current was increased. The lowest examined copper concentration (10 g dm^{-3}), however could not afford satisfactory levels of productivity, and the surface quality deteriorated rapidly by increasing the applied current density. Therefore the medium level of 15 g dm^{-3} copper concentration was selected for further operation.

The higher examined temperature (40 °C), reproduced the previously noted tendencies, although, the current efficiency and the cathode potential curves shifted notably to the higher current density ranges in Fig. 6. However, the relatively strong rate of evaporation causes technical complications in maintaining the optimum conditions, which would be disadvantageous when super pure copper is to be produced.

5.3. Special ways of improving performance

The effects of electrolyte agitation and periodic current reversal were tested with the selected 15 g dm^{-3} Cu–1 M HCl electrolyte. Agitation was implemented by gentle and strong magnetic stirring of the solution ($\sim$ about 50 and 500 r.p.m.). Continuous agitation of the electrolyte was not found advantageous, since the maximum attainable current efficiency was only about 60% even with gentle stirring.

Periodic current reversal (PCR) can be used to a great advantage in the case of $CuSO_4$ electrolysis [30–32], since it is capable of reducing concentration polarization and the associated harmful effects. However, it was found counterproductive in the chemically aggressive electrolyte, where the balance of the electrodeposition and the chemical dissolution processes are strongly dependent on the conditions of the boundary layer. Application of this technique caused a drastic drop in the current efficiency, although the surface quality did not improve.

To combine improved surface qualities with increased current efficiencies, a special method of intermittent stirring was tested. Short periods of

agitation were alternated with approximately 3–4 times longer periods of no agitation. Changes of the cathodic current efficiency, cathode potential and surface quality were examined with increasing intensity of the applied periodic agitation, expressed as the number of revolutions during the stirring intervals. The periods of stirring were kept approximately constant within the total cycle time of 16 s.

The current efficiency was not reduced significantly until the periodic stirring intensity reached a value of 5–10 revolutions per cycle, but the quality of the deposit improved considerably. Further increasing the periodic stirring intensity, however, caused strong chemical redissolution, which was similar to the case of continuous stirring.

Figure 7 shows a comparison between the operations with stagnant and periodically stirred electrolytes, containing $15 \, g \, dm^{-3}$ copper and $1 \, mol \, dm^{-3}$ hydrochloric acid at 25 °C. The characteristic surface micrographs revealed that cathodes produced by the periodic stirring method were not only dense but appeared also smooth up to about 10 h duration of electrolysis at a current density of $250–300 \, A \, m^{-2}$, and the precipitation of CuCl was avoided. The cross-section micrographs showed the characteristics of a mixed basis oriented reproduction and field oriented microtextures according to Fischer's classification [25, 26], implying low macroscopic porosity.

Although the surface of the cathode remains fine-grained and dense, the edges tend to deteriorate with long durations of electrodeposition. This tendency was found especially strong when the dimensions of the cathode were increased (Fig. 8(a)). To overcome the difficulties of edge roughening, the rectangular cathode shape was changed for a circular geometry and the edge was shielded with Teflon rings, fitted in a silicon rubber holder. Figure 8(b) shows the cathode assembly, together with the characteristic cross-sectional micrographs. The cathode deposits were analysed by glow discharge mass spectrometry (GDMS) for all the important impurity elements, and the results are summarized in Table 3.

6. Conclusions

The strong chemical corrosion of the copper cathode in $CuCl_2$–HCl electrolytes is attributable to the combined effect of the cupric and the chloride ions. Thermodynamic stability study of the different species in the electrolytes revealed the criteria of cuprous chloride precipitation.

Roughness of the deposits is related to the kinetic behaviour of the system, characterized by a highly reversible charge transfer and a rate determining mass transfer step.
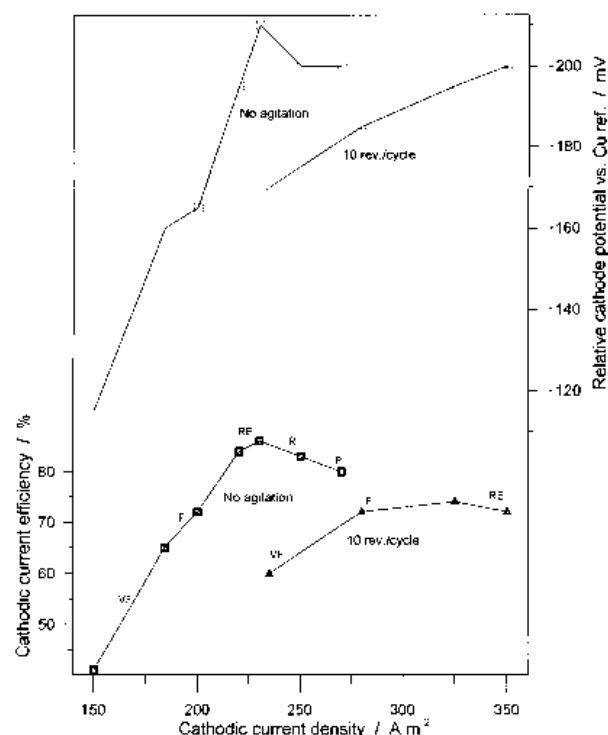

Fig. 7. Comparison of electrolysis characteristics obtained in nonagitated and periodically stirred pure $CuCl_2$–HCl electrolytes. Cycling time 16 s; stirring 3–4 s; no stirring 12–13 s. Data: $15 \, g \, Cu \, dm^{-3}$ and $1 \, M$ HCl at 25 °C. Surface quality code: (CC) considerable CuCl precipitation, (C) slight CuCl precipitation, (VF) very fine, (F) fine, (RE) rough edges, (R) rough, (PE) powdery edges, (P) porous–powdery.
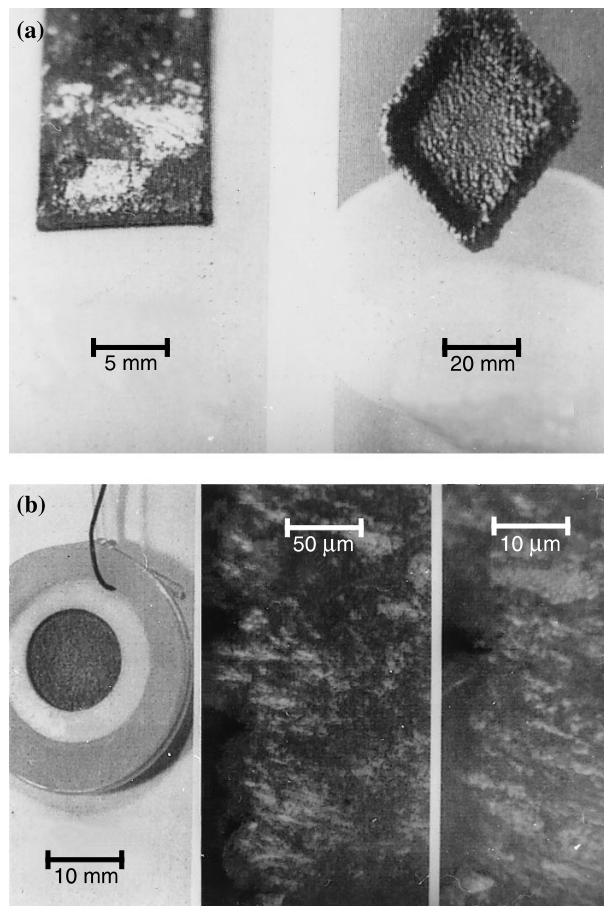

Fig. 8. Cathodes produced with longer durations of electrolysis. ($1 \, M$ HCl, $15 \, g \, dm^{-3}$ Cu, 25 °C, $250 \, A \, m^{-2}$, periodic stirring). (a) Small and larger cathodes obtained after 12 ks and 200 ks electrolysis runs, respectively; (b) surface and cross-section of the circular cathode with shielded edge (150 ks electrolysis).

Table 3. Analysed concentrations of the main impurities in the cathode copper produced from purified CuCl$_2$–HCl electrolytes[*] compared to the analysis of the 6 N standard Cu sample

Element	Na	Mg	Al	P	S	Cl	K	Ca	Ti	V	Cr	Fe	Mn
6N Cu	0.04	0.0009	0.0067	<0.003	0.01	0.013	0.0087	<0.02	0.027	<0.005	<0.002	0.0061	<0.001
Cathode	<0.005	<0.006	0.1	0.06	<0.1	<0.024	<0.007	<0.21	0.0047	<0.004	<0.005	<0.057	<0.005

Element	Ni	Co	Zn	As	Se	Zr	Nb	Mo	Ag	Sn	Sb	Te	Pb
6N Cu	<0.002	<0.001	<0.2	0.0064	<0.04	<0.002	0.0008	0.0005	0.113	0.024	<0.008	<0.06	0.0055
Cathode	0.0081	<0.004	<0.064	0.0088	0.0295	<0.009	0.007	<0.018	0.025	<0.053	0.006	<0.064	<0.019

[*] The solution was prepared from commerical grade CuCl and HCl, purified by anion-exchange and partially evaporated before electrolysis. The cathode was plasma melted, rolled and cut to prepare the specimens for analysis by glow discharge mass spectrometry.

The results of a fundamental experimental study pointed out the feasibility of obtaining dense and super pure electrodeposits of copper directly from the purified CuCl$_2$–HCl electrolyte containing no additive agents. The experiments revealed a strong effect of current density, electrolyte composition and temperature on the cathodic current efficiency and the quality of the deposit. Periodic stirring was found to facilitate the production of dense cathodes with acceptable current efficiency.

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