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Electrodeposition of Copper from a Choline Chloride based Ionic Liquid

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Abstract: The electrodeposition of copper from a solution containing copper chloride in either an ethylene glycol (EG)-choline chloride based or a urea-choline chloride based ionic liquid has been carried out onto a steel cathode by constant current and constant potential methods at room temperature. The influences of various experimental conditions on electrodeposition and the morphology of the deposited layers have been investigated by scanning electron microscopy (SEM) and X-ray diffraction (XRD). It is shown that very smooth, shiny and dense with good adherence and brown metallic coloured copper coatings can be obtained from both EG and urea based ionic liquids at the applied deposition potentials up to -0.45 V and applied deposition current densities up to $-4.0 \text{ A} \cdot \text{m}^{-2}$ at room temperature. The cathodic current efficiency for the deposition of copper is about 97%.

Key words: electrodeposition; ethaline; reline, copper; cyclic voltammetry

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Electrodeposition of copper is essential for a variety of industrial and decorative purposes including a large-scale use in the electronics industry for the production of printed circuit boards, semiconductor integrated circuits (IC's) for high performance advanced devices, selective case hardening of steel for engineering components, and production of electrotypes in the printing industry. Copper may be easily deposited and electroplated with other metals, and it is, therefore, particularly useful pre-coating for soft soldered work or for zinc alloy die-castings used in the automotive industry. Many of the technological developments seen in the electronics industry depend upon sophisticated electroplating including the use of exotic metals, and this is one of the drivers for new technology within the electroplating sector. The whole electroplating sector is based on aqueous solutions due to the high solubility of electrolytes and

metal salts resulting in high conducting solutions. The main metals that commercially deposited are Cr, Ni, Cu, Au, Ag, Zn and Cd together with a number of copper and zinc-based alloys. Uses of aqueous solutions as an electrolyte for metal deposition suffer from several drawbacks including toxic effluent, high energy consumption, air pollution, limited potential windows, passivation of metals and hydrogen embrittlement of the substrate due to gas evolution. The key technological goals include replacement of environmentally toxic metal coating, deposition of new alloys and semiconductors, and new coating methods for reactive metals.

During the last twenty years ionic liquids have found applications in a wide variety of electrochemical and synthetic processes^[1-2]. Most of the academic studies on ionic liquids have concentrated on imidazolium and pyridinium cations, however, their high

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cost and sensitivity to water have made them of little practical use for large-scale applications such as metal finishing. A relatively new class of moisture insensitive third generation ionic liquid based on eutectic mixtures of choline chloride with a hydrogen bond donor species either urea or ethylene glycol has been reported by Abbott et al.^[3-5]. The use of choline chloride as a quaternary ammonium salt has advantages as it is non-toxic, biodegradable and already used as a common component to numerous household and industrial products. These ionic liquids can be used for deposition of a range of metal coatings including Zn, Cr, Sn, Cu, and Ag at high current efficiency and also for metal dissolution processes such as electropolishing^[6-7]. In many cases, the use of ionic liquids solvents overcomes the need for strong inorganic acids (e.g., chromic acid, HF, H₃PO₄, H₂SO₄) and highly toxic salts (e.g., cyanide). The aim of the present work is to develop a copper coating on steel substrates by electrodeposition method from ionic liquids based on eutectic mixtures of choline chloride and hydrogen bond donors such as urea or ethylene glycol.

1 Experimental

1.1 Chemicals

Choline chloride (HOC₂H₄N(CH₃)₃Cl) (ChCl, Aldrich, 99%) was, when necessary, recrystallised from absolute ethanol, filtered and dried under vacuum. Urea (Aldrich > 99%) was dried under vacuum prior to use. Ethylene glycol (EG) (Aldrich > 99%), copper chloride dihydrate (CuCl₂·2H₂O) (Aldrich ≥ 98%), and all other chemicals were used as received.

1.2 Preparation of Ionic Liquids

The eutectic mixtures were formed by stirring the two components together, in the stated proportions, at 75 °C until a homogeneous, colourless liquid formed. The molar ratio for the eutectic compositions was found to be 1:2 for choline chloride (ChCl) with ethylene glycol (EG) or urea. The ionic liquids, once formulated, were kept in a thermostatic oven at 30 °C prior to use.

1.3 Electrochemical Measurements

Electrochemical investigations including poten-

tial step chronoamperometry, chronopotentiometry and cyclic voltammetry were carried out using a Hokudo Denko HAB-151 Potentiostat/Galvanostat (Tokyo, Japan), equipped with a potential sweeper. Data were recorded in a computer through data acquisition system (USA) using WinDaq software. A three-electrode system consisting of a platinum (50 mm × 5 mm × 0.1 mm) working electrode, a copper (50 mm × 10 mm × 0.1 mm) counter electrode and a silver wire quasi-reference electrode were used in all electrochemical studies. The working electrode was cleaned electrochemically in 1.5 mol·L⁻¹ H₂SO₄-1.0 mol·L⁻¹ H₃PO₄ mixtures, then rinsed with deionised water, and finally dried with acetone prior to use in all measurements. All voltammograms were obtained at 30 °C with various scan rates ranging from 5 to 100 mV·s⁻¹. A silver wire (immersed in ethaline/reline) quasi-reference electrode was used in all electrochemical experiments which have been shown to have stable reference potential in chloride based eutectics. All potentials in this work are quoted with respect to Ag|1:2 ChCl-EG/urea reference electrode (which will be written as Ag|Ag(I)) (note that the reference potential will be changed slightly with melts of different compositions).

1.4 Deposition of Copper

The electrodepositions of copper were carried out onto steel cathodes by constant current and constant potential methods from ionic liquids (ethaline/reline) containing CuCl₂·2H₂O at room temperature. The applied current densities and potentials for depositing in different plating operations were -2.0 ~ -6.0 A·m⁻² and -0.30 ~ -0.50 V, respectively. Following each deposition, the resulting deposit was soaked firstly in ethanol, then in deionised water, and finally washed with acetone to remove the residual ionic liquids. The deposit was then dried with cold air.

1.5 Deposit Characterization

The surface morphologies of the deposited samples were examined with scanning electron microscope (XL 30 SEM, PHILIPS). X-ray diffraction analysis was also performed with a Philips PW 1716 diffractometer using Cu K_α radiation (40 kV, 25 mA)

to explore the crystal structure of the deposits.

2 Results and Discussion

2.1 Cyclic Voltammetry of Cu(II) in ChCl:2EG (Ethaline) and ChCl:2Urea (Reline) Ionic Liquids

The cyclic voltammograms recorded on a platinum electrode in 1:2:0.05 (molar ratio) ChCl:EG:CuCl₂·2H₂O (A) and ChCl:urea:CuCl₂·2H₂O (B) ionic liquids at 30 °C with a scan rate of 10 mV·s⁻¹ are shown in Fig. 1. The rest potentials are 0.523 V in ethaline and 0.550 V in reline. The scan towards negative direction consists of first & second reduction waves C₁ & C₂ in Fig. 1A and C'₁ & C'₂ in Fig. 1B with the currents starting to increase at 0.515 V (C₁), -0.406 V (C₂), 0.510 V (C'₁) and -0.380 V (C'₂). Additional reduction waves C₃ in Fig. 1A and C'₃ in Fig. 1B are observed with the current increase starting again at

-1.160 V and -0.920 V, respectively. The reverse scan consists of first & second oxidation peaks P_{a1} (-0.114 V) and P_{a2} (0.483 V) in Fig. 1A, and P'_{a1} (-0.107 V) and P'_{a2} (0.490 V) in Fig. 1B with the current increases starting at 1.020 V for ethaline and also for reline. Compared with the voltammograms obtained in the absence of CuCl₂·2H₂O, the dotted curves in Fig. 1A and Fig. 1B, the reduction waves appeared at -0.720 V in ethaline and -0.860 V in reline correspond to the reduction of cationic species (Cat⁺) into these ionic liquids, while the oxidation waves appeared at 1.200 V in ethaline and 1.000 V in reline to the oxidation of chloride ions (anions) to molecular/gaseous chlorine according to the following reaction.



Fig. 2 shows the effect of cathodic sweeping potentials on the cyclic voltammograms recorded on a

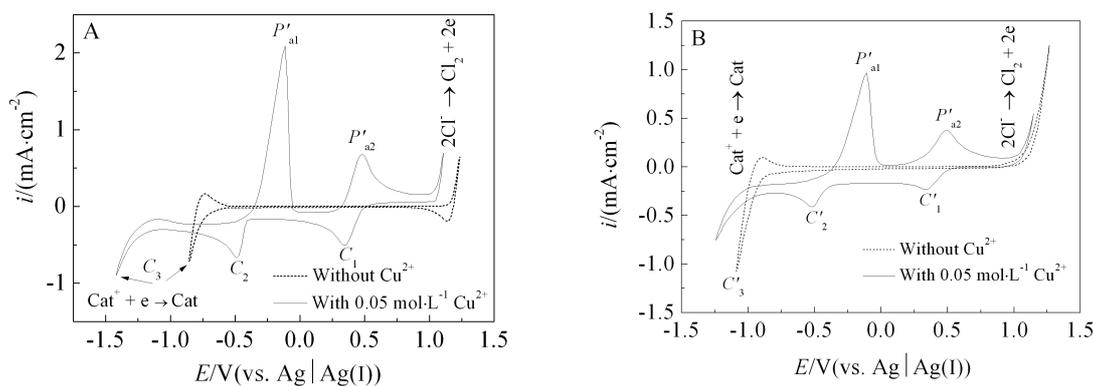


Fig. 1 Cyclic voltammograms recorded on a platinum electrode in ChCl:2EG (A) and ChCl:2urea (B) ionic liquids containing 0.05 mol·L⁻¹ CuCl₂·2H₂O at 30 °C with a scan rate of 10 mV·s⁻¹

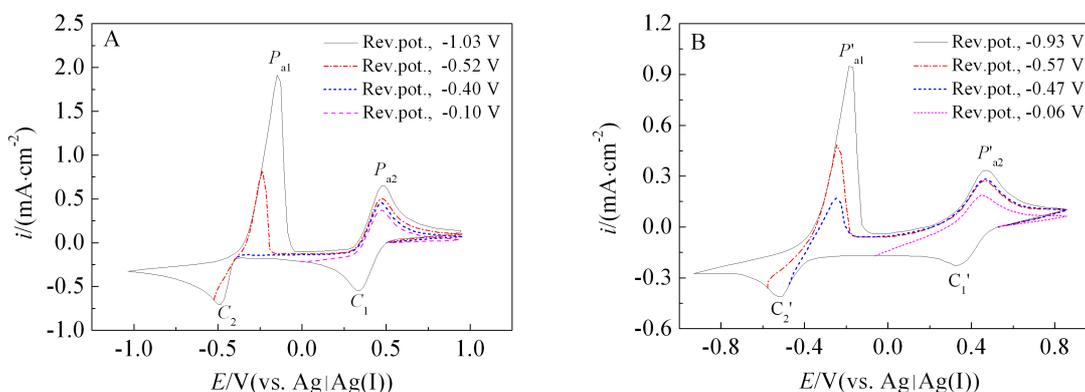


Fig. 2 Effect of sweeping potentials on the cyclic voltammograms recorded on a platinum electrode in ChCl:2EG (A) and ChCl:2urea (B) based ionic liquids containing 0.05 mol·L⁻¹ CuCl₂·2H₂O at 30 °C with a scan rate of 10 mV·s⁻¹

platinum electrode in 1:2:0.05 (molar ratio) ChCl:EG:CuCl₂·2H₂O (A) and 1:2:0.05 (molar ratio) ChCl:urea:CuCl₂·2H₂O (B) ionic liquids at 30 °C with a scan rate of 10 mV·s⁻¹. It is readily seen from the voltammograms that the first reduction waves C₁ and C'₁ correspond to the second oxidation peaks (P_{a2} and P'_{a2}), while the second reduction waves (C₂ and C'₂) to the first oxidation peaks (P_{a1} and P'_{a1}). From XRD and EDX analyses, pure copper has been detected in the deposit obtained at a deposition potential of -0.450 V (from the second reduction waves C₂ and C'₂) by constant potential method. Therefore, the increases of the negative currents in the second reduction waves (C₂ and C'₂) are obviously associated with the reductions of copper ions to metallic state. However, copper deposit could not be found on the cathode when deposition has been carried out by constant potential method from the first reduction waves C₁ and C'₁. These voltammograms indicate that there are two distinct reduction processes of copper corresponding to the reversible Cu(II)/Cu(I) couple at 0.515 V in ethaline and 0.510 V in reline, followed by the reduction of Cu(I) to Cu(0) at -0.406 V in ethaline and -0.380 V in reline, as shown below.

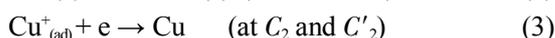


Fig. 3 shows the effect of CuCl₂·2H₂O concentrations on the cyclic voltammograms recorded on a platinum electrode in ChCl:2EG (A) and ChCl:2urea (B) ionic liquids at 30 °C with a scan rate of 10 mV·s⁻¹. It

is readily seen from these voltammograms that the magnitudes of current densities in the first and second reduction waves C₁ & C'₁ and C₂ & C'₂, which are attributed to the reductions of Cu(II) to Cu(I) and Cu(I) to Cu(0), increase with the increase of the CuCl₂·2H₂O concentrations added into the ionic liquids. The same phenomena are observed with the first and second oxidation peaks P_{a1} & P'_{a1} and P_{a2} & P'_{a2} in Fig. 3A and Fig. 3B, which also shows the increase in current densities with the increase of the CuCl₂·2H₂O concentrations. The increases in the magnitudes of Cu(II) and Cu(I) reduction current densities with the increase in CuCl₂·2H₂O concentrations into the ionic liquids indicate the higher discharge rates of copper ions to metallic copper at low over-potentials.

The effect of scan rates on the cyclic voltammograms recorded on a platinum electrode in ChCl:2EG:0.05CuCl₂·2H₂O (A) and ChCl:2urea:0.05CuCl₂·2H₂O (B) ionic liquids at 30 °C are presented in Fig. 4. For a reversible system, peak potential E_p is independent of scan rate (v), and peak current density (i_p) is proportional to the square root of scan rate (v^{1/2}). Variations in the peak potentials with scan rate (E_p vs. v) and peak current densities i_{pc1}, i'_{pc1}, i'_{pc2} and i'_{pc2} with square root of scan rate (i_p vs. v^{1/2}) are shown in Fig. 5A-B and Fig. 5C-D, respectively. It is evident from Fig. 5A-B that the peak potentials for the redox reactions of Cu(II)/Cu(I) and Cu(I)/Cu(0) couples are almost independent of the scan rate, indicating a reversible in nature. For a reversible system, the rela-

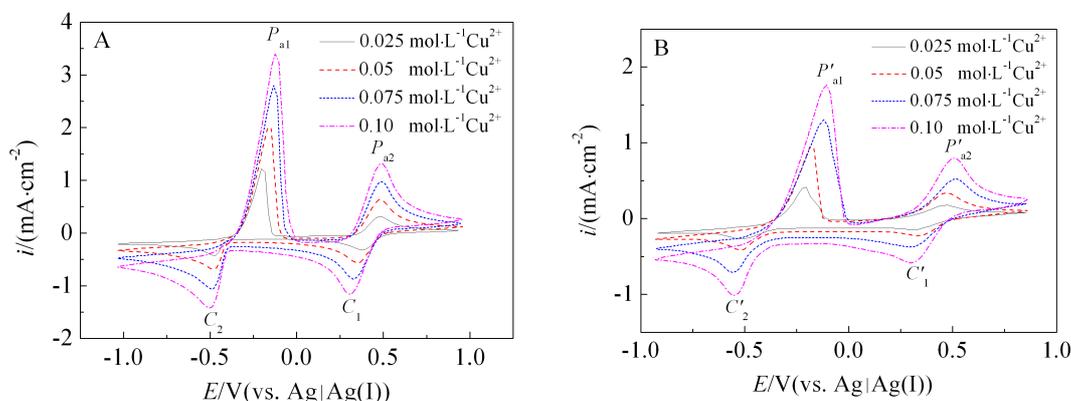


Fig. 3 Effect of CuCl₂·2H₂O concentrations on the cyclic voltammograms recorded on a platinum electrode in ChCl:2EG (A) and ChCl:2urea (B) ionic liquids at 30 °C with a scan rate of 10 mV·s⁻¹

tionship between the cathodic peak current density i_p and the square root of the scan rate $v^{1/2}$ is given by^[8]:

$$i_{pc1} = (2.69 \times 10^5)n^{3/2}AD_{Cu(II)}^{1/2}C_{Cu(II)}^*v^{1/2} \quad (\text{for } P_{c1} \text{ and } P'_{c1}) \quad (4)$$

$$i_{pc2} = (2.69 \times 10^5)n^{3/2}AD_{Cu(I)}^{1/2}C_{Cu(I)}^*v^{1/2} \quad (\text{for } P_{c2} \text{ and } P'_{c2}) \quad (5)$$

where $C_{Cu(II)^*}$ and $C_{Cu(I)^*}$ are the concentrations of

copper (II) and copper (I) ions, respectively, in the bulk solution, D is the diffusion coefficient of copper ions, A is the surface area of the electrode and n is the number of electron transferred during reduction reaction. The linear increases in the cathodic peak current densities i_{pc1} , i'_{pc1} , i'_{pc2} and i_{pc2} with the square root of scan rate, as shown in Fig. 5C-D, indicate that the re-

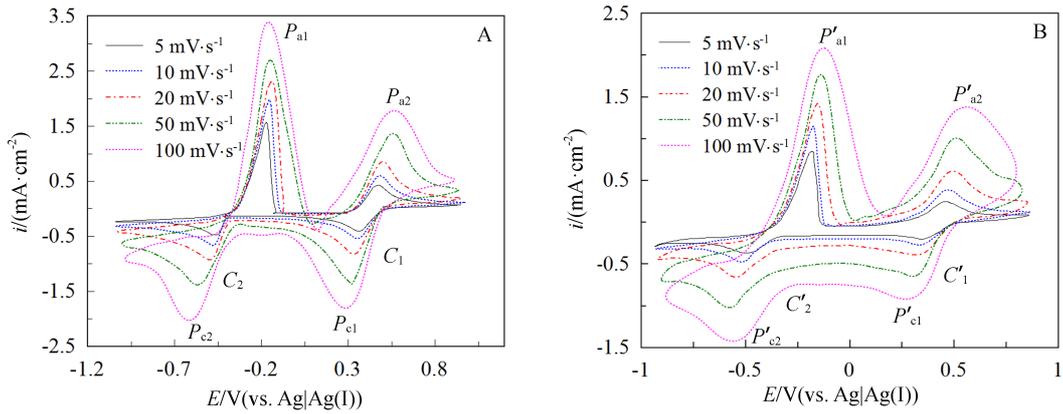


Fig. 4 Effect of scan rates on the cyclic voltammograms recorded on a platinum electrode in ChCl:2EG (A) and ChCl:2urea (B) ionic liquids containing $0.05 \text{ mol} \cdot \text{L}^{-1} \text{ CuCl}_2 \cdot 2\text{H}_2\text{O}$ at $30 \text{ }^\circ\text{C}$

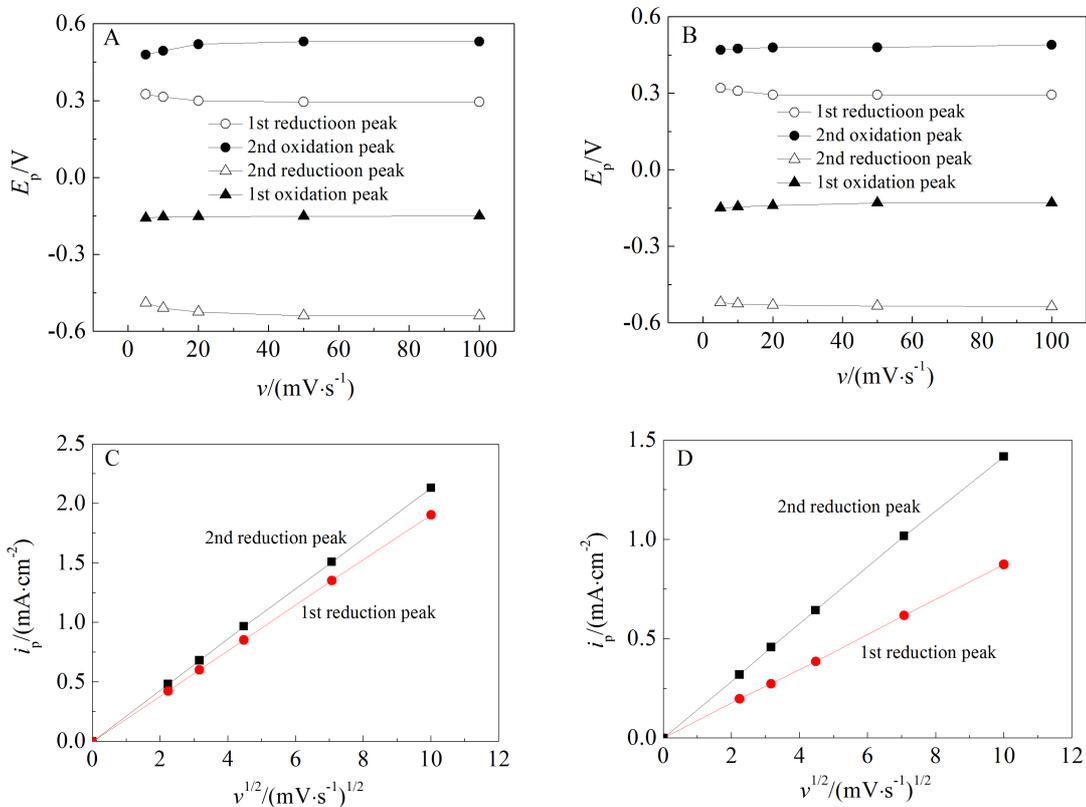


Fig. 5 Variations of peak potentials with scan rate in ethaline (A) and reline (B) or cathodic peak current densities with the square root of scan rate for the reduction of copper ions in ethaline(C) and reline(D) containing $0.05 \text{ mol} \cdot \text{L}^{-1} \text{ CuCl}_2 \cdot 2\text{H}_2\text{O}$

duction processes of copper ions in both ChCl:2EG and ChCl:2urea based ionic liquids are controlled by diffusion.

2.2 Electrodeposition of Copper from Ethaline and Reline

The camera images of the electrodeposited copper layers on steel cathodes by constant potential and constant current methods from both EG and urea based ionic liquids are shown in Fig. 6. All of the electrodeposits obtained on steel substrates at the applied deposition potentials of -0.30 V and -0.40 V (Fig. 6A-B), and the applied deposition current densities of -1.0 and -4.0 A·m⁻² (Fig. 6C-D) appear to be smooth, shiny, dense, and homogeneous with good adherence and brown metallic coloured copper. There is no apparent rupture on the deposit surface and the deposits do not peel off. However, the deposits obtained at the applied deposition potentials > -0.50 V are not smooth but with good adherence. Fig. 7 shows the SEM images of copper electrodeposits obtained from molar ratios of 1:2:0.10 in ChCl:EG:CuCl₂·2H₂O (A) and ChCl:urea:CuCl₂·2H₂O (B) ionic liquids at 30 °C by applying constant potentials of -0.40 V (A) and -0.45 V (B). The electrodeposited crystals are angular and also nodular in shape and in the order of 1.5 ~ 3 μm in size. There is no significant difference between the morphology of the deposits obtained at the two different ionic liquids.

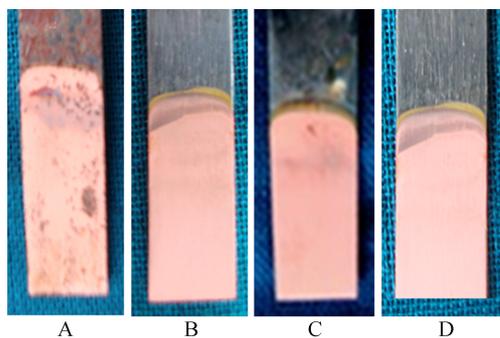


Fig. 6 Camera images of electrodeposited copper on steel cathodes from ethaline (A, B and C) and reline (D) containing 0.10 mol·L⁻¹ CuCl₂·2H₂O at 30 °C
Applied deposition potential: A. -0.30 V; B. -0.40 V
Applied deposition current density: C. -1.0 A·m⁻²; D. -4.0 A·m⁻²

There is no rupture on the deposit surface and it does not peel off. However, the size of the deposited particles decreases with the increase of applied deposition potentials and also current densities. The thicknesses of the deposited layers are approximately 5 ~ 6 μm, which has been calculated by weight gain method.

The acquired diffraction pattern for the deposit obtained from molar ratios of 1:2:0.1 in ChCl:urea:CuCl₂·2H₂O ionic liquid at applied deposition potential of -0.40 V is shown in Fig. 8. The diffraction peaks at 2θ = 43.3°, 50.45° and 74.1° are for Cu(111), Cu(200) and Cu(220), respectively. The diffraction peaks are very sharp, indicating that the deposit has the crystalline structure. The deposits obtained with this type of crystal structure are very smooth, shiny and dense and have good adherence to the surface. The current efficiency for the deposition of pure copper is about 97%. However, additional diffraction

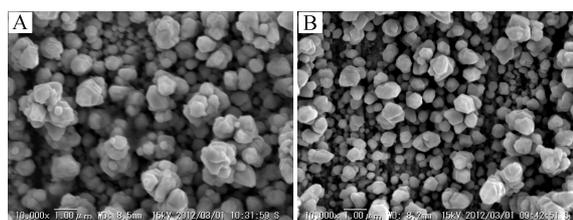


Fig. 7 SEM images of copper electrodeposits on steel substrates obtained from molar ratios of 1:2:0.1 in ChCl:EG:CuCl₂·2H₂O (A) and ChCl:urea:CuCl₂·2H₂O (B) Applied deposition potential: A. -0.40 V; B. -0.45 V

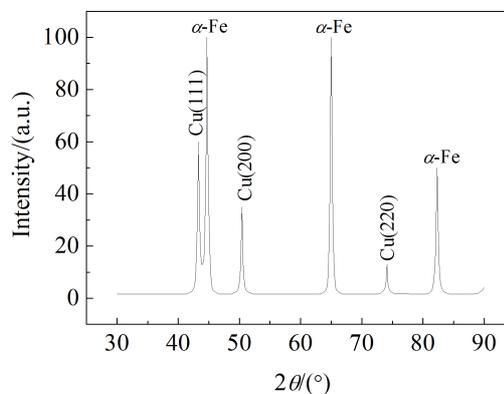


Fig. 8 X-ray diffraction pattern of copper electrodeposit obtained on steel from molar ratios of 1:2:0.1 in ChCl:EG:CuCl₂·2H₂O ionic liquid at 30 °C and -0.40 V

peaks at $2\theta = 44.7^\circ$, 65° and 82.3° corresponding to α -Fe (110), α -Fe (200) and α -Fe (211), respectively, are also observed in Fig. 8.

3 Conclusions

This work shows that ionic liquids based on eutectic mixtures of choline chloride and hydrogen bond donors such as ethylene glycol or urea can be used as electrochemical solvents. A dense, continuous, smooth and good adhering brown metallic coloured copper can be electrodeposited onto steel cathodes from ethaline and reline based ionic liquids containing $\text{CuCl}_2 \cdot 2\text{H}_2\text{O}$ at room temperature. The copper electrodeposits obtained at the applied deposition potentials up to -0.45 V and applied deposition current densities up to $-4.0\text{ A} \cdot \text{m}^{-2}$ are very smooth, dense, good adhering and of uniform size.

Acknowledgements

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基于氯化胆碱离子液体的铜电沉积研究

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摘要: 采用恒电流和恒电位方法, 基于含有氯化铜溶液的乙二醇-氯化胆碱或硫脲-氯化胆碱离子液体, 室温下在钢阴极上进行了铜的电沉积. 利用扫描电子显微镜和 X-射线衍射技术研究了各种实验条件对电沉积的影响以及沉积层的形貌. 结果表明, 室温下施加不超过 -0.45 V 的沉积电位和不超过 $-4.0\text{ A} \cdot \text{m}^{-2}$ 的沉积电流密度, 可以同时从氯化胆碱基乙二醇和硫脲离子液体中沉积得到非常光滑、有光泽、致密且具有良好结合力、色泽鲜艳的铜金属涂层. 铜的电沉积阴极电流效率约为 97%.

关键词: 电沉积; 乙二醇-氯化胆碱; 硫脲-氯化胆碱; 铜; 循环伏安法