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Electrodeposition of Zn, Cu, and Zn-Cu Alloys from Deep Eutectic Solvents

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Abstract

Deep eutectic solvents (DESs) comprising choline chloride (ChCl) with either urea or ethylene glycol (EG) have been successfully used as powerful and potential electrolytes for extracting metals from their corresponding metal oxide precursors. In this work, for electrodeposition of Zn and Zn-Cu alloys, ChCl/urea-based DES was employed. Cyclic voltammetry study demonstrates that the reduction of Zn(II) to Zn is a diffusion-controlled quasi-reversible, one-step, two electrons transfer process. Micro-/nanostructured Zn and Zn-Cu alloys films have been electrodeposited directly from their metal oxide precursors in DES, and the Zn and Zn-Cu alloy films exhibit homogeneous morphologies with controlled particle sizes. Besides, the electrodeposition of Cu from CuO in the eutectics based on ChCl with urea and EG has been investigated, respectively. The higher coordinated Cu species in the ChCl/urea-based DES are obviously more difficult to reduce, and higher overpotential is needed to drive the nucleation process compared with the lower coordinated Cu species in the ChCl/EG-based DES. The surface morphology of the Cu electrodeposits is significantly affected by the type of DES and the electrodeposition potentials. Furthermore, the Cu electrodeposits obtained in the ChCl/urea-based DES possess more dense microstructures than those produced in the ChCl/EG-based DES.

Keywords: electrodeposition, deep eutectic solvents, metal oxides, cyclic voltammetry, morphology

1. Introduction

The electrodeposition of Zn, Cu, and Zn-Cu alloys for corrosion-resistant coatings and electrochemical applications such as electrocatalysis and electronic devices has received considerable attention in recent years [1–7]. The electrodeposition of Zn, Cu, and Zn-Cu alloys

is commonly performed in aqueous electrolyte solutions. Traditional Zn plating is mainly carried out in sulfuric acidic aqueous baths [8, 9]. Generally, Zn is extracted from zinc sulfide ore. The ore is mined from the earth's crust and beneficiated by flotation methods that produce zinc sulfide concentrates. The mineral concentrates are oxidized to metal oxides during high temperature roasting and then the metal oxides are leached with sulfuric acid to produce zinc sulfate solution. Finally, the Zn electrodeposits are obtained from the zinc sulfate electrolyte under constant current electrolysis [10, 11]. However, the traditional Zn electrodeposition process is very sensitive to impurities and requires effective purification methods to produce pure Zn [12]. Copper electrodeposition is mostly performed in aqueous solutions, which possess high solubility of copper salts (e.g., CuCl_2 and CuSO_4) and high electrolyte conductivity. However, the acid- and cyanide-based aqueous electrolytes are corrosive and the inevitable hydrogen evolution reaction commonly occurs during the electrolysis process [13]. Consequently, finding new alternative electrolytes for the electrodeposition of Zn, Cu, and Zn-Cu alloy films at low temperature has become the focus in recent years.

More recently, the direct electrochemical reduction of metal oxides/compounds to metals/alloys in molten salts has been extensively studied because of its low energy consumption and environmental compatibility [14, 15]. This previous innovative work shows that the production of metallic/coating materials directly from their metal oxide precursors in liquid salt is a promising route. Low-temperature electrolytic production of iron film from iron oxide in alkaline solution has been studied in our previous work [16], which showed that metal oxide has the potential to be used as a precursor for the electrodeposition at low temperature; the electrochemical process can be controlled effectively and the electrodeposition process generally exhibits acceptable current efficiency. However, in comparison with aqueous solutions, room temperature ionic liquids (RTILs) have attracted much interest as promising electrolyte candidates for metal electrodeposition due to their remarkable characteristics, such as high thermal and chemical stability, negligible vapor pressure, wide electrochemical windows, high ionic conductivity, simplicity of handling, and good solubility for quite a lot of metal salts [17–19]. The hydrogen embrittlement and hydrogen evolution reactions occurring in aqueous solutions can be avoided by using ionic liquids as electrolytes. The electrodeposition of Zn has been investigated in many ionic liquids, particularly in AlCl_3 -based ionic liquids [20] and chlorozincate ionic liquids [21]. In addition, the electrodeposition of Zn from ZnCl_2 precursor has also been studied in choline chloride (ChCl)-based deep eutectic solvents (DESs) [22–26]. Liu et al. [27] illustrated the electrodeposition of Zn films from zinc triflate ($\text{Zn}(\text{TfO})_2$) in 1-butyl-1-methylpyrrolidinium trifluoromethylsulfonate ($[\text{Py}_{1,4}]\text{TfO}$) and 1-ethyl-3-methylimidazolium trifluoromethylsulfonate ($[\text{EMIm}]\text{TfO}$) ionic liquids. Zheng et al. [28] investigated the electrodeposition of Zn films from ZnO in imidazolium chloride/urea ionic liquid, which suggested that ZnO has appreciable solubility in the electrolyte. Besides, the electrochemical behavior of copper species (e.g., CuCl and CuCl_2) has been investigated in a range of ionic liquids such as Lewis acidic, basic chloroaluminate ionic liquids, and air-/water-stable ionic liquids based on $[\text{BF}_4]^-$, $[\text{N}(\text{CN})_2]^-$, and $[\text{Tf}_2\text{N}]^-$ [29–34]. Although these ionic liquids show many advantages in electrodeposition of Cu, issues such as toxicity, cost, and tedious synthesis procedures may limit their realistic applications [35]. Furthermore, many air-/water-stable ionic liquids are not

ideal electrolyte for copper salts such as nitrates, halides, and sulfates because of their poor solubilities [36]. Chen et al. [37] attempted to introduce the cuprous ions into the ionic liquid by the anodic dissolution of a Cu electrode, however, it is a time-consuming process. Therefore, searching for suitable ionic liquid-metal precursors systems for the electrodeposition of Zn, Cu, and Zn-Cu alloys is extremely needed.

DESs, which are made from quaternary ammonium salts mixed with hydrogen bond donors, such as carboxylic acids, alcohols, and amides, are promising electrolytes for electrodeposition application [38, 39]. The DESs are simple to prepare, relatively stable in air and moisture, many are biodegradable, and are relatively low cost [40–47]. Moreover, the DESs show considerable selective solubilities for many metal oxides, which may provide a new route for preparation of metals from metal oxide precursors in the DESs [48, 49]. In comparison with ZnCl_2 , CuCl , and CuCl_2 precursors [22–26], ZnO , Cu_2O , and CuO have potential to be used directly as new promising precursors for the electrodeposition of Zn, Cu, and Zn-Cu alloys films in DESs without chloridization pretreatment. ChCl /urea-based DES has been used as a potential solvent for Zn recovery from waste oxide residues [50]. Yang and Reddy [41, 42] studied the electrodeposition of Zn and Pb films from their oxide precursors in the ChCl /urea-based DES due to their relatively high solubilities in the DES. Tsuda et al. [43] investigated the electrochemical behavior of Cu_2O in the same DES, and they found that Cu can be directly electrodeposited from Cu_2O precursor. More recently, we have also found that micro-/nanostructured Zn and Cu films can be electrodeposited from ZnO and CuO precursors in DESs, respectively [44, 45]. Zhang et al. [46] also demonstrated that the electrochemical synthesis of uniform Cu nanoparticles from Cu_2O can be achieved in ChCl /urea-based DES. This previous work generally showed that zinc and copper oxides have the potential to be used as the precursors for the direct electrodeposition of Zn, Cu, and Zn-Cu alloys films in DESs.

2. Electrodeposition of Zn from ZnO in ChCl /urea-based DES

2.1. Cyclic voltammetry (CV) analysis

The blank CV curve obtained from a platinum working electrode in ChCl /urea-based DES at 333 K is illustrated in **Figure 1(a)**. The cathodic limit is approximately -1.2 V and the anodic limit is about 1.2 V. It can be seen from the blank CV that the electrochemical window of the ChCl /urea-based DES is approximately 2.4 V. **Figure 1(b)** shows the CV curve obtained from a platinum working electrode in the ChCl /urea-based DES dissolved with 0.1 M ZnO at 333 K and potential range of -1.3 to -0.1 V. As evidenced from this figure, the single cathodic current peak observed at about -1.1 V is attributed to the reduction of Zn^{2+} to the metal Zn, the anodic current peak occurred at approximately -0.95 V and is due to the stripping of the electrodeposited Zn.

In order to further investigate the electrochemical behavior of Zn, CV experiments using a platinum electrode as working electrode at different scan rates in ChCl /urea- ZnO (0.1 M) were also performed systematically, and the CV curves are shown in **Figure 2(a)**.

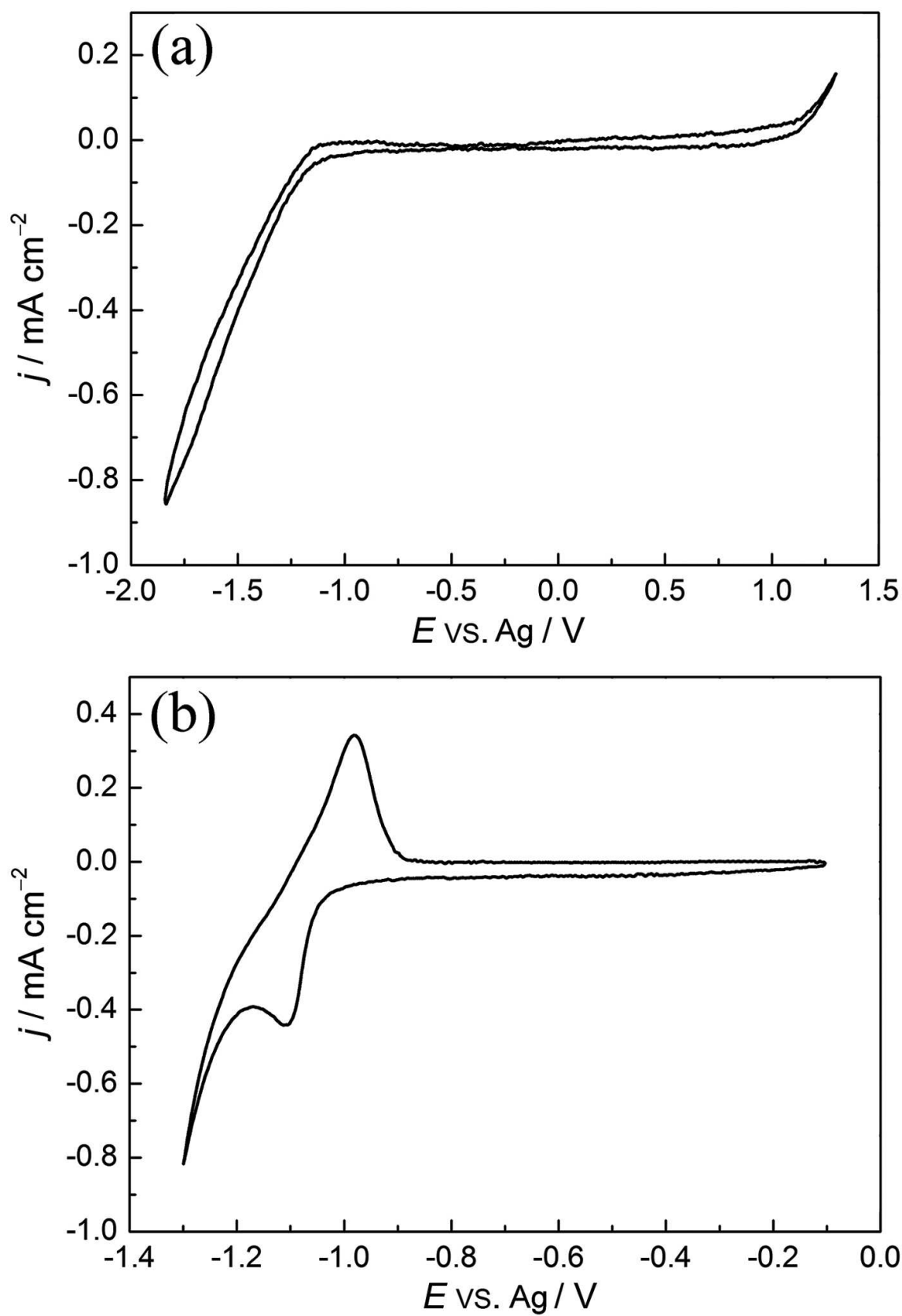


Figure 1. (a) CV curve of a Pt electrode in pure ChCl/urea at 333 K with a scan rate of 10 mV s^{-1} . (b) CV curve of a Pt electrode in ChCl/urea-ZnO (0.1 M) at 333 K with a scan rate of 10 mV s^{-1} .

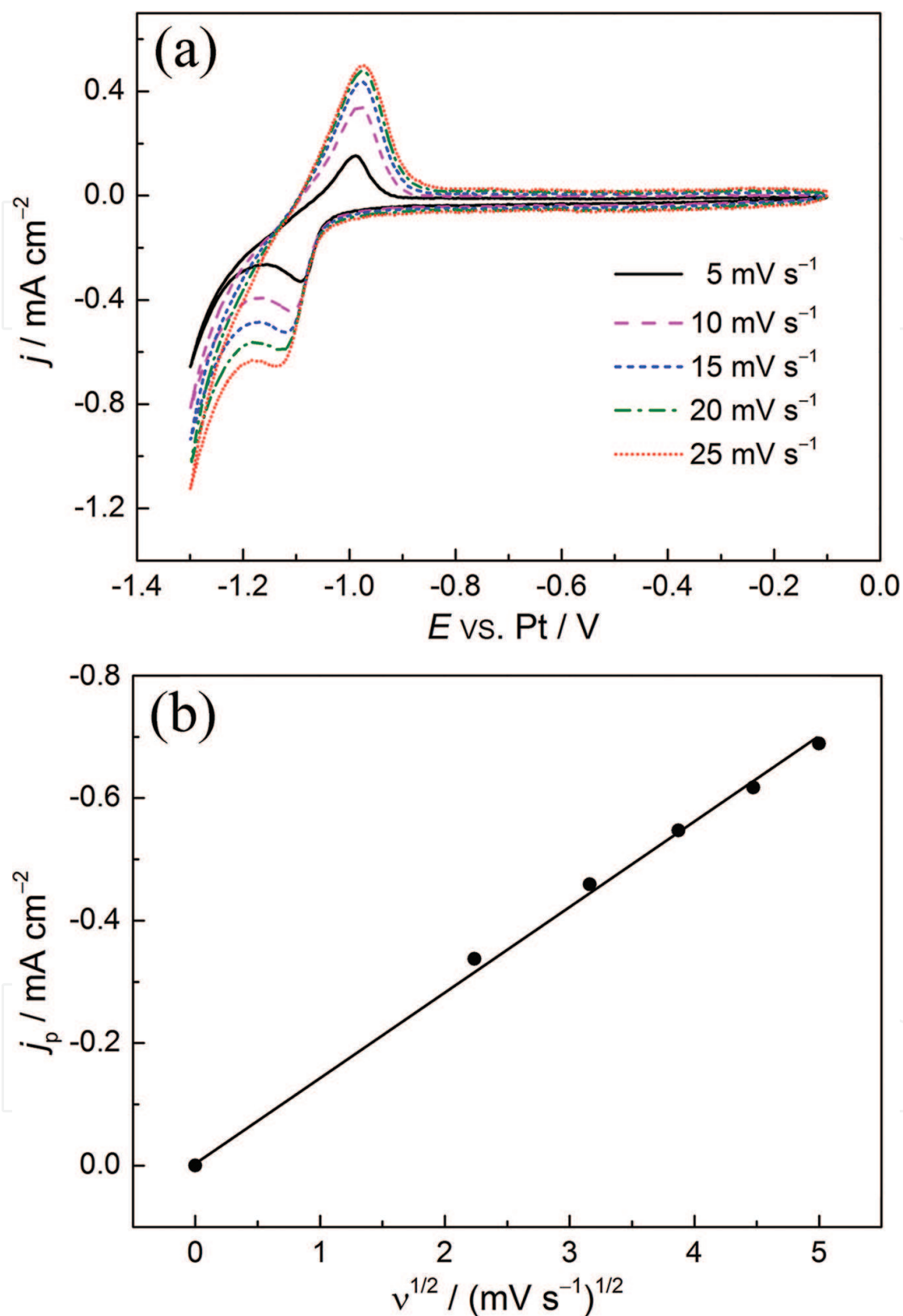


Figure 2. (a) CV curve of a Pt electrode in ChCl/urea-ZnO (0.1 M) at 333 K with different scan rates. The scan rates were 5, 10, 15, 20, and 25 mV s^{-1} , respectively. (b) Relationship between cathodic peak current density (j_{pc}) and square root of scan rate ($v^{1/2}$) calculated from (a).

The cathodic and anodic peak's current densities increase with the increase of scan rate, and the cathodic and anodic peak potentials shift to more negative and positive sides, respectively. In **Figure 2(b)**, the cathodic peak current density (j_{pc}) vary linearly as a function of the square root of scan rate ($v^{1/2}$), implying the reduction process of Zn(II) is mainly diffusion-controlled. Besides, the cathodic peak and half-peak potentials $|E_{pc} - E_{pc/2}|$ increase with the increase of scan rate. At the lowest scan rate, the difference in the value of 42 mV is larger than the value for the reversible process (31 mV at 333 K). All of these results suggest that the reduction of Zn(II) to Zn in ChCl/urea-based DES is a diffusion-controlled quasi-reversible process [51].

For a quasi-reversible charge transfer process, the diffusion coefficient of Zn(II) can be determined by the irreversible Randles-Sevcik equation (1) [51], which is applicable to the quasi-reversible systems as well [52, 53],

$$j_{pc} = 0.4958nFAC_{Zn(II)}D_{Zn(II)}^{1/2}\left(\frac{\alpha n_{\alpha}Fv}{RT}\right)^{1/2} \quad (1)$$

where j_{pc} is the cathodic peak current density, F is the Faraday constant, n is the number of exchanged electrons, $C_{Zn(II)}$ is the Zn(II) species concentration, A is the electrode area, $D_{Zn(II)}$ is the diffusion coefficient of Zn(II) species, v is the scan rate, α is the transfer coefficient, n_{α} is the electron transfer number in the rate determining step, R is the gas constant, and T is the absolute temperature. The value α can be obtained from Eq. (2) [51]:

$$|E_{pc} - E_{pc/2}| = 1.857RT/\alpha n_{\alpha}F \quad (2)$$

where E_{pc} and $E_{pc/2}$ are the cathodic peak potential and half-peak potential, respectively. According to Eq. (2) and the data obtained from **Figure 2(a)**, the average transfer coefficient can be calculated as 0.53. Substituting this and other parameters in Eq. (1), the diffusion coefficient of Zn(II) in ChCl/urea-based DES is determined to be $6.21 \times 10^{-9} \text{ cm}^2 \text{ s}^{-1}$ at 333 K, which is smaller than that of Zn(II) in $\text{Bu}_3\text{MeN-TFSI}$ ($1.6 \times 10^{-7} \text{ cm}^2 \text{ s}^{-1}$ [54]) and $\text{AlCl}_3\text{-EMIC}$ ($2.6 \times 10^{-6} \text{ cm}^2 \text{ s}^{-1}$ [55]) ionic liquids. The relatively low mobility of Zn(II) species may be ascribed to the formation of large, sterically hindered Zn-complex anions when ZnO is dissolved in the DES [44] and high viscosity of the ChCl/urea-based DES [56].

2.2. Morphology and phase composition analyses of the electrodeposited Zn films

The SEM images of the Zn films electrodeposited at different electrodeposition temperatures are shown in **Figure 3**. It is obvious that the microstructure of the Zn films changes gradually with increasing the electrodeposition temperature. As illustrated in **Figure 3(a)**, compact Zn films with particle size approximately 400 nm can be obtained at 333 K. The particle size of the Zn electrodeposits apparently increases with increasing electrodeposition temperature (**Figure 3b–d**). In addition, the interspaces between the Zn particles

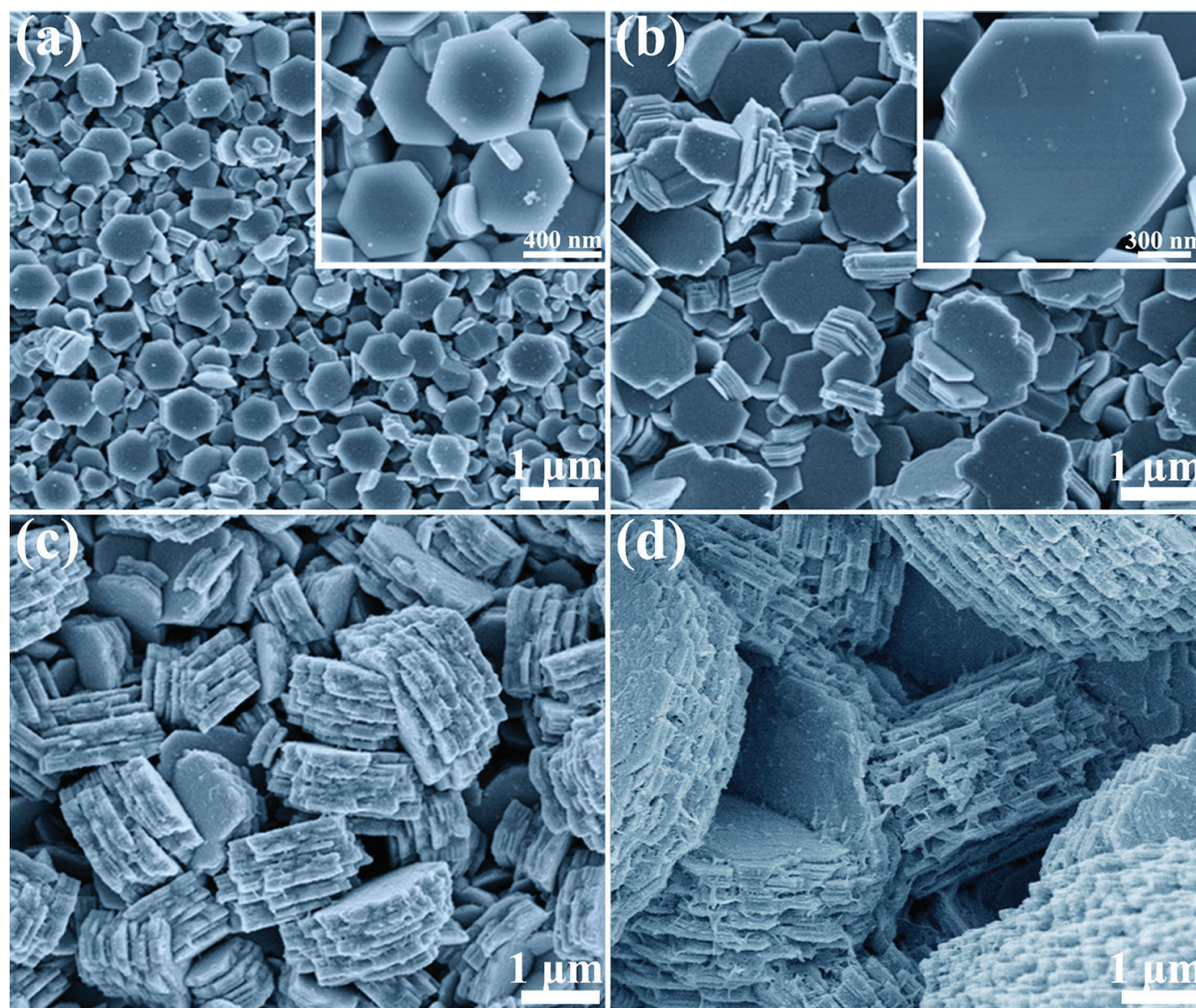


Figure 3. SEM images of the Zn electrodeposits obtained from ChCl/urea–ZnO (0.1 M) at -1.15 V on a Cu substrate at different temperatures: (a) 333 K, (b) 343 K, (c) 353 K, and (d) 363 K for 2 h.

also increase gradually with the growth of the particles, which result in the Zn films become porous. The Zn electrodeposits with hexagonal structure (**Figure 3a**) continue to further nucleate and grow to form polygonal Zn plates (**Figure 3b**) and then transform to multilayer structure (**Figure 3c–d**). The Zn particles gradually change from dispersive nanoparticle to multilayer microparticle with irregular shapes. It should be noted that the morphology change during the electrodeposition process is mainly attributed to the increased electrodeposition rate and the electrodeposition temperature. It is worth noting that the morphology of the electrodeposited Zn can be influenced by the electrodeposition temperature.

X-ray diffraction (XRD) pattern of the Zn electrodeposits on a Cu substrate obtained from 0.1 M ZnO in ChCl/urea-based DES is shown in **Figure 4**. It can be seen that only two metallic phases, Zn and Cu (substrate), are identified. It is obvious that the electrodeposit is composed of high purity Zn.

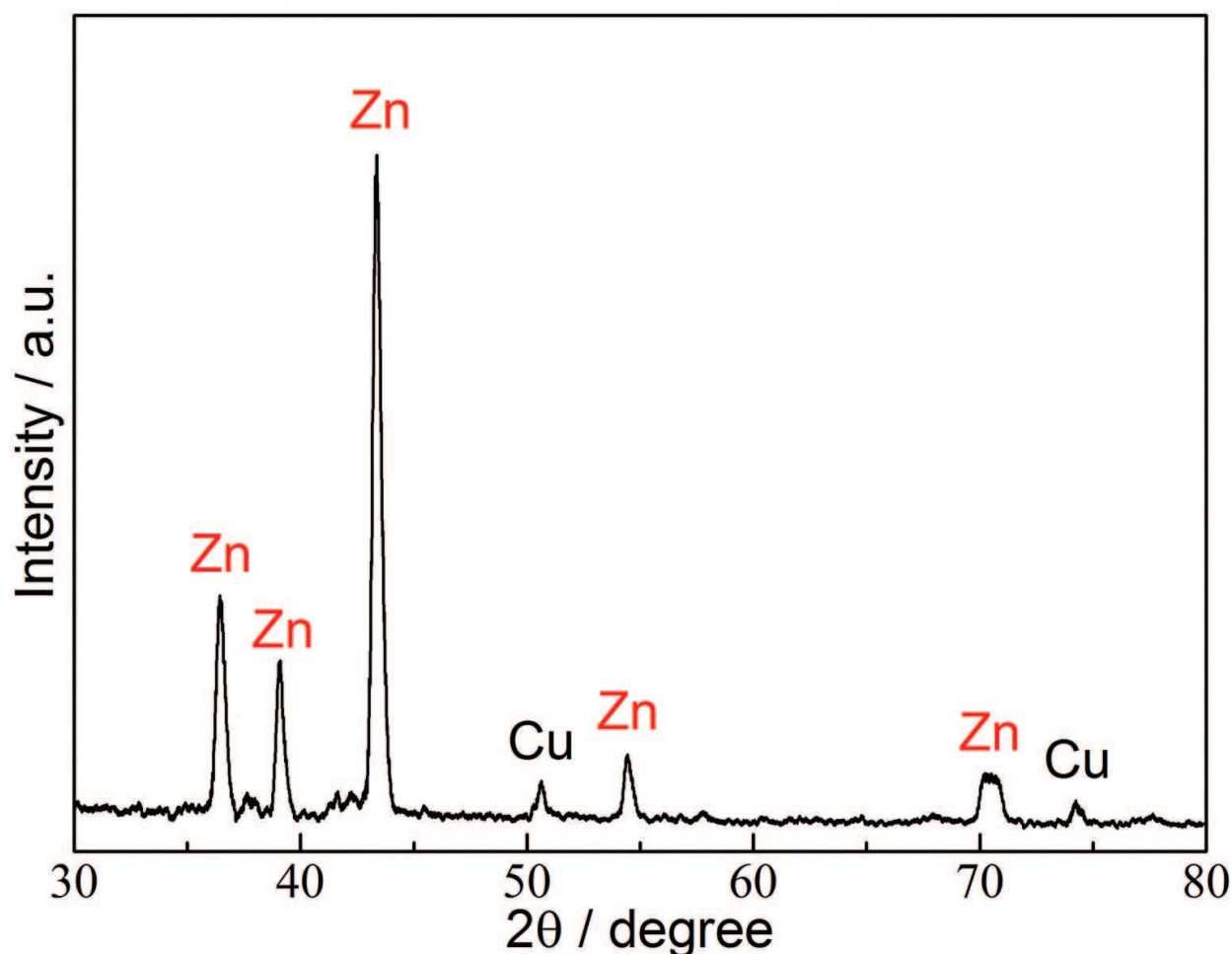


Figure 4. XRD pattern of the Zn electrodeposits obtained from ChCl/urea–ZnO (0.1 M) on a Cu substrate at -1.15 V and 333 K.

3. Electrodeposition of Cu from CuO in ChCl/EG and ChCl/urea-based DESs

3.1. CV study

In order to investigate the electrochemical behavior of Cu, CV analysis was carried out in ChCl/EG–CuO (0.01 M)- and ChCl/urea–CuO (0.01 M)-based DESs, and the CV curves are shown in **Figure 5**. For comparison, **Figure 5(a)** and **(b)** illustrates the voltammetric behavior of Cu(II) in the ChCl/EG–CuO (0.01 M) and ChCl/urea–CuO (0.01 M) electrolytes, respectively, and the CVs were recorded at 353 K with a scan rate of 10 mV s^{-1} . Two redox couples (c_1/a_1 and c_2/a_2) are occurred in each CV curve. The redox couple (c_1/a_1) is assigned to the reaction of $\text{Cu(II)} + e^- \leftrightarrow \text{Cu(I)}$, and the redox couple (c_2/a_2) is attributed to the reaction of $\text{Cu(I)} + e^- \leftrightarrow \text{Cu}$. As shown in **Figure 5(a)** and **(b)**, the peak current density for the reduction of Cu(I)/Cu(0) in the ChCl/EG system is higher than that in the ChCl/urea system. Moreover, the redox potentials of the Cu(II)/Cu(I) and Cu(I)/Cu(0) couples in the ChCl/urea system occur at potentials more negative than those observed in the ChCl/EG system. The different redox potentials

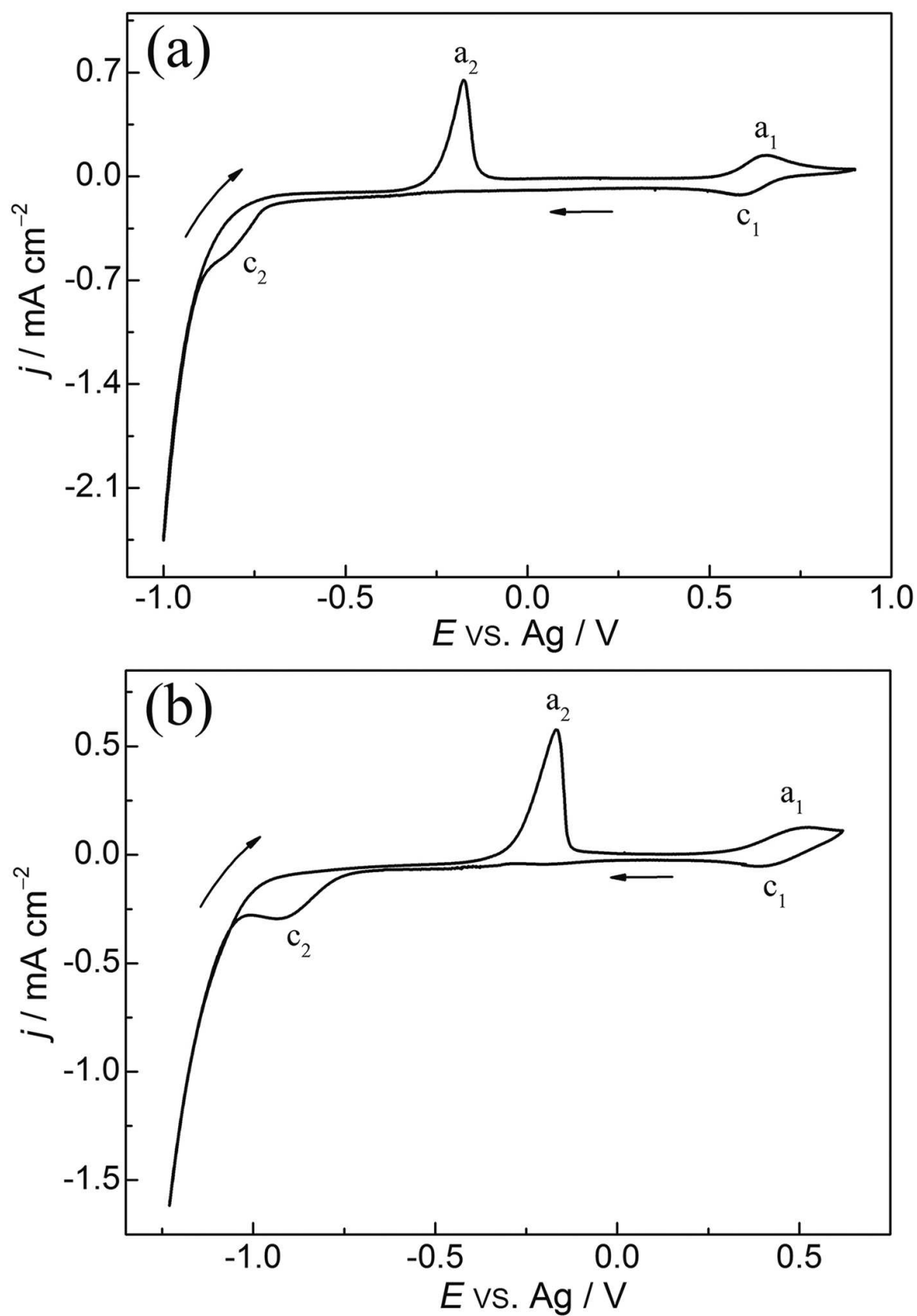


Figure 5. CV curves of a Fe electrode in (a) ChCl/EG-CuO (0.01 M) and (b) ChCl/urea-CuO (0.01 M) at 353 K with a scan rate of 10 mV s^{-1} .

may be attributed to the differences in ligand activity between the two DESs. There is a strong coordination between the chloride ions and urea, which can effectively decrease the activity of chloride compared with EG [25]. These results can be ascribed to the lower viscosity of the ChCl/EG system and the facile charge-transfer kinetics in the ChCl/EG system compared to that of the ChCl/urea system [41]. Therefore, the lower coordinated Cu species in the ChCl/EG ionic liquid are obviously more easier to be reduced, whereas the higher coordinated Cu species in the ChCl/urea ionic liquid are more difficult to be reduced.

3.2. Characterization of the Cu electrodeposits

The SEM images of the Cu films electrodeposited in ChCl/EG ionic liquid at different electrodeposition potentials are shown in **Figure 6**. In **Figure 6(a)**, a porous and nonuniform electrodeposit is formed. As the electrodeposition potential was made progressively negative to -0.80 V, the agglomeration of Cu particles occurred. The Cu particles generated at high cathodic potential are composed of some larger agglomerates with fine nanoscale particles (**Figure 6c**). **Figure 6(d)** shows the EDS spectra of the Cu film corresponding to **Figure 6(b)**. Only two elements Cu and Fe (substrate) are determined from the EDS spectra.

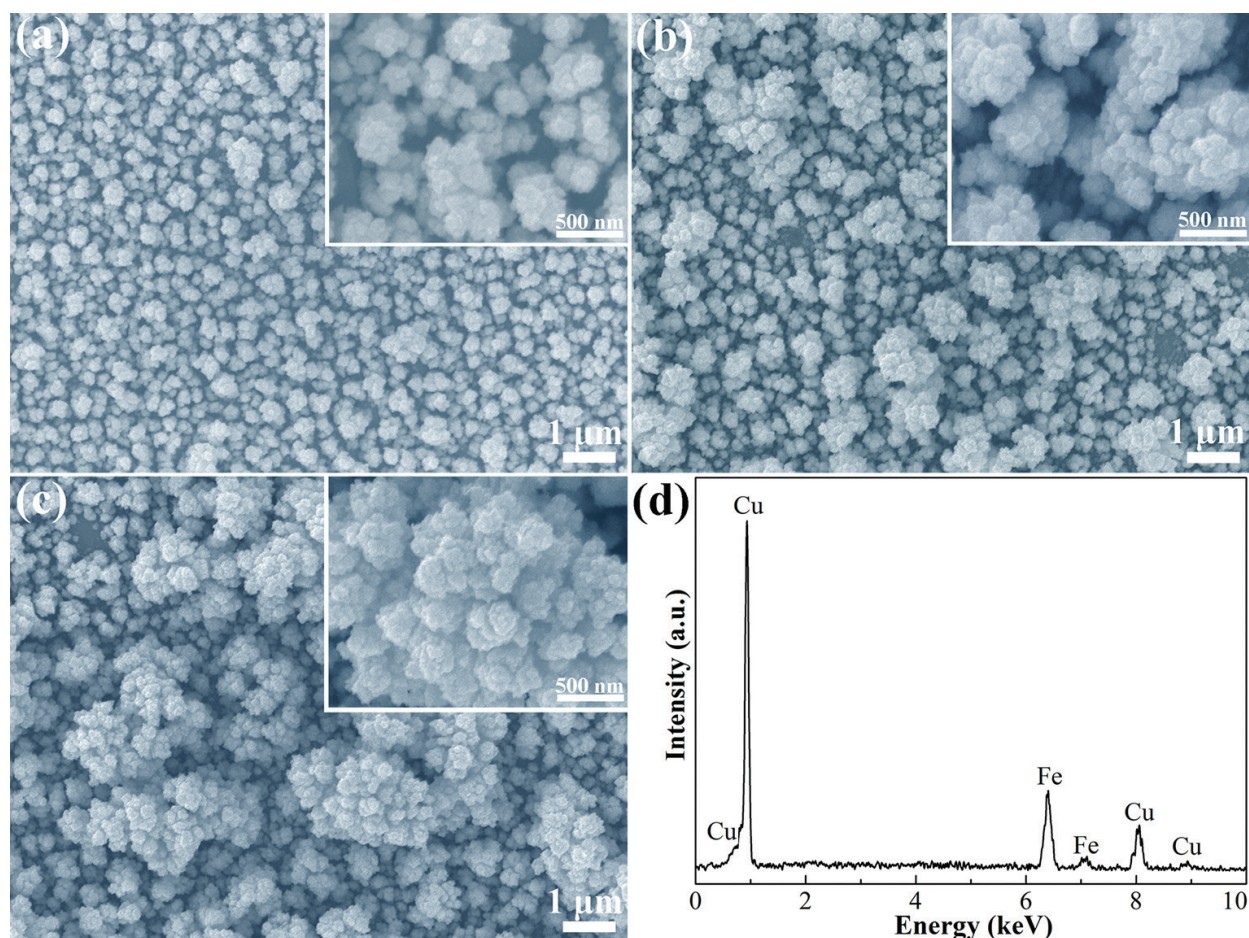


Figure 6. SEM images of the Cu electrodeposits obtained on a Fe substrate in ChCl/EG–CuO (0.01 M) at (a) -0.75 V, (b) -0.80 V, and (c) -0.85 V and 353 K for 3 h, and (d) EDS spectra of the electrodeposited Cu film corresponding to (b).

It is indicated that the electrodeposition potential has significant influences on the morphology of Cu electrodeposits.

The SEM images of the Cu films electrodeposited in ChCl/urea ionic liquid at different electrodeposition potentials are shown in **Figure 7**. As evidenced in **Figure 7(a)**, the uniform, dense, and compact electrodeposits are formed at -0.90 V. As the electrodeposition potential increases to -0.95 and -1.00 V, some spherical nodular electrodeposits are formed and become more porous (**Figure 7b** and **c**). **Figure 7(d)** shows the EDS spectra of the Cu film corresponding to **Figure 7(b)**. Only two elements Cu and Fe (substrate) are determined from the EDS spectra. The differences in morphology are probably due to the different Cu species formed in the electrolyte, the higher coordinated and lower superficial diffusion of Cu species in ChCl/urea ionic liquid results in a homogenous distribution of particles with particle size smaller than those observed in ChCl/EG ionic liquid.

XRD patterns of the Cu electrodeposits on a Fe substrate obtained from 0.01 M CuO in ChCl/EG and ChCl/urea ionic liquids are shown in **Figure 8(a)** and **(b)**. It can be seen that only two metallic phases Cu and Fe (substrate) are identified in both media. It is evidenced that the electrodeposit is composed of high purity Cu.

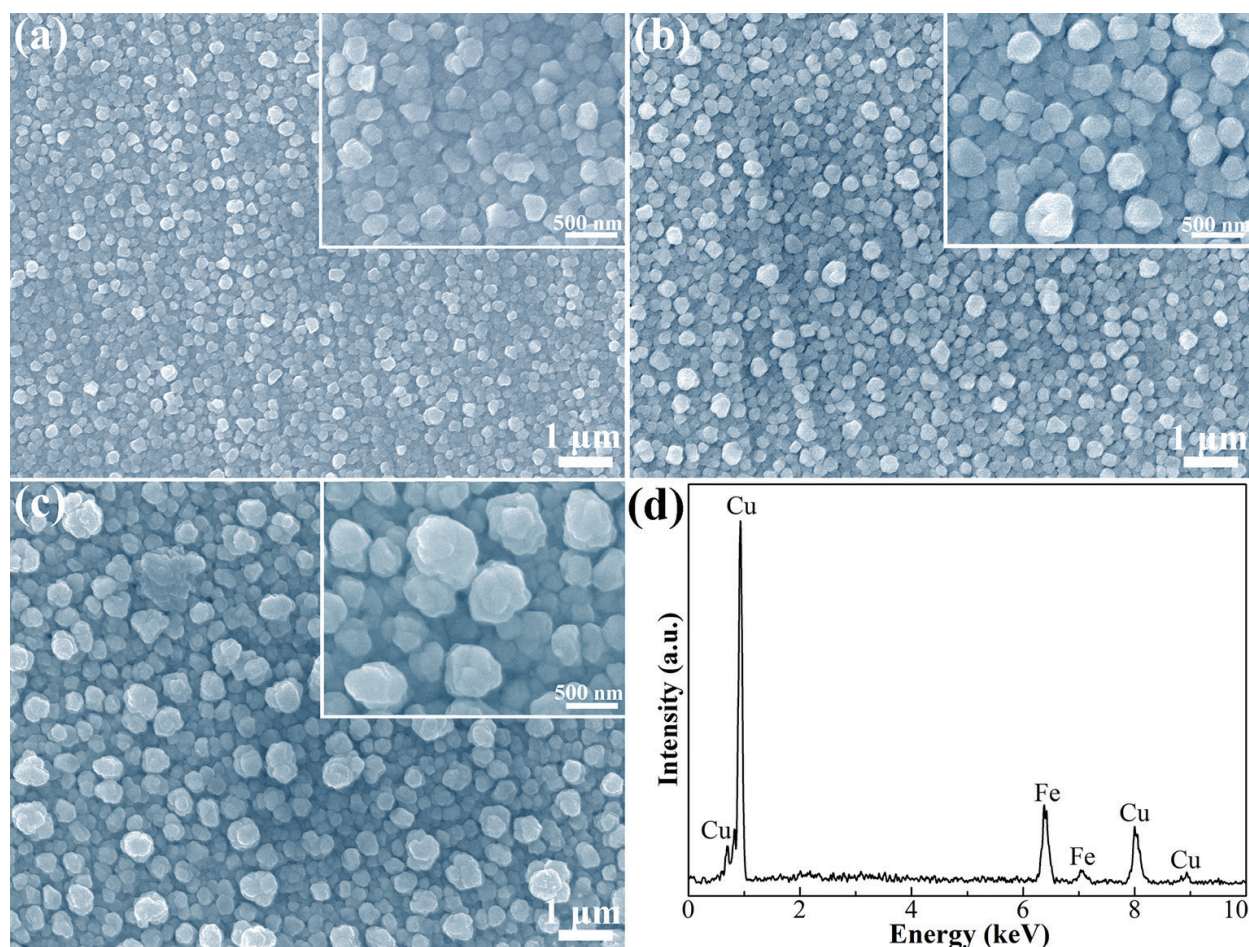


Figure 7. SEM images of the Cu electrodeposits obtained on a Fe substrate in ChCl/urea–CuO (0.01 M) at (a) -0.90 V, (b) -0.95 V, (c) -1.00 V and 353 K for 3 h, and (d) EDS spectra of the electrodeposited Cu film corresponding to (b).

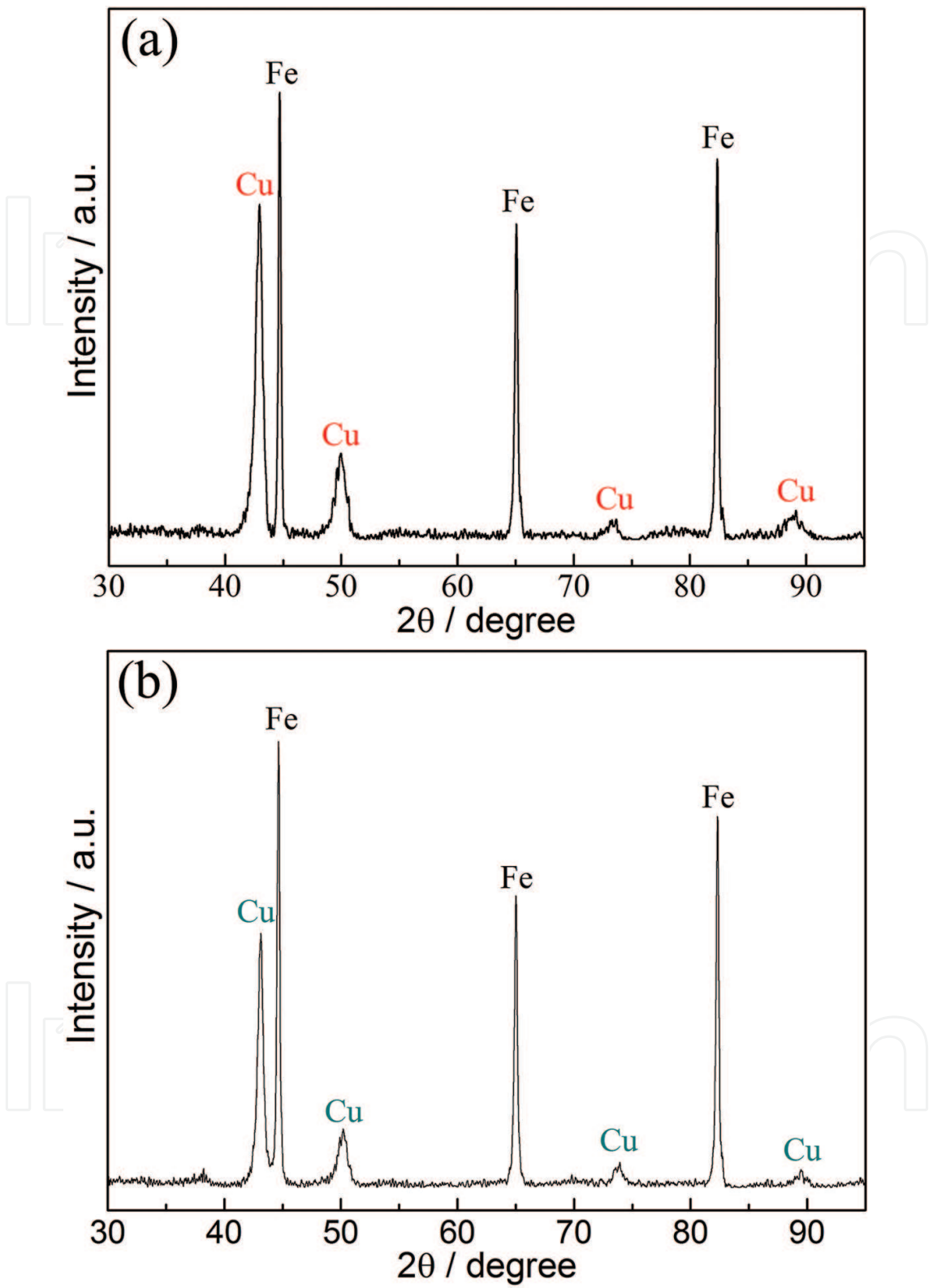


Figure 8. XRD patterns of the Cu electrodeposits obtained on a Fe substrate in (a) ChCl/EG–CuO (0.01 M) at –0.80 V and 353 K for 3 h and (b) ChCl/urea–CuO (0.01 M) at –0.95 V and 353 K for 3 h.

4. Electrodeposition of Zn-Cu alloys in ChCl/urea-based DES

4.1. CV analysis

Figure 9 shows the CV curve of the ChCl/urea ionic liquid dissolved with 0.01 M CuO and 0.1 M ZnO on a Fe electrode at 343 K with a scan rate of 10 mV s^{-1} . There are three reduction peaks on the cathodic branch of the voltammogram. The two cathodic reduction peaks observed at approximately 0.25 V (labeled as c_1) and -0.85 V (c_2) are attributed to the Cu(II) to Cu(I) reduction process and the Cu(I) to Cu reduction process, respectively. The reduction peak at about -1.15 V (c_3) can be ascribed to the Zn(II) to Zn reduction process. When the scan is reversed, four oxidation peaks (a_1 , a_2 , a_3 , and a_4), as shown in **Figure 9**, are observed in the potential range of -1.10 to 0.50 V . The oxidation peaks for pure Cu (a_1 and a_2) and pure Zn (a_4) are at about 0.32 , -0.30 , and -1.05 V , respectively, and the oxidation peak (a_3) is for the Zn-Cu electrodeposits between the two potentials (a_2 and a_4).

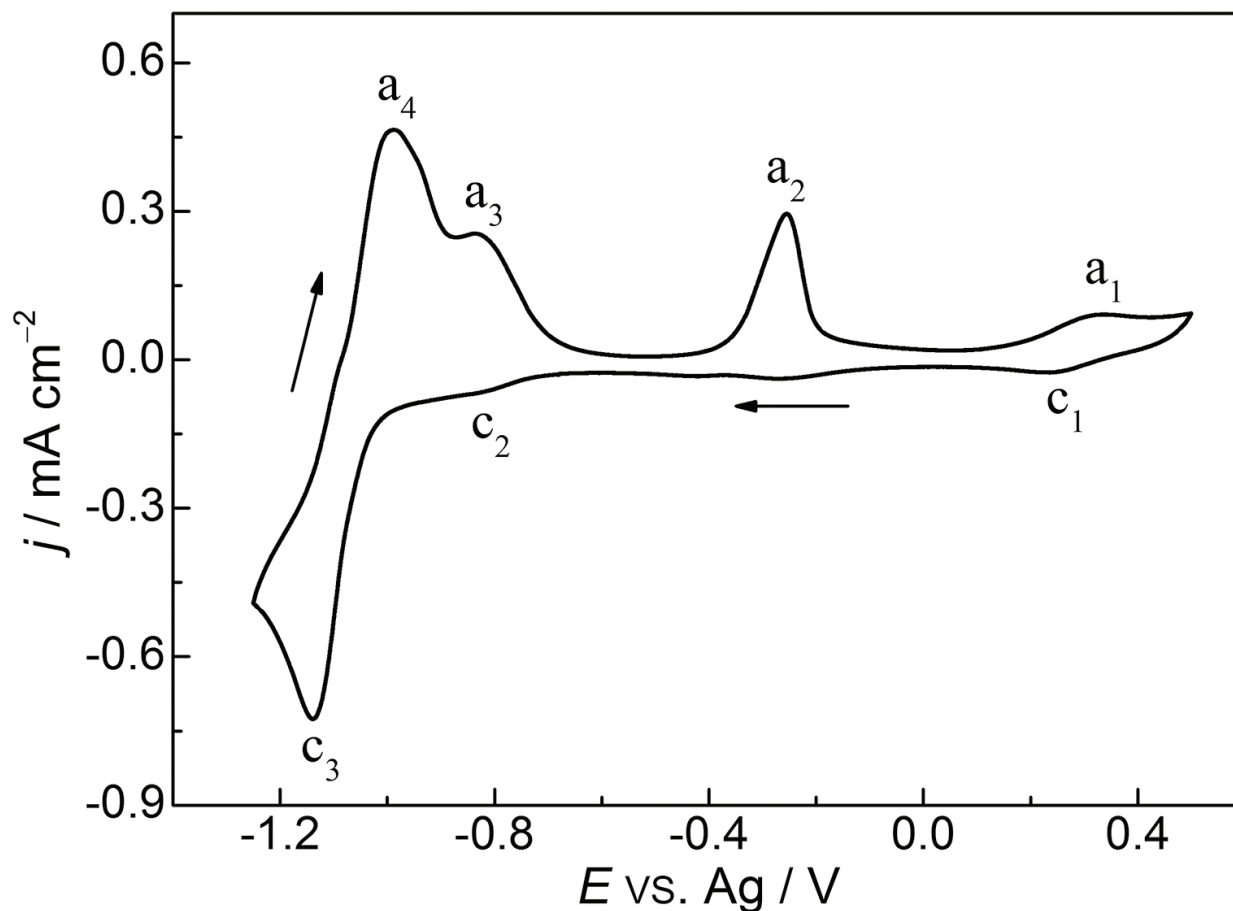


Figure 9. CV curve of a Fe electrode in ChCl/urea ionic liquid containing 0.1 M ZnO and 0.01 M CuO at 343 K with a scan rate of 10 mV s^{-1} .

4.2. Morphology and phase composition analyses of the electrodeposited Zn-Cu films

The XRD patterns of the Zn-Cu alloys electrodeposited on a Fe substrate in the ChCl/urea ionic liquid containing 0.1 M ZnO and 0.01 M CuO at different potentials and 343 K for 3 h are shown in **Figure 10(a)**. It can be seen that the dominate phases of the Zn-Cu films electrodeposited at -1.05 V are Cu_5Zn_8 and Cu (substrate). As the electrodeposition potential increases to -1.10 V, two new phases (CuZn_5 , Zn) are observed and the Cu_5Zn_8 phase is disappeared. It is mainly the result of increasing the Zn electrodeposition rate under more negative potential. **Figure 10(b)** and **(c)** shows the SEM images of the Zn-Cu alloys electrodeposited in the ChCl/urea ionic liquid containing 0.1 M ZnO and 0.01 M CuO at different cathodic potentials and 343 K for 3 h. The Zn-Cu electrodeposit obtained at -1.05 V is composed of spherical clusters with some void space between the particles (**Figure 10b**). When the potential changes from -1.05 to -1.10 V, the agglomeration of Zn-Cu particles is observed and the electrodeposits are porous and nonuniform (**Figure 10c**).

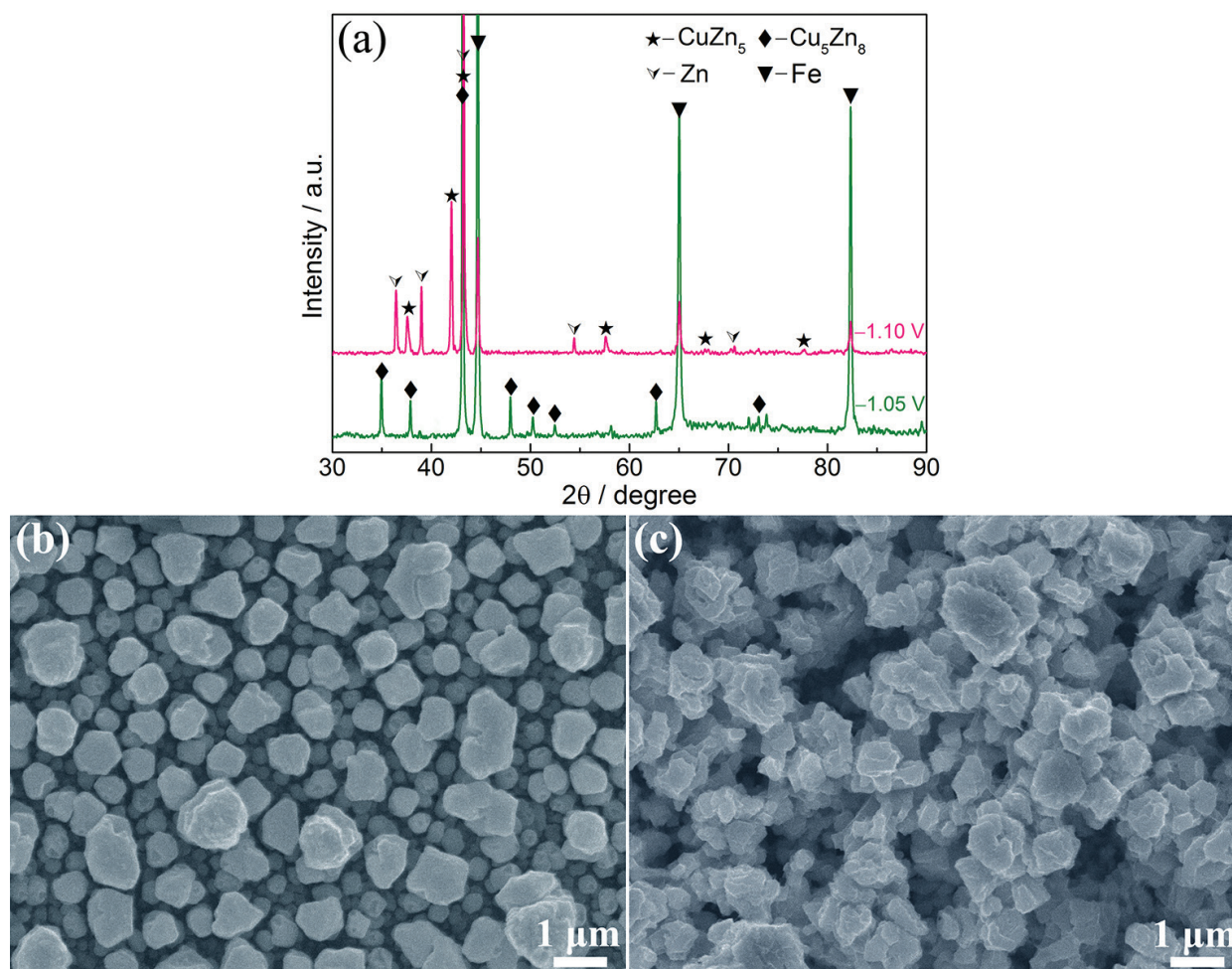


Figure 10. (a) XRD patterns of the Cu-Zn alloys electrodeposited on a Fe substrate in the ChCl/urea ionic liquid containing 0.1 M ZnO and 0.01 M CuO at different cathodic potentials and 343 K for 3 h. (b) and (c) SEM images of the Cu-Zn electrodeposits obtained on a Fe substrate in the 12CU ionic liquid containing 0.1 M ZnO and 0.01 M CuO at 343 K for 3 h, (b) -1.05 V and (c) -1.10 V.

5. Conclusions

The electrodeposition of Zn, Cu, and Zn-Cu alloys from ZnO/CuO precursors has been investigated in DESs. Electrochemical measurements showed that the Zn electrodeposition is a diffusion-controlled quasi-reversible, one-step, two electrons transfer process. The diffusion coefficient of Zn(II) was estimated to be $6.21 \times 10^{-9} \text{ cm}^2 \text{ s}^{-1}$ at 333 K. Uniform, dense, and compact Zn electrodeposits can form under suitable electrodeposition potentials and lower temperatures. Besides, the electrodeposition of Cu from CuO in the eutectics based on ChCl with urea and EG has been respectively investigated and compared. The voltammetric measurements show the electrodeposition of Cu in ChCl/EG and ChCl/urea systems through a two-step process. The higher coordinated Cu species in the ChCl/urea ionic liquid are more difficult to be reduced. The surface morphology of the Cu electrodeposits can be significantly affected by the ionic liquids and the electrodeposition potential. Furthermore, the Cu electrodeposits obtained in the ChCl/urea ionic liquid possess more homogenous microstructures than those produced in the ChCl/EG ionic liquid. In addition, the Zn-Cu alloy films have also been electrodeposited directly from their metal oxide precursors in ChCl/urea-based DES, the phase composition of the Zn-Cu alloys depends on the electrodeposition potential. These results may have implications on the electrodeposition of other alloy films from oxide precursors in DESs system.

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