Electrochemical Fabrication of Micro/Nanoporous Copper by Electrosynthesis-Dealloying of Cu–Zn Alloy in Deep Eutectic Solvent

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Abstract The electrodeposition of Cu–Zn alloy films on a Ni substrate from CuO and ZnO precursors in choline chloride (ChCl)/urea (1:2 molar ratio) based deep eutectic solvent (DES) was firstly carried out. Then, micro/nanoporous Cu films were fabricated by further electro-dealloying of the synthesized Cu–Zn alloy films. XRD analysis indicates that the phase compositions of the deposited Cu–Zn alloys are Cu_5Zn_8 and $CuZn_5$. Further investigation shows that the more-active component Zn would be dissolved during the electro-dealloying process, and porous Cu can be obtained. The result reveals that the electrosynthesis-dealloying process may provide a promising strategy for the production of micro/nanoporous Cu at low temperature.

Keywords Porous copper • Electrosynthesis • Dealloying • Cu–zn alloy
Deep eutectic solvent

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Introduction

Due to high surface areas, micro/nanoporous metals with superior physical and chemical properties have drawn broad attention in various applications, including catalysis, sensors, actuators, fuel cells, and batteries, etc. [1–4]. Several approaches have been proposed to fabricate micro/nanoporous metals, such as covering casting, melt gas injection, thermal evaporation, sputter deposition, vapor deposition technique, electrochemical methods, and dealloying [5, 6]. Among these techniques, the dealloying technique that refers to selective dissolution of one or more components from an alloy has attracted wide attention and becomes a promising process to produce micro/nanoporous metals. In addition, electrochemical dealloying method exhibits a relatively versatile superiority to prepare various micro/nanoporous metals, *e.g.*, gold, platinum, silver, nickel, tungsten, copper, and so on [7–9]. In recent year, nanoporous Cu with a relatively low cost and several exceptional features, such as low density, high modulus of elasticity and reaction activity, shows a promising application prospect [6]. However, the electrochemical fabrication of micro/nanoporous metals are usually carried out in acidic or alkaline media, which commonly involves the chemical/electrochemical etching of the substrate surface [10].

Room-temperature ionic liquids (RTILs) generally possess many distinct advantages such as extremely low vapor pressure, high ionic conductivity, wide electrochemical windows, high solubility of metal salts, and thermal stability [11, 12]. In particular, RTILs have gained considerable attention in comparison with aqueous solutions. In various kinds of RTILs, deep eutectic solvents (DESs) have been considered as the potential alternatives sharing most of physical and chemical properties of conventional RTILs [13]. Practically considering the cost and handling ionic liquids, DESs are obtained primitively by mixing quaternary ammonium salts with hydrogen-bond donors such as alcohols, amides, and acids [14, 15]. Moreover, the other merits of rifeness include low cost, nontoxicity and more accessible synthesis with high purity, make them attractive solvents for large-scale technological applications.

In this work, we report the electrosynthesis-dealloying of Cu–Zn alloy from CuO and ZnO precursors in DES on a Ni substrate. Moreover, the fabrication process for the micro/nanoporous copper is discussed.

Experimental

Electrolyte Preparation

Choline chloride [$HOC_2H_4N(CH_3)_3Cl$] (ChCl) (Aldrich 99%), urea [NH_2CONH_2] (Aldrich $>$ 99%), ZnO (Aldrich $>$ 99%) and CuO (Aldrich $>$ 99%) were used as received. To remove the water residue and trapped air, ChCl and urea were dried under vacuum at 333–363 K for at least 12 h. The eutectic mixture in the molar proportion of ChCl: urea = 1:2 was stirred under argon atmosphere using a polytetrafluoroethylene(PTFE)-coated magnetic stir bar in a beaker at 353 K until a homogeneous and colorless solution was formed. Thereafter, 0.01 M CuO and 0.1 M ZnO were dissolved in the ChCl-urea DES at 343 K and stirred until the blue transparent electrolyte was obtained.

Electrodeposition and Dealloying Experiments

Electrodeposition experiments were performed in a three-electrode system, consisting of a Ni foil (1 cm^2) as the working electrode, a platinum plate (0.6 cm^2) as the counter electrode, and a silver wire (99.995%, 1.0 mm in diameter) as the reference electrode. Approximately 50 mL of the ChCl-urea DES containing 0.01 M CuO and 0.1 M ZnO was used as the electrolyte for the electrodeposition experiments. The experimental device is shown in Fig. 1. Mirror polishing with 0.5 μm alumina paste, washing with 10 vol% H_2SO_4, degreasing with acetone, and rinsing with deionized water constitute the sequence in surface pretreating for the Ni substrate. Subsequently, the electrodeposition of alloy films on the Ni substrate was carried out at three different potentials (−1.1,−1.15 and −1.2 V versus Ag) by using chronoamperometry (CA) electrodeposition in the electrolytic cell at 343 K for 2 h. In order to minimize the water ingress into the electrolyte, all the electrodeposition experiments were conducted in a sealed cell. All final products were taken out from the cell, followed washing with distilled water and anhydrous alcohol, and then dried.

After the electrodeposition, the formed Cu–Zn alloy films were then dealloyed in the same system as the electrodeposition experiments at room temperature at −0.5 V verus Ag for a certain time (from 100 to 900 s). The dealloying potential was chosen from the cyclic voltammetry curve, and more negative than which will result in the dissolution of copper and more positive than which will lead to the dissolution of zinc [16]. Then, the as-prepared samples were removed from the solvent, carefully washed with anhydrous alcohol and distilled water, and dried finally by N_2 gas stream. The whole simplified process of electrodeposition and electrosynthesis-dealloying is shown in Fig. 2.

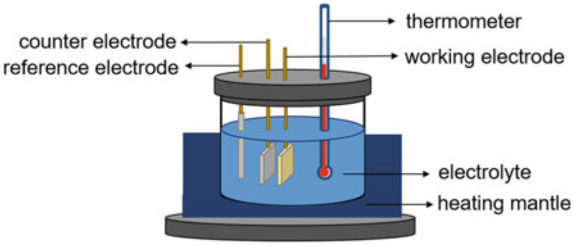


Fig. 1 Schematic illustration of the experimental device for the electrodeposition and dealloying processes

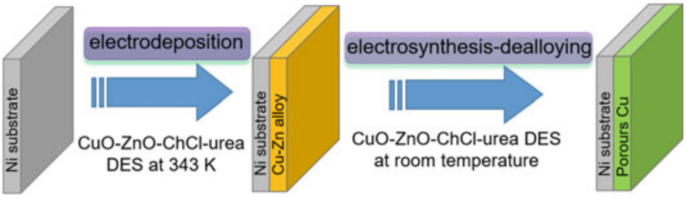


Fig. 2 Schematic illustration of the electrodeposition and electrosynthesis-dealloying processes

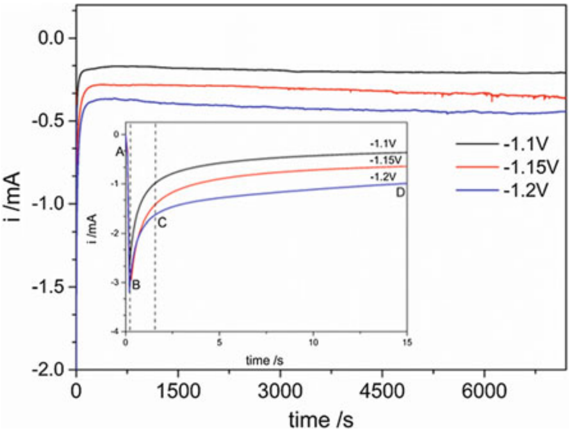
The microstructure of the electrodeposited Cu–Zn alloy films and the dealloyed products were examined with scanning electron microscope (SEM, JEOL JSM-6700F). The corresponding phase structures were analyzed by X-ray diffraction (XRD, Bruker-AXS D8Advance) with Cu-Kα radiation at a scan rate of $5^\circ\ \text{min}^{-1}$.

Results and Discussion

Electrodeposition of Cu–Zn Alloy Films

Chronoamperometry experiments were carried out in the potential range of −1.1 to −1.2 V. Typical current-time transient curves recorded in the ChCl-urea DES containing 0.01 M CuO and 0.1 M ZnO at 343 K for 2 h are shown in Fig. 3. From the enlarged part of Fig. 2, the drastically negative increasing of the initial current (A → B) may be caused by the double layer charging [17]. Then, as a result of the formation and growth of Cu-Zn alloy nuclei, the current (B → C) gradually shifts positively until a steady value (C → D). Compare the current-time curves recorded

Fig. 3 Current-time curve of the electrodeposition process on a Ni substrate in ChCl-urea DES containing 0.01 M CuO and 0.1 M ZnO at different potentials from −1.1 to −1.2 V at 343 K for 2 h



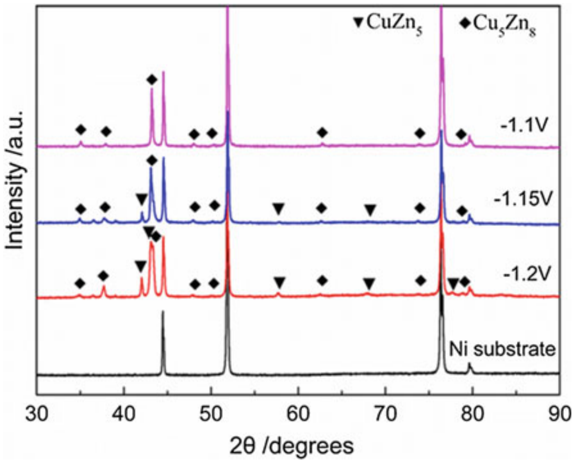


Fig. 4 XRD patterns of the electrodeposited Cu–Zn alloy films on a Ni substrate in ChCl-urea DES containing 0.01 M CuO and 0.1 M ZnO at different potentials and 343 K for 2 h

at different potentials, it is obvious that the final stable current increases with more negative potential.

Copper and zinc co-deposition was performed on a nickel foil at a constant potential, and the as-deposited samples were examined by XRD and SEM analysis. Figure 4 shows the XRD patterns the Cu–Zn alloy films electrodeposited at different potentials and 343 K for 2 h. The characteristic diffractions are attributed to Ni, $CuZn_5$ and Cu_5Zn_8 phases. Cu_5Zn_8 phase was produced at −1.1 V. As the potential becomes more negative, $CuZn_5$ electrodeposition becomes more distinct, owing to the increasing of the Zn electrodeposition rate at more negative potentials (−1.15 and −1.2 V) [18].

The corresponding SEM images of the samples electrodeposited at different potentials are shown in Fig. 5a–c. It can be observed that the particle size of the electrodeposits is approximately 800 nm (Fig. 5a). The pure Cu_5Zn_8 film electrodeposited at −1.1 V is uniform. As the electrodeposition potential increases to −1.15 V, the Cu–Zn alloy film is consisted of flower-shaped clusters (Fig. 5b). With further increasing the electrodeposition potential to −1.2 V, the Cu_5Zn_8 and

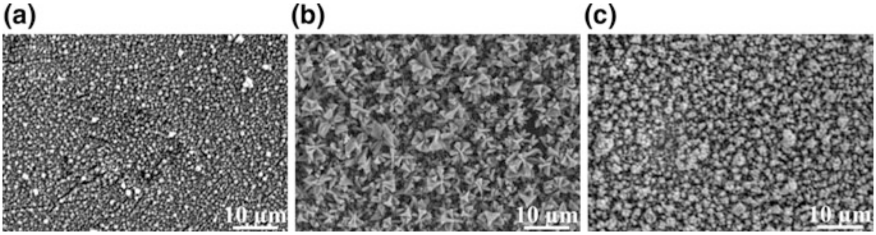


Fig. 5 SEM images of the electrodeposited Cu–Zn alloy films on a Ni substrate in ChCl-urea DES containing 0.01 M CuO and 0.1 M ZnO at different potentials: **a** −1.1 V, **b** −1.15 V, **c** −1.2 V at 343 K for 2 h

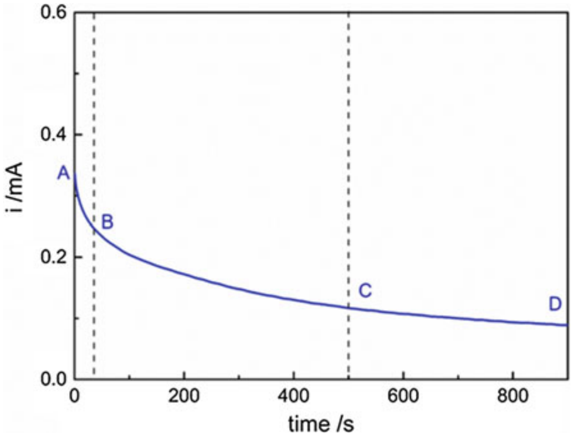


Fig. 6 Anodic stripping current-time curve of the dealloying of the formed Cu–Zn alloy film at −0.5 V and room temperature

$CuZn_5$ alloy films with conglobating structure are observed, owing to the Zn electrodeposition rate increases with more negative potential (Fig. 5c).

Synthesis of Porous Copper

The current-time curve recorded during the dealloying process of the Cu-Zn alloy film is shown in Fig. 6. The Cu-Zn film was firstly prepared on a Ni substrate in ChCl-urea DES containing 0.01 M CuO and 0.1 M ZnO at −1.15 V and 343 K for 2 h, then the electrochemical dealloying process was carried out at −0.5 V verus Ag and room temperature. As shown in Fig. 6, there are three stages in the anodic stripping current-time curve. The initial part (A → B) of the dealloying current decreases sharply, which is related to the quick dissolution of outmost zinc from the uppermost surface. The corresponding SEM examination of the film (Fig. 7b) shows that the flower-shaped clusters were gradually disappeared. As time goes by (B → C, C → D), the current decreases slowly and eventually stabilizes, implying more Zn atoms were dissolved (Fig. 7c–d, then porous Cu was obtained. The EDS spectrum confirms that the dealloyed product is Cu.

Conclusions

The electrochemical fabrication of micro/nanoporous copper films has been investigated by electrochemical alloying/dealloying of Cu-Zn alloy films in the ChCl/urea-based DES. It is suggested that the formation of Cu-Zn alloys including Cu_5Zn_8 and $CuZn_5$ alloy depends on the cathodic electrodeposition potential. More negative potential can contribute to the increasing of Zn electrodeposition rate.

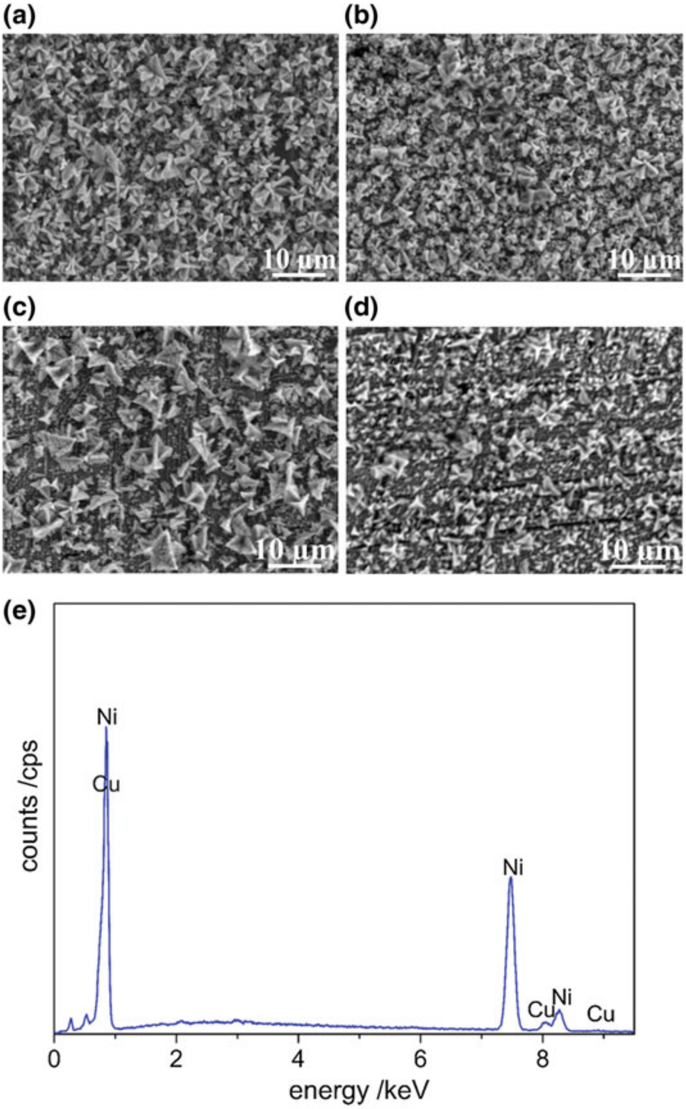


Fig. 7 SEM images of the electrodeposited Cu–Zn alloy films after being dealloyed for different times: **a** 0 s, **b** 70 s, **c** 400 s, **d** 900 s. and **e** EDS spectrum of after being dealloyed for 900 s

Comparing to the traditional acidic or alkaline solutions, the method of preparing micro/nanoporous copper in DES on the Ni substrate is more environmentally sustainable and recyclable, and spends less time (less than 1 h) in lower temperature. Moreover, this method may also have implications for the production of other porous metal materials.

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