Electrodeposition of Copper Metal from the 1-Ethyl-3-methylimidazolium Fluoride ([EMIM]F)-urea-H2O System Containing Cu2O

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ABSTRACT
In this work, [EMIM]F-urea-H2O system is capable of dissolving Cu2O, and then the metallic copper was electrodeposited from this system at room temperature. The reduction of Cu(I) in this system involves a quasi-reversible and one-step single-electron transfer process. The electrodeposition of copper was performed on a tungsten (W) substrate at –0.67 V (vs. Ag) and 353 K via potentiostatic electrolysis. The electrodeposits were identified as metallic copper, as verified by XRD and EDS. SEM image shows that uniform, polygonal nanoparticles of copper were obtained after the potentiostatic static electrolysis.

Keywords : Cu Electrodeposition, Imidazolium Fluoride, Urea, Copper

1. Introduction
Copper is often used for electronic components.1 Different production methods of copper have been mentioned in previous researches, such as vapor-deposition, plasma, mechanic-chemical reduction, and electrodeposition.2,3 Electrodeposition is attractive due to its low cost and less environmental impact. Industrially, the electrodeposition of copper is conducted in the copper sulfate solution.4,6

Room temperature ionic liquids (RTILs) were considered as an alternative electrolyte in laboratory studies during copper electrodeposition.8 For example, copper has been electrodeposited from various RTILs with CuCl, CuCl2, Cu(NO3)2, and CuTFSI, as copper sources, respectively.9-15 It is very interesting to use copper oxide as copper sources for electrodeposition in RTILs. However, most metal oxides are not soluble in molecular solvents except acesous acids or alkalies.16 Therefore, specific solvents were developed to dissolve copper oxide. Previously, Abbott had reported on the solubility of copper oxides in choline chloride (ChCl).17 Hussey et al. had presented the electrochemical behavior of copper (I) oxide in urea-ChCl at 323 K.18 Hua et al. had electrodeposited copper particles from Cu2O and CuO in the ChCl-based eutectics, respectively.19,20 Xu et al. had investigated the voltammetric behavior of CuO in ChCl-ethylene glycol and urea-ChCl.21 Xie et al. had electrochemically extracted copper-zinc alloy from CuO/ZnO in urea-ChCl.22,23 These unexpected solvating powers attract the processing of metal oxides and open a new route for metal electrodeposition from metal oxide precursors at room temperature. Compared with common EMIM salts, [EMIM]F can provide an interesting RTIL in a hydrated or solvated form for metal electrodeposition. Although [EMIM]F has been reported by Hagiwara et al.,24,25 Rogers et al.,26 Xiao et al.,27 and our group,28,29 to our best knowledge, the application of [EMIM]F in metal electrodeposition has not been elucidated so far. These findings expand the range of applications of [EMIM]F and provide a simple route to extract copper particles from precursors of metal oxides at room temperature. In this study, we report for the first time that [EMIM]F-urea-H2O system is capable of dissolving copper (I) oxide and electrochemically extracting copper. The electrochemical characteristics of copper in the [EMIM]F-urea was investigated via cyclic voltammograms (CV) and chronoamperometry. Metallic copper was electrodeposited via potentiostatic electrolysis.

2. Experimental
[EMIM]F was synthesized according to the procedure described in previous works.30,31 Water content in EMIF was measured to be 16.97% by Karl-Fischer titration. Urea, Cu2O, and Tungsten substrate were purchased and used according to the procedure earlier described.30 Also, urea and [EMIM]F were mixed in a molar ratio of 2:1 and then were used to dissolve 1.30 mmol Cu2O. This final mixture was labeled as [EMIM]F-urea-H2O system containing 1.30 mmol Cu2O.

Cu extraction and electrochemical investigation in this system were carried out according to the procedure reported in previous literature.30 A tungsten wire (0.05 cm in diameter) was used as the working electrode (WE), a platinum wire (0.05 cm in diameter) and silver wire (0.05 cm in diameter) were used as the counter electrode (CE) and the quasi-reference electrode (QRE), respectively.30 All the electrodes were sanded with sandpaper, ultrasonically degreased in an ethanol solution, and then washed with deionized water before use.30 The electrodeposition experiment was performed on a tungsten (W) substrate at –0.67 V (vs. Ag) and 353 K via potentiostatic electrolysis. The electrodeposits were characterized using XRD, SEM, and EDS.

3. Results and Discussions
CV curves (Fig. 1) were recorded using a tungsten electrode for [EMIM]F-urea-H2O system containing 1.30 mmol Cu2O. A reduction peak at –0.61 V (vs. Ag) was found. When potentiostatic electrolysis was carried out at –0.67 V, pure copper was obtained, as...
verified by both XRD and EDS. The reduction peak at 
-0.61 V could be assigned to the reduction of Cu (I). After negative
scanning, a single anodic peak was noted at 
-0.00 V, which corresponds to the dissolution of reduced copper on the surface of
the working electrode during a negative scan.

Figure 2 presents the chronoamperometric curves about the
copper nucleation/growth process in [EMIM]F-urea-H2O system
containing 1.30 mmol Cu2O at various potentials. These potentials
were stepped with a value that failed to cause nucleation
/growth and negatively increased to full nucleation
/growth. Chronoamperometric experiments were performed at -0.47, -0.57 and -0.67 V,
respectively. At the beginning, the transients at -0.57 V and
-0.67 V have a large decaying current due to the charge of the
double-layer on the surface of the electrode. After dropping to a
minimum value, these current densities reversely increase because
of the nucleation of copper. The current in this stage is referred as
Faraday current which gets a maximum point at t_m. All current
transients decay after time t_m. As the potentials negatively increased, t_m increases while t_m tends to decline. Here, t_m is referred to the maximum of current, t_m is referred to the time at the maximum of
current. This may be attributed to the shortening of time to overlap
with the discrete diffusion zone and the enhancement in nucleation rate and nucleation density at a higher cathodic potential.

Potentiostatic electrolysis was carried out on a tungsten substrate
in [EMIM]F-urea-H2O system containing 1.30 mmol Cu2O at
-0.67 V (vs. Ag) and 353 K for 20 minutes. After potentiostatic
electrolysis, electrodeposits are obtained on the tungsten substrate
and characterized by the following XRD, EDS, and SEM.

The observed 2° data of XRD in Fig.3 (43.30, 50.43, 74.13,
89.93, and 95.14 degree) are associated with copper crystals (ICCD
Files No. 04-0836), while the remaining peaks correspond to the
tungsten substrate. No peaks of copper oxide were discovered in this
XRD pattern, suggesting that Cu (I) in [EMIM]F-urea-H2O system
had been electro-reduced to Cu. Besides, Fig. 4 shows EDS analysis
about the electrodeposits. The peaks relate to copper, which agrees
with the results in XRD. These indicated that the electrodeposits were
a metallic copper.

Abbott et al. reported that copper (I) oxide has a good solubility
(8725 ppm) in urea melt since copper (I) oxide formed complexes
with urea. Hussey proposed complexes anion of copper (I) oxide
with urea. Based on these previous studies, we assumed the complexes anion of copper (I) oxide in this system as
[Cu2O·urea·F⁻]n⁻, and that these complexes are involved in the electrode reactions, as shown below.
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0.5O2

m

Cathodic potential: ¹

+ 

used to selectively dissolve Cu2O for electrochemical extraction Cu

H2O system via potentiostatic electrolysis, as veri-

fied copper were electrochemically extracted from [EMIM]F-urea-
single-electron transfer process. Uniform, polygonal nanoparticles
of Cu (I) in this electrolyte involves a quasi-reversible and one-step
at room temperature. Cyclic voltammetry shows that the reduction
Con

urea-H2O system containing 1.30 mmol Cu 2O (Substrate: W,

4. Conclusions

In this work, a new electrolyte, [EMIM][F-urea-H2O system was
used to selectively dissolve Cu2O for electrochemical extraction Cu
at room temperature. Cyclic voltammetry shows that the reduction
of Cu (I) in this electrolyte involves a quasi-reversible and one-step
single-electron transfer process. Uniform, polygonal nanoparticles
of copper were electrochemically extracted from [EMIM][F-urea-
H2O system via potentiostatic electrolysis, as verified by XRD, EDS,
and SEM.

Conflicts of Interest

There are no conflicts to declare.

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