Electrochemistry

Electrodeposition of Ni-Cu Alloys in an Air and Water Stable Room Temperature Ionic Liquid

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Due to the ligand property of the DCA anion, both CuCl and NiCl₂ are soluble in 1-ethyl-3-methylimidazolium dicyanamide (EMI-DCA) ionic liquid. Cyclic voltammograms of Ni(II), Cu(I), and Ni(II) + Cu(I), respectively, in EMI-DCA were recorded on the glassy carbon electrode at 30 °C. It is interesting to note that the thermodynamic deposition potentials of Ni and Cu are very close to each other. This is especially favorable for the electrodeposition of Ni-Cu alloys without any additive. The Ni-Cu alloys were electrodeposited using bulk controlled-potential electrolysis experiments. Energy-dispersive spectroscopy (EDS) data indicates that the composition of the Ni-Cu alloys not only depends on the deposition potential, but also on the Cu(I) and Ni(II) concentrations in the melt.

Key Words: Ni-Cu Alloys, Dicyanamide, EMI-DCA, Room Temperature Ionic Liquids

1 Introduction

Room temperature ionic liquids (RTILs) have been examined as electroplating baths and battery electrolytes, since they exhibit certain advantageous properties such as wide electrochemical window, high ionic conductivity, high chemical and thermal stability, negligible vapor pressure, nonflammability, and often the properties of the ILs can be tuned by varying the composition of the IL. Although the ILs containing anions such as tetrafluoroborate (BF₄⁻), hexafluorophosphate (PF₆⁻), and bis(trifluoromethanesulfonyl)imide (TFSI) are very popular for electrochemical studies, the literature indicated that transition metal halides generally exhibit very low solubility in these RTILs because of the very weak Lewis base nature of these anions. The solubility of transition metal halides can be increased by using anions that are capable of forming complex ions with transition metals. Recently, low viscosity RTILs based on dicyanamide (DCA) anion have been synthesized and characterized. The dicyanamide anion is a good ligand for the formation of soluble complex anions with transition metal cations, and facilitates the dissolution of metal halides in the IL.

Nickel and its alloys are interesting materials for corrosion resistance, electrocatalysis, and solar energy applications. The electrodeposition of Ni has been examined in a variety of ILs. For example, the electrodeposition of Ni and Ni-Al alloys was studied in chloroaluminate systems containing 1-ethyl-3-methylimidazolium (EMI⁺) and 1-butyl-3-methylimidazolium (BMI⁺). Ni-Zn alloys have been electrodeposited from EMICl-ZnCl₂. However, the electrodeposition of Ni-Cu from ILs has not been reported. In order to explore the utility of the DCA-based RTIL, the electrodeposition of Ni-Cu alloys from EMI-DCA RTIL was examined at 30 °C in this study. Both CuCl and NiCl₂ are soluble in the EMI-DCA IL. The Ni content in the deposits could be varied continuously from 12.3 to 82.6 mol.% by changing the deposition potential during the electrodeposition.

2 Experimental

2.1 Apparatus

All electrochemical experiments were performed under a purified nitrogen atmosphere in a glove box (Vacuum Atmospheres Co.), where both the moisture and oxygen contents were maintained below 1 ppm. The electrochemical experiments were accomplished with an AUTOLAB potentiostat/galvanostat controlled with the GPES software. Electrochemical experiments were performed in a three-electrode cell. For voltammetric experiments, the working electrode was a glassy carbon disk electrode. A Pt wire immersed in a ferrocene/ferrocnium (Fc/Fc⁺ = 50/50 mol%) N-butyl-N-methyl pyrrolidinium bis(trifluoromethyl-sulfonyl)amide (BMP-TFSI) solution contained in a glass tube with porous Vycor tip (Bioanalytical Systems, MF-2042) was used as the reference electrode. The counter electrode was a spiral Pt wire which was separated from the bulk ionic liquid by a glass frit. Electrodeposition experiments were conducted on W substrates. The surface morphology and elemental composition of the Ni-Cu coatings were investigated with a Philip XL-40FEG field-emission SEM.

2.2 Chemicals

The EMI-DCA ionic liquid was prepared and purified by following the previous literature. The ionic liquid was washed with acetone and dichloromethane sequentially and filtrated to remove NaCl precipitates, and dried at 393K under vacuum. Anhydrous NiCl₂ (99.99%, Aldrich), CuCl (99.999%, Strem), Pt wire (99.95%, Alfa Aesar) and W wire (99.9%, Aldrich) were used as pur-
chased.

3 Results and Discussion

3.1 Voltammetric studies

The dissolution of NiCl₂ to the EMI-DCA IL at room temperature gives green solutions. A typical cyclic voltammogram that was recorded at a glassy carbon electrode of 100 mM Ni(II) is shown in Fig. 1(a). The cyclic voltammogram exhibits a single reduction wave with a peak potential around −1.6 V during the cathodic scan, and a broad oxidation wave with a peak potential around −0.7 V during the anodic scan. A “current loop” in the −1.45 to −1.40 V potential region following scan reversal is observed. Such current loop is indicative of an overpotential driven nucleation-growth process that usually associated with the electrodeposition of a metal on a foreign substrate. Because the solubility of CuCl in the very weak Lewis basic ILs (such as TFSI, BF₃) is very limited, Cu(I) solution had to be generated by anodic dissolution or in the presence of excess chloride ions. However, CuCl is fairly soluble in the EMI-DCA. Figure 1(b) illustrates the cyclic voltammogram of a 100 mM Cu(I) solution in the EMI-DCA IL. The voltammograms exhibits two redox couples due to the Cu(II)/Cu(I) and Cu(I)/Cu(0) redox couples, respectively. In consistent with the fact that the DCA-based IL are more basic ligands and complex with the Cu(I) stronger than TFSI anion does, the redox potentials of both the Cu(II)/Cu(I) and Cu(I)/Cu(0) couples in the EMI-DCA IL occurred at potentials more negative than that were observed from other ILs made of very weak Lewis base anions. It is worthy to note that the deposition potentials of Ni and Cu are very close to each other in the EMI-DCA. This is especially favorable to the electrodeposition of Ni-Cu alloys. A typical cyclic voltammogram of a mixture of Ni(II) and Cu(I) are shown in Fig. 1(c). This figure shows that the reduction of Ni(II) and Cu(I) emerges into a broad reduction wave which shifts to slightly more negative potential with respect to the reduction waves of individual metals that were shown in Fig. 1a and 1b. The reduction current was low at the potential where the Ni(II) and Cu(I) reduction currents should appear in the Ni(II) and the Cu(I) solutions, respectively. However, Ni and Cu may still be codeposited at the potential where Ni and Cu are deposited. In the reverse scan of Fig. 1(c), a striking change is the appearing of a new anodic wave at −1.25 V. Furthermore, the anodic stripping waves of individual Ni and Cu seem to merge into one broad wave and the peak current is lower than those observed for the stripping of individual metals shown in Fig. 1a and 1b, respectively; the anodic stripping of the deposited Ni is likely inhibited by the presence of Cu in the deposits and the peak at less positive potential, −0.9 V, may be mainly results from the stripping of Cu. Similar behavior was observed on tungsten electrode.

3.2 Electrodeposition of Ni-Cu alloys and surface morphology

The electrodeposition of Ni-Cu alloys was investigated with bulk controlled-potential electrolysis experiments at W wires. The reduction currents were very stable during the electrodeposition process as long as the solutions were stirred constantly. The composition of the Ni-Cu alloys obtained by electrodeposition under stirring condition in the solutions with various Ni(II)/Cu(I) concentration ratios (C₆H₆:N₃⁻:Cu²⁺) are shown in Fig. 2. In this plot, the atomic ratio of Ni, which was determined by EDS, is plotted as a function of the deposition potential. This figure indicates that the Ni content of the Ni-Cu alloys could be increased from 12.3 to 82.6 mol.% during the electrodeposition. It is obvious that the compositions of Ni-Cu alloys not only change with deposition potential, but also depends on the C₆H₆:N₃⁻:Cu²⁺ ratio. The compositions of Ni-Cu alloys obtained from these solutions as the deposition potential became more negative, suggesting that it may be easy to control the composition of the Ni-Cu alloys.
alloys by adjusting the Ni(II)/Cu(I) concentration ratio.

Several selected samples of Ni-Cu alloys were examined by SEM. Their surface morphologies are shown in Fig. 3. The compositions of these samples are shown on each image. Pure Ni electrodeposits that was obtained from solution containing only Ni(II) is flat with cracks and consists mainly of spherical grains and pure Cu coating obtained from pure Cu(I) solution contains very small cubic grains. Similar features have been reported previously. As Fig. 3 shows, the surface morphologies of Ni-Cu alloys from Ni(II) + Cu(I) solutions depend on the alloy compositions which could be varied by deposition potential. The grain size of the surface coatings increases and some cracks appear as the Ni contents in the Ni-Cu alloys increases. Visual observation of these samples indicated that the color of the Ni-Cu alloy changed from a bright color to dark black as the Ni content is increased.

4 Conclusion

It was found that the ligand property of the DCA anion in the ILs can play an important role on electrodeposition potentials of the metals. The electrodeposition of Ni-Cu alloys was investigated with bulk controlled-potential electrolysis experiments. The compositions of Ni-Cu alloys not only change with deposition potential, but also depends on $C_{Ni}^{2+}/C_{Cu}^{+}$. The Ni content of the Ni-Cu alloys could be adjusted from 12.3 to 82.6 mol.% during electrodeposition from the EMI-DCA IL.

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References