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Electrochemical codeposition of copper and manganese from room-temperature *N*-butyl-*N*-methylpyrrolidinium bis(trifluoromethylsulfonyl)imide ionic liquid

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ABSTRACT

The voltammetric behavior of *N*-butyl-*N*-methylpyrrolidinium bis(trifluoromethylsulfonyl)imide ionic liquid (BMP-TFSI) containing Cu(I), Mn(II), or mixtures of Cu(I) and Mn(II) as well as the electrodeposition of copper–manganese alloy coatings (Cu–Mn alloy coatings) was studied at 323 K. The Cu(I) and Mn(II) species required to prepare these coatings were introduced into the BMP-TFSI by anodic dissolution of the relevant metallic electrodes. Electrodeposits of Cu, Mn, and Cu–Mn with various contents of Mn can be obtained by controlled-potential electrolysis. It was found that the compositions and surface morphology of the electrodeposited Cu–Mn alloy coatings depend on the deposition potentials and the concentration ratio of [Cu(I)]/[Mn(II)] in BMP-TFSI. The Cu–Mn alloy coatings obtained in this study were compact and adherent. They did not show any significant X-ray diffraction signal that could be assigned to the crystalline structures of Cu, Mn, or Cu–Mn alloys. In the aqueous solution containing 0.1 M NaCl, the Cu–Mn alloy coatings depondent was observed at the electrodes deposited with Cu or Mn.

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1. Introduction

The electrodeposition of sacrificial coatings on steel is a promising method of protecting steel parts from corrosion. Manganese (Mn) has a very negative redox potential. Therefore, it is a very promising sacrificial material. Compared with other frequently used sacrificial metals, such as Zn and Cd. Mn is more environmentally friendly. Cadmium ion dissolved from the sacrificial coatings is toxic to humans and to organisms [1-5]. Zinc ion, however, is a necessary nutrient but it is toxic and hazardous if its concentration is high [6–8]. Although Mn has superior sacrificial properties, pure Mn coatings on steel are not very practical because of their high reactivity and fast dissolution. Electrodeposited Mn is metastable and is in a centered tetragonal (ct) γ phase [9,10] that is ductile. At room temperature for several weeks, it transforms into a brittle body-centered cubic (bcc) α phase [11], which easily cracks upon impact. It has been shown that this phase transformation can be suppressed by codepositing γ -Mn with face-centered cubic (fcc) metals, especially Cu [10,12]. In addition to the corrosion resistance of Cu-Mn codeposits, several papers have pointed out that Cu-Mn coatings are good electrocatalysts for carbohydrates [13] and amino acids [14].

Copper–manganese (Cu–Mn) alloy coatings have been prepared by using electrodeposition in ammonium sulfate ($(NH_4)_2SO_4$) solutions [15–17]. A higher solution pH is more favorable for the electrodeposition of Cu–Mn alloy coatings because hydrogen evolution is suppressed and [Cu(NH₃)_{n=1-4}]²⁺ forms [17]. The formation of copper complexes leads to a negative shift in the reduction potential of Cu(II), moving it closer to the reduction potential of Mn(II). However, the electroplating bath is only stable for a limited time under higher pH conditions because hydrolysis and/or oxidation of Mn(II) induces turbidity in the solution. Although Cu–Mn alloy coatings can be obtained from the aforementioned solutions, low current efficiency is usually encountered and high current density must be applied.

It has been reported that the electrodeposition of Mn is feasible in room-temperature air- and water-stable ionic liquids. Extremely high current efficiencies (~100%) have been reported [18–20]. High efficiencies were obtained because no hydrogen evolution involved in the electrodeposition process. In addition, Mn(II) species dissolved in the ionic liquids is very stable. Precipitate was never observed. The characteristics of ionic liquids are well known. They include a wide electrochemical window, undetectable vapor pressure, large temperature ranges of the liquid, and no hydrogen evolution for aprotic ionic liquids. Ionic liquids are therefore promising electrolytes for the electrodeposition of metals and alloys. They are especially useful for reactive elements because no hydrogen evolution will be involved in the electrodeposition. The undetectable vapor pressure of ionic liq-

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uids implies that ionic liquids are inflammable and can be used under high temperatures without vaporization. Because the electrodeposition of Mn in ionic liquids has been proven to be feasible, it is possible to electrodeposit Cu-Mn alloy coatings in ionic liquids. Higher current efficiencies can be expected. However, there have been no reports of the electrodeposition of Cu-Mn alloy coatings in ionic liquids. In the present study, Cu-Mn alloy coatings were electrodeposited on tungsten (W) substrate in *N*-butyl-*N*-methylpyrrolidinium bis(trifluoromethylsulfonyl)imide (BMP-TFSI) ionic liquid to demonstrate the feasibility using ionic liquids in the electrodeposition of Cu-Mn alloy coatings. The voltammetric behaviors of Cu(I), Mn(II), or mixtures of Cu(I) and Mn(II) were also studied. The Cu-Mn layers were characterized with a scanning electron microscope (SEM) and an energy dispersive spectrometer (EDS). An anodic potentiodynamic scan was carried out in deaerated 0.1 M NaCl solution to assess the corrosion performance of the obtained Cu-Mn coatings.

2. Experimental

N-Butyl-N-methylpyrrolidinium bis(trifluoromethylsulfonyl)imide (BMP-TFSI) ionic liquid was prepared and purified by a previously published procedure [21]. However, in this study, chlorobutane was employed in the procedure instead of iodobutane. The ionic liquid was dried under vacuum for at least 1 day while being heated to 393 K. The water content of the ionic liquid was determined with a coulometric Karl Fischer titrator (Metrohm 756 KF) and the value was approximately 70 ppm. No Cl⁻ was detected with a platinum electrode by using cyclic voltammetry. Although the BMP-TFSI ionic liquid is air- and water-stable, all electrochemical experiments were performed inside a glove box (MBRAUN, UNI LAB-B) filled with purified nitrogen in order to prevent the interference produced from oxygen and moisture that are absorbed into the ionic liquid if it is exposed to a normal atmosphere. The concentrations of O₂ and H₂O inside the glove box were maintained under 1 ppm. Manganese block (99.9%), copper wire (99.9%), and tungsten wire (99.95%) were purchased from Alfa Aesar and used after being cleaned in concentrated nitric acid. Mn(II) and Cu(I) were introduced into the ionic liquid by electrolyzing a Mn anode and a Cu anode, respectively. Anodic dissolution was employed because the Mn and Cu compounds tested in this study cannot dissolve in BMP-TFSI. In addition, the effect of counter ions from Mn and Cu compounds on the electrochemical behavior of Cu(I) and Mn(II), respectively, can be avoided by employing anodic dissolution. Other compounds used in this study were at least reagent grade. Deionized water produced from a Milli-Q Gradient system (Millipore) was used to prepare all the aqueous solutions.

All electrochemical experiments were carried out with a Princeton Applied Research 263A potentiostat/galvanostat (PAR 263A). A conventional three-electrode electrochemical cell was used. The detailed constituents were reported in a previous study [19]. For the voltammetric study, a tungsten (W) disk electrode or a platinum (Pt) disk electrode was used as the working electrode. However, a piece of tungsten wire was employed as the working electrode for the electrodeposition of the Cu, Mn, or Cu-Mn alloy coatings. A platinum wire (Alfa Aesar, 99.95%) immersed in ferrocene/ferrocenium $(Fc/Fc^+ = 50/50 \text{ mol.}\%)$ BMP-TFSI solution contained in a glass tube with porous Vycor tip (Bioanalytical Systems, MF-2042) was used as a reference electrode; therefore, all values of potential are automatically reported with respect to the redox potential of Fc/Fc⁺. The counter electrode consisting of a platinum wire spiral immersed in BMP-TFSI was separated from the bulk ionic liquid by a porosity E glass frit. For aqueous solutions, Ag/AgCl saturated with NaCl was used as the reference electrode and a platinum wire that was directly immersed in the aqueous solutions was used as the counter electrode.

The surface morphologies and elemental compositions of the electrodeposits were investigated using a Philips XL-40FEG field emission scanning electron microscope (FE-SEM) coupled with an energy dispersive spectrometer (EDS) operating at 15 kV. The EDS was employed to semiquantitatively determine the compositions of the obtained Cu–Mn alloy coatings. The crystalline structure of the Cu, Mn, or Cu–Mn alloy coatings was also analyzed with the Shimadzu Model XD-D1 powder X-ray diffractometer (XRD).

3. Results and discussion

3.1. Voltammetric study of Mn(II) and Cu(I) species in BMP-TFSI ionic liquid

The electrochemical behavior of Mn(II) in BMP-TFSI is not discussed in detail here because it was carefully studied in our previous experiments [19]. The voltammetric behavior of Mn(II) is shown for readers' convenience. Because anodic dissolution of the Mn electrode was employed to introduce Mn(II) into the BMP-TFSI ionic liquid, cyclic voltammetry was carried out at the Mn electrode. The relevant cyclic voltammogram is shown in the inset of Fig. 1. The potential was initially scanned from -1.0V towards the positive direction. A sudden increase of the anodic current was observed when the potential reached -0.3 V, indicating that Mn can be oxidized in the ionic liquid. A current loop was observed during the reverse scan, implying that a fresh surface of Mn might be produced during the anodic scan [19]. The anodic current of Mn dissolution did not continuously increase. Instead, it reached a plateau, indicating that the oxidation reaction may be kinetically hindered. During the bulk electrolysis of the Mn electrode, the reaction occurring at the counter electrode was the oxidation of BMP⁺ (the cation of the BMP-TFSI ionic liquid). This reaction did not interfere with the system because the counter electrode was separated from the bulk solution. Fig. 1 shows the cyclic voltammogram of Mn(II) recorded at the W electrode. The potential was initially scanned from 0.0V towards the negative direction and then back to 0.0 V. The reduction wave of Mn(II) is very close to the cathodic limit of the BMP-TFSI ionic liquid. However, no interference was observed during the electrodeposition of Mn, as long as the applied potential was below the



Fig. 1. Cyclic voltammograms recorded at W electrode in BMP-TFSI containing 0.025 M Mn(II). The inset shows the cyclic voltammogram of a Mn electrode in BMP-TFSI. Scan rate: 50 mV s^{-1} . Temperature: 323 K.



Fig. 2. Cyclic voltammograms recorded at W electrode in BMP-TFSI containing 0.1 M Cu(I). The inset shows the cyclic voltammogram of a Cu electrode in BMP-TFSI. Scan rate: 50 mV s^{-1} . Temperature: 323 K.

limit. Our previous study pointed out that the current efficiency of Mn electrodeposition carried out in BMP-TFSI was very high (~100%) [19]. This indicates that decomposition of the ionic liquid did not happen at the potential of the Mn electrodeposition. In addition to the reduction wave of Mn(II), a typical stripping peak can be observed in the reverse scan, as shown in Fig. 1, indicating the reoxidation of the Mn deposited on the electrode surface during the cathodic scan. The deposited Mn, however, cannot be completely reoxidized from the electrode surface due to the shortage of the stripping peak area compared with the reduction wave area. This behavior is caused by the kinetically hindered oxidation of deposited Mn [18–20] and has been observed in several electrodeposition processes in air- and water-stable ionic liquids [23,24].

The voltammetric behavior of the Cu electrode and the Cu(I)/Cu(0) redox couple has also been studied in BMP-TFSI [22]. The electrochemistry of Cu(I) is discussed here in more detail. Cyclic voltammetry was carried out at the Cu electrode. The relevant cyclic voltammogram is shown in the inset of Fig. 2. The potential was initially scanned from -0.6 V in the anodic direction towards the switching potential and then back to -0.6 V. The anodic dissolution of Cu was apparent at +0.5 V, as indicated by the sudden increase in anodic current. The small reduction wave around +0.1 V is due to redeposition of dissolved Cu formed during the anodic scan. In order to determine the oxidation state of the dissolved Cu species, changes in the mass of the Cu electrode were determined after each passage of a given charge, Q_{exp}. The data obtained from several such controlled-potential coulometric experiments are collected in Table 1. In this table, ΔM is the change in the mass of the Cu electrode, *m* is the number of moles related to this mass change, and Q_{theory} (n = 1) is the charge based on m for n = 1 (where n is the number of electrons transferred during the anodic dissolution process). The experimental results shown in Table 1 imply that Cu(I) species were produced during the process of anodizing a Cu electrode in BMP-TFSI.

Fig. 2 shows the cyclic voltammograms recorded at the W electrode in BMP-TFSI containing 0.1 M Cu(I). The arrows indicate the initial direction of the potential scan. Two redox couples were

Table 1

Results of anodic dissolution of Cu electrode in BMP-TFSI ionic liquid.

$\Delta M(g)$	$10^4 m (\mathrm{mol})$	$Q_{\text{theory}}(n=1)(C)$	$Q_{\exp}(C)$	nª
0.0013	0.2046	1.97	1.91	0.97
0.0012	0.1888	1.82	1.81	0.99
0.0012	0.1888	1.82	1.80	0.99
0.0011	0.1731	1.67	1.80	1.08
0.0011	0.1731	1.67	1.70	1.02

^a Average value of *n* is 1.01 ± 0.04 .

observed, regardless of the initial scan direction. The conversion between Cu(I) and Cu(II) is a quasi-reversible reaction at the W electrode, indicated by the large separation of peak potentials (ΔE_p). This behavior indicates that this conversion is kinetically controlled, resulting from the change in the number of anions complexed to the Cu centers. On the other side of the voltammogram, a typical stripping peak was observed. It indicates that Cu(I) can be reduced to Cu metal and deposited onto the electrode surface during the cathodic scan and that the deposited Cu can be reoxidized from the electrode surface in the anodic scan, indicating that electrodeposition of Cu is feasible in this ionic liquid.

Because the codeposition of Cu and Mn would occur in BMP-TFSI, the voltammetric behavior of the Cu(I)/Cu(0) redox couple was studied in more detail. Fig. 3 shows the cyclic voltammograms of the Cu(I)/Cu(0) redox couple recorded at the Pt and W electrodes, respectively, in BMP-TFSI containing 0.1 M Cu(I).



Fig. 3. Cyclic voltammograms recorded at Pt and W electrodes, respectively, in BMP-TFSI containing 0.1 M Cu(I). Scan rate: 50 mV s^{-1} . Temperature: 323 K.

These cyclic voltammograms show that the potential was initially scanned towards the negative direction and then reversed at various potentials. As can be seen, the reduction of Cu(I) needs a higher overpotential at the W electrode than that observed at the Pt electrode because the reduction wave of Cu(I) was observed at a more negative region. In addition, a current loop was observed at the W electrode when the scan was reversed at more positive potentials, indicating that a nucleation process was involved in the reduction of Cu(I) at the W electrode. No current loop, however, was observed in the cyclic voltammograms recorded at the Pt electrode, even though the scan was reversed ahead of the peak potential. Fig. 3 also shows that the stripping peak increased when the scan was reversed at more negative potentials. The charge corresponding to the stripping peaks is almost identical to that of the reductive waves, indicating that the electrode posits of Cu adhered on the electrode surface well.

3.2. Voltammetric study of BMP-TFSI containing mixtures of Cu(I) and Mn(II)

The cyclic voltammograms recorded at the Pt electrode in BMP-TFSI containing Cu(I), Mn(II), and a mixture of Cu(I) and Mn(II) with a concentration ratio of [Cu(I)]/[Mn(II)] = 0.5 (0.033 M/0.067 M) are shown in Fig. 4a. By carefully examining these voltammograms, it can be found that the reduction wave of Cu(I) in the mixture is more negative than that observed in the solution containing Cu(I) alone. Mn(II) in the mixture was reduced to Mn(0) at more positive



Fig. 4. Cyclic voltammograms recorded at Pt electrode in BMP-TFSI containing Cu(I), Mn(II), and mixtures of Cu(I) and Mn(II), respectively. The concentrations of the metal ions are indicated. Scan rate: 50 mV s^{-1} . Temperature: 323 K.

potentials, as indicated by the positive shift in the reduction wave of Mn(II). This behavior implies that Cu(I) and Mn(II) may have certain interactions or even form some Cu-Mn compounds, resulting in a smaller separation of the reduction potentials. This behavior is beneficial to Cu-Mn codeposition. Similar behavior was observed for the mixture of Zn(II) and Mn(II), in which the electrodeposition of Zn-Mn coatings was carried out [20]. In that solution, the reduction wave of Zn(II) was not observed at the potential, in which Zn(II) should be reduced to zinc metal if the solution contains Zn(II) alone. In the mixture of Zn(II) and Mn(II), Zn(II) was reduced to zinc metal at the potentials where Mn(II) was reduced. Therefore, the reduction wave of Zn(II) seems to be disappeared. The reduction wave of Cu(I), however, was still observed in the mixture of Cu(I) and Mn(II). Fig. 4a also shows that the oxidative stripping peak of the deposited Cu shifted to a more positive potential. The separation of the peak potentials for the redox couple Cu(I)/Cu(II) increased when the cyclic voltammogram was performed in the mixture of Cu(I) and Mn(II). Again, this behavior indicates that Cu(I) may interact with Mn(II) in this solution.

Fig. 4b shows the cyclic voltammograms recorded in the mixtures of Cu(I) and Mn(II) with concentration ratios of Cu(I)/Mn(II) ranging from 0.5 to 2. In general, the reductive and oxidative waves of Cu(I) shifted to more negative and more positive potentials, respectively, with decreasing molar ratios of Cu(I)/Mn(II). Because the oxidation of deposited Mn is kinetically hindered, we believe that the stripping peak that occurred between 0 and 1 V was mostly from the oxidation of Cu deposited during the cathodic scan performed in the mixtures of Cu(I) and Mn(II).

Based on the cyclic voltammograms shown in Fig. 4, the codeposition of Cu–Mn should be possible if the applied potential is more negative than -1.5 V. The electrodeposition of Cu–Mn coatings is discussed in the following section.

3.3. Electrodeposition of Cu-Mn alloy coatings in BMP-TFSI

The electrodeposition of Cu–Mn alloy coatings was investigated by bulk controlled-potential electrolysis on tungsten wires in BMP-TFSI containing various [Cu(I)/[Mn(II)] concentration ratios. The reduction current of the electrodeposition was very stable as long as the solution was steadily stirred with a magnetic stirring bar derived by a magnetic stirrer. Good adherent coatings of Cu–Mn codeposits were obtained. The atomic ratios of Mn in the Cu–Mn alloy coatings were determined by EDS, and the results are shown in Fig. 5. It must be emphasized that EDS can only provide semiquantitative measurements and the results are not absolutely accurate



Fig. 5. Dependence of Mn contents contained in selected Cu–Mn coatings on the deposition potential. W wire was used as the substrate. The concentration ratios of [Cu(1)]/[Mn(II)] are shown in the inset. Electrodeposition temperature: 323 K.



Fig. 6. SEM micrographs of Mn, Cu, and Cu–Mn coatings electrodeposited at W wire in BMP-TFSI. The compositions of the Cu–Mn coatings are indicated as atomic ratios on each plot.

if the sample does not have a flat surface. However, the results still can provide a trend for us. As can be seen, the content of Mn in the Cu-Mn alloy coatings depends on the applied potential and the concentration ratio of [Cu(I)]/[Mn(II)]. The atomic ratio of Mn increased as the deposition potential (E_d) became more negative with each electroplating bath. At the same E_d , the content of Mn was richer when the Cu-Mn alloy coatings were prepared in the solution containing a higher concentration of Mn(II). This behavior is reasonable due to the different reduction potentials of Cu(I) and Mn(II). At the potentials at which the codeposition of Cu and Mn occurs, the reduction of Cu(I) is completely under the control of diffusion. The reduction rate of Mn(II), however, is controlled by the applied potentials and concentrations of Mn(II). Therefore, the content of Mn in the Cu-Mn codeposits increased with more negative applied potentials and higher concentrations of Mn(II). Fig. 5 shows that the content of Mn in the Cu-Mn coatings can be adjusted to any amount by regulating the applied potential and the concentration ratio of [Cu(I)]/[Mn(II)].

3.4. Surface morphology and corrosion resistance of Cu–Mn coatings

Several selected samples, whose compositions were determined with EDS and shown in Fig. 5, were studied with SEM. The surface morphology of these samples is shown in Fig. 6. For comparison, the coatings containing Mn and Cu alone, respectively, are also shown in the figure. The compositions determined with EDS for the coatings of Cu–Mn codeposits are shown on each micrograph. The SEM micrographs indicate that the Mn coating primarily consisted of spherical grains. The smaller grains aggregated together to form islands. The grain size of Cu coatings, however, is much smaller than that of Mn coatings. Therefore, the surface of the Cu coating is very smooth, even on a micrometer scale. The Cu–Mn alloy coatings had a totally different surface morphology. Their morphology was dependent on the compositions of the Cu–Mn codeposits. In general, the grain size of the Cu–Mn codeposits decreased as the Mn content in the Cu–Mn coatings increased. Regardless of the compositions of the Cu–Mn alloy coatings, the Cu–Mn codeposits exhibited good adherence on the substrate. The Cu–Mn coatings were also analyzed with XRD. However, no significant signal was observed that could be assigned to the crystalline structure of the Cu, Mn, or Cu–Mn alloys. This finding indicated that the Cu–Mn alloy coatings obtained in this study could be metallic glasses or amorphous. Amorphous Cu–Mn coatings have also been prepared by electrodeposition in sulfate-based electrolytes [16,17]. The authors indicated that the amorphous Cu–Mn alloy coatings did not show any structural transformation.

The potential corrosion resistance of two selected Cu-Mn coatings was assessed in a 0.1 M NaCl solution. Potentiodynamic anodic polarization curves recorded in a deaerated 0.1 M NaCl solution using the Cu-Mn alloy coatings electrodeposited on tungsten wire with BMP-TFSI ionic liquid are shown in Fig. 7. The behaviors of tungsten wires coated with Mn and Cu alone are also provided for comparison. It was found that the oxidation current of deposited Mn suddenly increased when the potential was more positive than -1.1 V (vs. Ag/AgCl saturated with NaCl). The current change was very rapid, indicating that the anodic dissolution of deposited Mn is thermodynamically and kinetically favorable in the chloride solution. The deposited Cu dissolved into the solution when the potential was more positive than 0V (vs. Ag/AgCl saturated with NaCl). However, the oxidation current changed in a slower manner, indicating that the rate of anodic Cu dissolution in the chloride solution was slower than that of the deposited Mn. Compared with the Mn and Cu coatings, the Cu-Mn alloy coatings demonstrated unusual voltammetric behavior, as shown in Fig. 7. Unlike the deposited Cu or Mn, the coatings of the Cu-Mn codeposits



Fig. 7. Potentiodynamic polarization curves recorded at Mn, Cu, and Cu–Mn coatings in deaerated 0.1 M NaCl aqueous solution. The compositions of the Cu–Mn coatings are indicated as atomic ratios on the plot. Scan rate: 1 mV s^{-1} .

were not continuously oxidized in the chloride solution, even at the potential where deposited Cu was seriously oxidized. Passive behavior was observed for the Cu–Mn alloy coatings, as indicated by the small oxidation wave at the potentials between 0 and 0.5 V (Fig. 6). Metal oxides that formed on the Cu–Mn alloy coatings during the process of electrochemical oxidation have been previously reported [17]. Oxide formation is a reasonable explanation for the passive behavior. Passivation inhibits the continuous dissolution of the Cu–Mn codeposits and possibly improves the corrosion resistance of the codeposits. Based on these observations, Cu–Mn alloy coatings prepared from BMP-TFSI ionic liquid may be a potential corrosion-resistant material for steel.

4. Conclusions

This study showed that the electrodeposition of Cu–Mn alloy coatings is feasible in the air- and water-stable room-temperature ionic liquid BMP-TFSI. The Cu(I) and Mn(II) species that are necessary to prepare the coatings must be introduced into the ionic liquid by anodic dissolution of the relevant metal electrodes. The content

of Mn in the Cu–Mn codeposits can be controlled by the applied potential and the concentration ratios of [Cu(I)]/[Mn(II)]. Based on the analysis of XRD, the coatings of Cu–Mn codeposits have no crystalline structure and are perhaps amorphous. The Cu–Mn alloy coatings prepared in this study displayed passive behavior during the anodic scan of potential in NaCl solutions. The passive behavior may be a result of oxide formation. The oxide layer may inhibit the anodic dissolution of the Cu–Mn alloy coatings, resulting in better corrosion resistance.

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