Electrodeposition of Metals from Quaternary Ammonium Imide Type Room Temperature Ionic Liquid

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Cathodic electrodeposition behavior of copper, zinc, nickel, magnesium, and lithium from a hydrophobic quaternary aliphatic ammonium-imide type room temperature ionic liquid, trimethyl-*n*-hexylammonium bis((trifluoromethyl)sulfonyl)amide (TMHA-Tf₂N), was investigated. The electrochemical window of TMHA-Tf₂N liquid was 5.6 V, *i.e.* -3.0 V to +2.6 V vs. I^{-}/I_{3}^{-} . Deposition of metallic Cu, Zn, and Ni took place at 50 °C at potentials negative to 0.0 V, -0.9 V, and -1.0 V, respectively, while metallic Mg, which cannot be electrodeposited from aqueous media, was obtained at -2.8 V or lower potentials. Deposition of a lustrous Cu layer proceeded from monovalent Cu(I) ions, which were formed spontaneously by the reaction of Cu(II) ions with Cu metal and were more stable than divalent Cu(II) ions in TMHA-Tf₂N. Electrochemical deposition and stripping of Li were also observed at around -3.0 V.

Key words: Electrodeposition, Ionic liquids, Room temperature molten salts, Non-aqueous solution, Redox

1. INTRODUCTION

Electrodeposition of metals and alloys from aqueous solutions is an important soft process for manufacturing thin-layered materials, surface finishing, and extractive metallurgy. However, the electrodeposition of base metals, such as such as zinc, chromium, and nickel, from aqueous media is inevitably accompanied by hydrogen evolution, which lowers the cathodic current efficiency of metal deposition. Since the electrodeposition of aluminium, magnesium, and rare earths from aqueous media is actually impossible due to their largely negative redox potentials, nonaqueous media such as aprotic organic solvent and high-temperature molten salts have been employed for the electrodeposition of these metals. Room temperature ionic liquids, or room temperature molten salts [1], have also been developed as promising electrolytes for the electrodeposition of base metals. In this field, chloroaluminates of alkylpyridinium or alkylimidazolium cation have been well investigated for aluminium or alluminium-alloy electroplating media [2]. On the other hand, in order to avoid high hygroscopicity arising from the use of aluminium chloride, attempts have been made to combine the alkylimidazolium cations with fluorine-containing hydrophobic anions, e.g. BF_4^{-} [3], $CF_3SO_3^{-}$ (TfO⁻) [4], (CF_3SO_2)₂N⁻ (Tf₂N⁻) [5], and to use the resulting liquids as electrodeposition media [6,7]. Recently, a new series of ionic liquids, commonly named "quaternary ammonium-imide," consisting of aliphatic tetraalkylammonium cations and Tf₂N⁻ anion, sometimes abbreviated as TFSI⁻ anion, was found to have a wide electrochemical window of >5 V [8,9] and thus seems to be suited for practical application as a solvent for electrochemical processes. In this paper, we review the electrochemical behavior of some metals in an ammonium-imide ionic liquid, trimethyl-n-hexylammonium bis((trifluoromethyl)sulfonyl)amide (TMHA-Tf₂N, melting point ca. 30 °C).

2. EXPERIMENTAL

2.1 Preparation of TMHA-Tf₂N

The ionic liquid TMHA-Tf₂N, n-C₆H₁₃(CH₃)₃N⁺N⁻ (SO₂CF₃)₂, was synthesized under ambient atmosphere by the reaction of trimethyl-*n*-hexylammonium bromide, n-C₆H₁₃(CH₃)₃NBr, with lithium bis((trifluoromethyl)sulfonyl)amide, LiN(SO₂CF₃)₂, as

$$n-C_6H_{13}(CH_3)_3NBr + LiN(SO_2CF_3)_2$$

 $\rightarrow n-C_6H_{13}(CH_3)_3N^+N^-(SO_2CF_3)_2 + LiBr$ (1)

Equimolar quantities (0.224 mol) of n-C₆H₁₃(CH₃)₃NBr and $LiN(SO_2CF_3)_2$ were weighed and each was dissolved in 100 cm³ of deionized water. The two aqueous solutions were mixed and agitated with a magnetic stirring unit for 1 hour at 70 °C. According to the above reaction, TMHA-Tf₂N was formed and separated from the aqueous phase as an organic phase. To extract the TMHA-Tf₂N completely from the aqueous phase, 100 cm³ of dichloroethane was added and stirred at room temperature. The organic phase, i.e. lower layer, was then separated using a separating funnel. The dichloroethane solution of TMHA-Tf₂N salt was washed with 100 cm³ of deionized water three times in order to remove residual LiBr. The dichloroethane was then distilled away with a rotating evaporator and the resulting crude TMHA-Tf₂N was dried with a vacuum desiccator at 120 °C for more than 3 days. The transparent colorless TMHA-Tf₂N was transferred into a glove box, in which further electrolytic experiments were carried out. The TMHA-Tf2N was identified by elemental analysis at the Center for Organic Elemental Microanalysis of Kyoto University.

2.2 Preparation of metal salts

To investigate the electrochemical properties of metal ions in TMHA-Tf₂N, a set of metal salts with the common anion, Tf₂N⁻, was prepared by the reaction of corresponding oxide or carbonates with bis((trifluoromethyl)sulfonyl)amine, HTf₂N. In the case of copper salt, for example, 17.8 mmol of HTf₂N was dissolved in 100 cm³ of deionized water and added dropwise over 1 hour to another 100 cm³ of deionized water suspended with excess copper(II) oxide, CuO, under stirring; the mixture was allowed to react for 2 hours at 70 °C as

$$CuO + 2HN(SO_2CF_3)_2 \rightarrow Cu[N(SO_2CF3)_2]_2 + H_2O$$
(2)

Unreacted CuO was then filtered off and the water was distilled away with a rotating evaporator, yielding a blue-colored hydrated salt, $Cu(Tf_2N)_2 \cdot xH_2O$. The hydrated salt was heated *in vacuo* at 120 °C for more than 3 days and the resulting greenish anhydrous $Cu(Tf_2N)_2$ was transferred into a glove box.

2.3 Electrochemical experiments

Preparation of sample solution, e.g. Cu(Tf₂N)₂ solution of TMHA-Tf₂N, and all electrolytic experiments, i.e. cyclic voltammetry and cathodic bulk deposition, were carried out in an argon filled glove box equipped with a molecular-sieve gas purification system. The water content of the glove box was less than 5 ppm. The electrolytic experiments were performed using a conventional three electrode setup comprising a potentiostat connected to a function generator and a coulometer. Cyclic voltammograms were taken by scanning the potential of the working electrode at a constant scan rate of 100 mV s⁻¹. Several kinds of electrode were employed for the working (WE) and counter electrodes (CE), e.g. Pt sheet, glassy carbon (GC) rod cemented in a resin, and oxygen free Cu sheet; the detailed combination of the electrodes is shown with the results. The Pt and Cu sheets were washed with diluted nitric acid before each use; the surface of the GC electrode was polished with 1 μm and 0.25 μm diamond abrasives. A $I^-\!/I_3^-$ electrode consisting of Pt wire immersed in TMHA-Tf_2N solution of 15 mM I_2 and 60 mM $(n-C_3H_7)_4$ NI (M = mol dm⁻³), contained in a glass tube with a ceramic frit at the bottom, was used as a reference; the electrode potential was checked by cyclic voltammogram for TMHA-Tf2N containing 10 mM ferrocene. A glass vessel (capacity 20 cm³) was used as an electrolytic cell. The electrolytic solution was agitated with a magnetic stirring unit. In order to keep the temperature of the solution at 50 °C for all runs, the electrolytic cell was placed in a double-walled glass heating jacket, in which warm water of 50 °C was circulated from outside the glove box.

Metal deposits obtained on the cathode by potentiostatic electrodepositions were identified by Xray diffractometry (XRD) using a molybdenum X-ray tube ($\lambda = 70.926$ pm). For the XRD measurement of powdery deposits, *e.g.* magnesium, the deposits were mounted on a glass plate with double-sided adhesive tape. In some cases, the current efficiency for the metal deposition was calculated as Q_M/Q_{total} , where Q_M is the charge estimated from a deposited mass of metal whose deposition is assumed to be one- or two-electron reduction (see results and discussion section). Q_{total} is the total quantity of charge passed during the electrodeposition.

3. RESULTS AND DISCUSSION

3.1 Electrochemical window of TMHA-Tf₂N

It was reported that quaternary ammonium-imide ionic liquids have a large electrochemical window compared to the ionic liquids containing alkylimidazolium cation. A cyclic voltammogram was undertaken to obtain the window of pure TMHA-Tf₂N prepared for the present study. The voltammogram (Fig. 1) was taken by scanning the potential of the Pt working electrode between -3.50 and +3.00 V vs. Γ/I_3^- . Steep onsets of cathodic and anodic currents appeared at -3.0 and +2.6 V, respectively, due to the reductive and oxidative decomposition of TMHA-Tf₂N, indicating that the electrochemical window was about 5.6 V at 50 °C. In the case of CG electrodes, the cathodic and anodic limits were recognized at -3.2 and +2.6 V and thus the window is slightly wider than that for Pt; this may have been due to a reduced electrochemical action of carbon against cathodic decomposition of organic TMHA-Tf₂N compound.



Fig. 1 Cyclic voltammogram for pure TMHA-Tf₂N at 50 $^{\circ}$ C. WE and CE: Pt sheets.



Fig. 2 Comparison of electrochemical window of TMHA-Tf₂N with those of several non-aqueous solvents. Data for non-aqueous solvents were taken from reference [11]. AN: acetonitrile; DME: 1,2-dimethoxy-ethane; DMF: dimethyl formamide; DMSO: dimethyl sulfoxide; PC: propylene carbonate; THF: tetrahydrofuran.

Since, the redox potential of ferrocene/ferricinium (Fc/Fc^{+}) ion systems is little affected by solvent, IUPAC recommended to measure the Fc/Fc⁺ redox in order to compare particular potential data with others [10]. A cyclic voltammogram for TMHA-Tf₂N containing 10

mM ferrocene gave a pair of reversible redox waves. According to the waves, the redox potential of Fc/Fc⁺ in TMHA-Tf₂N was determined to be +0.16 V vs. Γ/I_3^- , suggesting that the cathodic and anodic limits of TMHA-Tf₂N were -3.2 and +2.4 V vs. Fc/Fc⁺, respectively. Figure 2 summarizes the electrochemical windows of several organic solvents [11], which are usually employed for nonaqueous electrochemical processes, together with that of TMHA-Tf₂N. Although TMHA-Tf₂N has a wide electrochemical window, the cathodic limit is not as negative as for these organic solvents. From the standpoint of the electrochemical window, TMHA-Tf₂N does not appear to be an outstanding solvent for the cathodic electrodeposition process. In view of its nonflammable and non-volatile properties and of the high solubility of metal salts to ionic liquids, however, TMHA-Tf₂N may well also be an appropriate cathodic metal deposition medium.

3.2 Electrodeposition of metals and alloys

Table I summarizes the metals and alloys of which electrodeposition from TMHA-Tf₂N media have so far been investigated by the author's group.

Table I Metals and alloys for which electrodeposition from $TMHA-Tf_2N$ media has been investigated.

Metals	Bath composition	Cathode	Potential ^{a)}
Cu Zn Ni Ti Mg Zn-Mg	$\begin{array}{c} 0.04 \text{ M Cu}^{+} \\ 0.5 \text{ M Zn}^{2+} \\ 0.5 \text{ M Ni}^{2+} \\ 0.046 \text{ M Ti}^{4+b)} \\ 0.5 \text{ M Mg}^{2+} \\ 0.1 \text{ M Zn}^{2+}, 0.5 \text{ M Mg}^{2+} \end{array}$	Pt Cu Cu no depos Cu Cu	$\begin{array}{c} 0.0 \text{ V} \\ -0.9 \text{ V} \\ -1.0 \text{ V} \\ \text{ition} \\ -2.8 \text{ V} \\ \underline{-^{c)}} \end{array}$
Zu-wig	0.1 M ZII , 0.5 M Mg	Cu	

^{a)} maximum potential (V vs. Γ/I_3^{-}) for the deposition

^{b)} $0.2 \text{ cm}^3 \text{ TiCl}_4 \text{ in } 5.0 \text{ cm}^3 \text{ TMHA-Tf}_2 \text{N}$

^{c)} under investigation

Deposition of Cu: Potentiostatic bulk electrolysis was carried out at potential in the range 0.0 to -1.2 V vs. Γ/I_3^- using TMHA-Tf₂N containing 0.01 M Cu(Tf₂N)₂; cathode and anode were Pt and Cu sheets, respectively. Electrolysis at -1.2 V gave no deposit, while powdery black particles appeared in the solution. The powdery deposits were obtained also at -1.0, -0.8, and -0.4 V both on the cathode and in the solution bulk. In contrast, adhesive deposits were obtained at higher cathode potentials, or lower cathodic overpotentials, without the formation of the powder in the solution. Figure 3 depicts the X-ray diffraction of the deposit at 0.0 V, which had a metallic luster. Diffractions due to copper metal appeared at 20 of 19.6°, 22.7°, 32.3°, and 38.0° in addition to those from Pt substrate.

The current efficiencies for cathodic deposition (at 0.0 V) and concomitant anodic dissolution were estimated to be 185 and 226%, respectively, assuming that these were both two-electron reactions ($Cu^{2+} + 2e = Cu$). This suggests that the copper deposition and dissolution involved one-electron redox reactions. In other words, monovalent Cu(I) was formed spontaneously in the solution without electrolysis, whereas only divalent

copper salt was initially dissolved to TMHA-Tf₂N. To investigate the formation of Cu(I) species, a copper metal plate was immersed in 5 cm³ of TMHA-Tf₂N (50 °C) containing 0.02 M of Cu(II). It was found that the mass of the copper electrode decreased with the passage of time as shown in Figure 4 and, at the same time, the light-green color of the solution due to Cu(II) ions became paler, indicating the formation of colorless Cu(I) ions as $Cu^{2+} + Cu \rightarrow 2Cu^{+}$.

In consequence, copper metal was dissolved, or corroded, in the presence of Cu(II) ions, yielding monovalent copper species. Such a high stability of Cu(I) species in ionic liquids has been reported also for chloroaluminates [1] and tetrafluoroborate [6] based media. A bulk electrodeposition from TMHA-Tf₂N, saturated with Cu(I) ions, gave the copper deposition and dissolution current efficiency of 97 and 101%, which substantiated that the deposition and dissolution proceeded under a one-electron redox reaction (Cu⁺ + e = Cu).



Fig. 3 X-ray diffraction pattern for Cu layer electrodeposited on Pt sheet at 50 °C from TMHA-Tf₂N containing 0.04 M Cu(Tf₂N)₂. Deposition potential: 0.0 V vs. Γ/I_3^- .



Fig. 4 Variation of the weight of copper metal plate immersed in TMHA-Tf₂N containing 0.02 M $Cu(Tf_2N)_2$ at 50 °C.

Deposition of less-noble metals: Electrodepositions of several base metals have been achieved using the same media. Figure 5 summarizes the X-ray diffraction patterns for the deposits from TMHA-Tf₂N containing $M(Tf_2N)_2$ (M = Zn, Ni, or Mg). Zinc and nickel metals were obtained as grayish adhesive layers on Cu substrate and the current efficiencies were near 100%, assuming two-electron reduction processes (M²⁺ + 2e \rightarrow M). The deposit from the Mg²⁺-containing bath gave a set of weak but definite diffractions of elemental Mg (Fig. 5c). The magnesium metal deposited had a dendritic, or cotton-like, morphology and reacted vigorously with methanol, when the deposit was immersed in it after the

deposition, presumably accompanying the formation of a methoxide. Due to this less adhesive feature, the total deposited mass and thus the current efficiency of the Mg deposition could not be determined. It is still noteworthy, however, that elemental magnesium, one of the active metals, can electrodeposit under a relatively mild condition near ambient temperature. Electrodeposition of Mg metal is known to be impossible containing from ionic liauids alkylimidazolium as the cation component, since the potential of the decomposition of the cation, e.g. 1-ethyl-3-methyl imidazolium, is positive to that of magnesium deposition [12]. Considering the deposition of elemental Mg, it is expected that the deposition of alloys and intermetallic compounds containing magnesium with activities less than 1 can be electrodeposited at more positive potentials. Electrodeposition of Zn-Mg alloy layer, which is important for corrosion resistant coating, is hence currently under investigation.

Figure 6 shows a cyclic voltammogram for TMHA-Tf₂N containing 0.2 M LiNTf₂. A pair of clear redox currents of cathodic Li deposition and subsequent anodic stripping was recognized at around -3 V. Since the substrate was Pt sheet, the deposition may accompany a formation of Li-Pt alloy, but the result also demonstrates the wide electrochemical window of TMHA-Tf₂N and the potential applicability of this media for electrochemical processes which involve the deposition of active metal elements.

Although Mg and Li can be deposited, we have not yet succeeded in electrodepositing titanium metal. The addition of liquid TiCl₄ to TMHA-Tf₂N yielded a yellowish bath, from which, however, Ti(IV) ions were not reduced to metallic form at potentials between -2.0to -3.4 V vs. Γ/I_3^- , while anodic dissolution of Ti sheet, *i.e.* CE, proceeded uniformly. Such behavior seems to be attributable to the presence of stable intermediate valencies, *e.g.* Ti(III) and Ti(II), which, if formed on cathode, can be re-oxidized on the anode surface.

4. ACKNOWLEDGMENT

This work was supported by a Grant-in-Aid for Scientific Research (No. 13450309) and the 21st century COE program "United Approach to New Materials Science," both from the Ministry of Education, Culture, Sports, Science and Technology of Japan.

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Fig. 5 X-ray diffraction patterns for (a) Ni, (b) Zn, and (c) Mg electrodeposited on Cu sheet at 50 °C from TMHA-Tf₂N containing (a) 0.1 M Zn(Tf₂N)₂, (b) 0.5 M Ni(Tf₂N)₂, and (c) 0.5 M Mg(Tf₂N)₂. Deposition potentials: (a) -1.2 V, (b) -1.2 V, (c) -3.4 V vs. Γ/I_3^- .



Fig. 6 Cyclic voltammogram for TMHA-Tf₂N containing 0.2 M LiNTf₂ at 50 °C. WE and CE: Pt sheets.

(Received October 9, 2003; Accepted December 1, 2003)