ELECTROCHEMICAL BEHAVIOR OF SILVER(I) IN 1-ETHYL-3-METHYLIMIDAZOLIUM TETRAFLUOROBORATE PREPARED BY A NOVEL PROCEDURE

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A novel procedure was devised to prepare 1-ethyl-3-methylimidazolium tetrafluoroborate (EMIBF₄) via an intermediate liquid salt, EM(HF)₃F, obtained by the reaction of EMICl and anhydrous hydrogen fluoride. EMIBF₄ with adequate purity was also obtained by the reaction of EMICl and tetrafluoroboric acid. Silver tetrafluoroborate dissolves up to ~0.2 mol dm⁻³ in EMIBF₄. The electrochemical deposition and dissolution of silver were found possible in EMIBF₄. The rate of the charge transfer process of the reduction of silver(I) species in EMIBF₄ seems to be slower than that in aqueous solution.

INTRODUCTION

Several molten salt systems melting at ambient temperature have been investigated as the electrolytes for electroplating and rechargeable batteries. 1-ethyl-3-methylimidazolium chloride - aluminum trichloride (EMICl-AlCl₃) system is one of the most typical systems having low viscosity, high conductivity and wide electrochemical window. However, the hygroscopic nature of this system is not favorable for the practical use. Recently, some ambient temperature molten salt systems consisting of 1-ethyl-3-methylimidazolium (EMI⁺) and various anions, such as tetrafluoroborate (BF₄⁻), trifluoromethanesulfonate (CF₃SO₃⁻) and bis-(trifluoromethanesulfone) imide ((CF₃SO₂)₂N⁻), have been discovered in the exploration of the inflammable electrolytes for lithium rechargeable batteries (1, 2) and electrochemical capacitors (3, 4). These systems were reported to be stable against moisture while they have the similar characteristics to those of EMICl - AlCl₃ system. Therefore, these 'air-stable' molten salt systems are expected to be utilized in various industrial purposes.

1-ethyl-3-methylimidazolium tetrafluoroborate (EMIBF₄) has received much attention among the 'air-stable' molten salt systems because of its low reactivity against moisture (1, 2, 5, 6). EMIBF₄ has been prepared so far in aqueous or acetone solutions of EMICl by adding equimolar amount of tetrafluoroborate salts, such as AgBF₄, NaBF₄ and (NH₄)BF₄, to exchange Cl⁻ with BF₄⁻ (1, 2). In these methods, however, contamination of some impurities is unavoidable since the solubility of the chloride byproducts in the solutions is not negligible. Thus, it is necessary to develop more reliable procedures for preparing EMIBF₄. On the other hand, only a few electrochemical studies have been reported in EMIBF₄ system (1, 6). Besides, the absence of the well-defined reference electrode in this system prevents comparing the electrode potentials one another. Thus, it is necessary to find the reversible electrode reactions applicable to the reference electrode in order to accumulate the electrochemical data in this system.
In this study, some novel procedures for preparing EMIBF$_4$ were examined to reduce contamination of impurity. In addition, the electrochemical behavior of monovalent silver species was investigated in EMIBF$_4$ as a candidate for the reference electrode reactions.

EXPERIMENTAL

All the reagents after drying were handled in a glove box of argon atmosphere (Miwa Seisakujo, 1ADB-2+MM2-P15S). EMICl was prepared by the reaction of 1-methylimidazole and ethyl chloride (Tokyo Kasei) as described in the literature (7). Anhydrous hydrogen fluoride was distilled from K$_2$NiF$_6$ (Ozark-Mahoning) / HF solution to eliminate some reductive species, such as hydrogen and water. Boron trifluoride (BF$_3$, Nippon Sanso) was used as supplied. These gaseous reagents were handled with a stainless steel vacuum line. Tetrafluoroboric acid (42 vol%, Wako Chemicals) and silver tetrafluoroborate (AgBF$_4$, Aldrich) were used as supplied. Platinum or silver was used as working electrodes ($7.85 \times 10^{-3}$ cm$^2$). Gold was used as a counter electrode. The reference electrode consisted of silver electrode immersed in saturated AgBF$_4$ / EMIBF$_4$ solution separated from the test solution with G4 glass or Teflon membrane filter. All the potentials in this paper were represented against this electrode. The electrochemical measurements were performed with the aids of Potentiostat / Galvanostat (Toho Giken, PS-07) and a digital recorder (Yokogawa, OR100). The surface of the electrode was characterized by X-ray diffraction (XRD) with Rigaku apparatus (RINT-1300, CuK$\alpha$, Ni-filtered).

RESULTS AND DISCUSSION

Preparation of EMIBF$_4$ from EMICl, HF and BF$_3$

EMIBF$_4$ could be prepared by the acid-base reaction of 1-ethyl-3-methylimidazolium fluoride (EMIF) and BF$_3$ in the same way as EMICl-A1C$_1$$_3$ system. Thus, the reaction of EMICl and HF was examined to prepare the starting material, "EMIF", in the first place. EMICl was found to melt when it was interacted with excess amount of anhydrous HF in a Teflon reactor:

$$\text{EMICl} + (n + 1)\text{HF} \rightarrow \text{EMI(}\text{HF})_{n}\text{F + HCl} \quad [1]$$

Then, HCl and part of HF were removed under vacuum at ~70°C for several hours, finally giving a colorless liquid salt, EMI(HF)$_n$F. The composition of the salt was determined to be approximately EMI(HF)$_2$F by gravimetry, assuming that the ion exchange reaction of Cl$^-$ with (HF)$_2$F$^-$ proceeds completely because of the high electronegativity of fluorine. The vapor pressure of EMI(HF)$_2$F was almost negligible at ambient temperature (less than 1 Pa). This liquid salt is quite similar to EMIIHCl$_2$ prepared by the reaction of EMICl and HCl (8, 9). Simultaneously with our work, the preparation and some properties of EMII(HF)$_n$F have been studied by another group (10).
The reaction of EMI(HF)$_2$F and gaseous BF$_3$ resulted in liberation of the weak Lewis acid, HF, to give EMIBF$_4$:

\[
\text{EMI(HF)$_2$F + BF$_3$} \rightarrow \text{EMIBF}_4 + 2.5\text{HF}
\]

[2]

HF and excess BF$_3$ were removed under vacuum at ~70°C for several hours. The cyclic voltammogram of Pt electrode in the melt showed the absence of prominent impurities. The byproducts during the preparation of EMIBF$_4$ via EMI(HF)$_2$F are HCl and HF as in eqs. [1] and [2], which are volatile and easy to be removed from the main product. Moreover, this method enables to yield stoichiometric EMIBF$_4$ easily without weighing solid reagents.

The ion exchange reaction of EMI(HF)$_n$F can be used for the preparation of not only EMIBF$_4$ but also the salts of EMI$^+$ with various fluorides of metals and non-metals. However, The method described above is somewhat dangerous and must be performed with special instruments since the highly corrosive and toxic gases, HF and BF$_3$, are required for preparing EMI(HF)$_n$F and EMIBF$_4$. Thus, this method is effective when the products react with water or organic solvents.

### Preparation of EMIBF$_4$ from EMICl and HBF$_4$

The stability of EMIBF$_4$ against water enables its preparation in aqueous solution. EMIBF$_4$ can be prepared by pouring excess amount of aqueous HBF$_4$ solution into a Teflon beaker containing EMICl in the air:

\[
\text{EMICl + HBF}_4 \rightarrow \text{EMIBF}_4 + \text{HCl}
\]

[3]

HCl and H$_2$O were volatilized by heating the solution at ~120°C, followed by vacuum drying at ~130°C for several hours. The elimination of the byproduct was confirmed by the cyclic voltammogram of Pt electrode in the EMIBF$_4$ as shown in Fig. 1. The anodic current peaks around ~1.5 ~ 1.0 V seem to be ascribed to the oxidation of the reduced products of EMI$^+$ (2). The product is expected to have a high purity since all species except EMIBF$_4$ are volatile. This simple procedure is suitable for preparing a large quantity of EMIBF$_4$ and less dangerous than that via eqs. [1] and [2].

### Electrochemical behavior of Ag(I)

Figure 2 shows the cyclic voltammograms of Pt electrode in EMIBF$_4$ containing 21 mmol dm$^{-3}$ AgBF$_4$. The cathodic current peak around ~0.2 V was assigned to the reduction of Ag(I) to Ag(0) since deposition of metallic silver was confirmed by X-ray diffraction of a Pt electrode after potentiostatic cathodic reduction at ~0.2 V for several hours. The anodic current peak around ~0.1 V was ascribed to the dissolution of silver deposited during the cathodic scan as the ratio of anodic and cathodic quantities of electricity, $Q_a / Q_c$, was 1.1. The potentials of silver electrode depend linearly on the logarithmic concentration of AgBF$_4$ with a slope of ~60 mV / decade which is in good

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agreement with the theoretical value (59 mV) for one electron process at ambient temperature. Therefore, the reaction occurring around -0.1 V is represented as follows:

\[ \text{Ag(I)} + e^- = \text{Ag} \]  \[ (4) \]

The saturated concentration of AgBF$_4$ in EMIBF$_4$ was found to be ~0.2 mol dm$^{-3}$ at ambient temperature.

The cathodic peak potential shifted to more negative side with increase in the scan rate, as shown in Fig. 1, suggesting that the reduction of Ag(I) is electrochemically irreversible. The standard heterogeneous rate constant, \( k_0 \), for the reduction of Ag(I) to Ag(0) was calculated to be \( 1.2 \times 10^{-5} \) cm s$^{-1}$ from the plot of the logarithm of the peak current density, \( j_p \) (A cm$^{-2}$), for the reduction of Ag(I) and the difference of the peak and formal potentials, \( E_p \) and \( E_0^\circ \) (V), as shown in Fig. 2, according to the following equation:

\[ \ln j_p = \ln(0.227nFC_0 k_0^\circ) + \frac{an_s F}{RT} (E_p - E_0^\circ) \]  \[ (5) \]

where \( n, F, C_0^\circ, \alpha, n_s, F, R \) and \( T \) are number of involved electrons, bulk concentration of Ag(I) in mol cm$^{-3}$, transfer coefficient, number of electrons involved in the reduction process, Faraday constant in C mol$^{-1}$, gas constant in J mol$^{-1}$ K$^{-1}$, and absolute temperature in K, respectively. The \( \alpha \) value was estimated to be 0.65 from the slope of eq. \[ (5) \]. The slow kinetics of the deposition of silver has been observed also in an acidic EMICl-AlCl$_3$ system (11). The \( k_0^\circ \) value of the reduction of Ag(I) in the EMICl-AlCl$_3$ system was estimated to be \( 4 \times 10^{-4} \) cm s$^{-1}$ at 40°C from the data in the literature. These \( k_0^\circ \) values are rather smaller than that in aqueous solution system (~24 cm s$^{-1}$) (12). The slow kinetics of the reduction of Ag(I) in both EMIBF$_4$ and EMICl-AlCl$_3$ systems may be ascribed to the existence of the bulky EMI$^+$ cation, which may cover the surface of the cathodically polarized electrode and obstruct the charge transfer or nucleation of metallic silver.

The diffusion coefficient of Ag(I), \( D_{0s} \), in EMIBF$_4$ was estimated to be \( 3.0 \times 10^{-7} \) cm$^2$ s$^{-1}$ from the plot of the peak current density and the square root of scan rate, \( \nu \) (V s$^{-1}$), as shown in Fig. 3, from the following equation:

Table 1 Some kinetic parameters for the reduction of Ag(I) in EMIBF$_4$ and EMICl-AlCl$_3$ systems.

| System       | \( T / \) K | \( D / \) cm$^2$ s$^{-1}$ | \( 10^{10} D / T / \) g cm s$^{-2}$ K$^{-1}$ | \( \alpha n_s \) | \( k_0^\circ / \) cm s$^{-1}$ | Ref |
|--------------|------------|------------------------|---------------------------------|-----------------|-------------------|-----|
| EMIBF$_4$    | 298        | 3.0 \times 10^{-7}     | 3.8                             | 0.65            | 1.2 \times 10^{-5} | This work |
| EMICl-AlCl$_3$ | 313        | 1.2 \times 10^{-6}     | 3.8                             | 0.96            | 4.3 \times 10^{-4} | 11   |

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\[ j_p = 2.99 \times 10^8 n (\alpha n_j)^{1/2} C_0 \alpha D_0^{1/2} v^{1/2} \]  

The Stokes-Einstein product, \( \eta D / T \), value of Ag(I) in EMIBF₄ system was consistent with that in the EMICl-AlCl₃ system (11, 13), as listed in Table 1. The hydrodynamic radius of Ag(I) is calculated to be 0.19 nm, suggesting that Ag(I) exists as a substantially bare cation (Ag⁺) in these systems.

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Fig. 1  Cyclic voltammogram of Pt electrode in EMIBF$_4$ molten salt prepared by EMICl and tetrafluoroboric acid; scan rate : 100 mV s$^{-1}$.

Fig. 2  Cyclic voltammograms of Pt electrode in EMIBF$_4$ molten salt containing 21 mmol dm$^{-3}$ AgBF$_4$ at 25°C.
Fig. 3  Dependence of the logarithm of the peak current density for the reduction of Ag(I) on the difference in the peak and formal potentials in EMIBF$_4$ molten salt containing 21 mmol dm$^{-3}$ AgBF$_4$ at 25°C.

Fig. 4  Dependence of the peak current density for the reduction of Ag(I) on the square root of scan rate in EMIBF$_4$ molten salt containing 21 mmol dm$^{-3}$ AgBF$_4$ at 25°C.