ELECTROCHEMICAL BEHAVIOR OF VANADIUM (II / III) AND NIOBIUM (IV / V) IN BASIC 1-ETHYL-3-METHYLIMIDAZOLOM CHLORIDE-ALUMINUM TRICHLORIDE MOLTEN SALT

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The Electrochemical behavior of trivalent vanadium, V(III), and pentavalent niobium, Nb(IV), was investigated in a basic 1-ethyl-3-methylimidazolium chloride - aluminum trichloride (EMIC1-A1Cl3) molten salt. The reduction of V(III) to V(II) was observed on platinum electrode. The solubility of V(III) was estimated to be ~0.2 mol dm⁻³ in a highly basic EMIC1-A1Cl3 molten salt at room temperature. The reversible redox behavior of Nb(V) / Nb(IV) couple was observed at higher concentrations of Nb(V). NbCl₅ dissolved up to 0.9 mol dm⁻³ in a basic EMIC1-A1Cl3 molten salt regardless of the basicity.

INTRODUCTION

Rechargeable redox batteries using two pairs of soluble redox couples as the positive and negative half-cells have received much attention in the field of large-scale electricity storage for load leveling of energy. Most of the redox batteries are based on aqueous solutions, the electromotive force being limited within the electrochemical potential window of water. The wide electrochemical potential window of 1-ethyl-3-methylimidazolium chloride - aluminum trichloride (EMIC1-A1Cl3) molten salt system enables development of the redox batteries having larger electromotive forces. Furthermore, high energy density may be expected by using binary EMIC1-MCl₅ (M : transition metals) molten salt systems as the half-cells.

The transition metals in Group 5 (VA) are considered as the candidates for the active species of the half-cells since these elements have stable oxidation states from +2 to +5. In the case of vanadium, the reversible redox behavior between V(IV) and V(III) has been observed in the basic EMIC1-A1Cl3 molten salt (1). However, the reduction of V(III) to V(II) has not been confirmed in the molten salt while it is possible in acidic aqueous solution system (2). In the cases of niobium and tantalum, the reversible redox behaviors of Nb(IV) / Nb(V), Nb(III) / Nb(IV) and Ta(IV) / Ta(V) couples have been reported in the basic EMIC1-A1Cl3 molten salt (3 - 6), but there is no information on the solubility of the species and the electrochemical behavior at higher concentrations, which are important for considering the rechargeable redox batteries using these couples.

In this study, the dissolution and electrochemical behaviors of vanadium (II / III) and niobium (V / IV) were investigated in the basic EMIC1-A1Cl3 molten salts for determining their applicability for the rechargeable redox batteries based on EMIC1-A1Cl3 molten salt.
EXPERIMENTAL

EMICl was prepared by the reaction of 1-methylimidazole and ethyl chloride (Tokyo Kasei), as described in literature (7). AlCl3 (Fluka) was purified by sublimation in the presence of sodium chloride and aluminum under reduced pressure at 180°C. Anhydrous vanadium trichloride and niobium pentachloride (Aldrich) were used as supplied. All the reagents were handled in a glove box of dry argon atmosphere (Miwa Seisakujo, 1ADB-2+MM2-P15S). Platinum was used as working (7.85 × 10⁻³ cm²) and counter electrodes. Reference electrode consisted of aluminum wire immersed in an acidic EMICl-AlCl3 (0.333 : 0.667) molten salt separated by G4 glass filter from the test solution. All the potentials in this paper are presented against this electrode. The electrochemical measurements were performed in the glove box with the aid of Potentiostat / Galvanostat (Toho Giken, PS-07) and a digital recorder (Yokogawa, OR100).

RESULTS AND DISCUSSION

Electrochemical behavior of V(II) / V(III) couple

A violet solution was obtained when VCl3 was added to a basic EMICl-AlCl3 (N = 0.45, where N is the mole fraction of AlCl3) molten salt. The dissolution of VCl3 occurs forming the chloro complexes, VCl3+n− (n = 1, 2 and 3), as shown in the following equilibrium (1):

\[
\text{VCl}_3 + n\text{Cl}^- = \text{VCl}_{3+n}^{n-}
\]  

Figure 1 shows the cyclic voltammograms at a Pt electrode in the EMICl-AlCl3 (N = 0.45) molten salt containing various concentrations of VCl3 at 25°C. The cathodic and anodic current peaks around -0.5 and -0.4 V, respectively, were due to some impurities, such as HCl₂⁻ or H₂Cl₃⁻ (8, 9), since these peaks were also observed in the absence of VCl3. The cathodic current peak around -1.1 V was assigned to the reduction of trivalent vanadium species, V(III), as the current density increases with the increase in the concentration of VCl3 (10). The reduction of V(III) seems to occur rapidly on platinum electrodes while it has not been observed on glassy carbon electrodes (1), suggesting that the reduction mechanism of V(III) involves some chemical adsorption processes depending on the electrode materials. The anodic current peak around -0.7 V was ascribed to the oxidation of the reduced product of V(III), which is probably bivalent vanadium species, V(II), since the deposition of vanadium metal did not occur on Pt electrode after potentiostatic cathodic reduction at -1.4 V for several hours.

Figure 2 shows the cyclic voltammogram at a Pt electrode in the EMICl-AlCl3 (N = 0.45) molten salt containing 85.7 mmol dm⁻³ VCl3 at 25°C. The cathodic peak potential corresponding to the reduction of V(III) shifted to more negative potentials with increase in the scan rate, indicating that the reduction process is quasi-reversible or irreversible electrochemically. The transfer coefficient, α, was estimated to be 0.48 from the
difference between the cathodic peak and half peak potentials, $E_p$ and $E_{p/2}$, assuming that the number of electrons involved in the reduction process, $n_a$, equals one (11):

$$|E_p - E_{p/2}| = \frac{47.7}{cn_a}$$

[2]

It was difficult to determine the standard heterogeneous rate constant, $k^0$, of the reduction of V(III) since neither the formal potential nor half wave potential of V(II) / V(III) could be estimated from the cyclic voltammogram. There was a proportional relation between the peak current density for the reduction of V(III) and the square root of scan rate, as shown in Fig. 3. The peak current density was calculated by subtracting the residual current density from the actual peak current density in the cyclic voltammogram since the cathodic current peak of the impurity overlapped with that of V(III). The diffusion coefficient of V(III) was calculated from the slope of the line using the following equation (11);

$$j_p = 2.99 \times 10^3 n(cn_a)^{1/2} C_0 D_0^{1/2} \nu^{1/2}$$

[3]

where $j_p$, $n$, $C_0$, $D_0$ and $\nu$ are peak current density in A cm$^{-2}$, number of electrons, bulk concentration of V(III) in mol cm$^{-3}$, diffusion coefficient of V(III) in cm$^2$ s$^{-1}$ and scan rate in V s$^{-1}$, respectively. The diffusion coefficients of V(III) at different basicities were also calculated in the same way, as listed in Table 1. The Stokes-Einstein products, $nD / T$, of V(III), were calculated using the viscosities of the EMICl-AlCl$_3$ (12). The $nD / T$ values at the basicity of $N = 0.41$ and 0.37 is close to those of the hexacoordinated chloro complex anions of some trivalent metals, represented as $[MC_16]$$_3^-$ (13-20), in the basic EMICl-AlCl$_3$ molten salt systems. However, the $nD / T$ value at the basicity of $N = 0.45$ is quite different from the others, suggesting that the trivalent vanadium species exists not only as the $[VC_13]^+$ form.

Proportional relations were obtained between the cathodic peak current density for the reduction of V(III) in the EMICl-AlCl$_3$ ($N = 0.37, 0.41$ and 0.45) molten salt and the concentration of VC1$_3$, as shown in Fig. 4. The saturated concentrations of VC1$_3$ in the EMICl-AlCl$_3$ molten salt for $N = 0.37, 0.41$ and 0.45 were estimated to be 90, 130 and 200 mmol dm$^{-3}$, respectively, after which the cathodic peak current densities did not increase. The saturation concentration depends on the basicity of the EMICl-AlCl$_3$ molten salt, indicating that there exist some complicated equilibria among $[VC1_{3n}]^{+}$ (n = 1, 2 and 3) species (1).

**Electrochemical behavior of Nb(IV) / Nb(V) couple**

Pentavalent niobium species was added to the basic EMICl-AlCl$_3$ molten salt as EM$^+$NbCl$_5$ in order not to affect the basicity of the molten salt since NbCl$_5$ is much more soluble than VC1$_3$. Figure 5 shows the cyclic voltammograms at Pt electrode in the EMICl-AlCl$_3$ ($N = 0.45$) molten salt containing 28 mmol dm$^{-3}$ Nb(V) at 25°C. The
cathodic and anodic current peaks around 0.12 and 0.2 V were ascribed to the reduction of Nb(V) and the oxidation of Nb(IV), respectively. The separation between the cathodic and anodic peak potentials was ~0.076 V and did not vary with the scan rate, indicating the redox reaction of Nb(IV) / Nb(V) couple is nearly reversible electrochemically at low concentrations (3). On the other hand, the separation between the cathodic and anodic peak potentials increased with the addition of Nb(V), as shown in Fig. 6. The peak potential shifts may be caused by an ohmic loss arising from uncompensated solution resistance rather than a slow charge transfer. The reversible behavior was also observed in a more basic EMICl-AICl$_3$ ($N = 0.33$) containing lower concentrations of Nb(V) (~13 mmol dm$^{-3}$). The diffusion coefficients of Nb(V) species in EMICl-AICl$_3$ ($N = 0.33$ and 0.45) were calculated from the dependence of the cathodic peak current density on the square root of the scan rate, using the following equation (11):

$$j_p = 2.69 \times 10^5 n^{3/2} D_0^{1/2} v^{1/2} C_0$$

[4]

The obtained kinetic parameters are summarized in Table 2 with those of hexacoordinated chloro complexes of some pentavalent metals in the EMICl-AICl$_3$ molten salt system (3, 5). The diffusion coefficient of Nb(V) obtained at $N = 0.45$ in this work is smaller than those reported (3) mainly due to the difference in the temperature. However, the Stokes-Einstein product, $\eta D / T$, values, which were calculated using the $\eta$ values for plain EMICl-AICl$_3$ molten salt (12), were not consistent with those reported (3), suggesting that the viscosity of EMICl-AICl$_3$ molten salt containing NbCl$_5$ may be higher than that of the plain salt. The small diffusion coefficient of Nb(V) at high basicity ($N = 0.33$) is obviously owing to the high viscosity.

The saturated concentration of Nb(V) was found to be ~900 mmol dm$^{-3}$ regardless of the basicity from the dependence of the peak current density for the reduction of Nb(V) on the concentration of Nb(V) in EMICl-AICl$_3$ ($N = 0.33$ and 0.45), as shown in Fig. 7. This suggests that the dissolved species of NbCl$_5$ in the basic EMICl-AICl$_3$ is only $[\text{NbCl}_6]^{-}$ (3) in contrast to the case of vanadium.

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Table 1 Summary of the kinetic parameters of the hexacoordinated chloro complexes of some trivalent transition metals in the basic EMICl-AlCl₃ molten salt systems.

| Chloro complex | $N$  | $10^5 D / \text{cm}^2 \text{s}^{-1}$ | $10^{10} \eta D / T$ | $\alpha$ | $k^0 / \text{cm} s^{-1}$ | $T / \degree C$ | Ref.       |
|----------------|-----|----------------------------------|----------------------|---------|--------------------------|----------------|-----------|
| VCl₆⁻     | 0.37 | 0.69                             | 2.5                  | 0.5     | 25                       | This work      |           |
| VCl₆⁻     | 0.41 | 0.96                             | 1.8                  | 0.6     | 25                       | This work      |           |
| VCl₆⁻     | 0.45 | 3.5                              | 4.0                  | 0.5     | 25                       | This work      |           |
| CrCl₆³⁻    | 0.444 | 1.29                            | 1.2                  | 0.38    | $3.27 \times 10^{-6}$   | 29             | 13        |
| CrCl₆³⁻    | 0.490 | 3.31                            | 1.3                  | 0.37    | $5.79 \times 10^{-6}$   | 29             | 13        |
| MoCl₆³⁻    | 0.444 | 1.6                             | 1.9                  |         |                          | 40             | 14        |
| IrCl₆³⁻    | 0.444 | 1.9                             | 1.3                  |         |                          | 40             | 15        |
| IrCl₆³⁻    | 0.490 | 3.0                             | 1.3                  |         |                          | 40             | 15        |
| CeCl₆³⁻    | 0.490 | 4.0                             | 2.7                  | 0.5     | $1.0 \times 10^{-3}$    | 40             | 16        |
| EuCl₆³⁻    | 0.444 | 2.50                            | 1.7                  | 0.7     | $2.85 \times 10^{-4}$   | 40             | 17        |
| EuCl₆³⁻    | 0.490 | 3.75                            | 1.6                  | 0.43    | $1.41 \times 10^{-4}$   | 40             | 17        |
| YbCl₆³⁻    | 0.444 | 1.99                            | 1.4                  | 0.59    | $1.29 \times 10^{-4}$   | 27             | 18        |
| YbCl₆³⁻    | 0.490 | 3.54                            | 1.5                  | 0.61    | $1.16 \times 10^{-4}$   | 27             | 18        |
| TiCl₆⁻     | 0.400 | 0.80                            | 1.35                 | 0.2     |                          | 30             | 19        |
| TiCl₆⁻     | 0.444 | 1.46                            | 1.40                 | 0.2     |                          | 30             | 19        |
| UCl₆⁻      | 0.448 | 1.5                             | 1.7                  |         |                          | 28             | 20        |

Table 2 Summary of the kinetic parameters of the hexacoordinated chloro complexes of some pentavalent transition metals in the basic EMICl-AlCl₃ molten salt systems.

| Chloro complex | $N$  | $10^5 D / \text{cm}^2 \text{s}^{-1}$ | $10^{10} \eta D / T$ | $T / \degree C$ | Ref.       |
|----------------|-----|----------------------------------|----------------------|----------------|-----------|
| NbCl₆⁻     | 0.45 | 2.3                              | 2.7                  | 25             | This work      |           |
| NbCl₆⁻     | 0.33 | 0.36                             | 2.4                  | 25             | This work      |           |
| NbCl₆⁻     | 0.444 | 4.98                            | 3.4                  | 40             | 3           |
| NbCl₆⁻     | 0.490 | 8.21                            | 3.5                  | 40             | 3           |
| TaCl₆⁻     | 0.444 | 5.10                            | 3.5                  | 40             | 5           |
| TaCl₆⁻     | 0.490 | 8.18                            | 3.6                  | 40             | 5           |

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Fig. 1 Cyclic voltammograms at Pt electrode in the basic EMICl-AlCl₃ \((N = 0.45)\) molten salt containing various concentrations of VCl₃ at 25°C; scan rate : 50 mV s\(^{-1}\).

Fig. 2 Cyclic voltammograms at Pt electrode in the basic EMICl-AlCl₃ \((N = 0.45)\) molten salt containing 85.7 mmol dm\(^{-3}\) VCl₃ at 25°C.
Fig. 3 Dependence of the peak current density for the reduction of \( \text{VCl}_3 \) on the square root of the scan rate, \( v \), in the basic \( \text{EMICl-AlCl}_3 \) (\( N = 0.45 \)) molten salt containing 85.7 mmol dm\(^{-3}\) \( \text{VCl}_3 \) at 25°C.

Fig. 4 Dependence of the peak current density for the reduction of \( \text{VCl}_3 \) on the concentration of \( \text{VCl}_3 \) in the basic \( \text{EMICl-AlCl}_3 \) (\( N = 0.37, 0.41 \) and 0.45) molten salt at 25°C.
Fig. 5 Cyclic voltammogram at Pt electrode in the basic EMICl-AlCl$_3$ ($N = 0.45$) molten salt containing 28 mmol dm$^{-3}$ Nb(V) at 25°C.

Fig. 6 Cyclic voltammogram at Pt electrode in the basic EMICl-AlCl$_3$ ($N = 0.45$) molten salt containing various concentrations of Nb(V) at 25°C; scan rate : 50 mV s$^{-1}$.
Fig. 7 Dependence of the peak current density for the reduction of Nb(V) on the concentration of NbCl₅ in the cyclic voltammogram of Pt electrode in the basic EMICl-AlCl₃ (N = 0.33 and 0.45) molten salt at 25°C; scan rate : 50 mV s⁻¹.