Redox reaction in 1-ethyl-3-methylimidazolium–iron chlorides molten salt system for battery application

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Abstract

The redox reaction between divalent and trivalent iron species in binary and ternary molten salt systems consisting of 1-ethyl-3-methylimidazolium chloride (EMICl) with iron chlorides, $FeCl_2$ and $FeCl_3$, was investigated as a candidate of the half-cell reactions of novel rechargeable redox batteries based on low temperature molten salt systems. A reversible one-electron redox reaction between divalent and trivalent iron species was observed on a platinum electrode in EMICl–$FeCl_2$–$FeCl_3$ system at 130 °C. The voltammetric data indicated that divalent and trivalent iron species were $FeCl_3{}^-$ and $FeCl_4{}^-$ complex anions, respectively. Combined with another proper redox couple, this molten salt system can be utilized in a rechargeable redox battery on account of its low melting temperature and reversible redox reaction.
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Keywords: 1-Ethyl-3-methylimidazolium; Iron chloride; Redox battery; Molten salt

1. Introduction

Large-scaled rechargeable batteries having a long cycle life are required for the efficient operation of electric power supply. So-called 'redox flow batteries' are possible candidates for this purpose, where two couples of redox ions in aqueous solutions are employed for positive and negative half-cell reactions. The reactions involve neither chemical nor structural changes of the electrodes in contrast to usual rechargeable batteries using solid active materials, so that the charge and discharge cycles can be repeated without cycle deterioration in principle. Moreover, self-discharge can be avoided by storing the positive and negative half-cell solutions in separate tanks. These solutions are circulated between the tanks and the cell components consisting of electrodes and ion exchange membrane. In a vanadium cell, for example, V(V)/V(IV) and V(III)/V(II) couples are employed as positive and negative half-cell redox systems, respectively. The electromotive forces of aqueous redox flow cells are in the range from 1.0 to 1.4 V, which are limited necessarily by the electrochemical potential window of water. Therefore, the energy density of these redox batteries may be improved by using the electrolytes having wider electrochemical potential windows than water.

A room temperature molten salt consisting of 1-ethyl-3-methylimidazolium chloride (EMICl) and aluminum trichloride ($AlCl_3$) has low melting point and wide electrochemical potential window, which are favorable for the above application. A number of metal chlorides dissolve in EMICl–$AlCl_3$ molten salt due to its adjustable Lewis acid–base property. In the case of acidic condition, in which the mole fraction of $AlCl_3$, X_{AlCl_3}, is greater than 0.5, metal chlorides release chloride ions to form their cationic species. A lot of the metal chlorides behaving as Lewis base are in low oxidation states, and the reduction of the dissolved species results in electrodeposition of their metals. In the case of basic condition, in which X_{AlCl_3} is smaller than 0.5, metal chlorides accept chloride ions to form their chloro-complex anions. Most of soluble redox couples have been reported and studied under basic condition, as listed in Table 1 [1–16], probably because the metal species of several high oxidation states are stabilized after forming chlorocomplexes. The standard formal potentials of the redox couples of various metal chlorocomplexes are distributed widely within the electrochemical potential window of the basic EMICl–$AlCl_3$ molten salt. Thus, the rechargeable redox batteries having high cell voltages can be constructed by combining these redox couples in the basic EMICl–$AlCl_3$ molten salt.

On the other hand, the energy densities of the redox batteries depend not only on the cell voltages but also on

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Table 1
Redox couples reported in basic EMICl–AlCl$_3$ molten salt systems

Redox couple	X_{AlCl_3}	E^0 (V)[a]	T (°C)	Reference
[Yb(III)Cl$_6$]$^{3-}$/[Yb(II)Cl$_4$]$^{2-}$	0.444	−1.620	27	[1]
[Yb(III)Cl$_6$]$^{3-}$/[Yb(II)Cl$_4$]$^{2-}$	0.490	−1.554	27	[1]
[U(IV)Cl$_6$]$^{2-}$/[U(III)Cl$_6$]$^{3-}$	0.450	−1.35	28	[2]
[V(III)Cl$_6$]$^{3-}$/V(II)	0.450	−1.0	25	[3]
[Eu(III)Cl$_6$]$^{3-}$/[Eu(II)Cl$_4$]$^{2-}$	0.444	−0.908	40	[4]
[Nb(IV)Cl$_6$]$^{2-}$/[Nb(III)Cl$_6$]$^{3-}$	0.444	−0.900	40	[5]
[Nb(IV)Cl$_6$]$^{2-}$/[Nb(III)Cl$_6$]$^{3-}$	0.490	−0.900	40	[5]
[Re(IV)Cl$_6$]$^{2-}$/[Re(III)Cl$_6$]$^{3-}$	0.444	−0.885	40	[6]
[Re(IV)Cl$_6$]$^{2-}$/[Re(III)Cl$_6$]$^{3-}$	0.49	−0.866	40	[6]
[Eu(III)Cl$_6$]$^{3-}$/[Eu(II)Cl$_4$]$^{2-}$	0.490	−0.799	40	[4]
[W(IV)Cl$_6$]$^{2-}$/?	0.495	−0.792	40	[7]
[Cr(III)Cl$_6$]$^{3-}$/[Cr(II)Cl$_4$]$^{2-}$	0.444	−0.649	29	[8]
[Cr(III)Cl$_6$]$^{3-}$/[Cr(II)Cl$_4$]$^{2-}$	0.490	−0.596	29	[8]
[Re(III)$_2$Cl$_8$]$^{2-}$/[Re(II)$_2$Cl$_8$]$^{3-}$	0.444	−0.589	40	[9]
[Re(III)$_2$Cl$_8$]$^{2-}$/[Re(II)$_2$Cl$_8$]$^{3-}$	0.490	−0.566	40	[9]
[Ta(V)Cl$_6$]$^-$/[Ta(IV)Cl$_6$]$^{2-}$	0.444	−0.477	40	[10]
[Ta(V)Cl$_6$]$^-$/[Ta(IV)Cl$_6$]$^{2-}$	0.490	−0.457	40	[10]
[Re(III)$_3$Cl$_{12}$]$^{3-}$/[Re(II)$_3$Cl$_{12}$]$^{4-}$	0.444	−0.434	40	[9]
[Re(III)$_3$Cl$_{12}$]$^{3-}$/[Re(II)$_3$Cl$_{12}$]$^{4-}$	0.490	−0.337	40	[9]
[Tl(III)Cl$_6$]$^{3-}$/Tl(I)	0.400	−0.025	30	[11]
[Tl(III)Cl$_6$]$^{3-}$/Tl(I)	0.444	−0.005	30	[11]
[Nb(V)Cl$_6$]$^-$/[Nb(IV)Cl$_6$]$^{2-}$	0.444	0.182	40	[5]
[Nb(V)OCl$_5$]$^{2-}$/ [Nb(IV)OCl$_y$]$^{(2-y)-}$	0.444	0.182	40	[5]
[Nb(V)Cl$_6$]$^-$/[Nb(IV)Cl$_6$]$^{2-}$	0.490	0.191	40	[5]
[Fe(III)Cl$_4$]$^-$/Fe(II)	0.480	0.250	32	[12]
Au(III)/Au(I)	0.444	0.310	40	[13]
[Ir(IV)Cl$_6$]$^{2-}$/[Ir(III)Cl$_6$]$^{3-}$	0.444	0.344	40	[14]
[Ir(IV)Cl$_6$]$^{2-}$/[Ir(III)Cl$_6$]$^{3-}$	0.490	0.361	40	[14]
[W(V)Cl$_6$]$^-$/W(IV)	0.495	0.455	40	[7]
Ce(IV)/Ce(III)	0.490	0.600	40	[15]
[V(IV)Cl$_6$]$^{2-}$/[V(III)Cl$_6$]$^{3-}$	0.490	1.00	–	[16]

[a] Versus Al/Al(III).

the concentrations of the active species. If the redox couples listed in Table 1 are available without the supporting electrolyte (EMICl–AlCl$_3$), a high energy density redox cell may be realized. However, in contrast to the basic EMICl–AlCl$_3$ molten salt system, not only the melting points of such molten salt systems but also their electrochemical data have not been found except a few reports [17–19]. In this preliminary study, a novel low temperature molten salt systems consisting of EMICl and iron chlorides (FeCl$_n$) were studied. The electrochemical behaviors of the EMICl–FeCl$_n$ molten salt systems were investigated attempting to construct a rechargeable redox battery based on low temperature molten salt systems.

2. 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-methyli-midazole and ethyl chloride (Tokyo Kasei) as described in [20]. AlCl$_3$ (Fluka) was purified by sublimation in the

presence of sodium chloride (Merck) and aluminum (Soekawa Chemicals) under reduced pressure at 180 °C. Anhydrous FeCl$_2$ and FeCl$_3$ (Soekawa) were used as supplied. A mixture of EMICl and FeCl$_n$ was heated in a quartz beaker by a electric heater in the glove box. The melting of the mixture was confirmed by visual observation.

Platinum was used as working (7.85×10^{-3} cm^2) and counter electrodes. Reference electrode consisted of aluminum wire immersed in an acidic EMICl–AlCl$_3$ (0.333:0.667 in mole fraction) molten salt separated by G4 glass filter from the test melt. 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).

3. Results and discussion

A binary EMICl–FeCl$_3$ system with the mole fraction of FeCl$_3$, $X_{FeCl_3} = 0.500$ or 0.333 melted below room temperature to give a viscous liquid. In order to reduce the viscosity, it was necessary to elevate the working temperature up to 130 °C. If the temperature is elevated higher than 150–160 °C, the color of the melt changed probably due to the thermal decomposition of EMI$^+$ cations. The cyclic voltammograms on a Pt electrode in the EMICl–FeCl$_3$ molten salt systems are shown in Fig. 1. The anodic current arising from ∼1.0 V during anodic scan was due to the oxidation of free chloride ions to chlorine gas [21]. The irreversible cathodic current at ∼ −2.0 V was ascribed to the reductive decomposition of EMI$^+$ cations [22]. At both compositions, the cathodic and anodic current peaks were observed at the same potential, ∼0.1 V, and were assigned to the reduction of trivalent iron, Fe(III), species and the oxidation of divalent iron, Fe(II), species formed during the cathodic scan, respectively. The apparent viscosity of the melt increased when
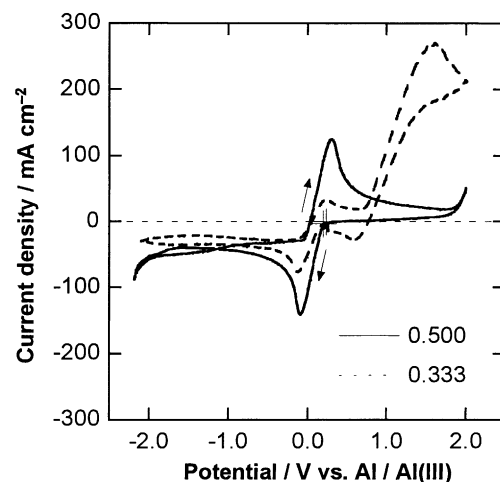

Fig. 1. Cyclic voltammograms at a Pt electrode in EMICl–FeCl$_3$ ($X_{FeCl_3} = 0.500$ and 0.333) at 130 °C; scan rate 100 mV s^{-1}.
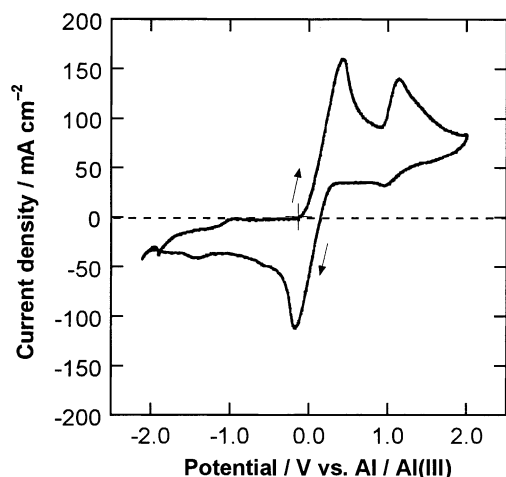
Fig. 2. Cyclic voltammogram at a Pt electrode in EMICl–FeCl$_2$ ($X_{FeCl_2} = 0.333$) at 130 °C; scan rate 100 mV s^{-1}.

Fig. 3. Dependence of the spontaneous potential of a Pt electrode in EMICl–FeCl$_2$–FeCl$_3$ ($X_{FeCl_2} + X_{FeCl_3} = 0.333$) on the logarithm of the X_{FeCl_3}/X_{FeCl_2} at 130 °C.

X_{FeCl_3} was decreased from 0.500 to 0.333. Consequently, the peak current density of Fe(III)/Fe(II) couple became lower with decreasing X_{FeCl_3}. The electrodeposition of metallic iron was not observed at both compositions within the electrochemical potential windows of this system, while the reduction of Fe(II) to metallic iron was reported in a buffered neutral EMICl–AlCl$_3$ molten salt [23].

The anodic current due to the oxidation of free chloride ions was not observed in EMICl–FeCl$_3$ ($X_{FeCl_3} = 0.500$) molten salt, indicating the absence of free chloride ions at this composition. In the case of EMICl–FeCl$_3$ ($X_{FeCl_3} = 0.333$) molten salt, on the other hand, the anodic current corresponding to the oxidation of free chloride ions appeared clearly. Thus, Fe(III) species in these melts is considered to be a tetracoordinated chlorocomplex anion, FeCl$_4^-$, formed by the following equation:

$$FeCl_3 + Cl^- \rightarrow FeCl_4^- \tag{1}$$

The existence of FeCl$_4^-$ anion has been confirmed also in basic chloroaluminate systems [12,23–25].

The binary EMICl–FeCl$_2$ system melted at 110 °C when the mole fraction of FeCl$_2$, X_{FeCl_2}, was 0.333. However, the melting temperature became higher than 130 °C when X_{FeCl_2} was 0.500. Fig. 2 shows the cyclic voltammogram at a Pt electrode in EMICl–FeCl$_2$ ($X_{FeCl_2} = 0.333$) molten salt at 130 °C. The anodic and cathodic current peaks were observed at ~0.1 V, which was close to those observed in the EMICl–FeCl$_3$ molten salt systems, so that they were ascribed to the redox reaction of Fe(II)/Fe(III) couple again. The formation of a chlorocomplex anion of Fe(II) species, FeCl$_4^{2-}$, was expected on the analogy of the basic chloroaluminate molten salt systems [12,23–25]. However, the anodic current due to the oxidation of free chloride ions was observed at ~1.0 V at the same time, although no free chloride ion should exist at this composition if the stoichiometric formation of FeCl$_4^{2-}$ is assumed. Thus, it was suggested that at least, a part of FeCl$_2$ forms some
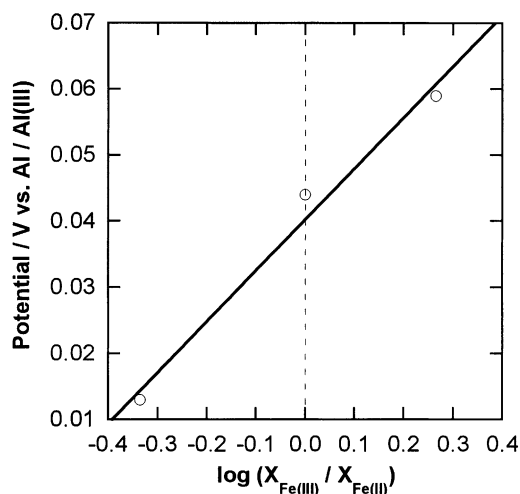
chlorocomplex anions having the atomic ratio of Cl/Fe < 4, such as FeCl$_3^-$ and Fe$_2$Cl$_7^{3-}$.

The spontaneous potential of a Pt electrode immersed in the ternary EMICl–FeCl$_2$–FeCl$_3$ ($X_{FeCl_2} + X_{FeCl_3} = 0.333$) molten salt changed linearly with the logarithm of the X_{FeCl_3}/X_{FeCl_2} ratio, as shown in Fig. 3, with a slope of 77 mV/decade, which was in accordance with the theoretical value for one-electron transfer reaction at 130 °C (80 mV/decade). Since the participation of polymeric anions is denied by the above dependence, the potential determining reaction should be represented as either of the following two equations:

$$FeCl_4^- + e^- \rightarrow FeCl_4^{2-} \tag{2}$$

$$FeCl_4^- + e^- \rightarrow FeCl_3^- + Cl^- \tag{3}$$
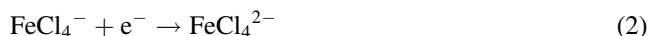
The latter seems more probable than the former since free chloride ions are present in EMICl–FeCl$_2$ ($X_{FeCl_2} = 0.333$) molten salt as described above. The Nernst equations corresponding to the above equilibria are given by

$$E = E'^0 + \frac{2.303RT}{F} \log \frac{X_{FeCl_3}}{X_{FeCl_2}} \tag{4}$$

$$E = E'^0 + \frac{2.303RT}{F} \log \frac{X_{FeCl_3}}{X_{FeCl_2}} - \frac{2.303RT}{F} \log X_{Cl^-} \tag{5}$$

where E, E'^0, R, T, F and X_{Cl^-} are electrode potential, formal potential, gas constant, absolute temperature, Faraday constant and mole fraction of free chloride ion, respectively. In either case, the spontaneous potential of the Pt electrode depends on the logarithm of the X_{FeCl_3}/X_{FeCl_2} ratio with the same slope. However, the spontaneous potential in the EMICl–FeCl$_2$–FeCl$_3$ ($X_{FeCl_2} = X_{FeCl_3} = 0.142$, $X_{Cl^-} = 0.716$) molten salt was lower than that in the EMICl–FeCl$_2$–FeCl$_3$ ($X_{FeCl_2} = X_{FeCl_3} = 0.167$, $X_{Cl^-} = 0.667$) molten salt by ~15 mV, indicating the dependence on X_{Cl^-}. Consequently,

dominant Fe(II) species in the present case may be represented as $FeCl_3^-$ rather than $FeCl_4^{2-}$. However, the difference of 15 mV is slightly larger than calculated one, 9 mV, between $X_{Cl^-} = 0.716$ and 0.667 after assuming that $FeCl_2$ forms $FeCl_3^-$ entirely in the melt. Therefore, there still remains a possibility that a part of Fe(II) exists as $FeCl_4^{2-}$ in the melt.

$$FeCl_2 + Cl^- \rightarrow FeCl_3^- \tag{6}$$

$$FeCl_3^- + Cl^- \rightarrow FeCl_4^{2-} \tag{7}$$
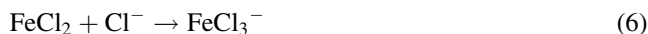
By the way, the Eq. (3) indicates that the oxidation of each $FeCl_2$ requires totally two chloride ions, so that no anodic current due to the oxidation of free chloride ions is expected in the cyclic voltammogram in Fig. 2. However, free chloride ions can be supplied from the bulk solution to the electrode surface after the consumption of most of free chloride ions which initially exist near the electrode surface, since the diffusion of small chloride ions is faster than that of large iron chlorocomplexes.

Fig. 4 shows the cyclic voltammograms at a Pt electrode in the EMICl–FeCl$_2$–FeCl$_3$ ($X_{FeCl_2} = X_{FeCl_3} = 0.167$) molten salt at 130 °C. The separation between the cathodic and the anodic peak potential for the Fe(III)/Fe(II) redox reaction exceeded 400 mV, which was ascribed to the ohmic loss in a low conductive melt rather than the slow electrode kinetics, since the significant cathodic and anodic currents were observed near the reversible potential, 0.04 V. This low conductivity of this melt is disadvantageous to the practical battery application. Although the actual conductivity of the melt was not measured in this study, it may be possible to increase the conductivity and lower the viscosity and the melting point by adding other room temperature ionic liquids or organic solvent. The quasi-steady-state anodic and cathodic polarization curves in the EMICl–FeCl$_2$–FeCl$_3$ ($X_{FeCl_2} = X_{FeCl_3} = 0.142$) molten salt at 130 °C were recorded separately, at a slow scan rate (0.5 mV s^{-1}) as
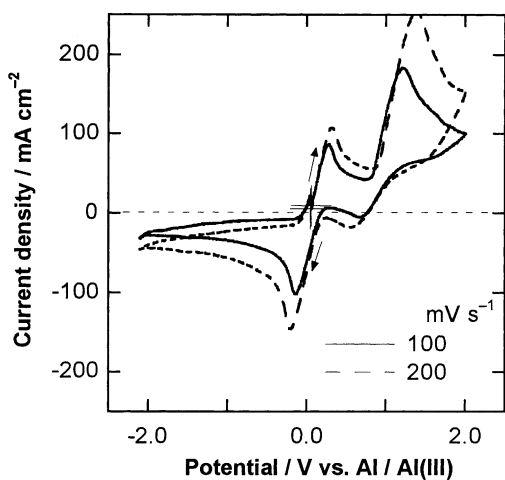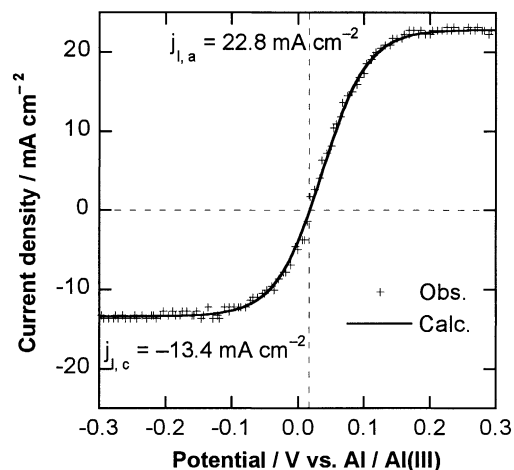

Fig. 5. Quasi-steady-state polarization curves at a Pt electrode in EMICl–FeCl$_2$–FeCl$_3$ ($X_{FeCl_2} = X_{FeCl_3} = 0.142$) at 130 °C; scan rate 0.5 mV s^{-1}.

shown in Fig. 5. Both curves could be fitted by a Nernstian current–potential relation as follows:

$$E = E_{rev} + \frac{RT}{F}\left\{ \ln\left(1 - \frac{j}{j_{l,c}}\right) - \ln\left(1 - \frac{j}{j_{l,a}}\right)\right\} \tag{8}$$

where $j_{l,c}$ and $j_{l,a}$ are the cathodic and anodic limiting current density. The anodic limiting current density is higher than the cathodic one in spite of the same bulk concentrations of Fe(II) and Fe(III), indicating that Fe(II) can diffuse faster than Fe(III) in this melt. In contrast, it has been reported that the diffusion coefficient of Fe(II) is smaller than that of Fe(III) in basic chloroaluminate systems [12,23–25]. In the present EMICl–FeCl$_2$–FeCl$_3$ molten salt, however, the difference in the diffusivity of iron species may be ascribed to the change of the composition near the electrode during the electrolysis. In the case of the cathodic reaction, the fraction of Fe(II) becomes much higher than that of Fe(III) in the diffusion layer at a steady state. Therefore, the limiting current density of Fe(III) observed under such a situation should be regarded as that measured in EMICl–FeCl$_2$ binary molten salt rather than in the original EMICl–FeCl$_2$–FeCl$_3$ molten salt. Similarly, the limiting current density of Fe(II) should be treated as that measured in EMICl–FeCl$_3$ binary molten salt. Since the viscosity of EMICl–FeCl$_2$ molten salt was apparently lower than that of EMICl–FeCl$_3$ molten salt, the limiting current density of Fe(III) became smaller than that of Fe(II) even if there is little difference in the sizes of these species.

Table 2 summarized the densities of EMICl–FeCl$_2$–FeCl$_3$ molten salt and related melts [26,27] in order to estimate the energy densities per volume or weight of general EMICl–MX$_n$ molten salt systems. The concentration of electroactive species amounts to several moles per dm^3 based on these data. For example, the concentration of Fe(III) in the EMICl–FeCl$_3$ ($X_{FeCl_3} = 0.333$) and EMICl–FeCl$_2$–FeCl$_3$ ($X_{FeCl_2} = X_{FeCl_3} = 0.142$) molten salts were 3.0 and 1.3 mol dm^{-3},

Fig. 4. Cyclic voltammogram at a Pt electrode in EMICl–FeCl$_2$–FeCl$_3$ ($X_{FeCl_2} = X_{FeCl_3} = 0.167$) at 130 °C.

Table 2
Density of EMICl–FeCl$_2$–FeCl$_3$ and some related systems

System	T (°C)	Density (g cm^{-3})	Weight (g)[a]	Volume (cm^3)[b]	Reference
EMICl–0.5FeCl$_3$	130	1.35	227.73	169	This work
EMICl–0.5FeCl$_2$	130	1.27	210.00	165	This work
EMICl–0.25FeCl$_3$–0.25FeCl$_2$	130	1.32	218.86	166	This work
EMICl–0.198FeCl$_3$–0.198FeCl$_2$	130	1.32	203.83	154	This work
EMICl–0.5AlCl$_3$	25	1.230	213.29	173.4	[26]
EMICl–AlCl$_3$	25	1.290	279.96	217.0	[26]
EMIBF$_4$	26	1.240	197.97	159.7	[27]
EMIPF$_6$	26	1.460	256.13	175.4	[27]

[a] Per 1 mol of EMI$^+$ (g (mol-EMI$^+$)$^{-1}$).

[b] Per 1 mol of EMI$^+$ (cm^3(mol-EMI$^+$)$^{-1}$).

respectively. The volume of the melt per 1 mol of EMI$^+$, V_{EMI^+}, was in the range from 150 to 170 cm^3 (mol-EMI$^+$)$^{-1}$ and almost independent of the composition, as listed also in Table 2. In addition, the V_{EMI^+} values are close to those in EMICl–AlCl$_3$ ($X_{AlCl_3} = 0.333$), EMIBF$_4$ and EMIPF$_6$ systems, suggesting that V_{EMI^+} is not effected significantly by coexisting anions in the melts. Consequently, the concentration of the halogenated complex anion of the metal in basic EMICl–MX$_n$ ($X_{MX_n} < 0.5$) system is estimated to be less than 5.0–6.5 mol dm^{-3}, assuming that the halogenated complex has almost identical size to the chlorocomplex anions of aluminum or iron. Therefore, the highest discharge or charge capacity per unit volume in binary EMICl–MX$_n$ ($X_{MX_n} < 0.5$) system is expected to reach at ~170 Ah dm^{-3} for one-electron reaction, although the capacity per unit weight is as low as ~60 Ah kg^{-1} in EMICl–FeCl$_2$–FeCl$_3$ ($X_{FeCl_2} = X_{FeCl_3} = 0.167$) molten salt system for example.

4. Conclusion

Combined with another proper redox couple, the EMICl–FeCl$_2$–FeCl$_3$ molten salt system may be utilized in a rechargeable redox battery. For example, when sodium chloride/sodium (mp = 7.8 °C) electrode is combined with this EMICl–FeCl$_2$–FeCl$_3$ molten salt, a high energy density per unit volume may be expected. Since Na(I)/Na couple in EMICl–AlCl$_3$ system has the formal potential of −2.15 V at room temperature [28], the electromotive force of ~2 V can be expected for the Na/EMICl–FeCl$_2$–FeCl$_3$ battery. This battery may have the advantage of a low operation temperature and a long cycle life against Na–S and Zebra cells. On the other hand, the EMICl–FeCl$_2$–FeCl$_3$ molten salt system itself is not necessarily suitable for the half-cell solution of the redox flow batteries presupposing the circulation of the half-cell solutions since the operation temperature must be higher than 110 °C. Thus, for this purpose, it is necessary to dilute the EMICl–FeCl$_2$–FeCl$_3$ molten salt system with other room temperature ionic liquids or aprotic organic solvents.

Although there are several problems to be solved, such as handling of hygroscopic chloride salts, low conductivity, high viscosity, and so on, the redox reactions in the similar molten salt systems, consisting of organic and transitionmetal chlorides, are expected to be utilized for new rechargeable batteries having high energy density and long cycle life.

Acknowledgements

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