ELECTROCHEMICAL BEHAVIOR OF IRON AND SEVERAL IRON COMPLEXES IN HYDROPHOBIC ROOM TEMPERATURE MOLTEN SALTS

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ABSTRACT

The electrochemical behavior of Fe(III)/Fe(II), FeCp2+/FeCp2, FeCl4+/FeCl42-, FeBr4-/FeBr42- and Fe(CN)63-/Fe(CN)64- couples in 1-n-butyl-1-methylpyrrolidinium bis(trifluoromethanesulfone) imide (BMPTFSI) room-temperature molten salt was studied by means of cyclic voltammetry. The electrode reaction of Fe(III)/Fe(II) on a platinum electrode was quasi-reversible due to the slow electron transfer while those of other iron complex couples were reversible. The slow electron transfer of the Fe(III)/Fe(II) couple may be related to the strong interaction of the Fe(III)/Fe(II) redox center with surrounding bulky TFSI- anions. Each iron complex couple showed its own redox potential, indicating the ligands of Cp*, Cl-, Br- and CN- are not replaced with TFSI- having a small donor number. The electrochemical behavior of Fe(CN)63-/Fe(CN)64- couples was also investigated in several molten salts which had different organic cations. The redox potential seems to be affected by the acceptor property of the organic cation.

INTRODUCTION

Room temperature molten salt (RTMS) systems containing bis(trifluoromethane-sulfone)imide (TFSI-) are attractive electrochemical reaction media, not only because they have many advantages common to RTMSs, such as wide electrochemical potential window, high ionic conductivity, high thermal stability and negligible vapor pressure, but also because they are hydrophobic and stable against moisture (16). Thus, TFSI- based RTMS systems are expected to be used for various practical applications, such as batteries, electroplating, chemical and electrochemical syntheses.

We have so far investigated the electrochemical reaction of samarium, europium and ytterbium in TFSI- based RTMSs (7). In case of Yb(III)/Yb(II), the cyclic voltammetric data revealed that the electrode reaction was quasi- or ir-reversible and the diffusion coefficients of related species were as low as ~10^-8 cm^2 s^-1. The low mobility suggests that they form some complex or have strong coulombic interaction with TFSI- anion. The donor number of BMPTFSI was estimated as ~7 based on the known correlation between the donor number and the polarographic halfwave potentials of Sm(III)/Sm(II), Eu(III)/Eu(II) and Yb(III)/Yb(II). The donor number of BMPTFSI is lower than that of other solvents.

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The redox couple of YbCp$_3$/[YbCp$_3$]$^-$ in BMPTFSI, on the other hand, showed reversible kinetics. The relatively large diffusion coefficient of YbCp$_3$ suggested that it has no strong interaction with other species in this BMPTFSI system. Thus, it is considered that the complex formation of a transition metal species in RTMSs affects its redox processes.

In the present study, the electrochemical behavior of several iron complexes in this melt was compared with that of ligand-free iron species.

**EXPERIMENTAL**

**Synthesis**

1-Ethyl-3-methylimidazolium bromide (EMIBr), 1-ethyl-2,3-dimethylimidazolium bromide (EDMIBr) were prepared by the reaction of 1-methylimidazole (Tokyo Kasei) and 1,2-dimethylimidazole (Tokyo Kasei) with ethyl bromide (Tokyo Kasei) at room-temperature, purified by recrystallization and finally dried under vacuum at 80°C for 12 hours. No impurity was detected by $^1$H-NMR. 1-n-Butylpyrrolidinium bromide (BMPBr) were prepared by the reaction of 1-methylpyrrolidine (Tokyo Kasei) and n-butyl bromide (Tokyo Kasei) as the same way of EMIBr and EDMIBr. 1-n-Butylpyridinium chloride (BPCl, Tokyo Kasei) and trimethyl-n-hexylammonium (TMHABr, Tokyo Kasei) was used as supplied. EMITFSI, EDMITFSI, BMPTFSI, BPTFSI and TMHATFSI were obtained by interacting LiTFSI with equimolar EMIBr, EDMIBr, BMPBr BPCl and TMHABr, respectively, in water at room temperature. These TFSI salts were extracted into dichloromethane and then vacuum dried for 1 day in at 120°C for 1 day.

Fe(TFSI)$_2$ salt was prepared by reacting Fe metal with HTFSI aqueous solution at 80 °C under agitation, followed by evaporation and vacuum drying at 200 °C for 48 hours. The product was confirmed by the UV-visible spectroscopy with the 1,10-phenanthroline for the probe and by the electrochemical methods.

Hexacyanoferric(III) acid (H$_3$Fe(CN)$_6$) was prepared by passing a aqueous solution of K$_3$Fe(CN)$_6$ through a cation-exchange column in the hydrogen form. The aqueous solution of the hydroxides of the organic cation, AOH (A = BP, EMI, EDM, BMP, TMHA), was prepared from their halides by passing through an anion-exchange column in the hydroxyl form. Finally, A$_3$Fe(CN)$_6$ was prepared by the neutralization of the corresponding hydroxide with H$_3$Fe(CN)$_6$ to pH of 7.0. The solution was evaporated under vacuum at room-temperature. The purity of these products was checked over by means of UV-visible spectroscopy and $^1$H-NMR. Almost all of these procedures were carried out in darkness under nitrogen atmosphere.

Anhydrous iron dibromide (FeBr$_2$, Soekawa Chemicals) and Iron dichloride (FeCl$_2$, Soekawa Chemicals) were used as supplied.

**Measurements**

All the electrochemical measurements were performed in an argon-filled glove box.
using a computerized potentio/galvanostat (Hokuto Denko, HZ-3000). A glassy carbon or a platinum disk was used as the working electrode. Platinum wire was used as a counter electrode. A silver wire immersed in a 0.1 mol dm\(^{-3}\) Ag(CF\(_3\)SO\(_3\))/EMITFSI was employed as the reference electrode. The reference electrode solution was separated from the main electrolyte by a Vycor glass.

RESULTS AND DISCUSSION

Electrode reaction of Fe in BMPTFSI

An divalent iron salt, Fe(TFSI\(_2\)), dissolved in BMPTFSI at room-temperature to give a pale brown solution. Figure 1(a) shows the cyclic voltammograms (CVs) of a Pt electrode in BMPTFSI containing 0.1 mol dm\(^{-3}\) Fe(TFSI\(_2\)). Two anodic current peaks were observed at +1.1 and -0.5 V, whereas two cathodic peaks appeared at +1.0 and -2.0 V. The electrodeposition of metallic Fe was confirmed after the potentiostatic cathodic reduction at -2.0 V. The anodic peak around -0.5 V was attributed to the anodic oxidation of metallic Fe. Another anodic peak around +1.1 V was ascribed to the oxidation of Fe(II), since the peak was observed only in the presence of Fe\(^{2+}\). Hence, the cathodic peak at +1.0 V was due to the reduction of Fe(III) formed during the preceding anodic scan.

The CVs of a Pt electrode in BMPTFSI containing 0.1 mol dm\(^{-3}\) Fe(TFSI\(_2\)) at various scan rates were shown in Fig. 1(b). The ratio of the anodic and cathodic peak current density, \(j_{\text{PA}}/j_{\text{PC}}\), increased with decreasing the scan rate, \(v\), and the separation between the cathodic and anodic peak potential, \(AE_{\text{pp}}\), exceeded 100 mV even for a low \(v\) of 1.0 mV s\(^{-1}\). These facts indicated that the Fe(III)/Fe(II) redox reaction should be regarded as quasi- or ir-reversible due to the slow electron transfer. The irreversible kinetics of the Fe(III)/Fe(II) couple may be explained by shielding the redox center of Fe(III)/Fe(II) with bulky TFSI\(^-\) anions, i.e., by the formation of a kind of complex of TFSI\(^-\) anions with Fe\(^{3+}\) and Fe\(^{2+}\) cations just like as found for lanthanide species (7).

The chronoamperometry (CA) for the oxidation of Fe(II) to Fe(III) in BMPTFSI was investigated at a Pt electrode in order to estimate the diffusion coefficient, \(D\), of the Fe(II) species as calculated from Cottrell equation

\[
j(t) = \frac{nFD^{1/2}C^*}{\pi^{1/2}t^{1/2}}\]  

where \(j\) is the current density, \(t\) is the time, \(C^*\) is the bulk concentration of the reactant, and \(n\) is the number of transferred electrons. The obtained CA data gave the \(D\) value of 9.7×10\(^{-8}\) cm\(^2\) s\(^{-1}\) for the Fe(II) species in BMPTFSI.

Fe complexes

FeBr\(_3\) dissolved readily in BMPTFSI at room-temperature to give an orange solution. Figure 2(a) compares the CVs of a Pt electrode in BMPTFSI solutions containing FeBr\(_3\) and BMPBr at different molar ratios. In the absence of BMPBr, two
pairs of redox peaks appeared at about $-0.6$ V vs. Ag/Ag(I), suggesting the existence of two different species of Fe(III). The electrodeposition of metallic iron occurred at $-2.0$ V. On the other hand, the redox peaks around $-0.6$ V appeared only in a 1:1 mixed solution of FeBr$_3$ and BMPBr, where FeBr$_4^{-}$ probably forms in BMPTFSI. The formation of FeBr$_4^{-}$ was also confirmed by UV-visible spectroscopy. The CV curves in a 0.1 mol dm$^{-3}$ FeBr$_4$/BMPTFSI solution at various scan rates were compared in Fig. 2(b). $\Delta E_p$ at $v = 1.0$ mV s$^{-1}$ was close to 60 mV as expected theoretically for a one electron reversible charge transfer at this temperature. In contrast to the Fe(III)/Fe(II) couple, the electrode reaction of the FeBr$_4^{-}$/FeBr$_4^{2-}$ couple is reversible probably because the redox center is surrounded by bromide ions, which are much smaller than TFSI$^-$. By analyzing the CA data during the reduction of FeBr$_4^{-}$ to FeBr$_4^{2-}$, the diffusion coefficient of FeBr$_4^{-}$ was found to be $1.1 \times 10^{-7}$ cm$^2$ s$^{-1}$ in BMPTFSI.

Figure 3 compares the typical CVs of a Pt electrode in BMPTFSI containing 0.012 mol dm$^{-3}$ FeCp$_2$, 0.1 mol dm$^{-3}$ FeCl$_4^-$ (equimolar amounts of FeCl$_3$ and BMPCl), 0.1 mol dm$^{-3}$ FeBr$_4^{-}$ or 0.1 mol dm$^{-3}$ BMP$_3$Fe(CN)$_6$. The separation between the anodic and cathodic peaks for these couples was approximately 60 mV, which was the theoretical value for a reversible one electron transfer reaction at 25°C. The redox potentials of Fe(III)/Fe(II), FeCp$_2^{+}$/FeCp$_2$, FeCl$_4^-$/FeCl$_4^{2-}$, FeBr$_4^{-}$/FeBr$_4^{2-}$ and Fe(CN)$_6^{3-}$/Fe(CN)$_6^{4-}$ were located at $+1.1$, $-0.4$, $-0.4$, $-0.6$ and $-1.5$ V, respectively. Since these iron complexes showed their characteristic redox potentials, the ligands, Cp, Cl, Br and CN$, seem to stay stable within the innermost sphere of the complex ions and not to be replaced with TFSI$^-$ having a small donor number (7, 8). The redox potential of these complexes Fe(III)/Fe(II) couples were lower than that of bare Fe(III)/Fe(II) probably due to the decreased free enthalpy (the increased stabilization energy) by complex formation. In other words, the bare Fe(III)/Fe(II) couple has a high redox potential owing to the small donor number of TFSI$^-$. The diffusion coefficient of Fe(II), FeCp$_2$, FeCl$_4^-$, FeBr$_4^{-}$ and Fe(CN)$_6^{3-}$ in BMPTFSI determined by CA methods was listed in Table 1 in addition to their Stokes radius, $a$, calculated by the following relation

$$D \eta T = k / 6 \pi a$$  \hspace{1cm} [2]$$

where $\eta$ is the viscosity, $T$ is the absolute temperature, and $k$ is the Boltzmann constant. The $\eta$ value of each solution was measured by the oscillational viscometer. In case of the anionic species, the diffusion coefficients in BMPTFSI varied as follows.

FeCp$_2$ > FeCl$_4^-$, FeBr$_4^{-}$ > Fe(CN)$_6^{3-}$

It seems that the diffusion of an anionic species in BMPTFSI becomes slower as the charge of the species increases. The mobility of Fe(CN)$_6^{3-}$ is lower than FeCl$_4^-$ or FeBr$_4^{-}$ probably because the coulombic interaction of BMP$^+$ with Fe(CN)$_6^{3-}$ is stronger than those with FeCl$_4^-$ or FeBr$_4^{-}$.  

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Table 1 Diffusion coefficient \( (D) \), viscosity \( (\eta) \) and the Stokes radius \( (a) \) for iron and iron complexes in BMPTFSI at 25 °C.

| Species      | \( 10^5 D \) / cm\(^2\) s\(^{-1} \) | Viscosity \( (\eta) \) / mPa s | \( a \) / nm |
|--------------|----------------------------------|-------------------------------|--------------|
| Fe(II)       | 0.97                             | 111                           | 0.20         |
| FeCp\(_2^\)  | 3.3                              | 70                            | 0.10         |
| FeCl\(_4^\)  | 1.1                              | 95                            | 0.21         |
| FeBr\(_4^\)  | 0.97                             | 107                           | 0.21         |
| Fe(CN)\(_6^3^-\) | 0.53                         | 138                           | 0.30         |

Figure 4 shows the \(^1\)H-NMR spectra of BMPTFSI in the absence or presence of BMP\(_3^\)Fe(CN)\(_6^\). All the peaks assigned to hydrogen atoms in BMP\(^+\) were shifted to lower field in the presence of BMP\(_3^\)Fe(CN)\(_6^\). This shift may be ascribed to the change in the intermolecular charge density arrangement due to the outer-sphere coordination, as follows.

Outer-sphere effects on the electrode reaction in RTMS

The A\(_3^\)Fe(CN)\(_6^\)/ATFSI (A = BP, EMI, EDMI, BMP, TMHA) solutions were prepared in order to study the effect of the cations on the redox potentials. BMP\(_3^\)Fe(CN)\(_6^\) and BP\(_3^\)Fe(CN)\(_6^\) were soluble in BMPTFSI and BPTFSI, respectively. EMI\(_3^\)Fe(CN)\(_6^\) and TMHA\(_3^\)Fe(CN)\(_6^\) were less soluble (less than 0.02 mol dm\(^{-3}\)) in EMITFSI and TMHATFSI, respectively. On the other hand, the solubility of EDMI\(_3^\)Fe(CN)\(_6^\) in EDMITFSI was very low (less than 0.005 mol dm\(^{-3}\)). Thus, the saturated solutions of EMI\(_3^\)Fe(CN)\(_6^\)/EMITFSI, EDMI\(_3^\)Fe(CN)\(_6^\)/EDMITFSI and TMHA\(_3^\)Fe(CN)\(_6^\)/TMHATFSI were used for the electrochemical measurements.

Figure 5 shows the CVs of a Pt electrode in these solutions. The potential was represented against the redox potential of the FeCp\(_2^\)/FeCp\(_2^+\) (= Fe/Fc\(^+\)) couple, which was used as an internal standard of the electrode potential (9). The redox reaction Fe(CN)\(_6^3^-\)/
Fe(CN)$_{6}^{4-}$ couples were observed at -0.68, -0.74, -0.74, -1.00 and -1.03 V vs. Fe/Fe$^+$ in EMITFSI, TMHATFSI, BPTFSI, EDMITFSI and BMPTFSI, respectively. In these systems, it is apparent that the redox potential of Fe(CN)$_{6}^{3-}$/Fe(CN)$_{6}^{4-}$ depends on the organic counter cation. This result is due to the fact that there is the outer-sphere effects on this electrode reaction in RTMS, which is due to the difference in the interaction between Fe(CN)$_{6}^{3-}$ and the counter cation.

The redox potential of Fe(CN)$_{6}^{3-}$/Fe(CN)$_{6}^{4-}$ has often been used as the index for the acceptor number (AN) of the medium(10). The solvent effect on this redox system lead to a shift of half-wave potentials to more positive values with increasing acceptor properties of the solvent. The relationship between the ANs and the redox potential of Fe(CN)$_{6}^{3-}$/Fe(CN)$_{6}^{4-}$ vs. Fe/Fe$^+$ is shown in Fig. 6. According to this relationship, the ANs of EMITFSI, EDMITFSI, BPTFSI, TMHATFSI and BMPTFSI was estimated as listed in Table 2.

Acceptor properties of the series of TFSI-based RTMS have been already reviewed by the groups of Gordon(13), Bartsch(14) and Matsumoto(15). They determined the the Dimroth-Reichardt $E_T$(30) values by the absorption spectra using the pyridinium-$N$-phenol betaine as the probe. The ANs of RTMSs can be estimated from $E_T$(30) values and listed in Table 2. The ANs estimated in this study is roughly consistent with those from $E_T$(30) values.

Table 2 ANs of the series of TFSI-based RTMSs.

| RTMS     | ANs in this study | ANs reported | Ref. |
|----------|-------------------|--------------|-----|
| EMITFSI  | 42 ± 6            | 34 ± 10      | 15  |
| EDMITFSI | 33 ± 6            | 25 ± 10      | 15  |
| BPTFSI   | 39 ± 6            | -            |     |
| BPBF$_4$ | -                 | 10 ± 10      | 16  |
| TMHATFSI | 39 ± 6            | -            |     |
| BMPTFSI  | 32 ± 6            | 24 ± 10      | 15  |

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Figure 1. (a) Typical CVs obtained at a Pt electrode in BMPTFSI with (—) and without (-----) 0.1mol dm$^{-3}$ Fe(TFSI)$_2$ at 25°C. Scan rate : 10 mV s$^{-1}$. (b) CVs for the electrode reaction of Fe$^{3+}$/Fe$^{2+}$ at various scan rates.

Figure 2. (a) CVs of a Pt electrode in BMPTFSI solutions containing FeBr$_3$/BMPBr at the ratios of 1/0 (-----) and 1/1(—). The total Fe concentration : 0.1 mol dm$^{-3}$. Scan rate : 10 mV s$^{-1}$. (b) CVs of a Pt electrode in BMPTFSI containing 0.1 mol dm$^{-3}$ Fe(TFSI)$_3$ at various scan rates.
Figure 3. CVs of a Pt electrode in BMPTFSI containing 0.012 mol dm$^{-3}$ FeCp$_2$ and 0.1 mol dm$^{-3}$ Fe(TFSI)$_2$, FeCl$_4^-$, FeBr$_4^-$ and Fe(CN)$_6^{3-}$.

Figure 4. $^1$H-NMR spectra of (a) (BMP)$_3$Fe(CN)$_6$/BMPTFSI solution and (b) BMPTFSI. TMS for external standard.
Figure 5. CVs of a Pt electrode in BMPTFSI containing (BP)$_3$Fe(CN)$_6$, (EMI)$_3$Fe(CN)$_6$, (EDMI)$_3$Fe(CN)$_6$, (BMP)$_3$Fe(CN)$_6$ and (TMHA)$_3$Fe(CN)$_6$, at 25°C.

Figure 6. Relationship between the half-wave potential of the reduction of Fe(CN)$_6^{3-}$/Fe(CN)$_6^{4-}$ vs. that of Fc/Fc$^+$ in various solvents and the acceptor numbers of these solvents.