

Electrochemical Behavior of Iron and Several Iron Complexes in Hydrophobic Room Temperature Molten Salts

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INTRODUCTION

Room temperature molten salts (RTMS) containing bis (trifluoromethane-sulfone) imide anions (TFSI) are attractive electrochemical reaction media since they are not only moisture-stable but also hydrophobic in addition to the various common advantages as RTMS systems, such as wide electrochemical potential window, high ionic conductivity, high thermal stability and negligible vapor pressure. Thus, these TFSI-based RTMS can be applicable to various practical uses, such as batteries, electroplating, chemical and electrochemical syntheses.

We have investigated the electrochemical reaction of various lanthanides in TFSI-based RTMSs.¹ The redox reaction of $\text{Yb}^{3+} / \text{Yb}^{2+}$ was quasi-reversible probably due to their strong interaction with TFSI, whereas cyclopentadienyl ytterbium (YbCp_3) showed reversible behaviors. Thus, 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) and 1-*n*-butylpyrrolidinium bromide (BMPBr) were prepared as described previously.¹ Trimethyl-*n*-hexylammonium (TMHABr) was used as supplied. EMITFSI, BMPTFSI and TMHATFSI were obtained by interacting LiTFSI with equimolar EMIBr, BMPBr 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.

An iron-TFSI 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. $\text{A}_3\text{Fe}(\text{CN})_6$ (A = EMI, BMP and TMHA) was obtained as described in a literature.²

Measurements. All the electrochemical measurements by a computerized system were performed in an argon-filled glove box. A glassy carbon rod or a platinum disk was used as the working electrode against the Pt counter electrode. A silver wire immersed in a 0.1 M $\text{Ag}(\text{CF}_3\text{SO}_3) / \text{EMITFSI}$ was employed as the reference electrode after separating the silver salt from the main electrolyte by a Vycor glass.

RESULTS AND DISCUSSION

Figure 1 shows the typical cyclic voltammograms for $\text{Fe}^{3+}/\text{Fe}^{2+}$, $\text{Fe}(\text{Cp})_2^+/ \text{Fe}(\text{Cp})_2$, $\text{FeBr}_4^+/ \text{FeBr}_4^-$ and $\text{Fe}(\text{CN})_6^{3+}/ \text{Fe}(\text{CN})_6^{4-}$ couples in BMPTFSI on a Pt electrode. The potential difference between anodic and cathodic peaks, ΔE_p , for $\text{Fe}^{3+}/\text{Fe}^{2+}$ exceeded 150 mV, suggesting quasi- or ir-reversible kinetics due to the slow electron transfer. ΔE_p for the other couples, in contrast, was close to 60 mV as expected theoretically for a reversible reaction at 25 °C. The irreversibility of the $\text{Fe}^{3+}/\text{Fe}^{2+}$ couple may be related to the direct interaction of the $\text{Fe}(\text{III})/\text{Fe}(\text{II})$ redox center with surrounding bulky TFSI anions, that is, a kind of complex formation of Fe^{3+} and Fe^{2+} cations with TFSI anions. Because the introduced iron complexes showed their characteristic redox potentials, the ligands of Cp, Br and CN seem to stay stable and are not replaced with TFSI having a small donor number. The redox potential of $\text{Fe}^{3+}/\text{Fe}^{2+}$ was high compared with other iron complexes probably due to the small donor number of TFSI, which has been suggested in the electrochemical study of lanthanide species.¹ Within the potential window of BMPTFSI, Fe^{2+} could be reduced to metallic Fe whose reoxidation peak appeared at around -0.3 V.

The redox potential of $\text{Fe}(\text{CN})_6^{3+}/\text{Fe}(\text{CN})_6^{4-}$ has often been

used as the index for the acceptor number of the medium.³ In a series of TFSI-based systems, the redox potential of $\text{Fe}(\text{CN})_6^{3+}/\text{Fe}(\text{CN})_6^{4-}$ depends on the kind of organic counter cation as in Fig. 2, where the potential was referred to the Fc/Fc^+ couple in the same media. After plotting the actually observed potentials in the present work on this dotted curve, the acceptor numbers of BMPTFSI, TMHATFSI and EMITFSI could be evaluated as about 32, 38 and 42, respectively.

ACKNOWLEDGEMENTS

This study was supported by a grant-in-aid for scientific research from the Ministry of Education, Culture, Sports, Science and Technology of Japan and by a JSPS Research Fellowships for Young Scientists.

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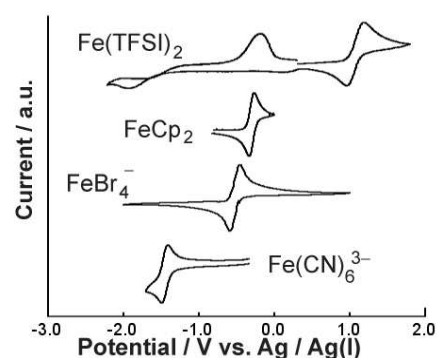


Fig. 1 CVs of a platinum electrode in BMPTFSI containing $\text{Fe}(\text{TFSI})_2$, FeCp_2 , FeBr_4^- and $\text{Fe}(\text{CN})_6^{3-}$.

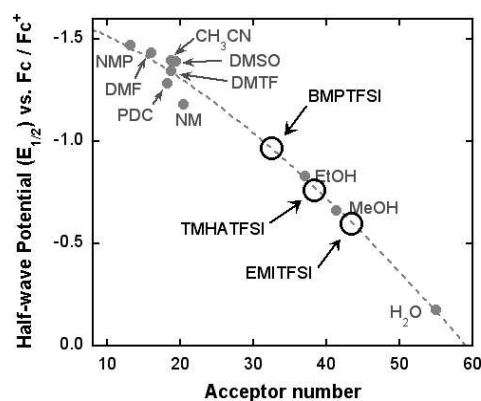


Fig. 2 Relationship between the half-wave potential of the reduction $\text{Fe}(\text{CN})_6^{3-} / \text{Fe}(\text{CN})_6^{4-}$ vs. that of Fc / Fc^+ in various solvents and the acceptor numbers of these solvents.