

SUMMARY OF Ph.D. DISSERTATION

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<p>Title</p> <p>The Electrochemical Behavior of Lanthanide and Iron Species in Hydrophobic Room-temperature Molten Salts</p>		
<p>Abstract</p> <p>Room-temperature molten salt (RTMS, often called as room-temperature ionic liquid) systems containing bis(trifluoromethylsulfonyl)imide (TFSI⁻) are attractive electrochemical reaction media, not only because they have many advantages common to RTMSs, such as wide electrochemical potential window, acceptable ionic conductivity, high thermal stability and negligible vapor pressure, but also because they are hydrophobic and stable against moisture. Thus, TFSI⁻-based RTMSs are expected to be used for various practical applications, such as batteries, electroplating, chemical and electrochemical syntheses. In order to apply the TFSI⁻-based systems for these practical purposes, however, it is necessary to investigate the chemical and electrochemical behavior of various species.</p> <p>The electrochemical behavior of lanthanides (Ln = Sm, Eu and Yb) was investigated in BMPTFSI (BMP⁺ = 1-<i>n</i>-butyl-1-methylpyrrolidinium) containing Ln(TFSI)₃. The redox reactions of Sm(III)/Sm(II), Eu(III)/Eu(II) and Yb(III)/Yb(II) were observed at -1.6, -0.3 and -1.0 V vs. Ag/Ag(I), respectively. In all cases, the electrode reactions were found to be quasi- or irreversible by the cyclic voltammetry. The diffusion coefficients of these lanthanides were estimated to be ~10⁻⁸ cm² s⁻¹ by chronoamperometry and chronopotentiometry, indicating that the mobility of these species is rather low probably due to the complex formation or the strong coulombic interaction with TFSI⁻. On the other hand, the redox reaction of YbCp₃/YbCp₃⁻ (Cp⁻ = cyclopentadienyl) in BMPTFSI was reversible, suggesting that the formation of a small complex species makes the redox center close to the electrode surface and leads to the fast electron transfer. According to the redox potentials of Ln(III)/Ln(II), it was found electrochemically that the donor property of TFSI⁻-based RTMS was lower than that of other conventional solvents.</p> <p>The electrode reaction of Fe(III)/Fe(II) was studied in BMPTFSI containing Fe(TFSI)₂. The quasi-reversible kinetics of Fe(III)/Fe(II) couple and the low diffusivity of Fe(II) are probably attributed to the interaction between these metal species and TFSI⁻. On the other hand, the electrochemical behavior of FeCp₂⁺/FeCp₂, FeCl₄⁻/FeCl₄²⁻, FeBr₄⁻/FeBr₄²⁻ and Fe(CN)₆³⁻/Fe(CN)₆⁴⁻ couples was investigated in BMPTFSI and TFSI⁻-based RTMSs with other quaternary ammonium cations. The cyclic voltammetric data indicated that these complexes were stable in BMPTFSI and that the redox reactions between the trivalent and divalent iron complexes are electrochemically reversible. The diffusion coefficients of these complexes were found to be affected by the size of the species and the viscosity of the RTMS. In addition, the redox potential of Fe(CN)₆³⁻/Fe(CN)₆⁴⁻ couple depended on organic cations reflecting the difference in the acceptor properties of the organic cations. The granular metallic Fe was electrodeposited from BMPTFSI containing Fe(TFSI)₂, while the film-like deposit was obtained with a additive, bipyridine. Both electrodeposits had low crystallinity, probably due to the inhibition of the crystal growth by the specific adsorption of BMP⁺.</p>		