

Electrochemical Behavior of Some Lanthanides in Imide Room Temperature Molten Salt Systems

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INTRODUCTION

Room temperature molten salt systems containing bis(trifluoromethanesulfone) imide (TFSI) are expected to be the alternative supporting electrolytes for electroplating and lithium rechargeable batteries because of their attractive characteristics, such as wide electrochemical potential window, high ionic conductivity, high thermal stability, negligible vapor pressure and hydrophobic nature. From these favorable properties, the redox flow batteries having high energy density may be also proposed by using the redox reactions of transition metals in the TFSI-based molten salt systems. However, few redox reactions of transition metals have been reported in the TFSI-based molten salt systems. In this study, the redox reactions of some lanthanides were examined as the candidates for the half cell reactions of the redox flow batteries using 1-ethyl-3-methylimidazolium and 1-n-butyl-1-methylpyrrolidinium bis(trifluoromethanesulfone) imide (EMITFSI and BMPTFSI) molten salt systems.

EXPERIMENTAL

BMPBr was prepared by the reaction of 1-methylpyrrolidine and n-butyl bromide (Tokyo Kasei) at room temperature for 6 hours. BMPBr was purified by recrystallization and dried under vacuum at 80°C for 12 hours. No impurity was detected by ¹H-NMR. The EMITFSI or BMPTFSI molten salt was prepared by interacting EMICI (Sanko Chemical Industry) or BMPBr with LiTFSI (3M) in water at room temperature, followed by extraction into dichloromethane and vacuum drying at 120°C for 1 day.¹⁾ The TFSI⁻ salts of lanthanides were prepared by the reaction of lanthanide oxides or carbonates with HTFSI aqueous solution with stirring at 80°C and dried under vacuum at 200°C for 48 hours.²⁾

All the electrochemical measurements were performed in argon-filled glove box (Miwa Seisakujyo, 1ADB-2+MM2-P15S). Electrochemical measurements were conducted with a computerized electrochemical measurement system (Hokuto Denko, HZ-3000). Glassy carbon and platinum were used as the working electrodes. Platinum was used as a counter electrode. The reference electrode consisted of a silver wire immersed in 0.1 M AgCF₃SO₃ / EMITFSI solution separated from the bulk solution with porous glass (Vycor).

RESULTS AND DISCUSSION

Eu(TFSI)₃ dissolved in both EMITFSI and BMPTFSI to give colorless solutions at room temperature. Figure 1 shows the cyclic voltammograms of a glassy carbon electrode in EMITFSI and BMPTFSI containing 100 mM Eu(TFSI)₃. A cathodic and an anodic current peak were observed at -0.5 and -0.1 V,

respectively, in each molten salt system. The cathodic current peak was ascribed to the reduction of Eu(III) to Eu(II) since no cathodic current was observed in the absence of Eu(TFSI)₃. The anodic current peak was assigned to the oxidation of Eu(II) formed during the preceding cathodic scan. The separation between the cathodic and anodic current peaks exceeded ~400 mV, indicating that the redox reaction of the Eu(III) / Eu(II) couple was irreversible electrochemically. The slow electrode kinetics may be due to the formation of some complexes of Eu(III) probably with TFSI⁻, which was suggested by UV-vis spectroscopy.

The further investigation of the electrochemical behavior of Eu and other lanthanides is under way.

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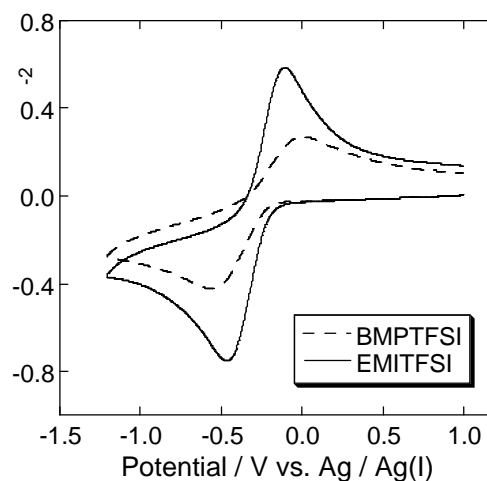


Fig. 1 Cyclic voltammograms at a glassy carbon electrode in EMITFSI and BMPTFSI containing 100 mM Eu(TFSI)₃; Scan rate : 20 mV s⁻¹.