Electrochemical Reduction of Oxygen in Some Hydrophobic Room Temperature Molten Salt Systems

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Introduction

Room temperature molten salt systems with bis(trifluoromethanesulfone)imide (TFSI) anion have high chemical and electrochemical stability, low volatility and incombustibility. In addition to these unique properties, they are not only stable against moisture but also immiscible with water.[1, 2] Thus, the TFSI-based molten salt systems are expected to be used for electrochemical processes conducted under the atmosphere. However, oxygen in the air may dissolve in the TFSI-base molten salt systems and affect electrochemical reactions to no small extent. On the other hand, the electrochemical behavior of oxygen is of importance in energy conversion and storage technology, especially for fuel cells and metal-air batteries. Thus, it is significant to clarify the electrochemical behavior of oxygen in the TFSI-based molten salt systems. In this study, the electrochemical reduction of oxygen was investigated in the TFSI-based molten salt systems having some different organic cations.

Experimental

1-butyl-1-methylpyrrolidinium bromide (BMPBr) was prepared by the reaction of 1-methylpyrrolidine and n-butyl bromide (Tokyo Kasei), purified by recrystallization and dried under vacuum. 1,2-dimethyl-3-propylimidazolium bromide (DMPIBr) was synthesized by the reaction of 1,2-dimethylimidazole with propyl bromide, followed by purification and vacuum drying. No impurity was detected in these compounds by ^{1}H-NMR. Anhydrous 1-ethyl-3-methylimidazolium chloride (EMICl, Sanko Chemical Industry) and trimehyl-n-hexylammonium bromide (TMHABr, Tokyo Kasei) were used as supplied. The TFSI-based molten salts were prepared by interacting the halides of the organic cations with LiTFSI (Stera Chemifa) in water at room temperature, followed by extraction into dichloromethane and vacuum drying.

All the hygroscopic reagents were handled in an argon-filled glove box (Miwa Seisakujyo, 1ADB-2+MM2-P15S). Electrochemical measurements were conducted with a potentio/galvanostat (Hokuto Denko, HABF-501) with a digital recorder. Platinum was used as a working and a counter electrode. The counter electrode was placed in a separated compartment with a glass filter. The reference electrode consisted of a silver wire immersed in 0.1 M $AgCF_3SO_3$ / EMITFSI solution separated from the bulk solution with porous glass (Vycor).

Results and Discussion

Figure 1 shows the cyclic voltammograms of a platinum electrode in EMITFSI after bubbling of argon and oxygen. An irreversible cathodic current below –1.5 V was observed after bubbling of oxygen while there was no electrolytic current within the sweep range after bubbling of argon. The cathodic current was ascribed to oxygen dissolved in EMITFSI, since the cathodic current was observed at the electrode immersed completely in the EMITFSI without three-phase interface.

The cyclic voltammograms of a platinum electrode in EMITFSI, DMPITFSI, TMHATFSI and BMPTFSI after saturation with oxygen were shown in Fig. 2. The anodic current peak corresponding to the reduction of oxygen was observed in both TMHATFSI and BMPTFSI. In the case of DMPITFSI, the anodic current peak was observed while its peak current density was smaller than that of the cathodic current peak. These results indicated that the reduced product of oxygen is more stable against aliphatic organic cations than aromatic ones.

The electrochemical reduction of oxygen in most anhydrous aprotic organic electrolyte systems leads to formation of superoxide anion, O_2^-, with one-electron transfer process, as follows:[3]

$$O_2 + e^- = O_2^- \qquad (1)$$

The same reaction is also expected to occur in the present TFSI-based molten salt systems. The superoxide is nucleophile and likely to attack the carbon atoms with low electron density. According to the *ab initio* MO calculation, the carbon atoms in the heterocycles of imidazoliums have positive charges and could be attacked by the superoxide. In contrast to aromatic organic cations, the superoxide is stable against aliphatic organic cations, which do not contain positively charged carbon atoms.

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References

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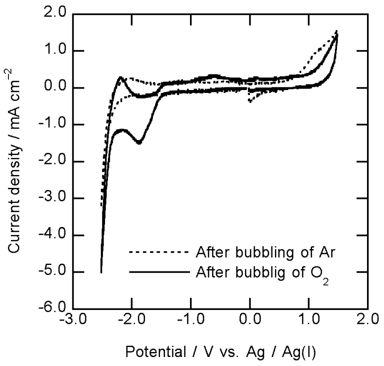

Fig. 1 Cyclic voltammograms of a platinum electrode in EMITFSI after bubbling of argon and oxygen at room temperature. Scan rate = 50 mV s^{-1}.

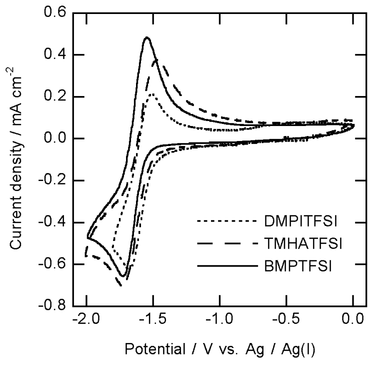

Fig. 2 Cyclic voltammograms of a platinum electrode in DMPITFSI, TMHATFSI and BMPTFSI after saturation with oxygen at room temperature. Scan rate = 50 mV s^{-1}.