Short communication

Lithium dope and undope reactions for tin in an ionic liquid electrolyte with some glymes

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A B S T R A C T

Lithium doped and undoped reactions for tin have been investigated in 1-butyl-1-methylpyrrolidinium bis(trifluoromethylsulfonyl)amide (BMPTFSA) containing 0.1 M LiTFSA with some glymes. Lithium doped and undoped for tin were found to be possible in the ionic liquid electrolyte in both absence and presence of glymes. The interfacial resistance for lithium doped and undoped reactions in the ionic liquid electrolyte was decreased by addition of 0.2 M glymes probably due to the coordination of the glymes to Li^+. It was suggested that the interfacial resistance is strongly affected by the coordination environment of Li^+ in the ionic liquid electrolyte.

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1. Introduction

There has been a growing demand to increase the safety of rechargeable lithium batteries that have been proposed for use in various power applications, such as hybrid and pure electric vehicles. Flammable organic electrolytes used in existing lithium-ion batteries may cause explosion and/or combustion in case of accidents. Therefore, employing non-flammable electrolytes is one of the effective measures for improving the safety of rechargeable lithium batteries. Ionic liquids have been investigated extensively as non-flammable electrolytes for rechargeable lithium batteries. Chloroaluminate ionic liquids have been studied at first [1–12]. However, the chloroaluminate ionic liquids having low melting points are only obtained with the aromatic cations, such as alkylated pyridinium and imidazolium, which are usually not stable against metallic lithium [1,2]. In addition, it has been known that the intercalation of the organic cations into graphite occurs in the absence of some additives, which forms passivation layer, often called as solid–electrolyte interphase (SEI) film [9–12]. Typical non-chloroaluminate ionic liquids based on bis(trifluoromethylsulfonyl)amide ($TFSA^-$) have been studied extensively for the electrolytes of rechargeable lithium batteries [13–34] since it is possible to obtain the ionic liquids having low melting points and acceptable conductivity with

the aliphatic organic cations, which are considered more stable against metallic lithium than the aromatic ones. However, some of the aliphatic cations are reported to be unstable against metallic lithium to form SEI film [18,19]. In addition, graphite is also not usable as anode materials in $TFSA^-$-based ionic liquids without additives due to the intercalation of the organic cations [27–31]. On the other hand, there are a few reports on lithium doped and undoped reactions for tin in these ionic liquids. Tin and its alloy anodes are expected to be the alternative anode materials of rechargeable lithium batteries since the specific capacity of tin is much higher than those of carbon-based materials. However, cycle performance of tin is known to be poor because of large volume change during charge–discharge cycle [35]. In the present study, the effect of some additives on the lithium doped and undoped reactions of a tin thin film electrode has been investigated in an electrolyte based on a hydrophobic ionic liquid, 1-butyl-1-methylpyrrolidinium bis(trifluoromethylsulfonyl)amide (BMPTFSA).

2. Experimental

BMPTFSA was purchased from Kanto Kagaku. The water content of BMPTFSA was less than 10 ppm. LiTFSA (Kanto Kagaku) was dissolved in BMPTFSA at a concentration of 1 M. Mono-glyme, diglyme, triglyme, and tetraglyme (Aldrich) were used as supplied. An organic electrolyte based on ethylene carbonate (EC) and dimethylcarbonate (DMC) containing 1 M $LiClO_4$ (Kishida Kagaku) was used as control. All the reagents were handled in

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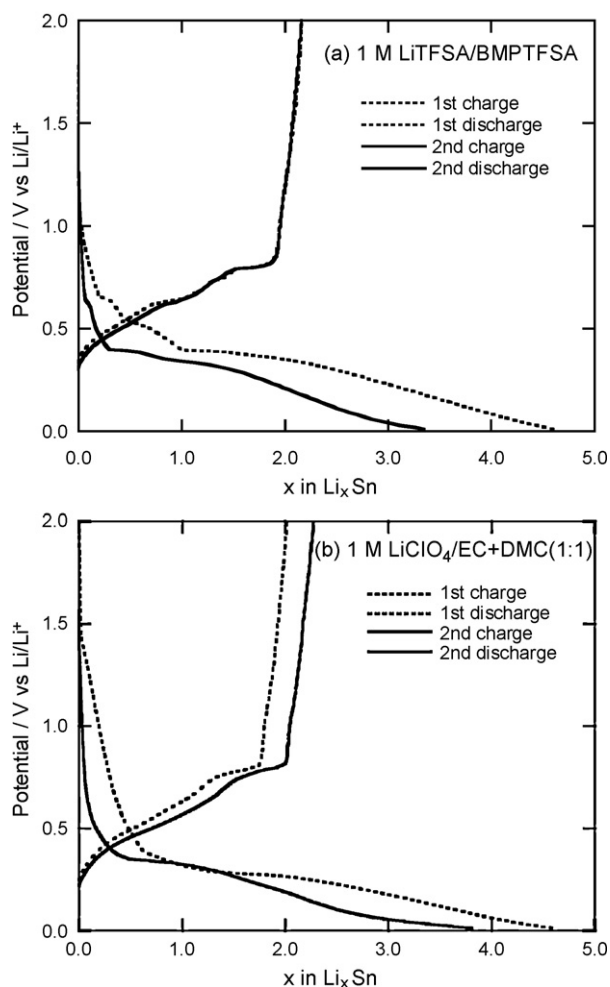E-mail address: katayama@applc.keio.ac.jp (Y. Katayama).

Fig. 1. Charge–discharge curves of a tin thin film electrode in (a) 1 M LiTFSA/BMPTFSA and (b) 1 M LiClO$_4$/EC + DMC (50:50 in vol.%) at 25 °C. Current density: 50 μA cm^{-2} (∼0.2C).

a glove box with a continuous gas purification apparatus (Miwa MFG Co. Ltd., DBO-1KP-KO2). A tin thin film electrode was prepared by electroplating on a copper substrate in a commercial tin plating bath (Meltex, SN-2650M). The copper substrate was degreased by electrolysis in an alkaline solution before electroplating. The thickness of the tin thin film was estimated to be 500 nm from the charge passed during electroplating. The electrochemical measurements were performed using an air-tight three-electrode beaker cell. The tin thin film electrode was used as the sample electrode. Lithium foil was used as a counter and a reference electrode. The electrochemical measurements were conducted with a potentiostat/galvanostat (Princeton Applied Research, PARSTAT2263) and a charge–discharge instrument (Hokuto Denko Corp., HJ-1001SM8). The impedance data were corrected at the rest potential with an amplitude of 10 mV.

3. Results and discussion

Fig. 1(a) shows the charge–discharge curves of a tin thin film electrode in 1 M LiTFSA/BMPTFSA. Some irreversible capacity was observed in the 1st cycle due to reduction of tin oxide on the electrode surface. The charge–discharge curves were similar to those in 1 M LiClO$_4$/EC + DMC shown in Fig. 1(b), indicating lithium doped and undoped reactions are possible in the ionic liquid electrolyte.
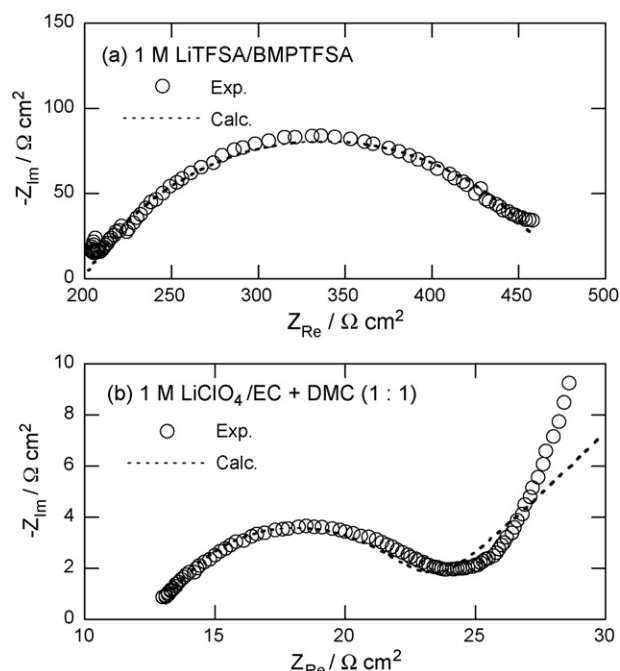

Fig. 2. Nyquist plots for a tin thin film electrode (LiSn) in (a) 1 M LiTFSA/BMPTFSA and (b) 1 M LiClO$_4$/EC + DMC at 25 °C.

Fig. 2 shows the Nyquist plots for the tin thin film electrode in the ionic liquid and the organic electrolyte. The composition of the tin alloy was LiSn for all the impedance measurements. A distorted semi-circle was obtained in the higher frequency range. The plots were fitted to a Randles-type equivalent circuit, as shown in Fig. 3. The solution resistance (R_{sol}) in the ionic liquid was larger than that in the organic electrolyte due to the low conductivity of the ionic liquid. It should be noted that the interfacial resistance (R_i) in the ionic liquid electrolyte was much higher than that in the organic electrolyte, indicating the reaction rate of lithium doped and undoped reactions in the ionic liquid electrolyte was much slower than that in the organic electrolyte. The slow electrode kinetics in BMPTFSA has been also reported for some outer-sphere electron transfer reactions [36,37] and electrodeposition of some metals [38–41]. Lithium doped and undoped reactions for tin are considered closely related to electrodeposition of metals. In case of electrodeposition of cobalt, it has been found that the over-potential of reduction of Co(II) to Co was reduced by addition of acetone, which is expected to coordinate Co^{2+} [40]. Based on these reports, the effect of addition of some glymes on the interfacial resistance for the tin thin film electrode was examined in the ionic liquid electrolyte. It has been reported that glymes coordinate Li$^+$ to form some complexes in some organic electrolytes [42]. Thus, formation of lithium–glyme complexes is also expected in the ionic liquid with addition of glymes. On the other hand, there has been
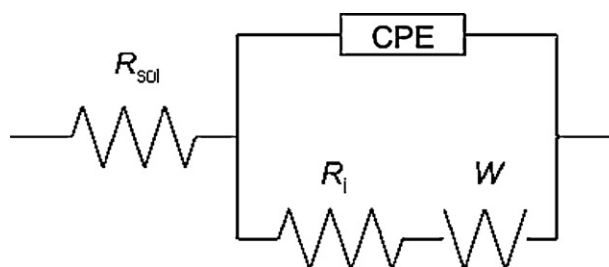

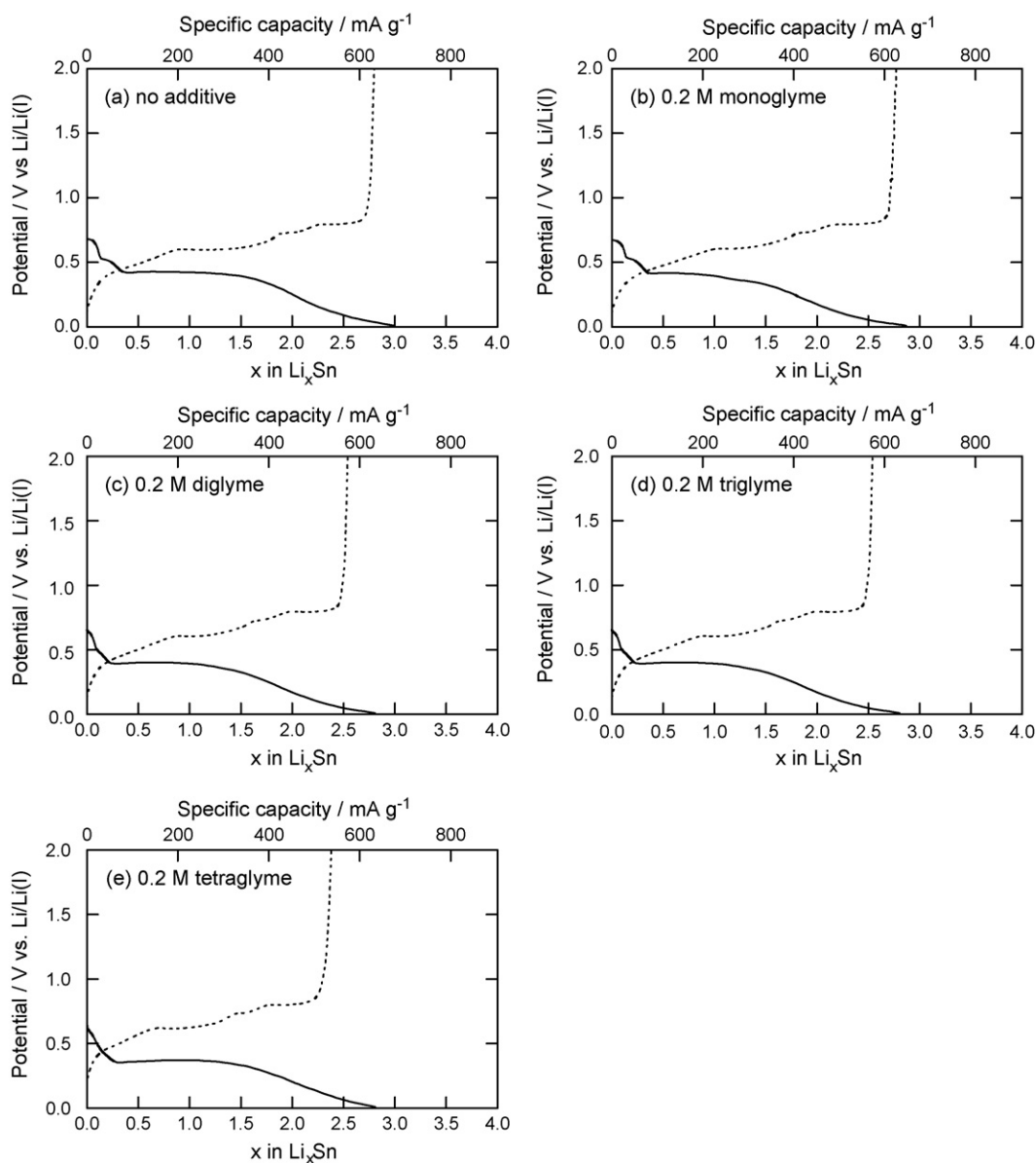**Fig. 3.** Equivalent circuit used for analyzing impedance data.

Fig. 4. Charge–discharge curves (2nd cycle) of a tin thin film electrode in (a) 1 M LiTFSA/BMPTFSA and 1 M LiTFSA/BMPTFSA containing 0.2 M (b) monoglyme, (c) diglyme, (d) triglyme, and (e) tetraglyme at 25 °C. Current density: 50 μA cm^{-2} (∼0.2C).

a report on lithium deposition and dissolution in the mixtures of some ionic liquids and glymes [43]. In this report, however, glymes should be regarded as a solvent since the amount of glymes was too much compared to the ionic liquids. In the present study, the concentrations of glymes were kept below that of LiTFSA.

Fig. 4 shows the charge–discharge curves of a tin thin film electrode in 1 M LiTFSA/BMPTFSA without and with 0.2 M glymes. The charge–discharge curves with glymes were close to those without glymes, indicating lithium doped and undoped reactions are possible in the ionic liquid electrolyte with glymes. On the other hand, the interfacial resistance was drastically decreased by addition of glymes according to the Nyquist plots shown in Fig. 5. The values of interfacial resistances are summarized in Fig. 6. It has been

reported that Li$^+$ is coordinated by TFSA$^-$ to form [Li(TFSA)$_2$]$^-$ in the ionic liquid [44,45]. In the presence of a glyme, TFSA$^-$ coordinating Li$^+$ is expected to be replaced by the glyme to form [Li(glyme)$_n$]$^+$. The number of glyme molecules coordinating Li$^+$ is considered unity for triglyme and tetraglyme and 2 or 3 for monoglyme and diglyme [42]. Therefore, the concentrations of lithium–glyme complexes ([Li(glyme)$_n$]$^+$) for triglyme and tetraglyme are expected to be higher than those for monoglyme and diglyme since the concentration of each glyme is fixed at 0.2 M. Although the detailed mechanism is unclear, the formation of lithium–glyme complex is expected to play an important role in reduction of the interfacial resistance in the ionic liquid electrolyte. Further investigation is under way.
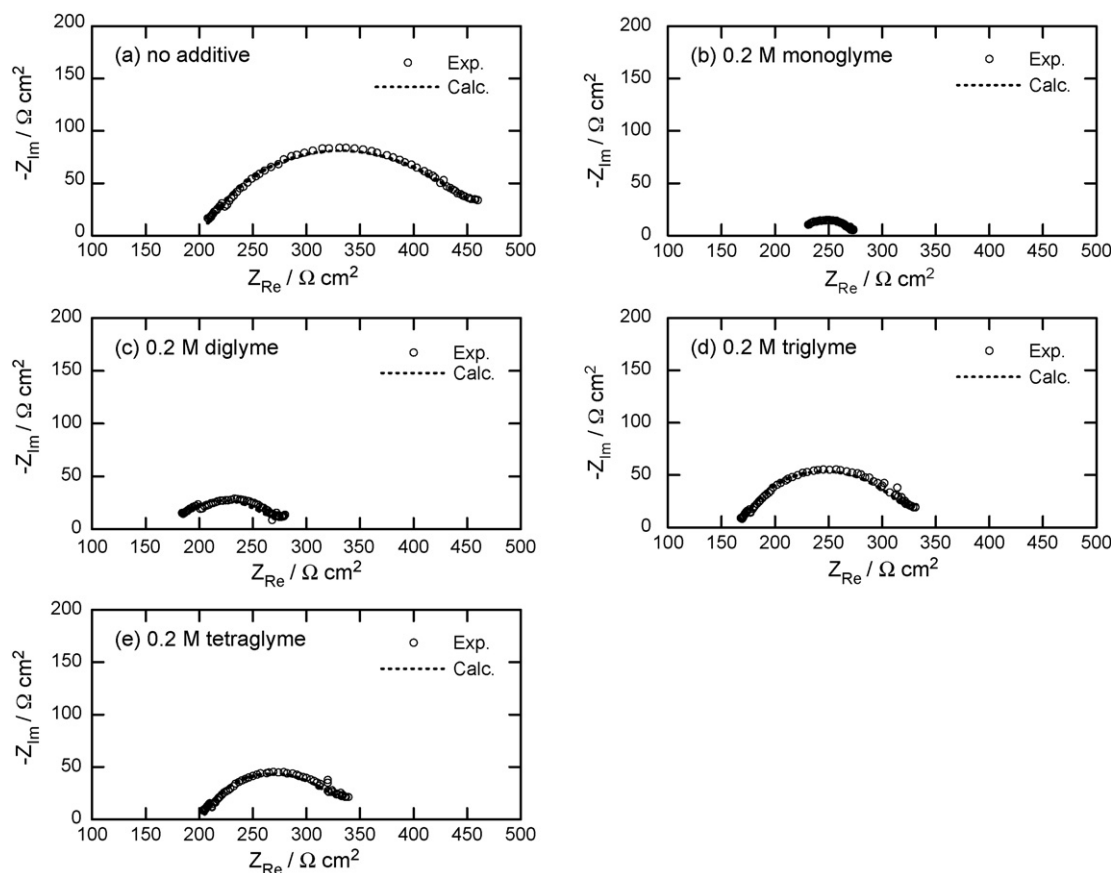
Fig. 5. Nyquist plots for a tin thin film electrode (LiSn) in (a) 1 M LiTFSA/BMPTFSA and 1 M LiTFSA/BMPTFSA containing 0.2 M (b) monoglyme, (c) diglyme, (d) triglyme, and (e) tetraglyme at 25 °C.
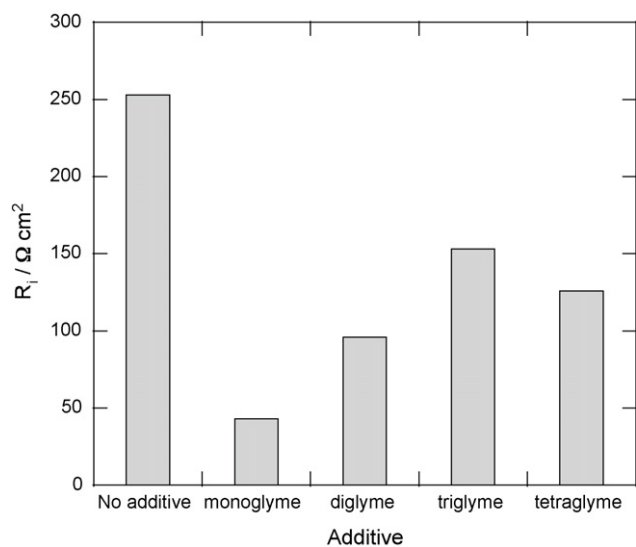

Fig. 6. Interfacial resistance for a tin thin film electrode (LiSn) in 1 M LiTFSA/BMPTFSA and 1 M LiTFSA/BMPTFSA containing 0.2 M monoglyme, diglyme, triglyme, and tetraglyme at 25 °C.

4. Conclusion

Lithium doped and undoped reactions for tin were found to be possible in 1 M LiTFSA/BMPTFSA. However, the interfacial resistance in the ionic liquid electrolyte was much larger than that in the organic electrolyte. The interfacial resistance could be reduced by addition of a small amount of glymes, suggesting the interfacial resistance is strongly affected by the coordination environment of Li$^+$ in the ionic liquid electrolyte.

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