Application of mix-salts composed of lithium borate and lithium aluminate in PEO-based polymer electrolytes

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Abstract

Mix-salts were prepared by mixing lithium borate (salt A or salt B) with lithium aluminate (salt C). Polymer electrolytes were prepared by dissolving lithium salt in PEO. Mix-salt polymer electrolytes exhibited higher ionic conductivities than pure-salt polymer electrolytes. The optimum-mixing ratio was investigated. Conductivity as high as $1 \times 10^{-4}\,\mathrm{S\,cm^{-1}}$ at $40\,^{\circ}\mathrm{C}$ was obtained for the optimized electrolyte system. A potential window of 4.3 V was determined for the mix-salt electrolyte. Good charge–discharge performance was observed for the mix-salt electrolyte composed cell, $\mathrm{LiNi_{0.8}Co_{0.2}O_2}$//salt A(3)/salt C(11.8) 2/1-PEO$_{22}$//Li.
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1. Introduction

Lithium ion batteries have been industrialized in 1990s for mobile applications with small size cells. However, they are not suitable to be applied in a large scale for vehicles until now, because flammable gas may be produced when the electrolyte decomposes at the carbon surface during cycling, especially in the case of batteries containing large amount of liquid electrolytes [1]. Therefore, lithium polymer battery received much attention due to its attractive properties of safety, ease of fabrication, high energy density. During recent two decades, many kinds of polymers like PEO, EO–PO copolymer, PVdF and PMMA have been reported as host polymers. Among them, PEO-based polymer electrolyte, which was first reported by Wright [2], has been regarded as the most promising material because of the high salt solubility and good ion prompting property of PEO. However, PEO-based polymer electrolytes exhibit acceptable conductivities only at high temperature (>60 °C) because PEO is easy to crystallize at low temperature [3,4]. It greatly restricts the application of such electrolytes. Many efforts have been focused on the depression of crystallinity and glass transition temperature

of PEO, such as the preparation of copolymers composed of short ethylene oxide (EO) chains and other monomers [5,6], blending PEO with ceramic fillers [7,8], and introduction of plasticizers [9,10]. Good effects were observed for these methods.

In this paper, we prepared several kinds of lithium salts, which contained short oligoether chains. Since the oligoether chain has a same structure as the polyethylene glycol ether, these salts were assumed to be able to work as plasticizers to PEO concomitantly. Pure-salt polymer electrolytes were obtained by dissolving the synthesized salts in PEO. Ionic conductivities of about $10^{-5}\,\mathrm{S\,cm^{-1}}$ at the room temperature were observed. It is still not enough for industry application. In order to further improve the performance of the electrolyte, lithium borate and lithium aluminate were first mixed and then were blended with PEO to get mix-salt polymer electrolytes. The electrochemical properties of these electrolytes were investigated.

2. Experimental

2.1. Preparation

LiAlH$_4$ (1.0 M solution in tetrahydrofuran (THF), Adrich), LiBH$_4$ (2.0 M solution in THF, Adrich),

pentafluorophenol (C$_6$F$_5$OH, Adrich), trifluoroacetic acid (CF$_3$COOH, Kanto Chemicals), and trifluoromethane-sulfonimide ((CF$_3$SO$_2$)$_2$NH, Aldrich) were used as supplied. Tri(ethylene glycol) monomethyl ether (TEGMME, Tokyo Kasei), poly(ethylene glycol) monomethyl ethers with average molecular weights of 350 and 550 (PEG-MME 350 (CH$_3$O(CH$_2$CH$_2$O)$_{7.2}$H) and PEGMME 550 (CH$_3$O(CH$_2$CH$_2$O)$_{11.8}$H)), poly(ethylene oxide) (PEO, Mw 5×10^6), lithium salts, LiNi$_{0.8}$Co$_{0.2}$O$_2$, acetylene black (AB) and solvents were rigorously dried prior to use. Unless otherwise stated, all manipulations were carried out on a dry nitrogen/vacuum line or in an argon-filled glove box for exclusion of moisture.

Lithium borates (salt A ($n = 3$ or 7.2) and salt B ($n = 7.2$)) were synthesized using the method we reported before [11]. LiBH$_4$/THF (2.0 M, 2.5 mL) diluted with 10 mL of THF was dropped with PEGMME 350 (3.500 g, 10 mmol)/THF solution at −78 °C. The mixture was slowly warmed to room temperature and was stirred for 4 h. The reaction mixture was then added dropwise to C$_6$F$_5$OH (1.841 g, 10 mmol)/THF solution at −78 °C. The mixture was recovered to room temperature and was stirred for another 12 h. After the solvent was removed, the residue was washed with toluene and hexane, and then was dried at 70 °C under the reduced pressure for 24 h. A clear viscous liquid, salt A (7.2), was obtained. Analytic results were as follows:

FT-IR (As$_2$Se$_3$ disc): 2878 cm^{-1} (C–H), 1474 cm^{-1} (CH$_2$O), 1507 cm^{-1} (C$_6$F$_5$), 1109 cm^{-1} (C–O).
^{1}H NMR (300 MHz, DMSO-d$_6$): 3.85 ppm (t, CH$_2$OB), 3.53 ppm (s, CH$_2$CH$_2$O), 3.25 ppm (s, CH$_3$O).

Salt A(3) and salt B(7.2) were synthesized using the same method described above. Lithium aluminate (salt C(11.8)) with two −N(SO$_2$CF$_3$)$_2$ groups bonded to the ate complex center (Al) was synthesized in the same way as we reported before [12]. The structures of synthesized lithium salts are presented in Fig. 1. Mix-salts were prepared by mixing lithium borate with lithium aluminate in an argon-filled glove box.

Calculated amounts of PEO and a lithium borate or a lithium aluminate or a mix-salt were dissolved in acetonitrile (AN). After removal of the solvent, polymer electrolytes were obtained. The composition of the mix-salt polymer electrolyte was expressed as "lithium borate/lithium aluminate a/b-PEO$_x$". a/b is the mole ratio of lithium borate to lithium aluminate. x is the ratio of EO/Li$^+$ in the electrolyte.
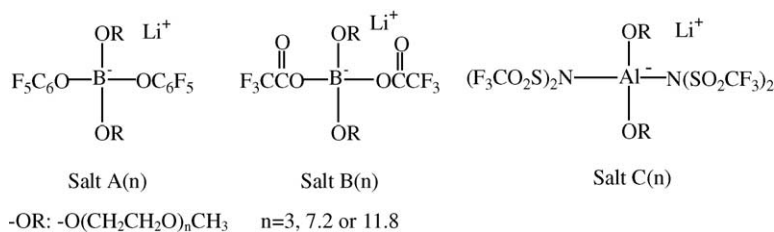
Table 1
Thermal characteristics of pure-salt polymer electrolytes and mix-salt polymer electrolytes

A(7.2)/C(11.8) a/b-PEO$_{25}$	T_g (°C)	T_m (°C)	$\Delta H/W$ (J/g)	χ
$a/b = 1/0$	−51.6	60.2	43.1	0.20
$a/b = 4/1$	−54.5	56.6	34.7	0.16
$a/b = 2/1$	−55.8	54.2	24.1	0.11
$a/b = 1/1$	−55.3	54.6	24.4	0.11
$a/b = 1/2$	−53.2	54.6	26.6	0.12
$a/b = 0/1$	−49.8	55.7	29.8	0.14

The composition of the composite cathode used in this paper was controlled as: LiNi$_{0.8}$Co$_{0.2}$O$_2$:polymer electrolyte (PEO/LiTFSI):AB = 65:20:15 (weight ratio).

2.2. Characterization

Thermal behavior of polymer electrolytes was investigated by differential scanning calorimeter (DSC) using a Perkin-Elmer Pris 1 DSC. Heat–cool–reheat cycles were performed at a rate of 10 °C min^{-1} in a temperature range of −100 to 150 °C. All thermal events were reported for the reheating cycle. Ionic conductivities were determined for the polymer electrolytes sandwiched between stainless steel blocking electrodes by ac impedance measurement (from 0 to 80 °C). The potential window of the electrolyte was evaluated by cyclic voltammetry at a scan rate of 10 mV s^{-1} at 60 °C. Stainless steel was used as a working electrode, and lithium as counter and reference electrodes. Charge–discharge cycles were performed using a galvanostatic method at a cut-off voltage of 2.5–3.8 V. The discharge capacity corresponds to that of LiNi$_{0.8}$Co$_{0.2}$O$_2$ in the cathode.

3. Results and discussion

All polymer electrolytes were flexible and homogeneous, and showed acceptable mechanic supports. Fig. 2 shows DSC thermograms of salt A(7.2)-PEO$_{25}$, salt C(11.8)-PEO$_{25}$ and salt A(7.2)/salt C(11.8) a/b-PEO$_{25}$ ($a/b = 4/1$, 2/1, 1/1 and 1/2). The thermal events obtained from the reheating cycle are summarized in Table 1. Each of the electrolytes presents an endothermic peak between 50 and 60 °C, suggesting the presence of a crystalline phase. It is related to the melting of PEO block. Almost all mix-salt polymer electrolytes show
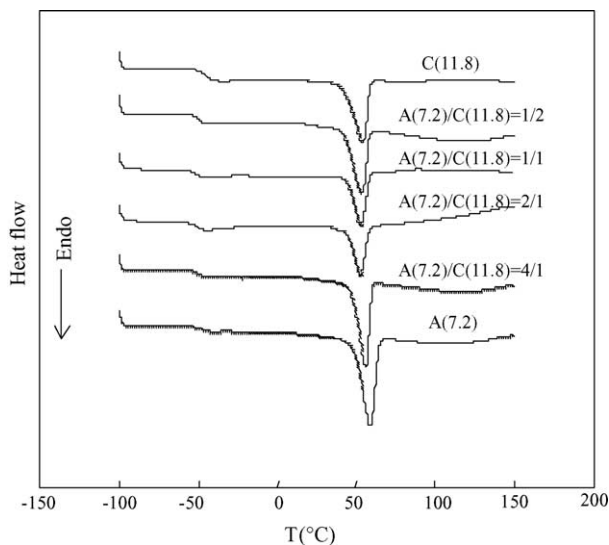

Fig. 1. Structures of synthesized lithium salts.

Fig. 2. DSC curves for salt A(7.2)-PEO$_{25}$, salt C(11.8)-PEO$_{25}$ and salt A(7.2)/salt C(11.8) a/b-PEO$_{25}$ at a scan rate of 10 °C min^{-1}.

Fig. 3. Temperature dependence of ionic conductivities of salt A(7.2)-PEO$_{25}$, salt C(11.8)-PEO$_{25}$ and salt A(7.2)/salt C(11.8) a/b-PEO$_{25}$ electrolytes.

lower χ than salt A(7.2)-PEO$_{25}$ and salt C(11.8)-PEO$_{25}$, indicating that mix-salts are more effective in depressing PEO crystallization. It is similar to a normal crystallization condition; when the total concentration of impurities is same, addition of two kinds of impurities is always more effective in hindering the crystallization process than addition of one kind of impurity. Since lithium ion conduction mainly takes place in amorphous phase, low crystallinity should be an advantage for ion transport in these electrolytes. It also can be seen that only one glass transition temperature (T_g) is observed on each DSC curve. salt A(7.2)-PEO$_{25}$ and salt C(11.8)-PEO$_{25}$ show well-defined T_g at −51.6 and −49.8 °C, respectively. Dissolving salt A(7.2) and salt C(11.8) mix-salt in PEO leads to lower T_g. Since T_g is concerned with the mobility of polymer chains and lithium ion transference in PEO-based electrolytes is greatly affected by such segmental motion; an electrolyte with low T_g always implies rapid ion conduction. Thus mix-salt polymer electrolytes were thought to be more conductive than pure-salt counterparts.

Fig. 3 shows the temperature dependence of ionic conductivities for salt A(7.2)-PEO$_{25}$, salt C(11.8)-PEO$_{25}$ and salt A(7.2)/salt C(11.8) a/b-PEO$_{25}$. It is obvious that the conductivities of mix-salt polymer electrolytes are higher than those of pure-salt polymer electrolytes. The reason for such mixing effect is attributed to the lower T_g and χ in mix-salt systems. In addition, another factor may also work. When the total concentration of lithium salts in the electrolyte is same, compared with pure-salt system, dissolving two kinds of salts in PEO (mix-salt electrolytes) will lead to lower concentration of each salt. It may cause less ion pairing because ion pairing increases with the concentration of the salt. In another word, larger amount of mobile charge carriers may be resulted in mix-salt polymer electrolytes. It may also partially contribute to the enhancement of ionic conductivity. The optimum-mixing ratio of salt A(7.2)/salt C(11.8) in these
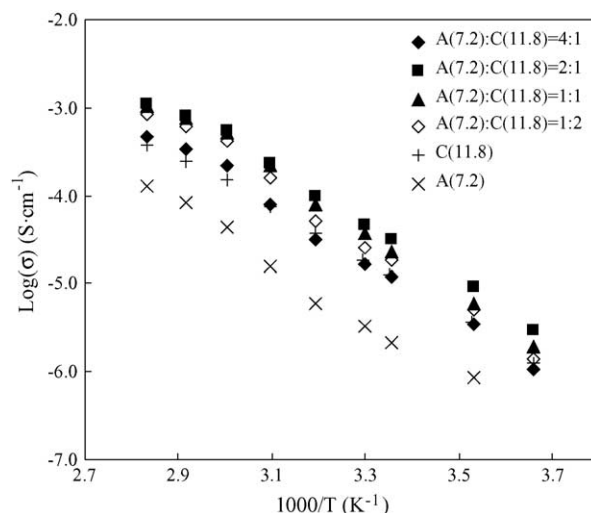
mix-salt electrolytes locates between 1/1 and 2/1. The conductivity of salt A(7.2)/salt C(11.8) 2/1-PEO$_{25}$ was determined to be 5×10^{-5} S cm^{-1} at room temperature (30 °C) and achieved 10^{-4} S cm^{-1} at 40 °C. Similar phenomenon was observed in salt B(7.2)/salt C(11.8) a/b-PEO$_{25}$ electrolyte system (Fig. 4). The mix-salt polymer electrolytes showed higher conductivities than salt B(7.2)-PEO$_{25}$ and salt C(11.8)-PEO$_{25}$. The optimum-mixing ratio for this mix-salt electrolyte system locates at about 1/1.

Addition of a lithium salt to PEO will lead to an increase of charge carriers, which contributes to the enhancement of conductivity. However, high concentration of ions may restrict the motion of EO chains concomitantly. The compromise of the two factors always leads to an optimized salt
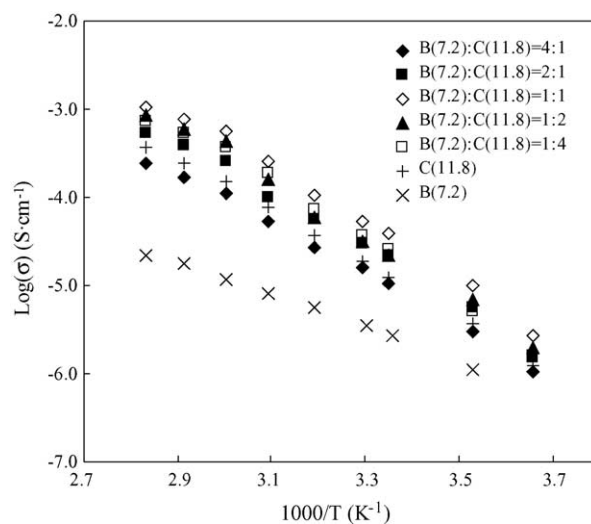

Fig. 4. Temperature dependence of ionic conductivities of salt B(7.2)-PEO$_{25}$, salt C(11.8)-PEO$_{25}$ and salt B(7.2)/salt C(11.8) a/b-PEO$_{25}$ electrolytes.
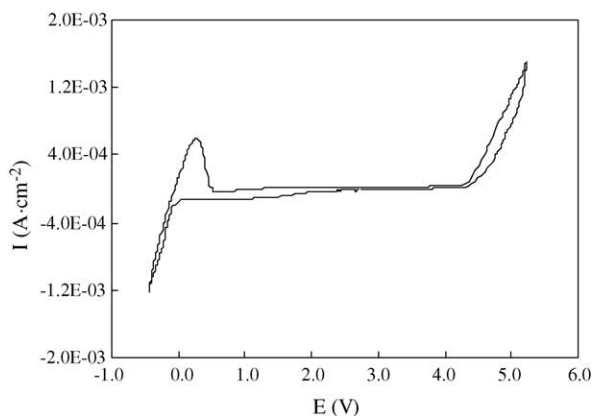
Fig. 5. Cyclic voltammetry of salt A(3)/salt C(11.8) 2/1-PEO$_{22}$ on a stainless steel working electrode and lithium counter and reference electrodes at 60 °C. Scan rate: 10 mV s^{-1}.

Fig. 6. Charge–discharge profiles for LiNi$_{0.8}$Co$_{0.2}$O$_2$//salt A(3)/salt C(11.8) 2/1-PEO$_{22}$//Li at 60 °C at different cycles. Cut-off voltage: 2.5–3.8 V. Current density: 0.1 mA cm^{-2}.

concentration. In this work, the effect of the salt concentration on the ionic conductivity was also investigated. Since conductivity maximum for LiX–PEO is always found at a ratio of EO/Li$^+$ = 15–30/1 [13], and mechanic strength is also important for polymer electrolytes, salt A(3), which contains relatively shorter oligoether chains as compared to salt A(7.2), and salt C(11.8) in a mixing ratio of 2/1 are used as doping salts. The conductivity maximum was found at the intermediate concentration of the mix-salt of EO/Li$^+$ = 22/1. The conductivity of salt A(3)/salt C(11.8) 2/1-PEO$_{22}$ (9.7 × 10^{-5} S cm^{-1} at 40 °C) is of the same level as that of salt A(7.2)/salt C(11.8) 2/1-PEO$_{25}$.

High electrochemical stability is essential for an electrolyte to be successfully applied in lithium secondary batteries. Fig. 5 shows the current–voltage response for the cell, SS//salt A(3)/salt C(11.8) 2/1-PEO$_{22}$//Li. Plating of lithium was observed at a potential lower than 0 V and stripping of lithium occurred at a potential between 0 V and 0.5 V. On the anodic side, the anodic potential limit was determined to be 4.3 V versus Li/Li$^+$, which was defined as the potential window of the electrolyte.

Since the electrolyte is designed for the lithium battery application. The best way to assess its performance is to do battery testing. In this paper, a composite cathode composed of LiNi$_{0.8}$Co$_{0.2}$O$_2$ as active material, PEO/LiTFSI as binder, and AB as a conducting material was prepared. salt A(3)/salt C (11.8) 2/1-PEO$_{22}$ was selected to check the cyclic performance of the mix-salt polymer electrolyte. Fig. 6 displays typical charge–discharge profiles for the cell, LiNi$_{0.8}$Co$_{0.2}$O$_2$//salt A(3)/salt C(11.8) 2/1-PEO$_{22}$//Li, at a cut-off voltage of 2.5–3.8 V at a current density of 0.1 mA cm^{-2} at 60 °C. No significant capacity loss was observed after 30 cycles of test. The capacities of the first several cycles are around 135 mAh g^{-1}. This value is a little lower than those of liquid electrolyte counterparts. It may be related to the higher interfacial and bulk resistances in the polymer electrolyte composed cell, which causes a larger cell voltage drop. The cycling efficiency rose from 65 to 98% during the
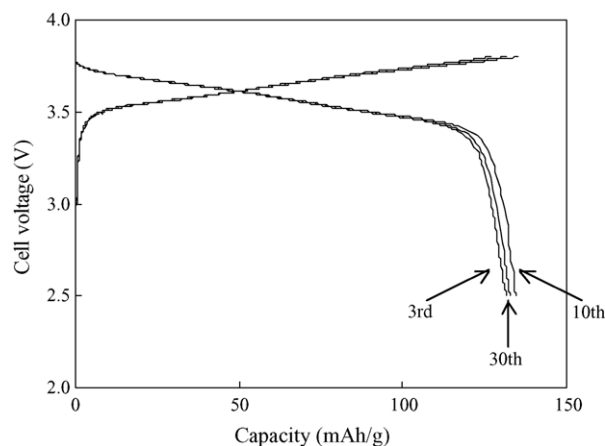
first three cycles and remained greater than 99% in the subsequent cycles, suggesting that the mix-salt polymer electrolyte was a promising material for lithium secondary battery application.

4. Conclusion

By doping PEO with the pure lithium salt or mix-salt, pure-salt polymer electrolytes or mix-salt polymer electrolytes were obtained. Mix-salt polymer electrolytes exhibited higher ionic conductivities than the corresponding pure-salt electrolytes. The optimum-mixing ratios for salt A(7.2)/salt C (11.8) a/b-PEO$_{25}$ and salt B(7.2)/salt C (11.8) a/b-PEO$_{25}$ were found to be in the range of 1/1–2/1 and around 1/1, respectively. The conductivity maximum for salt A(3)/salt C (11.8) 2/1-PEO was obtained at a salt concentration of EO/Li$^+$ = 22/1. Mix-salt polymer electrolytes exhibited acceptable electrochemical stability and good cyclic performance. Therefore, they are promising materials to be applied in solid-state lithium secondary batteries.

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