Short communication

Solid polymer electrolytes composed of polyanionic lithium salts and polyethers

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ABSTRACT

Solid polymer electrolytes are prepared by the combination of a polyether, poly(ethylene oxide) (PEO) or poly(ethylene oxide-*co*-propylene oxide) (P(EO/PO)), and a polyanionic lithium salt, (poly(lithium sorbate)(Poly(Li-Sorb)) or poly(lithium muconate)(Poly(Li-Muco)), and their ionic conductivities, lithium ion transference number, electrochemical stabilities, thermal properties, and mechanical strength were investigated in the absence and presence of $BF_3 \cdot OEt_2$. The ionic conductivities of all solid polymer electrolytes were enhanced by one to two orders of magnitude with addition of $BF_3 \cdot OEt_2$, because the dissociation of lithium ion and carboxylate anion was promoted by complexation with BF_3. The lithium ion transference number in these solid polymer electrolytes showed relatively high values of 0.45–0.88, due to the suppression of the transport of the large counter polymeric anion. These solid polymer electrolytes showed good electrochemical and thermal stabilities, and also, the mechanical strength of the solid polymer electrolytes was improved by the function of crystalline poly(lithium carboxylate)s as a sort of filler.

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1. Introduction

Dry polymer electrolytes have been attracting interest as safer alternatives to liquid electrolytes in the lithium secondary batteries. During the recent two decades, many kinds of polymers have been investigated as host polymers, and poly(ethylene oxide) (PEO)-based polymer electrolytes have been regarded as the most promising materials. However, they show high ionic conductivity at high temperature (>60 °C), but not at room temperature because of the crystallization of PEO. Many efforts have been made to suppress the crystallinity and lower the glass transition temperature, such as polymer structure modification, introduction of the inorganic fillers and plasticizers [1–7]. On the other hand, lithium ion transference number of the polymer electrolytes is another important factor to be required for practical battery application as well as the ionic conductivity. To attain the high lithium ion transference number, polyanionic lithium salts, lithium salts with weakly coordinating anion, and single ion-type polymer electrolytes have been designed [8–12]. And also, recently it was reported that complexation of carboxylate anion in the single-ion conductor by Lewis acid BF_3 might improve ionic conductivity [13,14]. In this work, we prepared poly(lithium carboxylate) type salts, poly(lithium sorbate) (Poly(Li-Sorb)) and poly(lithium muconate) (Poly(Li-Muco))

(Scheme 1), as crystalline polyanionic lithium salts, and investigated the properties of the polymer electrolytes composed of these polymeric salts and polyethers, PEO and a copolymer of ethylene oxide with propylene oxide (P(EO/PO)), in the absence and presence of $BF_3 \cdot OEt_2$.

2. Experimental

2.1. Materials

Poly(ethylene oxide) (PEO) (Aldrich, $M_w = 73 \times 10^4$), poly(ethylene oxide-*co*-propylene oxide) (P(EO/PO)) (Meisei Chemical Works, Ltd., EO/PO ratio of 85/15, $M_n = 6 \times 10^4$), and lithium bis(trifluoromethanesulfonimide) [$LiN(CF_3SO_2)_2$] (Fluka) were dried under vacuum at 120 °C prior to use and kept inside an argon-filled glove box. Methanol (Wako, bp 64.7 °C) was purified by distillation over metal magnesium, and acetonitrile (Sigma, $H_2O < 0.005\%$) and boron trifluoride etherate (Nacalai Tesque) were used as received.

2.2. Preparation of Poly(Li-Sorb) and Poly(Li-Muco)

Poly(1-naphthylmethylammonium sorbate) and poly(1-naphthylmethylammonium muconate) as precursors for the Poly(Li-Sorb) and the Poly(Li-Muco) were synthesized in 92% and 56% yields by the solid-state polymerizations under photo-irradiation of 1-naphthylmethylammonium sorbate,

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Poly(Li-Sorb)   Poly(Li-Muco)
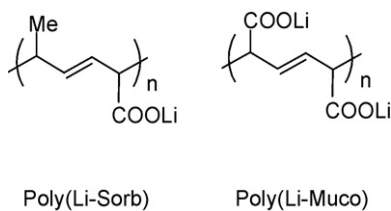
Scheme 1.

prepared in 70% yield by the reaction of sorbic acid with 1-naphthylmethylamine, and of 1-naphthylmethylammonium muconate, prepared in 94% yield by the reaction of muconic acid and 1-naphthylmethylamine, respectively [15–17]. Poly(1-naphthylmethylammonium sorbate) (1.90 g, 7.05 mmol) and lithium hydroxide (0.84 g, 35.3 mmol) were added into 50 mL of methanol, and the resulting suspension was refluxed with stirring for 24 h, and then filtered off. The formed insoluble ion-exchanged product was washed repeatedly with hot methanol, and dried under reduced pressure at 100 °C for 24 h. Poly(Li-Sorb) was obtained as white crystals: Yield 0.84 g (98%), IR (KBr): ν_{CH} 2970, $\nu_{C=O}$ 1597 cm^{-1}.

Poly(Li-Muco) was obtained as pale beige crystals from poly(1-naphthylmethylammonium muconate) (545.6 mg, 1.20 mmol) and lithium hydroxide (286.9 mg, 12.0 mmol) by the same procedure for the Poly(Li-Sorb): Yield 175 mg (95%), IR (KBr): ν_{CH} 2980, $\nu_{C=O}$ 1586 cm^{-1}; ^{1}H NMR (D$_2$O): δ 6.94 (d, $J = 2.5$ Hz, 2H), 5.94 (dd, $J = 2.5$ Hz, 2H); ^{13}C NMR (D$_2$O): δ 176.7 (C=O), 131.4 (–CH=CH–), 130.3 (–CH<). Both Poly(Li-Sorb) and Poly(Li-Muco) were broken into fine particles by grinding them in a mortar for 20–30 min before use. The particle sizes of the grinded polyanionic lithium salts were determined from SEM images to be 0.2–0.4 μm.

2.3. Preparation of solid polymer electrolytes

All preparation procedure carried out inside a dry argon-filled glove box kept at dew point of −85 °C to avoid moisture contamination. Given amounts of a poly(lithium carboxylate) (Poly(Li-Sorb) or Poly(Li-Muco)), a polyether (PEO or Poly(EO/PO)), and BF$_3$·OEt$_2$ (equivalent amount of polyanionic lithium salt) if necessary, were dissolved in a acetonitrile, and then stirred for 24 h. The resulting suspension was poured on a Teflon Petri dish and acetonitrile was evaporated very slowly at room temperature to prepare a casting film. Finally, the film was dried by heating at 90 °C for 24 h using the electric furnace equipped in the glove box. The obtained solid polymer electrolyte was peeled from the Teflon laboratory dish and stored inside the glove box.

2.4. Measurements

The ionic conductivities of the solid polymer electrolytes were measured by a two probe method after the samples were fixed inside a Teflon O-ring spacer with known thickness and sandwiched between two stainless steel (SS) electrode discs acting as ion-blocking electrodes and set in a thermostat oven chamber. Poly(Li-Sorb) and Poly(Li-Muco) are measured in pellets. The measurements were carried out using Solartron 1260 frequency response analyzer over a frequency range of 1 Hz to 1 MHz and in the temperature range of 0–130 °C with an amplitude of 100 mV. All samples were first kept at 130 °C for at least 12 h and then measured by cooling cycle. The measurements were carried out after keeping the samples for 1 h at each temperature to attain thermal equilibration. The data were processed by using an appropriate fitting program. Measurement was also carried out in heating cycle,

but no significant difference between the cooling cycle and heating cycle was observed. Multiple samples (three or four) were used for the measurements and their average values were shown in the figures and tables.

The electrochemical stability window of the solid polymer electrolytes was evaluated using Solartron 1287 electrochemical interface by running a linear sweep voltammetry (10 mV s^{-1}) at 80 °C in a Li/solid polymer electrolyte/SS cell, where Li and SS were used as a counter electrode and a blocking working electrode, respectively.

Lithium ion transference number (t_+) was determined at 80 °C by the two-impedance polarization coupling technique developed by Bruce and co-workers, where cells with symmetrical non-blocking lithium metal electrode were used [18,19].

Mechanical properties of the polymer electrolytes were measured by use of a TP-101 tension tester (Senteck, Japan) at 10 cm min^{-1} stretching speed at 30 °C. These measurements were carried out in a dry argon-filled glove box.

The thermal stability of the solid polymer electrolyte was investigated with thermogravimetry-differential thermal analysis instrument TG-DTA 6200 (Seiko Instruments) in the temperature range 20 to 400 °C at a heating rate of 5 °C min^{-1}. The glass transition temperature (T_g) of the solid polymer electrolytes were determined by the differential scanning calorimetry (DSC) using the EXSTER6000 thermal analysis instrument DSC 6200 (Seiko Instruments Inc.) in a nitrogen gas flow. About 10 mg amount of sample was weighted, loaded in an aluminum pan, and then sealed. The measurement was carried out in the temperature range −100 to 150 °C at a heating rate of 10 °C min^{-1}.

3. Results and discussion

3.1. Ionic conductivities and lithium ion transference numbers of the polymer electrolytes

The ionic conductivities of Poly(Li-Sorb) and Poly(Li-Muco) are as low as <10^{-10} S cm^{-1} even at 130 °C. The effect of the polyanionic lithium salt concentrations on the ionic conductivities for the PEO–Poly(Li-Sorb), P(EO/PO)–Poly(Li-Sorb), PEO–Poly(Li-Muco), and P(EO/PO)–Poly(Li-Muco) electrolytes was investigated in the temperature range of 0–130 °C, and the effect of BF$_3$·OEt$_2$ as an additive on the ionic conductivity of these polymer electrolytes was also investigated. Figs. 1 and 2 show the temperature dependence of the ionic conductivities for the PEO–Poly(Li-Sorb) and
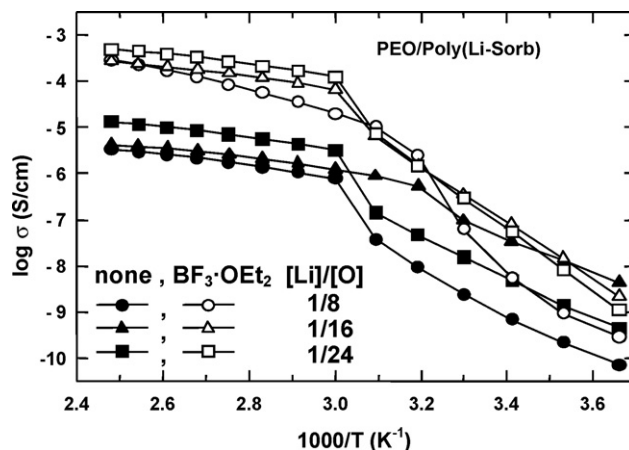

Fig. 1. Temperature dependence of ionic conductivity for the PEO–Poly(Li-Sorb) electrolyte at three different [Li]/[O] ratios of 1/8 (●), 1/16 (▲), and 1/24 (■) without BF$_3$·OEt$_2$ and of 1/8 (○), 1/16 (△), and 1/24 (□) with BF$_3$·OEt$_2$. PEO: $M_n = 60 \times 10^4$.
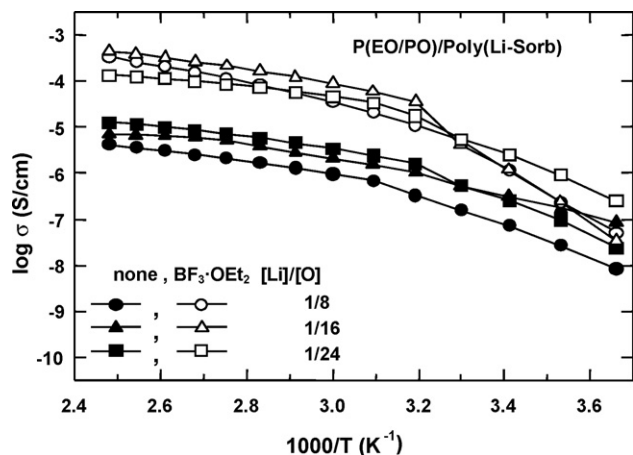
Fig. 2. Temperature dependence of ionic conductivity for the P(EO/PO)–Poly(Li-Sorb) electrolyte at three different [Li]/[O] ratios of 1/8 (●), 1/16 (▲), and 1/24 (■) without $BF_3 \cdot OEt_2$ and of 1/8 (○), 1/16 (△), and 1/24 (□) with $BF_3 \cdot OEt_2$. P(EO/PO): $M_w = 73 \times 10^4$.

P(EO/PO)–Poly(Li-Sorb) electrolytes with and without $BF_3 \cdot OEt_2$, respectively, in three different molar ratios of lithium ion to the ether oxygen (CH_2CH_2O or $0.85CH_2CH_2O/0.15CH_2CH(CH_3)O$ groups) of the matrix polymer ([Li]/[O] ratio) of 1/8, 1/16, and 1/24. Figs. 3 and 4 show the temperature dependence of the ionic conductivities for the PEO–Poly(Li-Muco) and P(EO/PO)–Poly(Li-Muco) electrolytes with and without $BF_3 \cdot OEt_2$, respectively, at three different [Li]/[O] ratios of 1/8, 1/16, and 1/24.

The ionic conductivities of these polymer electrolytes significantly decrease at around 50 °C, especially in the PEO-based electrolytes (Figs. 1 and 3). Crystallization temperature of PEO is reported to be around 50 °C, and it is considered, therefore, that the significant decrease of the ionic conductivities for these polymer electrolytes is due to the recrystallization of PEO. On the other hand, for the P(EO/PO)-based polymer electrolytes (Figs. 2 and 4), significant decrease of the ionic conductivity was not observed below 50 °C because of lower crystallinity of the P(EO/PO) as compared to PEO. This is strongly supported by the presence of the melting transitions and the difference in the heat of fusion observed for the all polymer electrolytes as will be mentioned later. The ionic conductivity of the solid polymer electrolytes without $BF_3 \cdot OEt_2$ decreased with an increase in the poly(lithium carboxylate)s concentrations at higher temperature than 50 °C, but the polymer
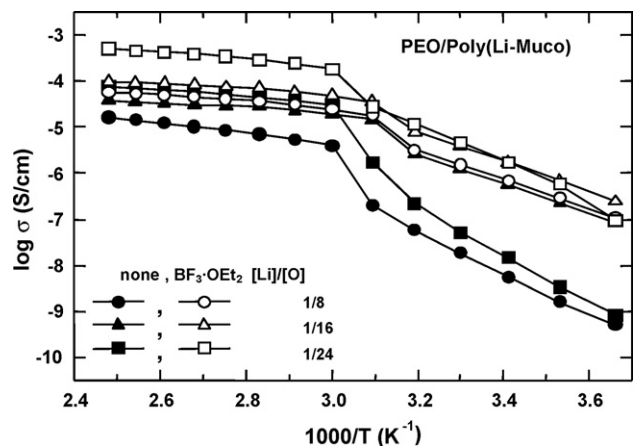

Fig. 3. Temperature dependence of ionic conductivity for the PEO–Poly(Li-Muco) electrolyte at three different [Li]/[O] ratios of 1/8 (●), 1/16 (▲), and 1/24 (■) without $BF_3 \cdot OEt_2$ and of 1/8 (○), 1/16 (△), and 1/24 (□) with $BF_3 \cdot OEt_2$. PEO: $M_n = 60 \times 10^4$.
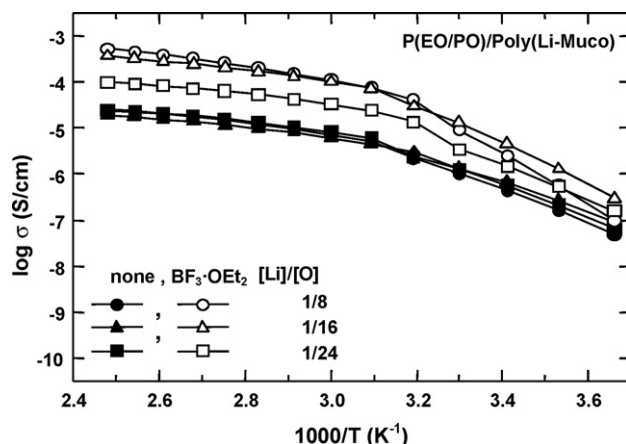

Fig. 4. Temperature dependence of ionic conductivity for the P(EO/PO)–Poly(Li-Muco) electrolyte at three different [Li]/[O] ratios of 1/8 (●), 1/16 (▲), and 1/24 (■) without $BF_3 \cdot OEt_2$ and of 1/8 (○), 1/16 (△), and 1/24 (□) with $BF_3 \cdot OEt_2$. P(EO/PO): $M_w = 73 \times 10^4$.

electrolyte at the [Li]/[O] ratio of 1/16 exhibited higher ionic conductivity than other two polymer electrolytes at the [Li]/[O] ratios of 1/8 and 1/24 at the temperature below 50 °C. Similar behavior is observed for the polymer electrolytes with $BF_3 \cdot OEt_2$. The difference in the structures of the polyanionic lithium salts does not significantly affect the ionic conductivities of their polymer electrolytes. In this study, it is interesting that when $BF_3 \cdot OEt_2$ was added to the polymer electrolytes, the ionic conductivity of the all polymer electrolytes increased by one to two orders of magnitude. Sadoway et al. reported that in the single-ion graft copolymer electrolyte of poly[(oxyethylene)$_9$ methacrylate-*ran*-lithium methacrylate]-*graft*-poly(dimethyl-siloxane), conversion of lithium methacrylate units via addition of BF_3, Lewis acid, that is, a large increase in the number of mobile cations and an effective delocalization of the carboxylate anion charge through complexation with BF_3 ($COOBF_3^-$) enhanced the ionic conductivity by two orders of magnitude [12,13]. In order to obtain the evidence of this effect in the poly(lithium carboxylate)-based polymer electrolytes, we measured the infrared spectra for the Poly(Li-Sorb) and the PEO–Poly(Li-Sorb) ([Li]/[O] = 1/16) electrolytes without and with $BF_3 \cdot OEt_2$. Their infrared spectra are shown in Fig. 5a–c.

The asymmetric stretching vibration of the carboxylate ion, measured in KBr disc, is observed at 1566 cm^{-1} for the Poly(Li-Sorb). In the PEO–Poly(Li-Sorb) electrolyte, the asymmetric stretching vibration of the carboxylate ion is observed at 1654 cm^{-1}. This shift to higher frequency can be linked to an enhanced dissociation of lithium cation and carboxylate anion, that is, a shift of the carboxylate anion stretch to higher wave numbers due to ion-dipole interactions between the lithium cation and oxygen in PEO. Addition of the $BF_3 \cdot OEt_2$ into the PEO–Poly(Li-Sorb) electrolyte induced the shift to higher frequency, which is observed at 1670 cm^{-1}, for the asymmetric stretching vibration of the carboxylate ion. $BF_3 \cdot OEt_2$ strongly associates with the carboxylate anion to form a complex such as $COOBF_3^-$, where OEt_2 in the $BF_3 \cdot OEt_2$ is exchanged to more basic COO^-, and induces further ion dissociation of poly(lithium carboxylate). And also, in the PEO–Poly(Li-Muco) electrolytes with and without $BF_3 \cdot OEt_2$, a shift from 1583 cm^{-1} in the case without $BF_3 \cdot OEt_2$ to 1705 cm^{-1} in the case with $BF_3 \cdot OEt_2$ was observed for the asymmetric stretching vibration of the carboxylate ion. It is considered, therefore, that the enhancement of the ionic conductivity observed in these polymer electrolyte systems is due to the increased dissociation of lithium ion and carboxylate anion complexed with BF_3. Moreover, when the large polymeric anion was used instead of small anion such
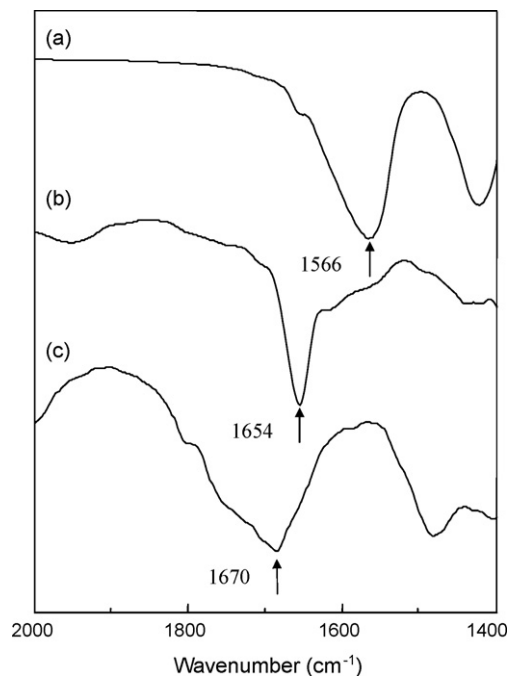
Fig. 5. Infrared spectra of (a) Poly(Li-Sorb) salt, (b) PEO–Poly(Li-Sorb) electrolyte, and (c) PEO–Poly(Li-Sorb) electrolyte with $BF_3 \cdot OEt_2$, respectively.

as $LiN(CF_3SO_2)_2$, the lithium ion transference number would be expected to increase because the transport of the polymeric anion is greatly restricted in the solid polymer electrolytes. So, the lithium ion transference numbers were measured at 80 °C for the solid polymer electrolytes with $BF_3 \cdot OEt_2$ at two [Li]/[O] ratios of 1/16 and 1/24, and the results are summarized in Table 1, together with those of the PEO–$LiN(CF_3SO_2)_2$ at the [Li]/[O] ratio of 1/20 and the P(EO/PO)–$LiN(CF_3SO_2)_2$ electrolytes at the [Li]/[O] ratio of 1/15, respectively.

These solid polymer electrolytes showed the lithium ion transference number of 0.45–0.88, and they have much larger values than the PEO–$LiN(CF_3SO_2)_2$ ($t_+ = 0.1$) and the P(EO/PO)–$LiN(CF_3SO_2)_2$ ($t_+ = 0.14$) electrolytes. Watanabe et al. reported that the usage of polymer analogs, poly(2-oxo-1-difluoroethylene sulfonylimide lithium) and poly(5-oxo-3-oxy-4-trifluoromethyl-1,2,4-pentafluoropentylene sulfonylimide lithium), of the $LiN(CF_3SO_2)_2$ as the lithium salt in the polymer electrolytes might improve the lithium ion transference number to 1 and the enhancement of the lithium ion transference number is ascribed to the restricted mobility of the polymeric anion [20,21]. Lithium ion transference numbers for all these polymer electrolytes are expected to be unity, but less than

unity. This indicates that polyanionic part of both Poly(Li-Sorb) and Poly(Li-Muco) salts still might move in the solid polymer electrolytes. Probably, the molecular weight of the polyanionic part is not enough to prevent the transport of the polyanionic part completely. Anyway, it is concluded that the observation of higher lithium ion transference number in this work is attributed to the suppressed transport of polymeric anions compared with monomeric anion in the polymer matrix.

3.2. Thermal and electrochemical properties of the polymer electrolytes

DSC measurements were carried out in the temperature range −100 to 150 °C for the PEO–Poly(Li-Sorb), the P(EO/PO)–Poly(Li-Sorb), the PEO–Poly(Li-Muco), and the P(EO/PO)–Poly(Li-Muco) electrolytes with and without $BF_3 \cdot OEt_2$ at the [Li]/[O] ratio of 1/16. The glass transitions and melting transitions were observed in all solid polymer electrolytes, and their temperatures (T_g and T_m) and the heat of fusion (ΔH_m) are summarized in Table 2.

Observation of the T_m in all solid polymer electrolytes is linked to a decrease in the ionic conductivity at the low temperature region, especially at around 45–60 °C. Moreover, lower ΔH_m values of the P(EO/PO)-based polymer electrolytes compared to the PEO-based polymer electrolytes might explain well the gentle decrease of the ionic conductivity below 50 °C. Here, the solid polymer electrolytes with $BF_3 \cdot OEt_2$ showed the higher glass transition temperatures than the solid polymer electrolytes without $BF_3 \cdot OEt_2$. This indicates that $BF_3 \cdot OEt_2$ does not act as a plasticizer, but promotes the dissociation of lithium cation and carboxylate anion in the solid polymer electrolytes. This increased dissociation leads to the physicochemical cross-linking formation of the linear chain by the formation of multiple ions, resulting in an increase in T_g.

The thermal stabilities of the PEO–Poly(Li-Sorb), the P(EO/PO)–Poly(Li-Sorb), the PEO–Poly(Li-Muco), and the P(EO/PO)–Poly(Li-Muco) electrolytes with $BF_3 \cdot OEt_2$ under air were investigated for the solid polymer electrolytes at the [Li]/[O] ratio of 1/16, and the decomposition temperatures and the 10% weight loss temperatures for these four polymer electrolytes are summarized in Table 2. These solid polymer electrolytes are relatively thermally stable. The electrochemical stabilities of the PEO–Poly(Li-Sorb), the P(EO/PO)–Poly(Li-Sorb), the PEO–Poly(Li-Muco), and the P(EO/PO)–Poly(Li-Muco) electrolytes with $BF_3 \cdot OEt_2$ at the [Li]/[O] ratio of 1/16 were determined by linear sweep voltammetry using a lithium metal/solid polymer electrolyte/stainless steel cell at 80 °C, and the breakdown voltages of these solid polymer electrolytes are summarized in Table 1, together with those of the PEO–$LiN(CF_3SO_2)_2$ and the P(EO/PO)–$LiN(CF_3SO_2)_2$ electrolytes. The electrochemical windows observed for these polymer electrolytes are to be 4.13–4.36 V.

3.3. Mechanical property of the polymer electrolytes

The tensile strengths of the PEO–Poly(Li-Sorb), the PEO–Poly(Li-Muco) and the P(EO/PO)–Poly(Li-Sorb) electrolytes with and without $BF_3 \cdot OEt_2$ were investigated at the [Li]/[O] ratio of 1/16 at 30 and 60 °C, and the results are summarized in Table 3 together with the tensile strengths of the PEO–$LiN(CF_3SO_2)_2$ electrolyte at the [Li]/[O] ratio of 1/20 and the P(EO/PO)–$LiN(CF_3SO_2)_2$ electrolytes at the [Li]/[O] ratio of 1/15, respectively.

Poly(lithium carboxylate)s-based polymer electrolytes exhibited much better mechanical strength than the $LiN(CF_3SO_2)_2$-based polymer electrolytes. Better tensile strength observed for the poly(lithium carboxylate)s-based polymer electrolytes is attributed to that the crystalline poly(lithium carboxylate)s with

Table 1
Lithium ion transference number (t_+) and breakdown voltage for the solid polymer electrolytes with $BF_3 \cdot OEt_2$ at 80 °C.

Polymer electrolytes	Transference number, t_+, at 80 °C		Breakdown voltage at 80 °C/V
	[Li]/[O]		
	1/16	1/24	
PEO–Poly(Li-Sorb)–$BF_3 \cdot OEt_2$	0.65	0.88	4.24
P(EO/PO)–Poly(Li-Sorb)–$BF_3 \cdot OEt_2$	0.75	0.83	4.13
PEO–Poly(Li-Muco)–$BF_3 \cdot OEt_2$	0.45	0.48	4.36
P(EO/PO)–Poly(Li-Muco)–$BF_3 \cdot OEt_2$	0.46	0.51	4.31
PEO–$LiN(CF_3SO_2)_2$ ([Li]/[O] = 1/20)	0.10		4.50
P(EO/PO)–$LiN(CF_3SO_2)_2$ ([Li]/[O] = 1/15)	0.14		4.70

Table 2
Glass transition temperatures (T_g), melting temperatures (T_m), heat of fusion (ΔH_m), decomposition temperatures, and 10% weight loss temperatures for the solid polymer electrolytes with and without $BF_3 \cdot OEt_2$ at the [Li]/[O] ratio of 1:16.

Polymer electrolytes	$T_g/°C$	$T_m/°C$	$\Delta H_m/J\,g^{-1}$	Decomposition temperature/°C	10% weight loss temperature/°C
PEO–Poly(Li-Sorb)	−47.5	61.9	38.7		
PEO–Poly(Li-Sorb)–$BF_3 \cdot OEt_2$	−38.3	62.0	26.6	188	276
P(EO/PO)–Poly(Li-Sorb)	−63.5	44.5	25.1		
P(EO/PO)–Poly(Li-Sorb)–$BF_3 \cdot OEt_2$	−38.5	43.9	19.9	222	313
PEO–Poly(Li-Muco)	−41.9	64.9	46.9		
PEO–Poly(Li-Muco)–$BF_3 \cdot OEt_2$	−38.4	65.1	38.4	204	322
P(EO/PO)–Poly(Li-Muco)	−58.1	46.6	20.8		
P(EO/PO)–Poly(Li-Muco)–$BF_3 \cdot OEt_2$	−46.4	45.4	20.4	212	333

Table 3
Tensile strength of the solid polymer electrolytes at 30 and 60 °C.

Polymer electrolyte ([Li]/[O])	Tensile strength/MPa	
	At 30 °C	At 60 °C
PEO–Poly(Li-Sorb) (1/16)	12.89	6.98
PEO–Poly(Li-Muco) (1/16)	13.10	7.09
PEO–Poly(Li-Sorb)–$BF_3 \cdot OEt_2$ (1/16)	15.54	9.06
P(EO/PO)–Poly(Li-Sorb)–$BF_3 \cdot OEt_2$ (1/16)	6.47	
PEO–$LiN(CF_3SO_2)_2$ (1/20)	3.55	1.73
P(EO/PO)–$LiN(CF_3SO_2)_2$ (1/15)	0.66	0.20

fine particle size might act as a sort of fillers as an inorganic filler such as TiO_2 and SiO_2 do.

4. Conclusions

The ionic conductivity, lithium ion transference number, electrochemical stability, thermal property, and mechanical strength of solid polymer electrolytes composed of a polyether (PEO or P(EO/PO)) and a polyanionic lithium salts (Poly(Li-Sorb) or Poly(Li-Muco)) with and without $BF_3 \cdot OEt_2$ were investigated. The ionic conductivities of all solid polymer electrolytes were enhanced by one to two orders of magnitude with addition of $BF_3 \cdot OEt_2$, because the dissociation of lithium ion and carboxylate anion was promoted by complexation with BF_3. The lithium ion transference number in these solid polymer electrolytes showed relatively high values of 0.45–0.88, due to the suppression of the transport of the large counter polymeric anion. The solid polymer electrolytes with $BF_3 \cdot OEt_2$ showed good electrochemical and thermal stabilities. And also, the solid polymer electrolytes based on poly(lithium carboxylate)s showed high mechanical strength because crystalline poly(lithium carboxylate)s act as a sort of filler.

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