

Composite polymer electrolytes of poly(ethylene oxide)/BaTiO₃/Li salt with hyperbranched polymer

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Abstract

Composite polymer electrolytes composed of poly(ethylene oxide) (PEO), BaTiO₃ as a ceramic filler, LiN(CF₃CF₂SO₂)₂ as a lithium salt, and hyperbranched polymer (HBP) (poly[bis(triethylene glycol)benzoate] capped with an acetyl group) as a plasticizer were examined as the electrolyte for all solid-state lithium polymer batteries and the ionic conductivity was optimized. The optimized 90 wt.% [(80 wt.% PEO–20 wt.% HBP)₁₂(LiN(CF₃CF₂SO₂)₂)]–10 wt.% BaTiO₃ electrolyte, where the PEO with M_n of 60×10^4 , HPB with M_n of 15,000, and BaTiO₃ with a particle size of 0.5 μm were used, showed the ionic conductivity of 1.3×10^{-4} S/cm at 30 °C and 1.6×10^{-3} S/cm at 80 °C, respectively. The optimized composite polymer electrolyte has an electrochemical stability window of 4.0 V and also it was stable until 307 °C under air. Interfacial stability of the LiN(CF₃CF₂SO₂)₂-based composite polymer electrolyte for a lithium metal electrode was found to be better than that of LiN(CF₃SO₂)₂-based one.

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Keywords: Composite polymer electrolyte; Poly(ethylene oxide); Hyperbranched polymer; LiN(CF₃CF₂SO₂)₂; Ionic conductivity; Thermal stability; Electrochemical stability; Interfacial stability

1. Introduction

Solid polymer electrolytes have received much attention as the electrolyte materials for all solid-state rechargeable lithium batteries and many polymer electrolytes have been developed [1–4]. Poly(ethylene oxide) (PEO)-based polymer electrolyte have been found to be the best candidate as electrolytes for the lithium polymer batteries in view of ionic conductivity and mechanical properties. However, the most significant disadvantage of the polymer electrolytes is poor conductivity at lower temperatures. Considerable research effort has been made to lower the operating temperature of the polymer electrolytes to the room temperature region. The addition of ceramic fillers in the PEO-based polymer electrolytes was one of the most successful modifications. For example, Scrosati and coworkers reported an increase in cation transference numbers and improvement of the interfacial stability between the polymer electrolytes and the lithium metal electrode by addition of SiO₂, TiO₂, γ-LiAlO₂ as ceramic fillers [5,6], and also Yamamoto and coworkers reported an increase of the electrical conductivity, especially

at lower temperature, and a decrease of the interfacial resistance between the lithium anode and the polymer electrolyte [7] by addition of the ferroelectric material, BaTiO₃. Moreover, they investigated the particle size effect of the BaTiO₃ on the ionic conduction of composite polymer electrolytes and pointed out that large particle size BaTiO₃ would increase the salt dissociation because of ferroelectric domains developed in the ceramics [8,9]. In addition to the composite polymer electrolytes, a blend-based polymer electrolyte, composed of two conductive components and lithium salts, is another example with favorable electrical properties and, for example, there are (PEO–poly[bis(methoxyethoxyethoxide)phosphazene])–LiN(CF₃SO₂)₂ and (PEO–poly[bis(triethylene glycol)benzoate] capped with an acetyl group)–LiN(CF₃SO₂)₂ systems [10–12]. One conductive component in the blend-based polymer electrolytes acts as a plasticizer to reduce the non-conductive crystalline phase of PEO, leading to an increase in the ionic conductivity at low temperatures. In a previous paper, we investigated a novel composite polymer electrolyte with the hyperbranched polymer, PEO–BaTiO₃–LiN(CF₃SO₂)₂ with poly[bis(triethylene glycol)benzoate] capped with an acetyl group (HBP), in expectation of promising electrolyte materials by combination of the composite polymer electrolytes and the blend-based polymer

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electrolytes, and then we found that this material showed a high ionic conductivity of 5.2×10^{-3} S/cm at 80 °C and 2.5×10^{-4} S/cm at 30 °C [13]. Recently, it was reported that an aluminum current collector, which is used widely as a cathode current collector in lithium secondary batteries, was subjected to serious corrosion in carbonate-based electrolyte solutions containing $\text{LiN}(\text{CF}_3\text{SO}_2)_2$ [14]. To overcome this disadvantage, lithium bis(perfluoroethylsulfonimide) ($\text{LiN}(\text{CF}_3\text{CF}_2\text{SO}_2)_2$) with high corrosion resistant property for aluminum has been proposed as an electrolyte in lithium batteries and also it exhibited a higher dissolution voltage compared to $\text{LiN}(\text{CF}_3\text{SO}_2)_2$ in liquid electrolyte [15].

In this work, characteristics of the composite polymer electrolyte composed of the PEO, HBP, BaTiO_3 , and $\text{LiN}(\text{CF}_3\text{CF}_2\text{SO}_2)_2$ for all solid-state lithium-ion batteries were investigated in comparison with $\text{LiN}(\text{CF}_3\text{SO}_2)_2$ -based composite polymer electrolyte.

2. Experimental

2.1. Materials

The hyperbranched polymer, poly[bis(triethylene glycol)]-benzoate capped with an acetyl group (HBP), was prepared according to the procedure reported previously [16] and its number-average molecular weight (M_n) was determined to be 15,000 by gel permeation chromatography (Tosoh HLC-803D with two columns of Tosoh TSKgel Multipore $\text{H}_{\text{XL}}\text{-M}$) with standard polystyrenes as a reference and tetrahydrofuran as an eluent. PEO (Aldrich Co., $M_n = 40 \times 10^4$, 60×10^4 , 90×10^4 , 100×10^4 , 200×10^4) were used as received. Lithium bis(trifluoromethanesulfonimide) [$\text{LiN}(\text{CF}_3\text{SO}_2)_2$] (Fluka Co.) and lithium bis(perfluoroethylsulfonimide) [$\text{LiN}(\text{CF}_3\text{CF}_2\text{SO}_2)_2$] (3M Company) were dried under vacuum at 120 °C prior to use and kept inside an argon-filled glove box. Barium titanate (BaTiO_3) powders [Sakai Chem. (0.5 and 0.1 μm) and Aldrich Co. (nano-size)] were dried under vacuum at 100 °C for 24 h just prior to use. Acetonitrile (bp 82 °C) was refluxed over calcium hydride for 12 h and then distilled under nitrogen.

2.2. Preparation of composite polymer electrolytes with HBP

All preparation procedures were performed inside an argon-filled glove box kept at a dew point of -85 °C to avoid moisture contamination. Given amounts of HBP and PEO were dissolved in a purified acetonitrile by magnetic stirring to form a first solution. A second solution was prepared by dispersing an appropriate amount of BaTiO_3 in a purified acetonitrile. The two solutions were then mixed and vigorously stirred for 12 h. To the homogeneous slurry was added a given amount of lithium salt and further magnetically stirred for 12 h. Subsequently, the slurry was poured on a Teflon laboratory dish and then the acetonitrile was allowed to

evaporate slowly at 40–60 °C, and then finally dried under vacuum at 70–100 °C for 3 days by using an electric furnace equipped in the glove box. The dried composite polymer electrolyte films with HBP were peeled from the Teflon laboratory dish and stored inside the glove box.

2.3. Ionic conductivity

The ionic conductivity of the composite polymer electrolytes with HBP was 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 electrode discs acting as ion-blocking electrodes and set in a thermostat oven chamber. The measurements were carried out using Solartron 1260 frequency response analyzer over a frequency range of 1 Hz to 1 MHz and in temperatures of 30–80 °C with amplitude of 10 mV. All samples were first kept at 80 °C for at least 12 h and then measured by cooling cycle. The measurements were carried out after keeping the samples for 3 h at each temperature to attain thermal equilibration. The data were processed by using an appropriate fitting program.

2.4. Electrochemical stability window

The stability of the composite polymer electrolytes with HBP was evaluated at room temperature by running (10 mV/s) a linear sweep voltammetry in two electrode cells as a Li/polymer electrolyte/stainless steel (SS) cell, where lithium metal and SS were used as a counter electrode and a blocking working electrode, respectively. A Solartron Schlumberger 1287 electrochemical interface was used for the voltammetry measurement.

2.5. Thermal analysis

Glass transition temperature (T_g) of the composite polymer electrolyte with HBP was determined by the differential scanning calorimetry (DSC) instrument (Model DSC-8230, Rigaku Co.) in a nitrogen gas flow. About 20 mg amount of samples was weighed, loaded in an aluminum pan, and then sealed hermetically. The measurement was carried out in temperatures of -100 to 100 °C at a heating and cooling rate of 10 °C/min to record the DSC curves.

The thermal stability of the composite polymer electrolytes with HBP was investigated with thermogravimetry-differential thermal analysis (TG-DTA) apparatus (Model TAS-200, Rigaku Co.) in air. The heating rate was 5 °C/min.

3. Results and discussion

3.1. Electrical properties

To find the composite polymer electrolyte with high ionic conductivity over a wide temperature range as well as the

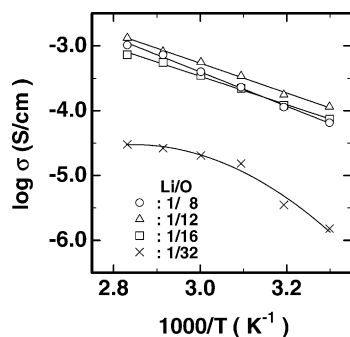


Fig. 1. Temperature dependence of the ionic conductivity in the 90 wt.% [(80 wt.% PEO–20 wt.% HBP)_x(LiN(CF₃CF₂SO₂)₂)]–10 wt.% BaTiO₃ at [Li]/[O] ratios of 1/8 (○), 1/12 (△), 1/16 (□), and 1/32 (×). PEO: $M_n = 60 \times 10^4$; HBP: $M_n = 15,000$; BaTiO₃ = 0.5 μm .

(PEO–HBP)–BaTiO₃–LiN(CF₃SO₂)₂ system reported previously [13], effects of lithium salt concentrations, amounts and molecular weights of PEO and HBP, and amounts and particle sizes of BaTiO₃ on the ionic conductivity of the (PEO–HBP)–BaTiO₃–LiN(CF₃CF₂SO₂)₂ system were investigated.

For the composite polymer electrolyte with a fixed composition of 90 wt.% [(80 wt.% PEO–20 wt.% HBP)]–10 wt.% BaTiO₃, where PEO with M_n of 60×10^4 , HBP with M_n of 15,000, and BaTiO₃ with a particle size of 0.5 μm were used, the effect of salt concentration on the ionic conductivity was investigated. Fig. 1 shows the temperature dependence of the ionic conductivity for the 90 wt.% [(80 wt.% PEO–20 wt.% HBP)_x(LiN(CF₃CF₂SO₂)₂)]–10 wt.% BaTiO₃ electrolyte at four different [Li]/[O] ratios of 1/8, 1/12, 1/16, and 1/32, where [O] means oxygen atoms in both PEO and HBP. The ionic conductivity of the composite polymer electrolytes increased with an increase in lithium salt concentration, reached a maximum value, and then decreased at the lithium salt concentration as high as 1/8. The highest ionic conductivity was found at the [Li]/[O] ratio of 1/12 as well as the (PEO–HBP)–BaTiO₃–LiN(CF₃SO₂)₂ electrolyte reported previously [13] and was to be 1.3×10^{-4} S/cm at 30 °C and 1.6×10^{-3} S/cm at 80 °C, respectively. Fig. 2 shows the PEO molecular weight dependence of the ionic conduc-

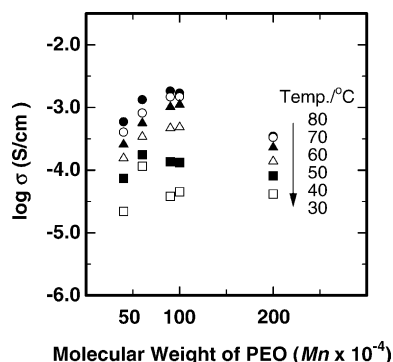


Fig. 2. PEO molecular weight dependence of the ionic conductivity for the 90 wt.% [(80 wt.% PEO–20 wt.% HBP)₁₂(LiN(CF₃CF₂SO₂)₂)]–10 wt.% BaTiO₃ at 30 °C (□), 40 °C (■), 50 °C (△), 60 °C (▲), 70 °C (○), and 80 °C (●). PEO: $M_n = 60 \times 10^4$; HBP: $M_n = 15,000$; BaTiO₃ = 0.5 μm .

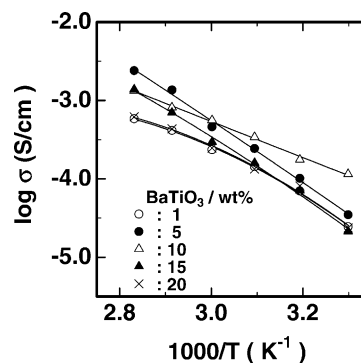


Fig. 3. Temperature dependence of the ionic conductivity in the (100 – x) wt.% [(80 wt.% PEO–20 wt.% HBP)₁₂(LiN(CF₃CF₂SO₂)₂)]– x wt.% BaTiO₃ at BaTiO₃ contents of 1 wt.% (○), 5 wt.% (●), 10 wt.% (△), 15 wt.% (▲), and 20 wt.% (×). PEO: $M_n = 60 \times 10^4$; HBP: $M_n = 15,000$; BaTiO₃ = 0.5 μm .

tivity at a temperature region of 30–80 °C for the 90 wt.% [(80 wt.% PEO–20 wt.% HBP)₁₂(LiN(CF₃CF₂SO₂)₂)]–10 wt.% BaTiO₃ electrolyte, where PEO with five different M_n of 40×10^4 , 60×10^4 , 90×10^4 , 100×10^4 , and 200×10^4 and HBP with M_n of 15,000, and BaTiO₃ with a particle size of 0.5 μm were used. The composite polymer electrolytes for PEO with M_n of 90×10^4 and 100×10^4 showed higher ionic conductivity compared to that for PEO of 60×10^4 at temperatures over 50 °C, but ionic conductivity at lower temperature region of 40–30 °C was lower. The ionic conductivity for PEO with M_n of 40×10^4 and 200×10^4 was lower than that of 60×10^4 . Therefore, it seems that the composite polymer electrolyte at PEO with M_n of 60×10^4 was the best one among them as well as (PEO–HBP)–BaTiO₃–LiN(CF₃SO₂)₂ electrolyte reported previously [13]. Fig. 3 shows the filler content dependence of the ionic conductivity at a temperature region of 30–80 °C for the (100 – x) wt.% [(80 wt.% PEO–20 wt.% HBP)₁₂(LiN(CF₃CF₂SO₂)₂)]– x wt.% BaTiO₃ electrolyte at five different BaTiO₃ contents of 1, 5, 10, 15, and 20 wt.%, where PEO with M_n of 60×10^4 , HBP with M_n of 15,000, and BaTiO₃ with a particle size of 0.5 μm were used. Among them, the [(80 wt.% PEO–20 wt.% HBP)₁₂(LiN(CF₃CF₂SO₂)₂)] electrolyte with addition of 10 wt.% BaTiO₃ showed the relatively high ionic conductivity over a wide temperature range, especially at lower temperatures. This behavior would be explained by a ferroelectricity of the BaTiO₃ filler. At low filler contents, ferroelectricity of the BaTiO₃ would contribute to dissociation of lithium salt, resulting in enhancement of total ionic conductivity, but at higher filler contents, continuous non-conductive phase built up by large amount of fillers as an electrically inert component would block up lithium ion transport, resulting in increase in the total resistance of the composite polymer electrolyte. Fig. 4 shows the temperature dependence of the ionic conductivity for the 90 wt.% [(80 wt.% PEO–20 wt.% HBP)₁₂(LiN(CF₃CF₂SO₂)₂)]–10 wt.% BaTiO₃ electrolyte at three different BaTiO₃ particle sizes of nano-size, 0.1 and 0.5 μm , where PEO with M_n of 60×10^4 and HBP with M_n of 15,000 were used. It is

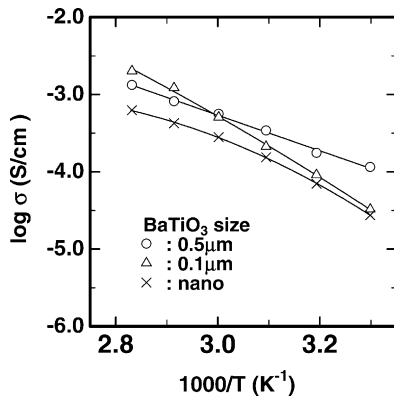


Fig. 4. Temperature dependence of the ionic conductivity in the 90 wt.% [(80 wt.% PEO–20 wt.% HBP)₁₂(LiN(CF₃CF₂SO₂)₂)]–10 wt.% BaTiO₃ at different BaTiO₃ particle sizes of 0.5 μm (○), 0.1 μm (△), and nano-size (×). PEO: $M_n = 60 \times 10^4$; HBP: $M_n = 15,000$.

concluded that a particle size of 0.5 μm is the best one among three particle sizes tested because of significant enhancement of the ionic conductivity at lower temperature. Takeuchi et al. investigated the relationship of the property of the BaTiO₃ with the grain sizes in detail and concluded that the lower permittivity in smaller grain size BaTiO₃ was attributed to poor development of ferroelectric domains in the ceramics, which originated from incomplete development of the tetragonal structure as well as the presence of a local orthorhombic structure [9]. Capiglia et al. investigated the particle size effect on the ionic conductivity by addition of BaTiO₃ with particle size of 0.06 and 0.5 μm into the (PEO)₁₂LiN(CF₃CF₂SO₂)₂ electrolyte, and pointed out that the addition of particle size of 0.5 μm predominantly increases salt dissociation because of the larger ferroelectricity, resulting in the higher ionic conductivity [8]. Therefore, the high ionic conductivity observed in this work would be due to the same reason. Fig. 5 shows the temperature dependence of the ionic conductivity of the 90 wt.% [(100–x) wt.% PEO–x wt.% HBP]₁₂(LiN(CF₃CF₂SO₂)₂)]–10 wt.% BaTiO₃ electrolytes at four different HBP contents of 0, 10, 20, and 30 wt.%, where the PEO with M_n of 60×10^4 , HPB with M_n of 15,000, and BaTiO₃ with a particle size of 0.5 μm were used, and also in the Fig. 5 the temperature dependence of the ionic conductivity for the 90 wt.% [(80 wt.% PEO–20 wt.% HBP)₁₂(LiN(CF₃SO₂)₂)]–10 wt.% BaTiO₃ electrolyte reported previously [13] as the most promising electrolyte is shown for comparison. Addition of HBP did not improve significantly the ionic conductivity, but slight enhancement of ionic conductivity was observed at the addition of HBP amount of 20–30 wt.%. It is concluded, therefore, that the most promising composite polymer electrolyte is to be the 90 wt.% [(80 wt.% PEO–20 wt.% HBP)₁₂(LiN(CF₃CF₂SO₂)₂)]–10 wt.% BaTiO₃ electrolyte, which showed the ionic conductivity of 1.3×10^{-4} S/cm at 30 °C and 1.6×10^{-3} S/cm at 80 °C, respectively. This optimized composite polymer electrolyte has a same composition to the LiN(CF₃SO₂)₂-based one reported previously [13], but its ionic conductivity is lower compared to LiN(CF₃SO₂)₂-based

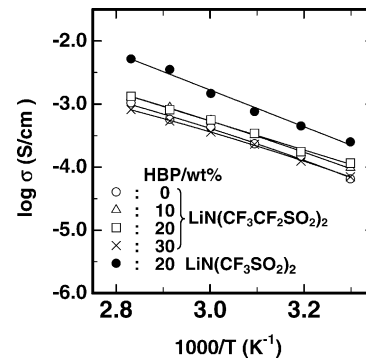


Fig. 5. Temperature dependence of the ionic conductivity in the 90 wt.% [(100–x) wt.% PEO–x wt.% HBP]₁₂(LiN(CF₃CF₂SO₂)₂)]–10 wt.% BaTiO₃ at various HBP content: 0 wt.% (○), 10 wt.% (△), 20 wt.% (□), and 30 wt.% (×) and in the 90 wt.% [(80 wt.% PEO–20 wt.% HBP)₁₂(LiN(CF₃SO₂)₂)]–10 wt.% BaTiO₃. PEO: $M_n = 60 \times 10^4$; HBP: $M_n = 15,000$; BaTiO₃ = 0.5 μm.

composite polymer electrolyte, which showed ionic conductivity of 2.6×10^{-4} S/cm at 30 °C and 5.2×10^{-3} S/cm at 80 °C, respectively. It is concluded that LiN(CF₃SO₂)₂-based composite polymer electrolyte is superior to LiN(CF₃CF₂SO₂)₂-based one from the view of the ionic conductivity.

Electrochemical stability is the one of key criteria of the polymer electrolyte for practical battery applications. To know the electrochemical stability of the optimized composite polymer electrolyte 90 wt.% [(80 wt.% PEO–20 wt.% HBP)₁₂(LiN(CF₃CF₂SO₂)₂)]–10 wt.% BaTiO₃, where the PEO with M_n of 60×10^4 , HPB with M_n of 15,000, and BaTiO₃ with a particle size of 0.5 μm were used, linear-sweep voltammetry measurement was carried out at room temperature by using Li/composite polymer electrolytes/SS cells. The sweep was run from open circuit voltage to about 5 V at a scan rate of 10 mV/s. The potential at which the current density reaches 0.2 mA/cm² was defined as the breakdown voltage for the polymer electrolytes as shown in [17]. The results are summarized in Table 1. The potential window was found to be 4.0 V as well as that of the LiN(CF₃SO₂)₂-based composite polymer electrolyte [13].

3.2. Interface property

Compatibility of composite polymer electrolytes with electrode materials is an important factor for polymer battery applications. In order to evaluate interfacial stability between a lithium metal and the both composite polymer electrolytes, 90 wt.% [(80 wt.% PEO–20 wt.% HBP)₁₂(LiN(CF₃CF₂SO₂)₂)]–10 wt.% BaTiO₃ and 90 wt.% [(80 wt.% PEO–20 wt.% HBP)₁₂(LiN(CF₃SO₂)₂)]–10 wt.% BaTiO₃, ionic conductivity was measured by using the Li metal/composite polymer electrolyte/Li metal cells at 70 °C and monitored for 10 days. The results are shown in Fig. 6. For the 90 wt.% [(80 wt.% PEO–20 wt.% HBP)₁₂(LiN(CF₃SO₂)₂)]–10 wt.% BaTiO₃ electrolyte, there seems a transition at 7 days. At present, it is not explained clearly, but there is a possibility of the crystallization of PEO during long cure time even though

Table 1

Breakdown voltages, decomposition temperatures and 10% weight loss temperatures for the 90 wt.% [(100 - x) wt.% PEO-x wt.% HBP]₁₂(LiN(CF₃CF₂SO₂)₂)-10 wt.% BaTiO₃ and the 90 wt.% [(100 - x) wt.% PEO-x wt.% HBP]₁₂(LiN(CF₃SO₂)₂)-10 wt.% BaTiO₃ electrolytes

Composite polymer electrolyte	HBP content (wt.%)	Breakdown voltage (V) at room temperature	Decomposition temperature (°C)	10% weight loss temperature (°C)
90 wt.% [(100 - x) wt.% PEO-x wt.% HBP] ₁₂ (LiN(CF ₃ CF ₂ SO ₂) ₂)-10 wt.% BaTiO ₃	0		198	351
	10	4.0	277	371
	20		307	362
	30		315	371
90 wt.% [(100 - x) wt.% PEO-x wt.% HBP] ₁₂ (LiN(CF ₃ SO ₂) ₂)-10 wt.% BaTiO ₃	0		207	350
	10	4.0	277	365
	20		312	364
	30		316	362

HBP was added as plasticizer. The ionic conductivity of both composite polymer electrolytes decreased with time, but the decrease of the 90 wt.% [(80 wt.% PEO-20 wt.% HBP)₁₂(LiN(CF₃CF₂SO₂)₂)-10 wt.% BaTiO₃ electrolyte is much larger than that of the 90 wt.% [(80 wt.% PEO-20 wt.% HBP)₁₂(LiN(CF₃SO₂)₂)-10 wt.% BaTiO₃ one. As the ionic conductivity of both composite polymer electrolytes observed by using SS/composite polymer electrolyte/SS cells did not change during monitored time, the decrease in the ionic conductivity would be due to the increase in the electric resistance of the interface between the electrolyte and lithium metal. It is concluded, therefore, that the interfacial stability for the LiN(CF₃CF₂SO₂)₂-based electrolyte is better than that for the LiN(CF₃SO₂)₂-based electrolyte.

3.3. Thermal property

DSC measurements were carried out at temperatures of -100 to 100 °C for the composite polymer electrolytes. DSC trace of the 90 wt.% [(80 wt.% PEO-20 wt.% HBP)₁₂(LiN(CF₃CF₂SO₂)₂)-10 wt.% BaTiO₃ electrolyte showed only T_g of -35.2 °C and no evidence of melting transition, indicating that it is completely amorphous. TGA measurements were

carried out under air in order to know the thermal stability of the 90 wt.% [(100 - x) wt.% PEO-x wt.% HBP]₁₂(LiN(CF₃CF₂SO₂)₂)-10 wt.% BaTiO₃ electrolytes at four different HBP contents. The decomposition temperatures and 10% weight loss temperatures of these composite polymer electrolytes are summarized in Table 1, together with corresponding 90 wt.% [(100 - x) wt.% PEO-wt.% HBP]₁₂(LiN(CF₃SO₂)₂)-10 wt.% BaTiO₃ electrolytes for comparison. The decomposition temperatures of the polymer electrolytes increased significantly by addition of HBP and also increased with an increase in the HBP content, indicating that the HBP could contribute significantly to enhancement of thermal stability of the composite polymer electrolytes, due to the presence of the aromatic rings in the HBP.

4. Conclusion

Composite polymer electrolytes composed of PEO, BaTiO₃ as a ceramic filler, LiN(CF₃CF₂SO₂)₂ as a lithium salt, and HBP as a plasticizer were examined as the electrolyte for all solid-state lithium polymer batteries and the ionic conductivity was optimized. The composite polymer electrolyte of 90 wt.% [(80 wt.% PEO ($M_n = 60 \times 10^4$)-20 wt.% HBP ($M_n = 15,000$))]-10 wt.% BaTiO₃ (0.5 μm)-LiN(CF₃CF₂SO₂)₂ showed the highest ionic conductivity in a [Li]/[O] ratio of 1/12 and the conductivity was found to be 1.3×10^{-4} S/cm at 30 °C and 1.6×10^{-3} S/cm at 80 °C, respectively. The optimized composite polymer electrolyte has an electrochemical stability window of 4.0 V and also it was stable until 307 °C under air. Interfacial stability of the LiN(CF₃CF₂SO₂)₂-based composite polymer electrolyte for a lithium metal electrode was found to be better than that of LiN(CF₃SO₂)₂-based one.

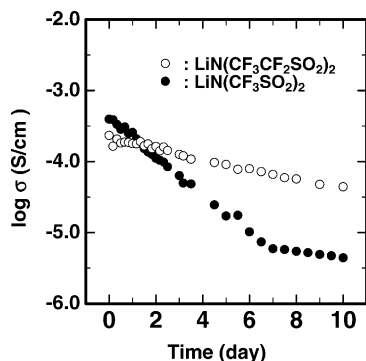


Fig. 6. Ionic conductivity change at 70 °C of the 90 wt.% [(80 wt.% PEO-20 wt.% HBP)₁₂(LiN(CF₃CF₂SO₂)₂)-10 wt.% BaTiO₃ and the 90 wt.% [(80 wt.% PEO-20 wt.% HBP)₁₂(LiN(CF₃SO₂)₂)-10 wt.% BaTiO₃ as a function of the time by using a symmetrical Li/composite polymer electrolyte/Li cells. PEO: $M_n = 60 \times 10^4$; HBP: $M_n = 15,000$; BaTiO₃ = 0.5 μm.

Acknowledgements

We greatly appreciate the helpful discussion with Dr. Takeda and Dr. Imanishi, Department of Chemistry for

Materials, Mie University. The financial support from Genesis Research Institute, Inc. is gratefully acknowledged.

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