

Short communication

Properties of the cross-linked composite polymer electrolytes using hyperbranched polymer with terminal acryloyl groups

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Abstract

The cross-linked composite polymer electrolytes composed of poly(ethylene oxide) (PEO), hyperbranched polymer with terminal acryloyl groups (poly-1b), poly(ethylene glycol) methyl ether methacrylate (PEOMA), $\text{LiN}(\text{CF}_3\text{SO}_2)_2$ were prepared, and their ionic conductivities, mechanical strength, electrochemical and thermal properties, and interfacial stabilities with electrodes were investigated. The ionic conductivity increased with an increase in the PEOMA content in the cross-linked composite polymer electrolyte, and the highest ionic conductivity was obtained at the [80% PEO/20% (poly-1b/PEOMA)]₁₂($\text{LiN}(\text{CF}_3\text{SO}_2)_2$) electrolyte with the poly-1b/PEOMA ratio of 1/3. However, the tensile strength decreased with an increase in the PEOMA content in the cross-linked composite polymer electrolytes. The cross-linked composite polymer electrolyte with the highest ionic conductivity has three times higher tensile strength than non-cross-linked (80% PEO/20% poly-1a)₁₂($\text{LiN}(\text{CF}_3\text{SO}_2)_2$) electrolyte. The addition of the PEOMA unit into the cross-linked composite polymer electrolyte improved both the ionic conductivity and mechanical property at the same time. And also, the cross-linked composite polymer electrolyte containing the PEOMA unit showed the good interfacial stability with both lithium metal and cathode electrodes.

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Keywords: Cross-linked composite polymer electrolyte; Hyperbranched polymer; Cross-linkable groups; Electrical and mechanical properties; Interfacial stability

1. Introduction

Solid polymer electrolytes serve as both the electrolyte and the separator for all solid-state rechargeable lithium batteries, and they can provide advantages such as safety, mechanical properties, low cost design, flexibility in sizes and shapes, and high-energy density over commercial liquid electrolytes, which make them potential candidates for portable electric devices and electric vehicle batteries [1–6]. Polymer electrolytes consisting of poly(ethylene oxide) (PEO) with a wide variety of lithium salts have been studied. However, the practical use of PEO-based polymer electrolytes is often hindered due to their low ionic conductivity at room temperature and poor mechanical properties. Considerable research effort has been made to lower the operating temperature of the polymer electrolytes to the room temperature region [1–6]. We have investigated the polymer electrolytes based on hyperbranched

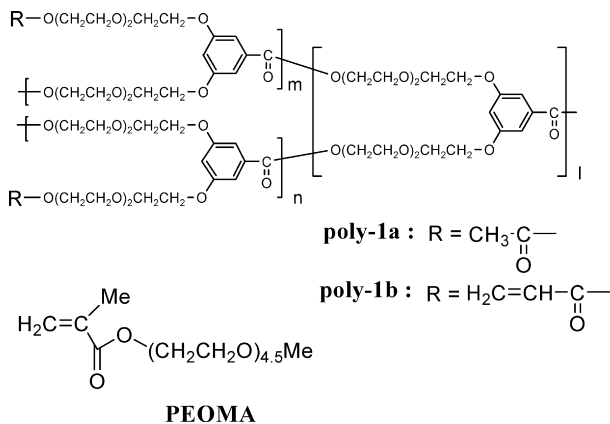
polymer poly[bis(triethylene glycol)benzoate], which is completely amorphous and has large number of branch ends with highly segmental motion ability. We have reported that the composite polymer electrolytes composed of PEO, $\text{LiN}(\text{CF}_3\text{SO}_2)_2$ as a lithium salt and poly[bis(triethylene glycol)benzoate] with terminal acetyl groups (poly-1a) as a plasticizer show high ionic conductivity over the wide temperature range [7], and also the use of HBP with terminal acryloyl groups (poly-1b) instead of poly-1a could improve the mechanical property of the composite polymer electrolytes, though their ionic conductivity decreased largely [8]. Therefore, to improve both the ionic conductivity and mechanical property at the same time, we have investigated the addition effect of the poly(ethylene glycol) methyl ether methacrylate (PEOMA) into the cross-linked composite polymer electrolyte based on poly-1b. Because the polymerizable methacryloyl group in the PEOMA unit is expected to behave as a spacer to reduce the cross-linking density, and also the short ethylene oxide (EO) chain with the fast segmental motion ability is expected to contribute to the lithium ion transport.

In this work, the cross-linked composite polymer electrolytes composed of PEO, poly-1b, PEOMA and $\text{LiN}(\text{CF}_3\text{SO}_2)_2$ were

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prepared, and their some properties such as ionic conductivity, mechanical strength, electrochemical and thermal properties, and interfacial stabilities with electrodes were investigated.



2. Experimental

2.1. Materials

Poly(ethylene oxide) (PEO) (Aldrich Co., $M_n = 60 \times 10^4$) and acetonitrile (Sigma, $\text{H}_2\text{O} < 0.005\%$) were used as received. Benzoyl peroxide (BPO) was purified by recrystallization from methanol and poly(ethylene glycol) methyl ether methacrylate (PEOMA) (Aldrich Co., average $M_n \sim 300$) was purified by distillation over the calcium hydride, respectively. Lithium bis(trifluoromethanesulfonimide) [$\text{LiN}(\text{CF}_3\text{SO}_2)_2$] (Fluka Co.) was dried under vacuum at 120°C prior to use and kept inside an argon-filled glove box.

Poly[bis(triethylene glycol)]benzoate] (HBP) was prepared according to the method reported previously [9] and the number-average molecular weight (M_n) of the polymer was determined to be 3000 by gel permeation chromatography (GPC).

The HBP (4.05 g, 9.35 mmol) and an acryloyl chloride (4.00 mL, 28.1 mmol) were dissolved in 10 mL of dichloromethane at room temperature, a triethylamine (2.30 mL, 28.1 mmol) solution in 15 mL of dichloromethane added, and stirred for 24 h at room temperature. The reaction mixture was washed with a saturated sodium chloride aqueous solution and dried over anhydrous magnesium sulfate. The filtrate was concentrated and then poured into an excess of isopropyl ether to precipitate the polymer, poly[bis(triethylene glycol)benzoate] with acryloyl groups (poly-1b) at terminals, which was purified in three or more cycles of a redissolution–reprecipitation method. Dichloromethane and isopropyl ether were used as solvent and precipitant, respectively. The polymer obtained was dried under reduced pressure at room temperature until a constant weight was reached. Poly-1b was obtained in 3.23 g (76% yield) as pale brown viscous oils: IR (NaCl): $\nu_{\text{C-H}}$ 2880, $\nu_{\text{C=O}}$ 1722, $\nu_{\text{C=C}}$ 1595, $\nu_{\text{C-O-C}}$ 1125 cm^{-1} . ^1H NMR (CDCl_3 , δ (ppm)): 7.19 (Ar, br 2H), 6.68 (Ar, br 1H), 6.38 (*trans*-CH=, d, $J = 17.2$ Hz), 6.15 (=CH, dd, $J = 10.2$ and 17.2 Hz), 5.85 (*cis*-CH=, d, $J = 10.2$ Hz), 4.45 (benzoyl-OCH₂), 4.31 (acryloyl-OCH₂), 4.13 (CH₂-O-Ar), 3.84–3.72 (CH₂). ^{13}C NMR (CDCl_3 , δ (ppm)): 166.1 (C=O), 165.6 (C=O), 159.2 (Ar),

131.4 (Ar), 130.5 (CH₂=), 127.8 (=CH), 107.7 (Ar), 106.3 (Ar), 70.6 (CH₂), 69.1 (CH₂), 68.6 (CH₂), 67.2 (CH₂), 63.7 (CH₂), 63.1 (CH₂), 51.7 (CH₃). $M_n = 3200$.

2.2. Preparation of the composite polymer electrolytes

All preparation procedures were carried out inside a dry argon-filled glove box kept at dew point of -85°C to avoid moisture contamination. Given amounts of poly-1b, PEOMA, and BPO (10 wt.% for a total amount of poly-1b and PEOMA) were dissolved in an acetonitrile, and then to the solution a given amount of PEO was added and stirred for 6 h. Subsequently, to the resulting solution was added an appropriate amount of lithium salt ($\text{LiN}(\text{CF}_3\text{SO}_2)_2$) and further stirred for 24 h. The viscous solution 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 and cross-linked by heating at 90°C for 24 h using electric furnace equipped in the glove box. The obtained cross-linked composite polymer electrolyte was peeled from the Teflon laboratory dish and stored inside the glove box. The composite polymer electrolytes were obtained as rubber-like materials with different hardness, depending upon the PEOMA content.

2.3. Measurements

The ionic conductivities of the cross-linked composite 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. The measurements were carried out using Solartron 1260 frequency response analyzer over a frequency range of 1 Hz to 1 MHz and in a temperature range of 0 – 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 1 h at each temperature to attain thermal equilibration. The data were processed by using an appropriate fitting program.

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

Lithium ion transport number (T_+) was determined by the two-impedance polarization coupling technique developed by Bruce and co-workers [10] and Bruce and Vincent [11], where cells with symmetrical non-blocking lithium metal electrode were used.

Mechanical properties of the composite polymer electrolytes were measured by use of a TP-101 tension tester (Sentek, 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 cross-linked composite polymer electrolyte was investigated with thermogravimetry–differential

thermal analysis instrument TG–DTA 6200 (Seiko Instruments Inc.) at a heating rate of $5\text{ }^{\circ}\text{C min}^{-1}$ in air. The glass transition temperature (T_g) values of the cross-linked composite polymer electrolytes were determined by the differential scanning calorimetry (DSC) using 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 a temperature range of -100 to $110\text{ }^{\circ}\text{C}$ at a heating rate of $10\text{ }^{\circ}\text{C min}^{-1}$.

3. Results and discussion

3.1. Ionic conductivity

The effect of the PEOMA content on the ionic conductivity of the $[80\% \text{ PEO}/20\% (\text{poly-1b/PEOMA})]_{12}(\text{LiN}(\text{CF}_3\text{SO}_2)_2)$ electrolyte was investigated at the poly-1b/PEOMA ratios of 1/0, 1/1, 1/2, 1/3, 1/4.5, and 1/20. The temperature dependence of the ionic conductivity of their cross-linked composite polymer electrolytes at 0 – $80\text{ }^{\circ}\text{C}$ was shown in Fig. 1. The ionic conductivity of the cross-linked composite polymer electrolytes increased with an increase in the PEOMA content, reached a maximum value and then decreased. Addition of a large amount of the PEOMA unit induced a decrease in the ionic conductivity, and at the poly-1b/PEOMA ratio of 1/20, a rapid decrease in the ionic conductivity was observed at around $40\text{ }^{\circ}\text{C}$, which is due to the suppression of the polymer chain motion by the crystallization of PEO, probably comes from the poor plasticizing effect caused by a less amount of the poly-1b. The highest ionic conductivity for the $[80\% \text{ PEO}/20\% (\text{poly-1b/PEOMA})]_{12}(\text{LiN}(\text{CF}_3\text{SO}_2)_2)$ electrolyte was found at the poly-1b/PEOMA ratio of 1/3, and it was to be $1.2 \times 10^{-4} \text{ S cm}^{-1}$ at $30\text{ }^{\circ}\text{C}$ and $1.8 \times 10^{-3} \text{ S cm}^{-1}$ at $80\text{ }^{\circ}\text{C}$, respectively. This indicates that the PEOMA unit may act as a spacer between the cross-linking terminal groups of the poly-1b to reduce the cross-linking density, supported by the decrease in the mechanical strength of the cross-linked composite polymer electrolytes as described later, and also induce the acceleration of lithium ion transport by the help of the PEO side chains with highly segmental motion ability.

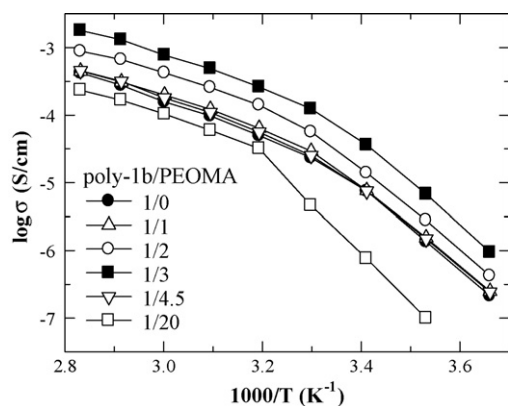


Fig. 1. Temperature dependence of the ionic conductivity for the $[80\% \text{ PEO}/20\% (\text{poly-1b/PEOMA})]_{12}(\text{LiN}(\text{CF}_3\text{SO}_2)_2)$ electrolytes at six different poly-1b/PEOMA ratios of 1/0 (●), 1/1 (△), 1/2 (○), 1/3 (■), 1/4.5 (▽), and 1/20 (□). PEO: $M_n = 60 \times 10^4$; poly-1b: $M_n = 3200$.

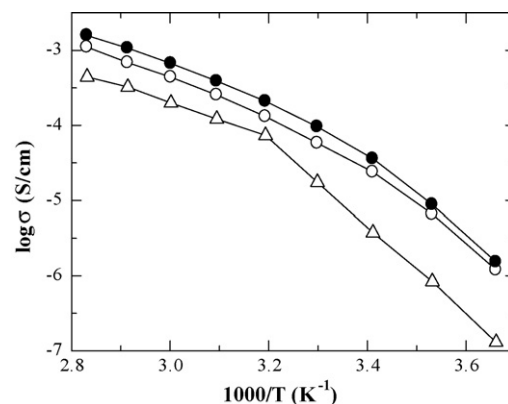


Fig. 2. Temperature dependence of the ionic conductivity for the $[80\% \text{ PEO}/20\% (\text{poly-1b/PEOMA})]_x(\text{LiN}(\text{CF}_3\text{SO}_2)_2)$ electrolytes at three different $[\text{Li}]:[\text{O}]$ ratios of 1:8 (○), 1:12 (●), and 1:16 (△). PEO: $M_n = 60 \times 10^4$; poly-1b: $M_n = 3200$.

The effect of the lithium salt concentration on the ionic conductivity of the $[80\% \text{ PEO}/20\% (\text{poly-1b/PEOMA})]_x(\text{LiN}(\text{CF}_3\text{SO}_2)_2)$ electrolyte with a fixed poly-1b/PEOMA ratio of 1/3 was investigated at three different $[\text{Li}]:[\text{O}]$ ratios of 1:8, 1:12, and 1:16, respectively. The temperature dependence of the ionic conductivity of their composite polymer electrolytes at 0 – $80\text{ }^{\circ}\text{C}$ was shown in Fig. 2. The ionic conductivity of the cross-linked composite polymer electrolytes increased with increasing lithium salt concentration, reached a maximum value at the $[\text{Li}]:[\text{O}]$ ratio of 1:12, and then decreased for the lithium salt concentration at 1:8 ratio. This behavior is similar to the linear PEO-based polymer electrolyte with lithium salt systems. For the cross-linked composite polymer electrolyte at the $[\text{Li}]:[\text{O}]$ ratio of 1:16, a rapid decrease in the ionic conductivity was observed at around $40\text{ }^{\circ}\text{C}$, due to the suppression of the polymer chain motion by the crystallization of PEO. The highest ionic conductivity was found at the $[\text{Li}]:[\text{O}]$ ratio of 1:12.

The effect of the (poly-1b/PEOMA) content on the ionic conductivity of the $[(100-x)\% \text{ PEO}/x\% (\text{poly-1b/PEOMA})]_{12}(\text{LiN}(\text{CF}_3\text{SO}_2)_2)$ electrolyte with a fixed lithium salt concentration and a fixed poly-1b/PEOMA ratio of 1/3 was investigated at three different (poly-1b/PEOMA) contents of 10, 20, and 30 wt.%. The temperature dependence of the ionic conductivity of their cross-linked composite polymer electrolytes at 0 – $80\text{ }^{\circ}\text{C}$ was shown in Fig. 3. The ionic conductivity of the cross-linked composite polymer electrolytes increased with increasing the (poly-1b/PEOMA) content, reached a maximum value at the 20 wt.% content, and then decreased at the 30 wt.% content. Relatively high ionic conductivity over a wide temperature range was observed for the $[\text{PEO}-(\text{poly-1b/PEOMA})]_{12}(\text{LiN}(\text{CF}_3\text{SO}_2)_2)$ electrolyte with a 20 wt.% (poly-1b/PEOMA). This composite polymer electrolyte was a rubber-like material in physical appearance.

3.2. Mechanical property

The tensile strengths of the $[80\% \text{ PEO}/20\% (\text{poly-1b/PEOMA})]_{12}(\text{LiN}(\text{CF}_3\text{SO}_2)_2)$ electrolytes at $30\text{ }^{\circ}\text{C}$ were investigated at six different poly-1b/PEOMA ratios of 1/0, 1/1,

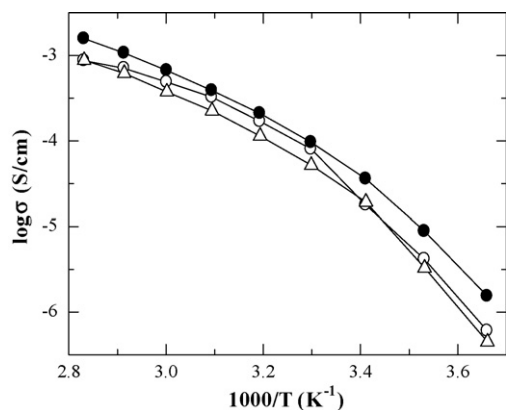


Fig. 3. Temperature dependence of the ionic conductivity for the [(100- x)% PEO/ x % (poly-1b/PEOMA)]₁₂(LiN(CF₃SO₂)₂) electrolytes with a fixed lithium salt concentration and a fixed poly-1b/PEOMA ratio of 1/3 at three different (poly-1b/PEOMA) contents of 10 (○), 20 (●), and 30 (△) wt.%. PEO: $M_n = 60 \times 10^4$; poly-1b: $M_n = 3200$.

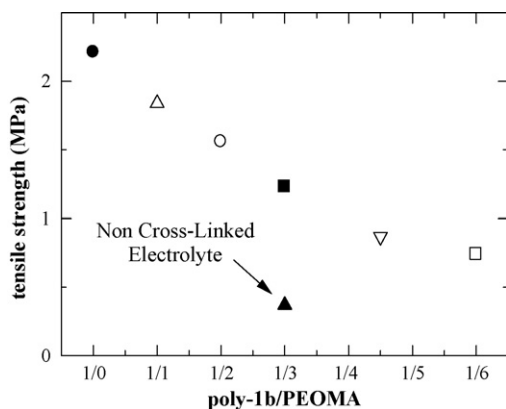


Fig. 4. Tensile strengths of the [80% PEO/20% (poly-1b/PEOMA)]₁₂(LiN(CF₃SO₂)₂) electrolyte at 30 °C at six different poly-1b/PEOMA ratios of 1/0 (●), 1/1 (△), 1/2 (○), 1/3 (■), 1/4.5 (▽), and 1/6 (□). PEO: $M_n = 60 \times 10^4$; poly-1b: $M_n = 3200$.

1/2, 1/3, 1/4.5, and 1/6, and the results were shown in Fig. 4 together with the tensile strength of non cross-linked one, composed of PEO, poly-1a, and LiN(SO₂CF₃)₂, and in Table 1, respectively. The tensile strength decreased monotonically with an increase in the PEOMA content as shown in Fig. 4. This decrease is considered to be due to a decrease in the cross-linking density to be produced in the cross-linked composite polymer electrolytes, that is, the PEOMA may act as a spacer to reduce the cross-linking density. The cross-linked composite polymer

electrolyte at the poly-1b/PEOMA ratio of 1/3 revealed one-half tensile strength of the corresponding one containing no PEOMA unit, but it has three times higher tensile strength in comparison with the (80% PEO/20% (poly-1a)₁₂(LiN(CF₃SO₂)₂) electrolyte (tensile strength: 0.37 MPa) [8]. The cross-linked composite polymer electrolyte with good mechanical property and relatively high ionic conductivity was successfully obtained by an introduction of the PEOMA unit into the cross-linked composite polymer electrolytes.

3.3. Electrochemical and thermal properties

The electrochemical stability, thermal stability, and transference number of the lithium ion for the [80% PEO/20% (poly-1b/PEOMA)]₁₂(LiN(CF₃SO₂)₂) electrolyte, which shows the highest ionic conductivity and relatively high mechanical property, were investigated in comparison with the (80% PEO/20% poly-1b)₁₂(LiN(CF₃SO₂)₂) electrolyte not containing PEOMA, and the results were summarized in Table 1. The breakdown voltages for the composite polymer electrolytes were found to be 4.2 V for the [80% PEO/20% (poly-1b/PEOMA)]₁₂(LiN(CF₃SO₂)₂) electrolyte and 4.3 V for the (80% PEO/20% poly-1b)₁₂(LiN(CF₃SO₂)₂) electrolyte at 80 °C, respectively. This indicates that an introduction of the PEOMA unit in the composite polymer electrolytes does not significantly affect the electrochemical stability. And also, T_+ value increased from 0.105 to 0.121 by an introduction of the PEOMA unit in the composite polymer electrolytes. This improvement is probably due to the effect of the short EO chain with fast segmental motion ability in the PEOMA unit. Both composite polymer electrolytes were stable until 300 °C, and the temperature at 5% weight loss was 330 °C for the [80% PEO/20% (poly-1b/PEOMA)]₁₂(LiN(CF₃SO₂)₂) electrolyte and 313 °C for the (80% PEO/20% poly-1b)₁₂(LiN(CF₃SO₂)₂) electrolyte, respectively. An incorporation of the PEOMA unit in the composite polymer electrolytes did not affect significantly the thermal stability of the composite polymer electrolyte. Glass transition temperatures (T_g) for the [80% PEO/20% (poly-1b/PEOMA)]₁₂(LiN(CF₃SO₂)₂) electrolyte were measured at the poly-1b/PEOMA ratios of 1/0, 1/1, 1/2, 1/3, 1/4.5, and 1/6, and the results were summarized in Table 1. The observed T_g values were found to be in a temperature range of -40.9 to -39.0 °C, indicating that an introduction of the PEOMA unit also did not affect significantly the thermal property of the composite polymer electrolytes.

Table 1

Glass transition temperatures (T_g) and tensile strengths for the [80% PEO/20% (poly-1b/PEOMA)]₁₂(LiN(CF₃SO₂)₂) electrolytes at various poly-1b/PEOMA ratios and breakdown voltages, transport numbers of Li⁺ (T_+), and decomposition temperatures and 5 wt.% loss temperatures at the poly-1b/PEOMA ratios of 1/0 and 1/3

Poly-1b/PEOMA	Tensile strength (MPa)	T_g (°C)	Breakdown voltage (V)	T_+ at 80 °C	Decomposition temperature (°C)	5 wt.% loss temperature (°C)
1/0	2.21	-40.6	4.2	0.105	300	313
1/1	1.84	-39.0				
1/2	1.56	-40.1				
1/3	1.39	-40.9	4.2	0.121	300	330
1/4.5	0.87	-40.4				
1/6	0.74	-40.6				

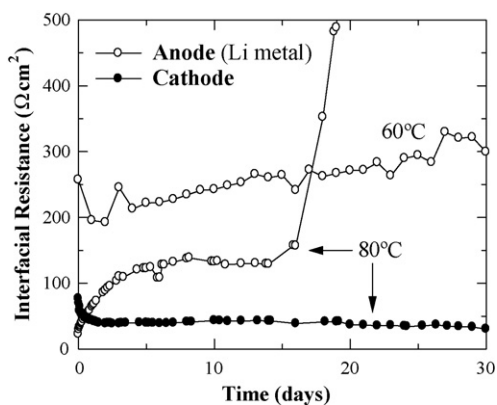


Fig. 5. The changes in the interfacial resistance with time at 60 and 80 °C by using Li/cross-linked composite polymer electrolyte/Li cell and for the [80% PEO/20% (poly-1b/PEOMA)]₁₂(LiN(CF₃SO₂)₂) electrolyte and the cathode mixture/cross-linked composite polymer electrolyte/cathode mixture at 80 °C, where the cathode mixture is composed of 50 wt.% LiNi_{0.8}Co_{0.2}O₂: 40 wt.% polymer electrolyte (30 wt.% PEO:10 wt.% LiN(CF₃SO₂)₂):10 wt.% acetylene black.

3.4. Interfacial property

Control of the cross-linked composite polymer electrolyte/electrode interface is an important factor for success in polymer battery applications. The interfacial stability was evaluated for the cells, the Li metal/cross-linked composite polymer electrolyte/Li metal at 60 and 80 °C and the cathode mixture/cross-linked composite polymer electrolyte/cathode mixture at 80 °C, where the cathode mixture is composed of 50 wt.% LiNi_{0.8}Co_{0.2}O₂:40 wt.% polymer electrolyte (30 wt.% PEO:10 wt.% LiN(CF₃SO₂)₂):10 wt.% acetylene black, and the cross-linked composite polymer electrolyte is the [80% PEO/20% (poly-1b/PEOMA)]₁₂(LiN(CF₃SO₂)₂) electrolyte at the ratios of 1/3, respectively. The changes in the interfacial resistance with time at 60 and 80 °C for 30 days were shown in Fig. 5. The cathode interfacial resistance at 80 °C is almost constant, keeping a value less than 50 Ω cm² even in 30 days. This indicates that stable interface might be formed between the cross-linked composite polymer electrolyte and the cathode electrode. On the other hand, the lithium metal interfacial resistance at 80 °C increased gradually with time for 14 days, and reached to 129 Ω cm² in 14 days, and afterward a rapid increase of the interfacial resistance was observed, over 3000 Ω cm² in 30 days, indicative of the formation of a high-resistance film at the interface between the lithium metal and the composite polymer electrolyte. Some reaction occurred at the interface, but it is not clear what reaction took place at present. At 60 °C, it was 260 Ω cm² in 14 days and 300 Ω cm² even in 30 days, respectively, though the lithium metal interfacial resistance gradually increased. It seems that at lower temperature, this reaction might be suppressed.

4. Conclusion

The cross-linked composite polymer electrolytes composed of PEO, poly-1b, PEOMA and LiN(CF₃SO₂)₂, were prepared, and the some properties of the cross-linked composite polymer electrolyte were investigated. The ionic conductivity increased with an increase in the PEOMA content in the cross-linked composite polymer electrolyte, and the highest ionic conductivity was obtained at the poly-1b/PEOMA ratio of 1/3. Although the tensile strength of the cross-linked composite polymer electrolyte decreased with an increase in the PEOMA content in the cross-linked composite polymer electrolytes, the cross-linked composite polymer electrolyte with the highest ionic conductivity revealed three times higher tensile strength than non cross-linked composite polymer electrolyte. The addition of the PEOMA unit into the cross-linked composite polymer electrolytes improved both the ionic conductivity and mechanical property at the same time by the reduction of the cross-linking density and acceleration of the ion transport by the short EO chain with the fast motion ability in the PEOMA. And also, the cross-linked composite polymer electrolyte containing the PEOMA unit showed the good interfacial stability with a lithium metal at 60 °C and with a cathode electrode at 80 °C.

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