

Blended polymer electrolytes based on poly(lithium 4-styrene sulfonate) for the rechargeable lithium polymer batteries

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Abstract

Single ion conducting polymer electrolytes composed of poly(ethylene oxide) (PEO) and poly(lithium 4-styrenesulfonate) (PLSS) were prepared and characterized. Transference number of lithium ion in the blended polymer electrolyte was 0.85. For the blended polymer electrolytes under this study, the optimum concentration for maximum ionic conductivity was found to be [EO]/[Li] = 8.0.

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1. Introduction

Development of portable electronic devices has been remarkable in the last decade. High performance batteries with high energy density are indispensable for further development of the portable electronic equipments. A lithium secondary battery using solid polymer electrolyte is an attractive energy source for the portable devices, since the use of solid polymer electrolyte makes the fabrication of safe batteries possible and permits the development of thin batteries with design flexibility. In the conventional electrolytes, both the anions and cations are mobile the other side, which has a salt concentration gradient and polarization. It impedes further ionic movement and thus increases resistance of electrolyte [1]. In order to decrease the salt concentration gradient, it is necessary to develop single-ion conductor. A lot of researchers focus on the works for anchoring the anion to the polymer matrix [2–4]. This work is for the development of new single ionic conducting polymer electrolytes based on polymer blends. In this paper, we report the synthesis and some of electrical properties of blended polymer electrolytes

composed of poly(ethylene oxide) (PEO) and poly(lithium 4-styrenesulfonate) (PLSS).

2. Experimental

2.1. Polymer synthesis and characterization

Poly(lithium 4-styrenesulfonate) was synthesized via ion exchange method. The molar ratio of poly(sodium 4-styrenesulfonate) (PSSS): LiOH·H₂O was 1:10. PSSS and LiOH·H₂O were added into dimethyl sulfoxide (DMSO) gradually while the temperature was maintained to be 30 °C in the glass reactor equipped with a nitrogen inlet, a reflux condenser, an additional funnel, and a mechanical stirrer. The mixture was stirred for 12 h at 90 °C. Then the polymer solution was precipitated by using a large amount of tetrahydrofuran. Polymer was isolated by filtration and washed successively with ethyl alcohol to remove any impurities such as residual LiOH and NaOH. The product was then dried in a vacuum oven at 60 °C for 24 h. White powder was obtained as a final product. FT-IR studies were performed using Magna-IR 760 spectrometer in the range of 400–4000 cm⁻¹. The substitution of Na to Li was analyzed by atomic absorption

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spectroscopy (AAS). DSC measurements were performed to measure the thermal properties of polymers, with a heating rate of 10 °C/min.

2.2. Preparation of single ion conductor

Single ion conducting polymer electrolytes were prepared by solution casting method. PLSS was first dissolved in anhydrous DMSO at 90 °C. After the polymer was completely dissolved, PEO was added and solution was further stirred. The resulting viscous solution was cast with a doctor blade onto Teflon plate and left to evaporate solvent slowly at 35 °C for 48 h. The films were finally dried under vacuum at 60 °C for 24 h. Film thickness was in the range of 50–80 μm. All procedures for preparing the single ion conducting polymer electrolytes were carried out in a dry-room.

2.3. Electrical measurements

The ac impedance measurements were performed for ionic conductivity measurement using Zahner Elektrik IM6 impedance analyzer over the frequency range of 100 Hz to 100 KHz with an amplitude of 10 mV. The lithium ion transference number, t_{Li^+} was measured in a cell of Li | polymer electrolyte | Li by the combination of ac impedance and dc polarization measurements, which has been described by Bruce and Vincent [5,6].

3. Results and discussion

FT-IR spectra of PSSS and PLSS are shown in Fig. 1. Full description of absorption band assignments has been reported in the previous literature [7]. The OH stretching vibration of H₂O in the region of 3000–3700 cm⁻¹ and H₂O scissor vibration in the region of 1570–1700 cm⁻¹ were observed in the FT-IR spectra of PSSS and PLSS. In the range of 800–1500 cm⁻¹, PLSS yielded very different spectra than PSSS. The characteristic peaks of PLSS were found at about 833, 1070, 1430 and 1500 cm⁻¹, as shown in Fig. 1. The S=O antisymmetric vibration peaks can be assigned to the peaks at 1430 and 1500 cm⁻¹ [8]. Peaks appeared at 833 and 1070 cm⁻¹ can be assigned to the symmetric vibration of S–O [8]. This result indicates that ion exchange between sodium of PSSS and lithium of LiOH·H₂O has taken place. The substitution of sodium to lithium was also confirmed by AAS, and the ratio of substitution was measured to be 97%.

Fig. 2 shows the ionic conductivity of single ionic conductor as a function of the PLSS concentration. It is found that ionic conductivity passes a maximum value (3.0×10^{-8} S/cm) at [EO]/[Li] = 8.0. An increase of ionic conductivity at the low concentration region (high [EO]/[Li] region) can be attributed to both the increase in the number of carrier ions and the decrease in crystallinity of polymer electrolyte. The less ordered regions become more flexible, which results in an increase of segmental motion of the polymer chain.

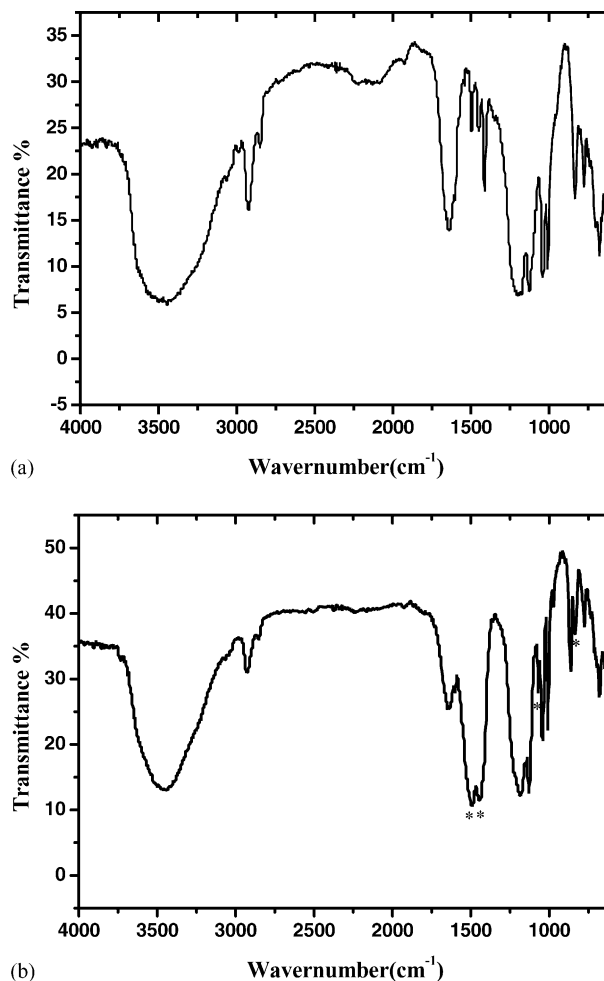


Fig. 1. FT-IR spectra of (a) PSSS and (b) PLSS. The characteristic peaks of PLSS are indicated by symbol (*).

At the higher concentration region (low [EO]/[Li] region), the ionic conductivity decreased beyond maximum point. This result is due to the fact that styrene unit in the PLSS tends to impede ionic movement by acting as an insulator.

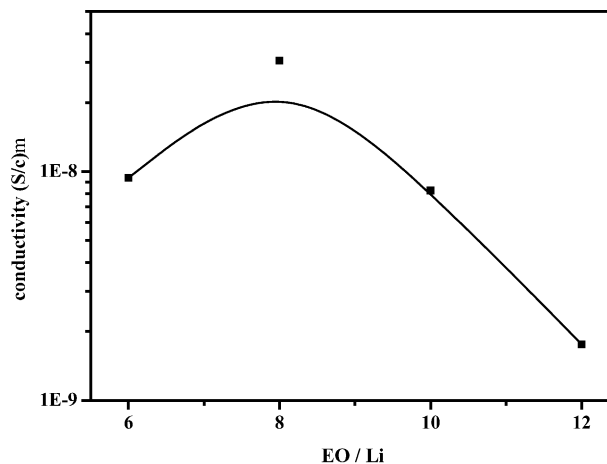


Fig. 2. Variation of ionic conductivity with PLSS content in the blended polymer electrolyte based PEO and PLSS.

Table 1
DSC result of the single ion conducting polymer electrolytes composed of PEO and PLSS

[EO]/[Li]	T_m (°C)	ΔH_m (J/g)	Crystallinity (%)
6	66.4	48.2	23.8
8	67.4	73.6	36.2
10	66.1	85.4	42.1
12	67.0	100.2	49.4
14	66.6	102.0	50.2

Transference number in the blended polymer electrolyte was measured to be 0.85, which means that the blended polymer electrolytes composed of PEO and PLSS exhibit a single ion conducting behavior.

DSC results of single ionic conducting polymer electrolytes are summarized in Table 1. In this table, the enthalpy of melting (ΔH_m) is represented as that per unit weight of PEO, and crystallinity is estimated from the ratio of the experimentally determined ΔH_m to the value of 203 J/g reported in the literature for the enthalpy of melting of 100% crystalline PEO [9]. It is found that the crystallinity is decreased with increasing the PLSS content. This result is due to the intermolecular crosslinking of PEO through ion-dipole interaction with lithium ion in PLSS. Reduction of crystallinity may also arise from random distribution of PLSS into PEO, which may introduce the topological disorder to the polymer electrolyte.

Fig. 3 shows the scanning electron micrographs of the surface for single ion conducting polymer electrolytes. The PLSS are observed to be uniformly distributed from [PEO]/[PLSS] = 14 to [PEO]/[PLSS] = 8, but the PLSS

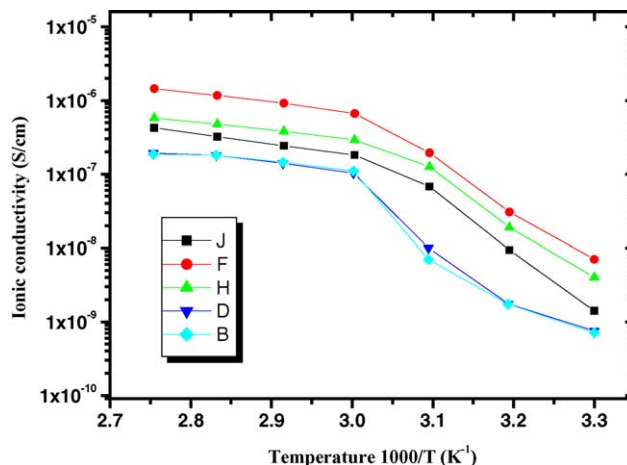


Fig. 4. Temperature dependence of ionic conductivity for the blended polymer electrolytes composed of PEO and PLSS.

agglomeration is observed in the polymer electrolyte of [PEO]/[PLSS] = 6, which means that blended polymer electrolyte having higher PLSS content may exhibit a tendency to separate into phase. This result suggests that the PLSS content should be properly maintained to prevent phase discontinuities in the polymer electrolyte.

Fig. 4 shows the temperature dependence of ionic conductivity for the single ion conducting polymer electrolytes. The optimum PLSS content was determined to be [PEO]/[PLSS] = 8 through ionic conductivity measurements. All the polymer electrolytes show an abrupt decrease in ionic conductivity around 60 °C, which is related to the crystallization of PEO as previously explained from DSC results.

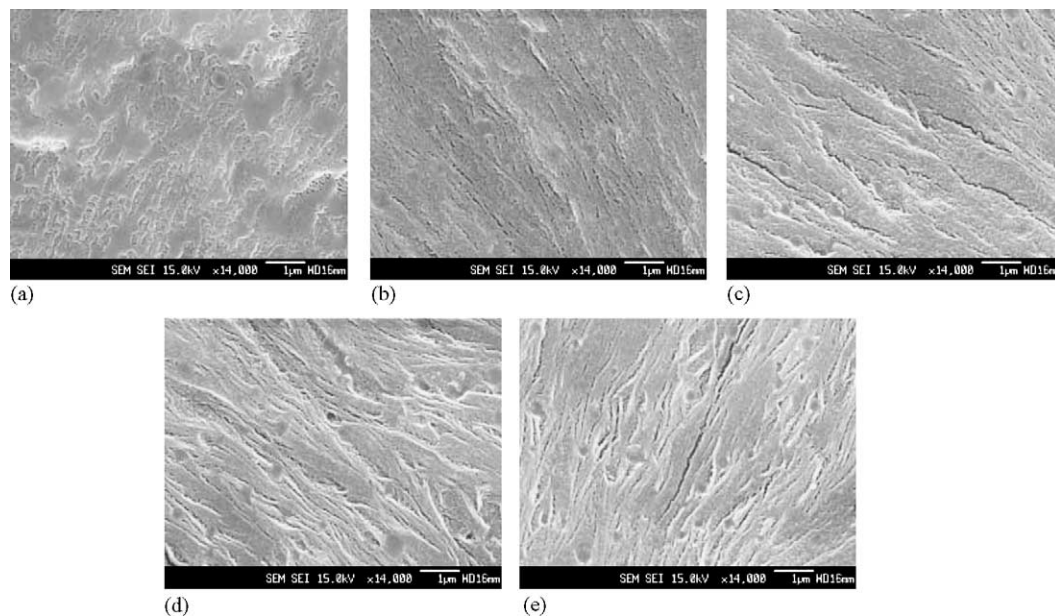


Fig. 3. Scanning electron micrographs of blended polymer electrolytes. (a) [EO]/[Li] = 6, (b) [EO]/[Li] = 8, (c) [EO]/[Li] = 10, (d) [EO]/[Li] = 12, (e) [EO]/[Li] = 14.

4. Conclusions

Poly(lithium 4-styrenesulfonate) was synthesized by ion exchange method from poly(sodium 4-styrenesulfonate). Blended polymer electrolytes composed of PEO and PLSS exhibited a single ion conducting behavior. A reasonably high concentration of PLSS in the blended polymer electrolytes was necessary to affect both the ionic conductivity and crystallinity. The optimum in [EO]/[Li] was proved to be 8.0 in terms of ionic conductivity.

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