

Characteristics of new-type solid polymer electrolyte controlling nano-structure

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Available online 1 August 2005

Abstract

Both high ionic conductivity and excellent mechanical properties are required to solid polymer electrolytes (SPEs) for all-solid lithium polymer batteries. We synthesized a solid polymer electrolyte with micro phase separation structure and its electrochemical characteristics were investigated.

The highest value of ionic conductivity was obtained at a concentration of 5 mol% of lithium salt to ethyleneoxide unit ([EO]). The ionic conductivity of this SPE was $2 \times 10^{-4} \text{ S cm}^{-1}$ at 30 °C. An all-solid state lithium polymer battery, Li/SPE/Li CoO₂ composite cathode cell, exhibited an excellent charge/discharge character with keeping a discharge capacity of 100 mAh g⁻¹ after 100 cycles at room temperature. This SPE was electrochemically stable and did not decompose up to 4.5 V.

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Keywords: Polymer electrolyte; Ionic conductivity; Micro phase separation

1. Introduction

Present lithium ion batteries contain flammable organic solvents, so that a problem has been left in the aspect of safety. Therefore, researches on all-solid state polymer electrolytes without organic solvents have been progressed in the world. Polymer electrolytes have been studied for more than 20 years since the first investigation reported by Armand et al. [1]. However, practical electrolytes have not been developed, yet.

The desirable characteristics of solid polymer electrolyte (SPE) are high ionic conductivity and excellent mechanical properties. However, ionic conductivity and excellent mechanical properties are incompatible and insufficient to practical use [2–6]. We studied SPE with micro phase separation structure to satisfy these requirements. The SPE consists of polystyrene (PSt) block to improve the mechanical properties and polyethylene oxide (PEO) moiety to provide the ionic conductivity. As is well-known, the ionic conductivity depends on the mobility of a polymer chain, so

that poly(ethylene glycol) methyl ether methacrylate (PME) with PEO of low molecular weight was used. PPME-*b*-PSt block copolymers were prepared by using living polymerization technique. In general, block copolymers essentially form micro phase separation structure (Fig. 1).

The sequence type of block copolymer used in this work was BAB (PSt-*b*-PPME-*b*-PSt). Here, A is the initial polymerized unit and B is the consecutive unit in block copolymer. The pseudo-crosslinking effect is expected due to the both ends of PSt parts. The preparation method of PPME-*b*-PSt using living anionic polymerization has been reported [7]. However, it is difficult to prepare PSt-*b*-PPME-*b*-PSt copolymer by the anionic polymerization technique due to the restriction of block polymerizable sequence. In addition, high molecular weight copolymer (MW > 100,000) is hardly prepared by the anionic polymerization technique. This difficulty can be explained by the fact that anionic propagation ends are susceptible to oxygen and moisture. Therefore, BAB block copolymer was synthesized using the living radical polymerization technique [8] with ruthenium(II) complexes and bifunctional initiator. Fig. 2 shows the structure of BAB-block copolymer.

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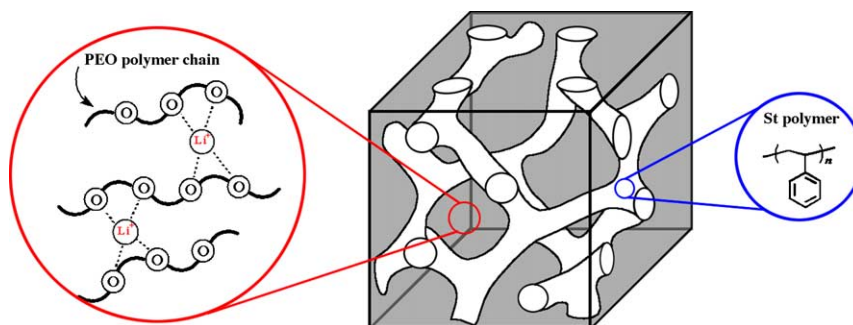


Fig. 1. Schematic illustration of novel nano-structure-controlled solid polymer electrolyte.

Furthermore, a rechargeable cell was prepared by using this BAB block copolymer and the electrochemical characteristic was investigated at room temperature.

2. Experimental

2.1. Synthesis of BAB-block copolymers

BAB-block copolymers were synthesized by the living radical polymerization technique with ruthenium(II) complexes as shown in Fig. 2. In the first step, poly(ethylene glycol) methyl ether methacrylate, $\text{H}_2\text{C}=\text{C}(\text{CH}_3)\text{COO}-(\text{CH}_2\text{CH}_2\text{O})_n\text{CH}_3$ (PME-550; $\text{DP}_{\text{PEO}} = 13$, PME-1000; $\text{DP}_{\text{PEO}} = 23$; PME monomers were supplied by NOF corporation), were polymerized in toluene at 80°C . This polymer was used as macroinitiator after the removal of both ruthenium complexes and residual monomers by silica column treatment. Block copolymerization with styrene was carried out in toluene at 100°C .

2.2. Preparation of SPE film

BAB-block copolymer and LiClO_4 (in a ratio of $[\text{Li}]/[\text{EO}] = 0.03\text{--}0.08$) were dissolved in acetone, the mixture solution was cast on an aluminum plate. The solvent was allowed to evaporate at room temperature in the glove

box overnight and successively under high vacuum for 5 h at 120°C . The thickness of SPE film was about $80\ \mu\text{m}$.

2.3. Preparation of SPE cells

Cathode was consisted of 70 wt% of LiCoO_2 , 15 wt% of Ketjen Black (KB) as an electronic conductor and 15 wt% of polyvinylidene fluoride (PVdF) as a binder. Cathode films were prepared by casting the appropriate *N*-methyl pyrrolidone (NMP) slurry on an aluminum foil with a doctor blade, and then dried under high vacuum. The obtained SPE and LiClO_4 were added into acetone, and this solution was added on the cathode. The polymer solution was infiltrated into the cathode matrix by holding for 10 min under weak reduced pressure. The composite cathode was obtained by repeating this procedure several times. Then, SPE film layer was formed on the above composite cathode by depositing SPE and LiClO_4 to insulate from anode (lithium metal). Finally, the cell was produced by sticking lithium metal and copper collector.

2.4. Electrochemical measurements of SPE cells

The ionic conductivity was measured in the temperature range from 20 to 60°C by ac impedance method using an impedance analyzer (Solartron SI-1260) over a frequency range from 0.1 to $10\ \text{MHz}$.

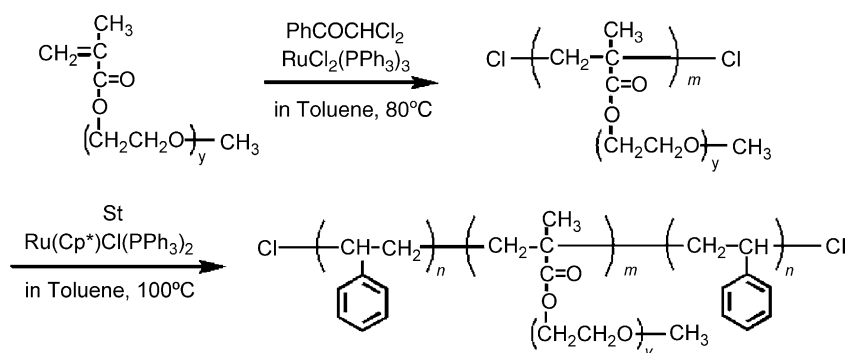


Fig. 2. Synthesis scheme of the BAB-block polymers with micro phase separation structure.

Electrochemical properties of SPE cells were measured at room temperature. Charge and discharge tests were measured by using power supply (HOKUTO DENKO HJ1001SM8). Cut off voltages for charge and discharge cycle test were 3.0 V on discharge and 4.5 V on charge.

3. Results and discussion

3.1. Temperature dependence of ionic conductivity

Fig. 3 shows the temperature dependence of ionic conductivity. The highest value of ionic conductivity was observed at the concentration of 5 mol% of lithium salt to [EO]. The ionic conductivity was $2 \times 10^{-4} \text{ S cm}^{-1}$ at 30°C . This value is relatively high compared with reported values for developed SPE.

Fig. 4 shows the relationship between PEO content and the ionic conductivity.

The ionic conductivity became higher with increasing of PEO content. The ionic conductivity exceeded $1 \times 10^{-4} \text{ S cm}^{-1}$ at room temperature when PEO content exceeded 80%. On the other hand, the ionic conductivity did not change with EO length.

In the case of PME-1000/St block copolymers, the relationships between PEO content and ionic conductivity or tensile strength are shown in Fig. 5. The ionic conductivity became higher as PEO content increased. On the other hand, tensile strength became weak. The ionic conductivity of $1 \times 10^{-4} \text{ S cm}^{-1}$ or more at room temperature was realized by SPE over 80% of PEO content, and its tensile strength was about 3 MPa.

In order to investigate the effect of micro phase separation structure on ionic conductivity and tensile strength, each micro structure of SPE films was observed with transmission electron microscope (TEM). TEM images of SPE are shown

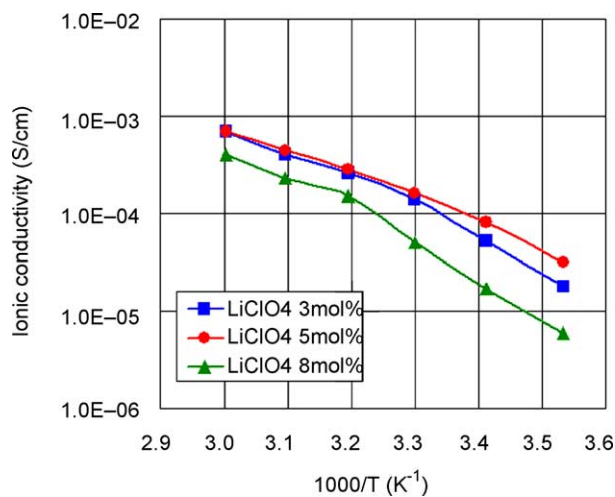


Fig. 3. Temperature dependence of ionic conductivity of novel nano-structure-controlled solid polymer electrolyte containing various concentrations of LiClO_4 : (a) 3 mol%, (b) 5 mol% and (c) 8 mol%.

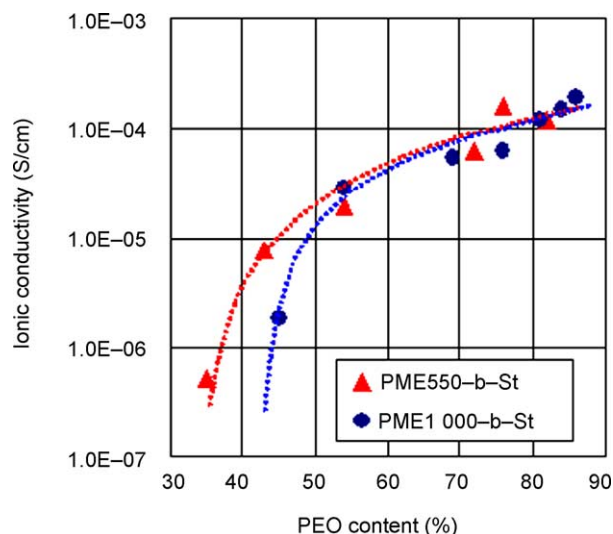


Fig. 4. Effects of PEO content on the ionic conductivity for two different length polymers: (a) PME550-*b*-St and (b) PME1000-*b*-St.

in Fig. 6. The micro phase separation with a continuous phase of PEO forming a network structure was observed when the PEO content exceeded 70%. The formation of the continuous phase of PEO gives the high ionic conductivity. When styrene moiety increased, PEO phase could not form the continuous phase. Consequently, the ionic conductivity was decreased with decreasing PEO content.

3.2. Electrochemical properties of SPE cells

An all-solid state rechargeable lithium cell of $\text{LiCoO}_2/\text{SPE}/\text{Li}$ was prepared by using this BAB-block polymer successfully, and its electrochemical characteristic was investigated at room temperature.

Fig. 7 shows the discharge and charge curves of the $\text{LiCoO}_2/\text{SPE}/\text{Li}$ cell. SPE cells showed the high discharge capacity at discharge rate of 0.1 C. The discharge capacity was maintained over 100 mAh g^{-1} against the theoretical capacity 140 mAh g^{-1} . Moreover, the cycle performance was

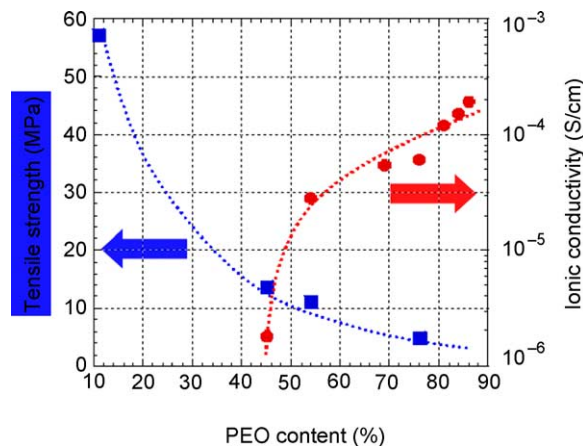


Fig. 5. Effects of PEO content on ionic conductivity and film strength.

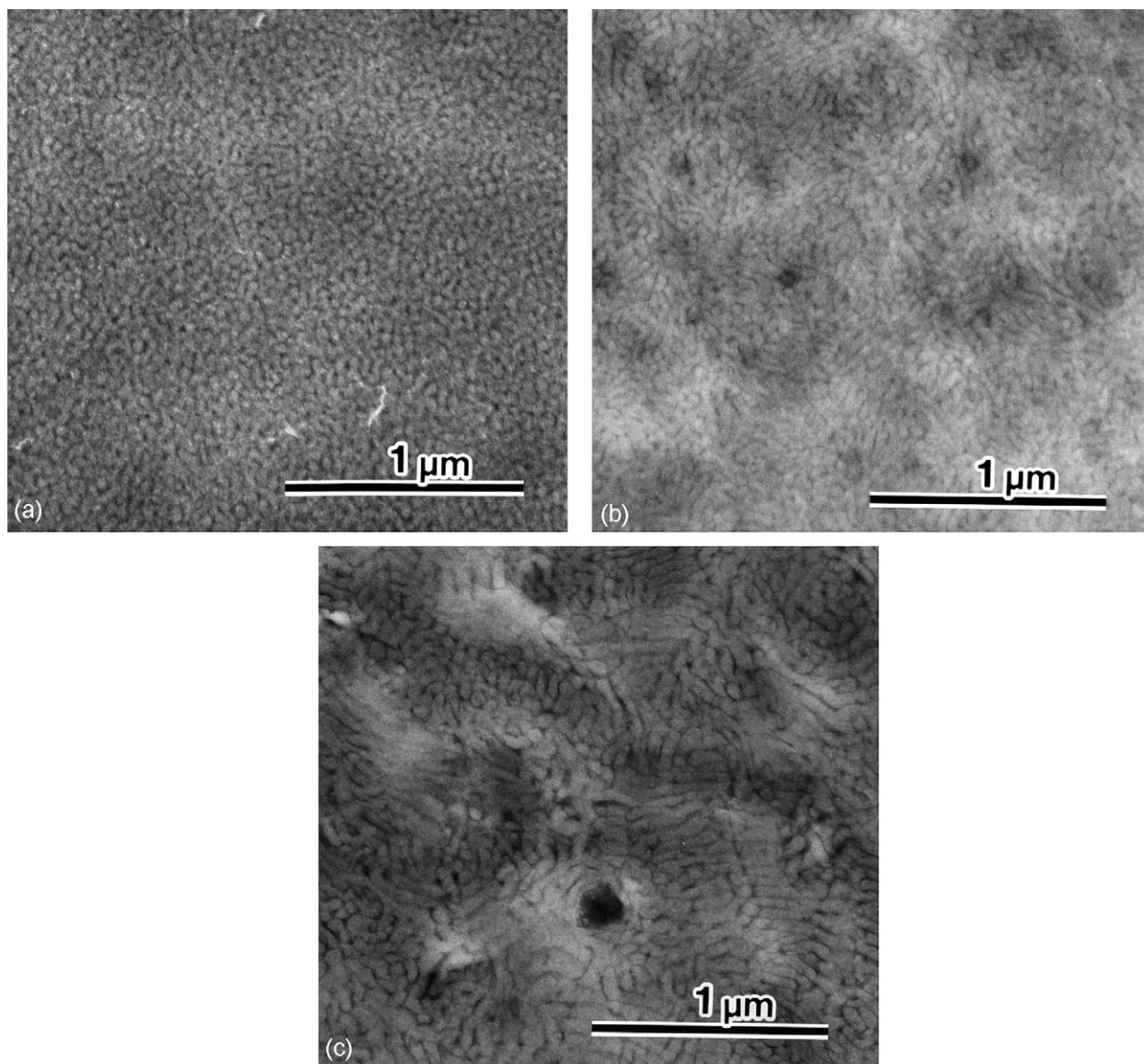


Fig. 6. TEM images of SPE with (a) 70%, (b) 50–70% and (c) 30–50% PEO content.

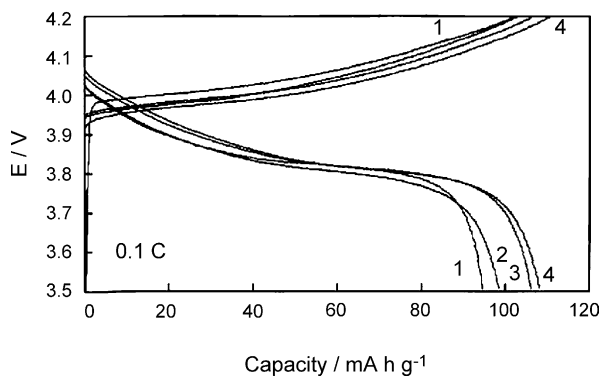


Fig. 7. Charge and discharge curves of Li/SPE/LiCoO₂ cell at 0.1 C.

confirmed over 100 cycles. And this SPE was electrochemically stable and did not decompose up to 4.5 V.

4. Conclusions

A novel nano-structure-controlled BAB-block copolymers have been used as a matrix of solid polymer electrolytes. The micro phase separation with the continuous phase of PEO forming a network structure was observed, when PEO content exceeded 70%. The SPE containing LiClO₄ exhibited a high ionic conductivity of $2.0 \times 10^{-4} \text{ S cm}^{-1}$ at 30 °C. The formation of the continuous phase of PEO is very important to realize the high ionic conductivity.

An all-solid state SPE cell of Li/SPE/LiCoO₂ had an excellent charge and discharge characteristics with keeping a

discharge capacity of 100 mAh g^{-1} after 100 cycles at room temperature. Moreover, this SPE was electrochemically stable and did not decompose up to 4.5 V.

From the above results, this SPE is expected to the application of a room-temperature-operation-type battery.

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