

Short communication

Electrochemical characterization of blend polymer electrolytes based on poly(oligo[oxyethylene]oxyterephthaloyl) for rechargeable lithium metal polymer batteries

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Abstract

Solid polymer electrolytes composed of poly(ethylene oxide)(PEO), poly(oligo[oxyethylene]oxyterephthaloyl) and lithium perchlorate have been prepared and characterized. Addition of poly(oligo[oxyethylene]oxyterephthaloyl) to PEO/LiClO₄ reduced the degree of crystallinity and improved the ambient temperature ionic conductivity. The blend polymer electrolyte containing 40 wt.% of poly(oligo[oxyethylene]oxyterephthaloyl) showed an ionic conductivity of $2.0 \times 10^{-5} \text{ S cm}^{-1}$ at room temperature and a sufficient electrochemical stability to allow application in the lithium batteries. By using the blend polymer electrolytes, the lithium metal polymer cells composed of lithium anode and LiCoO₂ cathode were assembled and their cycling performances were evaluated at 40 °C.

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1. Introduction

Solid polymer electrolytes have received considerable attention as solid electrolyte materials in the rechargeable lithium batteries, because the use of a solid polymer electrolyte makes the fabrication of safe batteries possible and permits the development of thin batteries with design flexibility [1–5]. A large number of studies to date have been carried out on solid polymer electrolytes based on poly(ethylene oxide)(PEO) containing the alkali metal salts. However, these materials have a major drawback that the ionic conductivity for the practical applications can only be reached at around 100 °C, due to the high degree of crystallinity inherent in these complexes at room temperature. Because of the inherent drawback of PEO-based solid polymer electrolytes, various attempts such as grafting [6,7], block copolymerization [8,9], interpenetration polymer network [10,11] have been tried to incorporate PEO into a macromolecular sequence which inhibits crystallization, while maintaining

a low value of the glass transition temperature. Although these novel approaches are promising, the fact that their preparation requires nontrivial synthetic processes is a drawback for practical application. Therefore, it is of considerable importance to develop easier method for preparing the solid polymer electrolytes with higher ionic conductivities and dimensional stability. In this regard, previous works on the preparation of polymer electrolytes by blending polymers are of interest [12–16]. The main advantages of these blend-based polymer electrolytes are simplicity of preparation and easy control of physical properties by compositional changes. Thus, the detailed studies of the blend-based polymer electrolytes can furnish valuable information on the relative importance of various factors which affect the electrical, thermal and mechanical properties of the solid polymer electrolytes.

With the aim of developing highly conductive solid polymer electrolytes, we synthesized poly(oligo[oxyethylene]oxyterephthaloyl) as a matrix polymer. It has ethylene oxide units for dissolving lithium salt in the polymer backbone and lower crystallinity than PEO. The solid polymer electrolytes based on poly(oligo[oxyethylene]oxyterephthaloyl) showed high ionic conductivity at room temperature. However, their

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poor mechanical property prevented the preparation of dimensional stable thin films necessary for practical use in the electrochemical devices. In order to overcome this problem, we blended it with a high molecular weight PEO, enabling the fabrication of thin film with acceptable ionic conductivity. In this work, we present the ionic conductivity and thermal properties of the blended polymer electrolytes composed of PEO, poly(oligo[oxyethylene]oxyterephthaloyl) and lithium salt. By using the blend polymer electrolytes, lithium metal polymer cells composed of lithium anode and LiCoO₂ cathode are assembled and their cycling performances are evaluated.

2. Experimental

2.1. Polymer synthesis and characterization

Poly(oligo[oxyethylene]oxyterephthaloyl) was synthesized in benzene with triethylamine as a catalyst via solution polycondensation in a glass reactor equipped with a nitrogen inlet, reflux condenser, an additional funnel and a mechanical stirrer. Poly(ethylene glycol)(PEG, MW = 1000) dissolved in benzene with a catalytic amount of triethylamine was fed into a glass reactor. A solution of slight molar excess of terephthaloyl chloride in benzene was added to the reactor dropwise over a period of 1 h with vigorous agitation at room temperature. After the terephthaloyl chloride solution was completely added, the reaction temperature was raised to 60 °C, and the reaction solution was stirred for a further 10 h. After the end of the reaction, the triethylamine salt (TEA·HCl) was filtered off, and the polymer was recovered by precipitating the filtrate into an excess of diethyl ether under mechanical agitation. The obtained polymer was then dried in a vacuum oven at room temperature for 24 h. White waxy powder was obtained as a product. ¹H NMR spectra were obtained in DMSO-*d*₆ solvent on a Bruker-DRX-300 NMR spectrometer with tetramethylsilane (TMS) as an internal standard reference.

2.2. Preparation of blend polymer electrolyte

Appropriate amounts of poly(oligo[oxyethylene]oxyterephthaloyl), PEO(MW: 1,000,000) and LiClO₄ were dissolved together in anhydrous acetonitrile. The solution was well stirred and cast on a Teflon plate, then left to evaporate the solvent at room temperature. The resulting film was dried in a vacuum oven at 60 °C for at least 24 h. The polymer electrolyte film was sandwiched between two stainless steel (SS) electrodes for conductivity measurements. The ac impedance measurements were performed using a Zahner Elektrik IM6 impedance analyzer at 25 °C, over the frequency range 10 Hz–100 kHz. The ionic conductivity (σ) was calculated from the impedance data, using the relation $\sigma = t/RA$, where t and A are the thickness and area of the polymer electrolyte, and R was bulk resistance derived from the ac impedance spectrum. A linear sweep voltammetry was performed on a SS working electrode at 25 °C, with counter and reference electrodes of lithium, at a scanning rate of 1.0 mV s⁻¹. DSC thermal analysis was carried out to measure the T_g , T_m ,

ΔH_m values of the polymer electrolytes with a heating rate of 10 °C min⁻¹ from -100 to 100 °C.

2.3. Cell assembly and electrical measurements

Lithium metal polymer cell was assembled by sandwiching the polymer electrolyte between lithium anode and LiCoO₂ cathode. The anode consisted of 50 μm thick Li foil (Cyprus Foote Mineral Co.) pressed onto copper current collector. The cathode was composed of LiCoO₂ (Japan Chemical), polymer electrolyte and super-P carbon on an aluminum foil. Its active area was 4 cm² and its active mass loading corresponded to the capacity of about 2.0 mAh cm⁻². The cell was enclosed in a metallized plastic bag and vacuum-sealed. All assemblies of the cells were carried out in a dry box filled with argon gas. The charge and discharge cycling tests of lithium-metal polymer cells were conducted in the voltage range of 3.0–4.2 V at 40 °C with Toyo battery test equipment (TOSCAT-3000U).

3. Results and discussion

The chemical structure of poly(oligo[oxyethylene]oxyterephthaloyl) was characterized by ¹H NMR spectra, a typical example of which is shown in Fig. 1. The formation of ester linkage from the condensation reaction between PEG and terephthaloyl chloride causes a down-field shift of the H_α and H_β peaks compared with the peaks of H_γ hydrogens in the internal oxyethylene units (Fig. 2), resulting in a distinct peak for H_α ($\delta = 4.41$ ppm) and H_β ($\delta = 3.75$ ppm), respectively. The

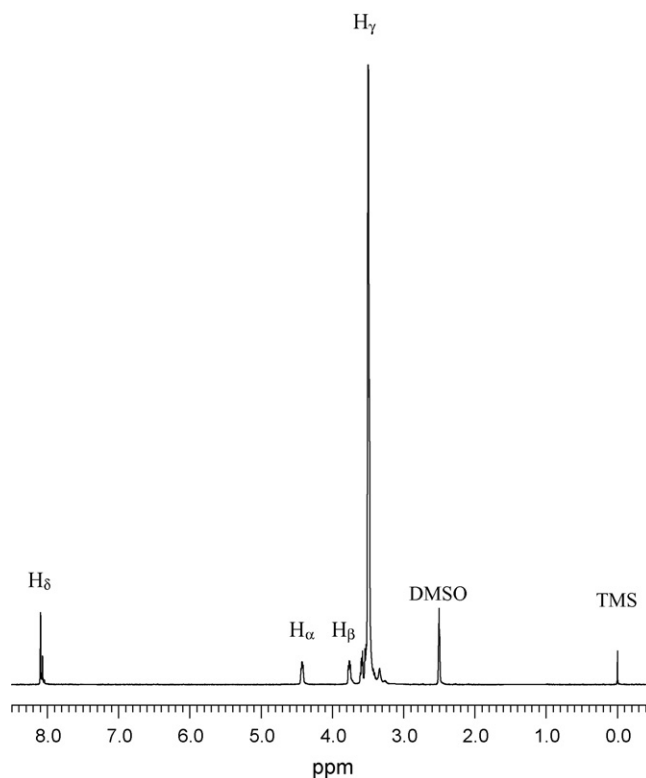


Fig. 1. ¹H NMR spectrum of poly(oligo[oxyethylene]oxyterephthaloyl) in DMSO-*d*₆.

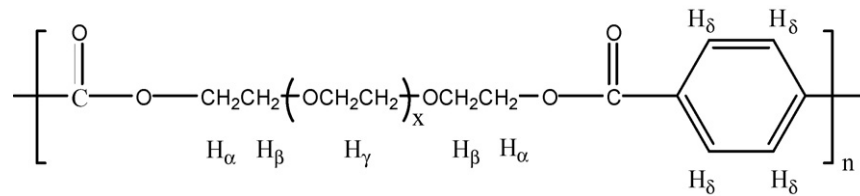


Fig. 2. Chemical structure of poly(oligo[oxyethylene]oxyterephthaloyl) and nomenclature of the protons for assigning the peaks shown in ^1H NMR spectrum.

peaks for the aromatic hydrogens (H_δ) in the terephthaloyl unit appeared at 8.10 ppm. The intensity ratio of $\text{H}_\alpha:\text{H}_\beta:\text{H}_\gamma:\text{H}_\delta$ in Fig. 1 was approximately 1.0:1.1:22.6:1.1, which was consistent with the theoretical value (1.0:1.0:20.3:1.0) calculated from the expected polymer structure. The number average molecular weight of poly(oligo[oxyethylene]oxyterephthaloyl) was measured to be 27,000 by gel permeation chromatography (GPC). Thus, the number average degree of polymerization is estimated to 23.9. From the DSC results, the degree of crystallinity for poly(oligo[oxyethylene]oxyterephthaloyl) was observed to be significantly reduced compared with that of the corresponding PEG. The values of ΔH_m for PEG and poly(oligo[oxyethylene]oxyterephthaloyl) are 157.7 and 68.3 J g^{-1} , respectively. Poly(oligo[oxyethylene]oxyterephthaloyl) has also lower T_m (31.2 $^\circ\text{C}$) than that (37.7 $^\circ\text{C}$) of the PEG. The reduction of crystallinity and melting temperature may be attributed to the alternating introduction of terephthaloyl units between ethylene oxide units in the polymer backbone.

When the lithium perchlorate was incorporated into poly(oligo[oxyethylene]oxyterephthaloyl) for making the polymer electrolyte, the resulting film was sticky and glutinous, and thus was difficult to handle. In order to improve the dimensional stability of the film, we blended it with a high molecular weight PEO. All the films prepared with different blend composition were very stable and did not phase separate, which suggests that homogeneous polymer electrolytes are formed over all the blend compositions. The addition of lithium perchlorate probably facilitates uniform film formation, because the lithium cation can interact simultaneously with the oxygen atoms of both polymers. Fig. 3 shows the ionic conductivity measured at 25 $^\circ\text{C}$ and crystallinity of the solid polymer electrolytes as a function of the blend composition. The crystallinity was estimated from the ratio of the experimentally determined ΔH_m to the value of 203 J g^{-1} reported in the literature [17] for the heat of fusion for 100% crystalline PEO. It is found that the crystallinity of the polymer electrolyte decreases with increasing poly(oligo[oxyethylene]oxyterephthaloyl) content. It can be attributed to the formation of less perfect crystalline lamellae, resulting from the dispersion of poly(oligo[oxyethylene]oxyterephthaloyl) having the crystal defects. Ionic conductivity increases with an increase of the poly(oligo[oxyethylene]oxyterephthaloyl) content, which is due to the increase of amorphous character stemming from the presence of poly(oligo[oxyethylene]oxyterephthaloyl). However, the polymer electrolytes containing high amount of poly(oligo[oxyethylene]oxyterephthaloyl) exhibited poor mechanical property. Thus, it can be concluded that 40 wt.% of

poly(oligo[oxyethylene]oxyterephthaloyl) is an optimum composition in consideration of both the ionic conductivity and the mechanical stability. The ionic conductivity of the optimized solid polymer electrolyte was $2.0 \times 10^{-5} \text{ S cm}^{-1}$, and it is a rubbery film with dimensional stability. In further experiments, the composition of poly(oligo[oxyethylene]oxyterephthaloyl) in the blended polymer electrolyte will be restricted to 40 wt.%. The electrochemical stability of blended polymer electrolyte was evaluated by linear sweep voltammetric measurement at 25 $^\circ\text{C}$. It was performed by applying an anodic voltage to a cell consisting of the solid polymer electrolyte (SPE) sandwiched between a lithium electrode and an inert SS electrode. Fig. 4 shows a typical linear sweep voltammetry curve of the Li/SPE/SS cell. From the figure, the decomposition voltage is found to be high, which is acceptable for high voltage cathode materials, such as LiCoO_2 , LiNiO_2 and LiMn_2O_4 .

We investigated the interfacial behavior of the lithium electrode in contact with the polymer electrolyte under a prolonged timescale. Fig. 5 shows the time evolution of ac impedance response of the Li/SPE/Li cell under open circuit potential conditions at 25 $^\circ\text{C}$. As shown in figure, a progressive extension of the low-frequency semicircle can be easily noticed initially, indicating an increase of the interfacial resistance, which may be associated with the growth of a passivation layer on the lithium electrode. A large interfacial resistance observed in this figure may be attributed to the formation of thick passive layer on the lithium electrode. It may contain the product of the corrosion reaction between the lithium electrode and the polymer, the

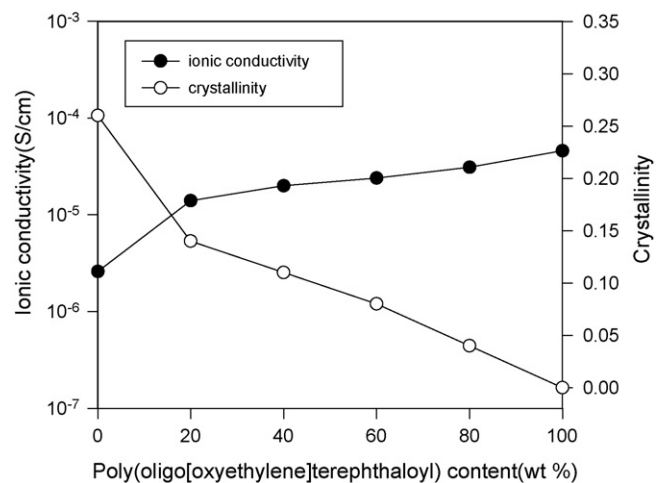


Fig. 3. Ionic conductivity and crystallinity of the blended polymer electrolytes as a function of the blend composition. Ionic conductivity is measured one at 25 $^\circ\text{C}$.

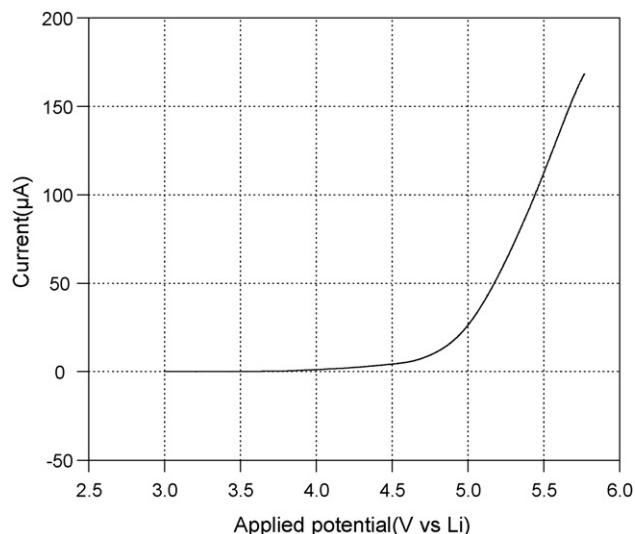


Fig. 4. Current–voltage curve of the Li/SPE/SS cell, which is measured at 25 °C. Scan rate is 1.0 mV s⁻¹.

salt, the residual solvent and other impurities. To demonstrate the usefulness of the blend polymer electrolyte in rechargeable lithium metal cells, we fabricated the Li/SPE/LiCoO₂ cell. Fig. 6 shows the charge–discharge curves of the cell with number of cycles at 40 °C, which are obtained at a constant current density of 0.1 mAh cm⁻². Ambient temperature conductivity of solid polymer electrolyte in the cell is too low to test the cell performance at room temperature. Thus, the cycling performances of the cell assembled with solid polymer electrolyte were evaluated at 40 °C. Ionic conductivity of the solid polymer electrolyte is 6.0×10^{-5} S cm⁻¹ at 40 °C. As shown in Fig. 6, the cell initially delivered a discharge capacity of 123 mAh g⁻¹ based on LiCoO₂ active material in the cathode. The coulombic efficiency, which is defined as a ratio of the discharge capacity to the charge

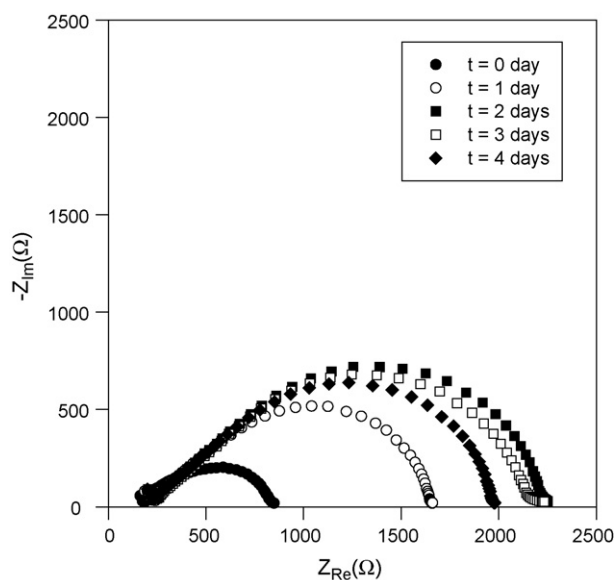


Fig. 5. AC impedance spectra of the Li/SPE/Li cell as a function of a storage time, which are measured at 25 °C.

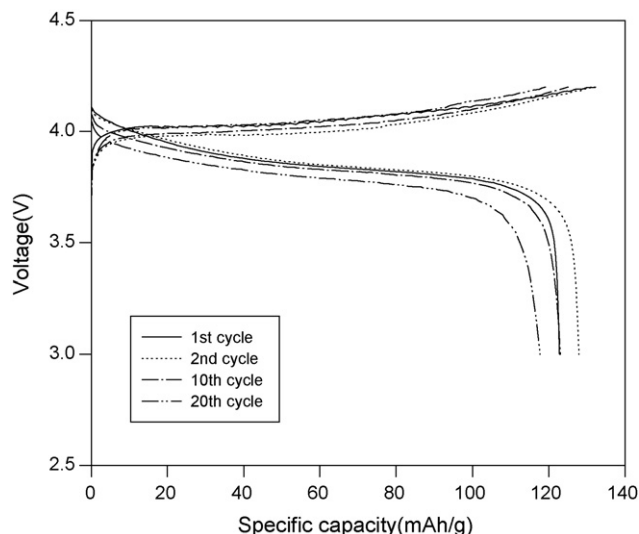


Fig. 6. Charge and discharge curves of the Li/SPE/LiCoO₂ cell at a constant current density of 0.1 mAh cm⁻², which are measured at 40 °C.

capacity, is 93% in the first cycle. The low coulombic efficiency observed at the initial cycle may be caused by the formation of a passivating film, often called the solid electrolyte interphase (SEI) on the surface of lithium electrode. The discharge capacity reached a maximum value (128 mAh g⁻¹) at the second cycle, and then slowly decreased with further cycling. The coulombic efficiency of the cell is maintained to be higher than 98.5% through cycling after the initial few cycles. Further research is being conducted in the authors' laboratories improve the cycling performances of the rechargeable lithium metal cells using the solid polymer electrolytes.

4. Conclusions

Blend-based solid polymer electrolytes composed of PEO, poly(oligo[oxyethylene]oxyterephthaloyl) and lithium salt have been prepared and characterized. Addition of poly(oligo[oxyethylene]oxyterephthaloyl) to PEO/LiClO₄ reduced the degree of crystallinity and improved the ionic conductivity at room temperature. The ionic conductivity of the blended polymer electrolyte containing 40 wt.% of poly(oligo[oxyethylene]oxyterephthaloyl) was 2.0×10^{-5} S cm⁻¹ at 25 °C, and it is a rubbery film with dimensional stability. Lithium metal cell consisted of lithium anode, solid polymer electrolyte and LiCoO₂ cathode gave a specific discharge capacity of 128 mAh g⁻¹ at 40 °C.

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