

# Lithium polymer batteries using the highly porous membrane filled with solvent-free polymer electrolyte

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## Abstract

Solid polymer electrolyte supported by a microporous membrane was prepared and characterized. The polymer electrolyte was prepared by penetrating the highly conductive solvent-free polymer electrolyte based on poly(oligo [oxyethylene] oxyterephthaloyl) into the pores of the highly porous membrane. The electrochemical characteristics of the solid polymer electrolytes are presented, and we discuss the possibility of them as an electrolyte material for lithium polymer batteries.

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## 1. Introduction

Solid polymer electrolytes have been paid much attention in rechargeable lithium batteries, because of absence of risk for leakage of liquid electrolytes, high energy density and design flexibility. Development of a truly solid-state lithium polymer battery is dependent upon the successful identification of a suitable solid polymer electrolyte. Solvent-free solid polymer electrolytes used in the rechargeable lithium polymer batteries are mainly poly(ethylene oxide)(PEO)-based polymers containing the lithium salts [1]. However, these materials have a major drawback that the ionic conductivity for practical application can only be reached at high temperature, 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 [2,3], block copolymerization [4,5], interpenetration polymer network [6,7] 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 appli-

cation. Besides, their mechanical properties were often very poor, and the films had to be hardened by curing. In order to overcome these problems, the microporous separator of polyolefins impregnated with gel polymer electrolytes have been developed as an electrolyte material for lithium batteries. Morigaki et al. manufactured a lithium secondary battery using a microporous polyolefin separator, the pores of which were filled with gel polymer electrolyte [8]. In another example, a solution consisting of ethylene carbonate, propylene carbonate, tetraethylene glycol dimethyl ether, tetraethylene glycol diacrylate, LiAsF<sub>6</sub> and a small amount of a photopolymerization initiator is impregnated into the porous polyolefin separator and polymerized to form a solid electrolyte [9]. Recently, the porous polymer coated on polyethylene separator has been used for preparing gel polymer electrolyte [10]. However, the use of solvents in the previous works can cause another problems related to loss of organic solvents by evaporation and high reactivity towards the lithium metal anode.

With the aim of developing highly conductive solid polymer electrolytes, we synthesized the solid polymer electrolytes based on poly(oligo [oxyethylene] oxyterephthaloyl), which showed high ionic conductivity at room temperature. However, their poor mechanical property prevented the preparation of dimensional stable thin film necessary for practical use. In order to improve the poor mechanical strength, this solvent-free polymer electrolyte was penetrated into the pores of the highly porous

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separator. In this system, mechanically robust porous separator can protect against shortage to assure safety reliability and to make a feasible thin film. By using the separator filled with solvent-free polymer electrolyte, lithium metal polymer cells composed of lithium anode and  $\text{LiCoO}_2$  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 = 3400) 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  $60^\circ\text{C}$ , and the reaction solution was stirred for a further 10 h. After the end of the reaction, the triethylamine salt ( $\text{TEA}\cdot\text{HCl}$ ) 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.  $^1\text{H}$  NMR spectra were obtained in  $\text{DMSO-d}_6$  solvent on a Bruker-DRX-300 NMR spectrometer with tetramethylsilane (TMS) as an internal standard reference.

### 2.2. Preparation of the polymer electrolyte

Appropriate amounts of poly(oligo [oxyethylene] oxyterephthaloyl) and  $\text{LiClO}_4$  were dissolved together in anhydrous acetonitrile. A microporous polyethylene(PE) separator(Asahi Kasei, thickness:  $18\ \mu\text{m}$ , porosity: 50%) was then immersed in the polymer solution. The resulting separator was taken out and left to evaporate to the solvent slowly at room tempera-

ture. After evaporation of acetonitrile, the separator was dried in a vacuum oven at  $60^\circ\text{C}$  for 24 h. The PE separator filled with polymer electrolyte was sandwiched between two stainless steel (SS) electrodes for conductivity measurements. The a.c. impedance measurements were performed using an impedance analyzer over the frequency range 10 Hz–100 kHz at  $25^\circ\text{C}$ . The ionic conductivity ( $\sigma$ ) 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 a.c. impedance spectrum. A linear sweep voltammetry was performed on a SS working electrode, with counter and reference electrodes of lithium, at a scanning rate of  $1.0\ \text{mV/s}$ . The surface morphology of PE separator and PE separator filled with polymer electrolyte was examined using a scanning electron microscope. DSC thermal analysis was carried out to measure the  $T_g$ ,  $T_m$ ,  $\Delta H_m$  values of the polymer electrolytes with a heating rate of  $10^\circ\text{C/min}$  from  $-100$  to  $100^\circ\text{C}$ .

### 2.3. Cell assembly and electrical measurements

Lithium metal polymer cell was assembled by sandwiching the PE separator filled with polymer electrolyte between lithium anode and  $\text{LiCoO}_2$  cathode. The anode consisted of  $50\ \mu\text{m}$  thick Li foil (Cyprus Foote Mineral Co.) pressed onto copper current collector. The cathode was composed of  $\text{LiCoO}_2$  (Japan Chemical), polymer electrolyte and super-P carbon on an aluminum foil. Its active area was  $4\ \text{cm}^2$  and its active mass loading corresponded to the capacity of about  $2.0\ \text{mA h/cm}^2$ . 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  $3.0$ – $4.2\ \text{V}$  at  $40^\circ\text{C}$  with Toyo battery test equipment (TOSCAT-3000U).

## 3. Results and discussion

The chemical structure of poly(oligo [oxyethylene] oxyterephthaloyl) was characterized by  $^1\text{H}$  NMR spectra, a

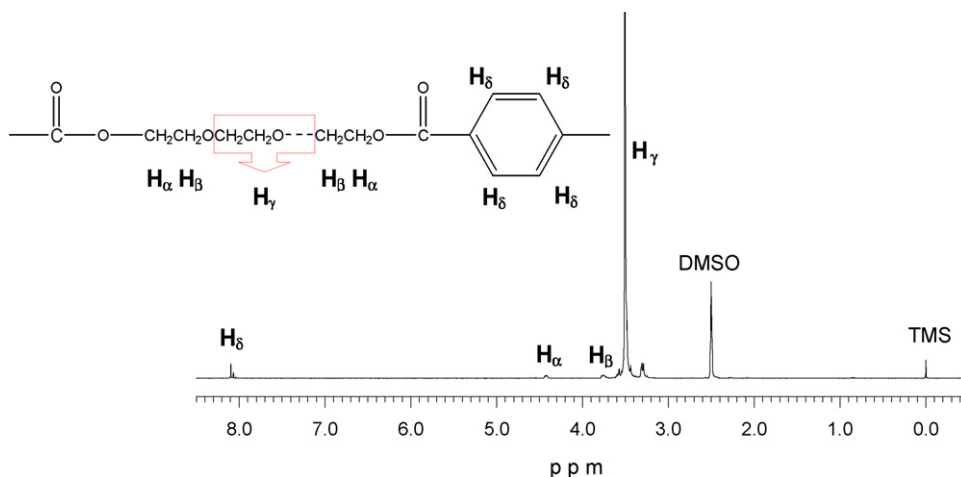


Fig. 1.  $^1\text{H}$  NMR spectrum of poly(oligo [oxyethylene] oxyterephthaloyl) in  $\text{DMSO-d}_6$ .

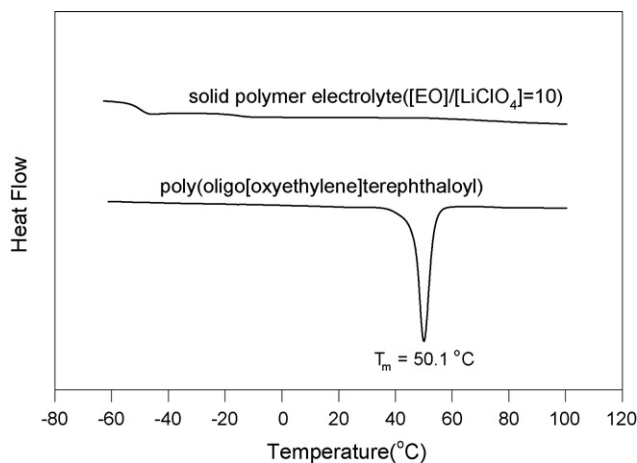


Fig. 2. DSC thermograms of poly[oligo(oxyethylene)terephthaloyl] and solid polymer electrolyte containing LiClO<sub>4</sub> ([EO]/[LiClO<sub>4</sub>]=10).

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<sub>α</sub> and H<sub>β</sub> peaks compared with the peaks of H<sub>γ</sub> hydrogens in the internal oxyethylene units, resulting in a distinct peak for H<sub>α</sub> (δ=4.43 ppm) and H<sub>β</sub> (δ=3.76 ppm), respectively. The peaks for the aromatic hydrogens (H<sub>δ</sub>) appeared at 8.07 ppm. The <sup>1</sup>H NMR spectrum shown in Fig. 1 was consistent with the expected polymer structure. Poly(oligo [oxyethylene] oxyterephthaloyl) was also confirmed to be free of residual solvents such as benzene and diethyl ether by the <sup>1</sup>H NMR spectrum.

We prepared the solid polymer electrolyte composed of poly(oligo [oxyethylene] oxyterephthaloyl) and lithium perchlorate. The salt concentration was fixed to be constant ([LiClO<sub>4</sub>]/[EO]=0.10). DSC thermograms of poly(oligo [oxyethylene] oxyterephthaloyl) and solid polymer electrolyte are shown in Fig. 2. An endothermic peak due to the melting of crystalline poly(oligo [oxyethylene] oxyterephthaloyl) is observed at 50.1 °C with a fusion heat of 136.9 J/g. This value is lower than the fusion heat (188.3 J/g) of melting transition observed at 60.0 °C for the corresponding PEG(MW:3,400) used for synthesizing poly(oligo [oxyethylene] oxyterephthaloyl). The reduction of crystallinity may be attributed to the alternating introduction of terephthaloyl unit between ethylene oxide units in the backbone of poly(oligo [oxyethylene] oxyterephthaloyl). With the incorporation of LiClO<sub>4</sub> into the poly(oligo [oxyethylene] oxyterephthaloyl) polymer, the melting peak was completely disappeared and the glass transition could be clearly detected, which indicates that the solid polymer electrolyte becomes fully amorphous by incorporating LiClO<sub>4</sub>. The destruction of crystalline structure is due to the intermolecular crosslinking of the polyether chains through ion-polymer interactions with the lithium cations.

Fig. 3 shows the a.c. impedance spectrum of SS/SPE/SS cell (SPE: solid polymer electrolyte), which is measured at 25 °C. The intercept on the real axis gives the electrolyte resistance. Ionic conductivity was calculated to be  $3.2 \times 10^{-4}$  S/cm from the a.c. impedance result. High ionic conductivity of the solid polymer electrolyte results from the fully amorphous structure.

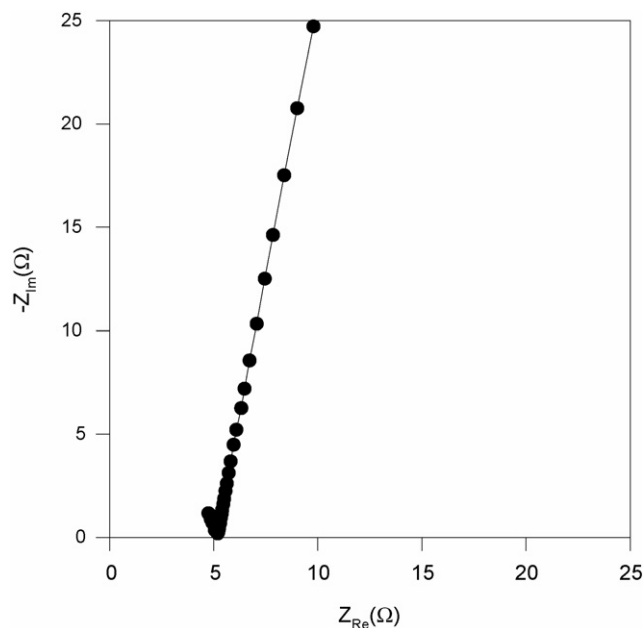
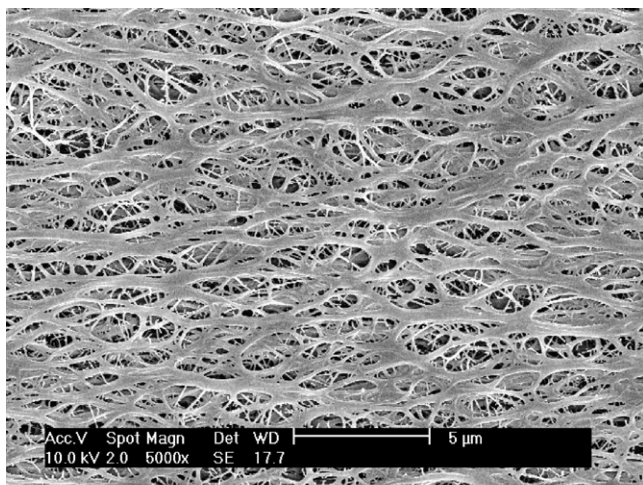


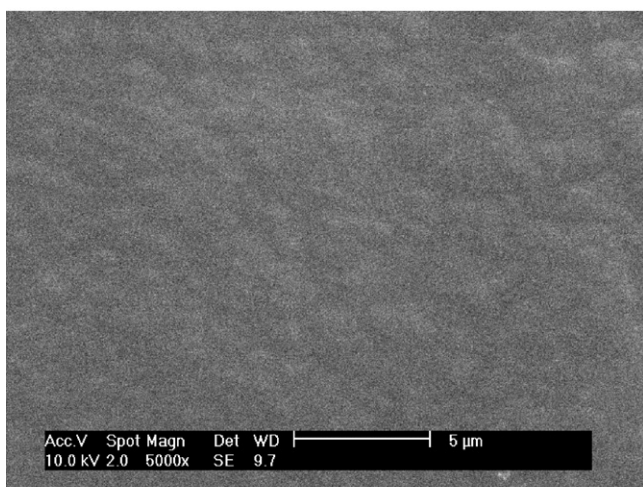
Fig. 3. AC impedance spectrum of the SS/SPE/SS cell at room temperature.

However, the polymer electrolyte film was sticky and glutinous, and thus was difficult to handle. Its poor mechanical strength prevented the preparation of dimensionally stable film. In order to overcome the poor mechanical strength, we tried to penetrate the sticky polymer electrolyte based on poly(oligo [oxyethylene] oxyterephthaloyl) into the pores of the highly porous separator. Fig. 4(a) shows the scanning electron micrograph of the porous PE separator used in this study. This separator is characterized by highly porous structure. It has a nominal thickness of 18 μm and its porosity is 50%. When the separator is filled with polymer electrolyte, the pores of the separator become fully covered by the polymer electrolyte, as shown in Fig. 4(b). From the SEM image of the cross section of the separator filled with polymer electrolyte, the solid polymer electrolytes are observed to be penetrated into the pores of the porous separator. From the a.c. impedance measurements, its ionic conductivity was estimated to be  $2.1 \times 10^{-5}$  S/cm. By filling solid polymer electrolyte into the pores of the separator, ionic conductivity is decreased about an order of magnitude as compared to that ( $3.2 \times 10^{-4}$  S/cm) of solid polymer electrolyte, but the mechanical strength was significantly enhanced. In the separator filled with polymer electrolyte, sticky polymer electrolyte plays an effective role of an ionic conduction inside of the separator, and can assist in adhering the electrodes to the separator. The mechanical strength of the separator filled with solid polymer electrolyte was of the same order as that of the PE separator itself. The electrochemical stability of the solid polymer electrolyte supported by PE separator was evaluated by linear sweep voltammetric measurement. From the linear sweep voltammetry curve of the Li/SPE/SS cell, the decomposition voltage was found to be over 4.4 V versus Li.

In order to evaluate the electrochemical performance of lithium metal polymer cell using the PE separator filled with solid polymer electrolyte (PE-SPE), we fabricated a Li/PE-SPE/LiCoO<sub>2</sub> cell. Fig. 5 shows the charge–discharge curves of



(a)



(b)

Fig. 4. SEM images of (a) PE separator and (b) PE separator filled with polymer electrolyte.

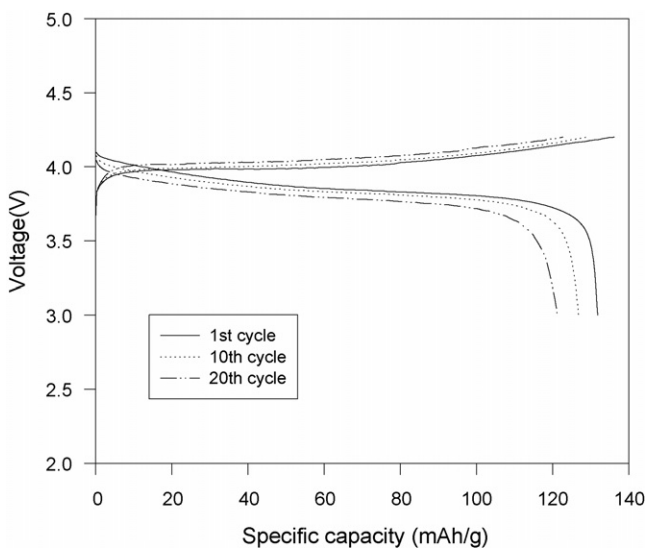


Fig. 5. Charge and discharge curves of the lithium metal polymer cell at a constant current density of  $0.1 \text{ mA/cm}^2$ , which are measured at  $40^\circ\text{C}$ .

the cell with number of cycles at  $40^\circ\text{C}$ , which are obtained at a constant current density of  $0.1 \text{ mA/cm}^2$ . The cell initially delivered a discharge capacity of  $132 \text{ mA h/g}$  based on  $\text{LiCoO}_2$  active material in the cathode. The coulombic efficiency of the cell was maintained to be higher than 98.5% through cycling after the initial few cycles. The discharge capacity slowly decreased with cycling. The capacity decline of the cell may be mainly related to the deterioration of interfacial contacts of composite cathode, as a result of lattice change of the cathode active material during the charge–discharge cycling. An increase of the interfacial resistance of the composite cathode has been confirmed by a.c. impedance analysis of the  $\text{Li/gel}$  polymer electrolyte/ $\text{LiCoO}_2$  cell, as similar to the analysis previously reported [11]. It is thought that the morphology and composition of the composite cathode should be optimized to improve the cell performance.

#### 4. Conclusions

We synthesized the solvent-free polymer electrolytes based on poly(oligo[oxyethylene] oxyterephthaloyl) containing lithium perchlorate. They showed fully amorphous structure and high ionic conductivity at room temperature. In order to prepare the mechanically robust film, solid polymer electrolyte was penetrated into the pores of the highly porous membrane. Polymer electrolyte could play an effective role of an ionic conduction inside pores of the membrane. The good electrochemical and mechanical properties enabling the use of this electrolyte system in rechargeable lithium polymer batteries have been confirmed by the charge/discharge cycling of the lithium metal polymer cell.

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