

# High ionic conductivity and electrode interface properties of polymer electrolytes based on high molecular weight branched polyether

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## Abstract

Ionic conductivity and electrode interface properties of solid polymer electrolytes (SPE) based on high-molecular-weight branched polyethers have been studied for their application to solid state rechargeable lithium batteries. High molecular weight ( $10^5$ – $10^6$ ) comb-shaped polyethers, poly[ethylene oxide-co-2-(2-methoxyethoxy)ethyl glycidyl ether] [P(EO/MEEGE)], allow to give elastic and self-standing polymer electrolyte films without cross-linking. With increasing the MEEGE composition, the conductivity appreciably increases and takes a maximum at MEEGE compositions of 0.2–0.3, due to the fast ion transport assisted by highly mobile ether side-chains. Interfacial resistance ( $R_i$ ) at the lithium electrode interface decreases with increasing ionic conductivities of the polymer electrolytes, which are affected by the MEEGE composition and lithium salt species complexed with the copolymers. An all-solid lithium polymer battery, Li/P(EO/MEEGE = 91/9)-LiClO<sub>4</sub>/LiCoO<sub>2</sub> composite cathode cell, exhibited a discharging life of over 7 h at 0.1 mA/cm<sup>2</sup> and a low cell impedance of 96 Ω cm<sup>2</sup> after full charge at 60°C. © 1999 Elsevier Science S.A. All rights reserved.

**Keywords:** Polymer electrolyte; Ionic conductivity; Electrode interface; Lithium polymer battery

## 1. Introduction

Highly conducting polymer electrolytes have been developed for application to reliable electrochemical devices, e.g., solid state lithium-polymer-batteries [1–3]. Our studies on polymer electrolytes having flexible and ion-coordinating ether side chains are based on the concept of the coupling of fast ionic transport and fast side-chain motion. Several kinds of network polymer electrolytes having free side-chain ends have achieved comparably high ionic conductivity, and the effect of the coupling of fast ionic transport and fast side chain motion to achieve high ionic conductivity has been proved [4–6].

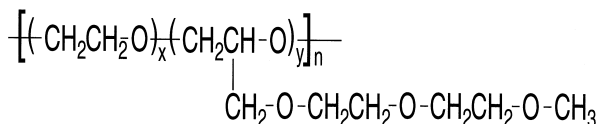
In the previous study [7], high-molecular-weight ( $10^5$ – $10^6$ ) comb-shaped polyethers, P(EO/MEEGE) (Scheme 1), were used as host polymers for polymer electrolytes. The P(EO/MEEGE) polymer electrolytes, containing several mol% of MEEGE, exhibited much higher conductivity than conventional poly(ethylene oxide) based polymer electrolytes especially at low temperatures [7]. In this study, the effects of introduction of flexible ether side

chains on the ion transport in the polymer electrolytes have been investigated in detail by comparing the conductivity data for P(EO/MEEGE) electrolytes having seven copolymer compositions. The lithium electrode interface properties for the polymer electrolytes have also been evaluated by using Li/polymer electrolyte/Li symmetrical cells. Furthermore, in order to explore composite cathode interface properties, charge–discharge tests and the cell impedance measurements for a lithium polymer battery using a P(EO/MEEGE) electrolyte have been carried out.

## 2. Experimental

High-molecular-weight branched polyethers P(EO/MEEGE) were prepared by ring-opening copolymerization of ethylene oxide (EO) with 2-(2-methoxyethoxy)ethyl glycidyl ether (MEEGE) in hexane at 20°C, using a condensation product of dibutyltin oxide and tributylphosphate as a highly active catalyst [8]. The molar ratio of MEEGE in P(EO/MEEGE) copolymers was determined from <sup>1</sup>H-NMR spectra. Glass transition temperature ( $T_g$ ), melting temperature ( $T_m$ ), and heat of the fusion ( $\Delta H_m$ ) of the copolymers were measured by differential scanning calorimetry (DSC). The degree of crystallinity of the

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Scheme 1. Structure of P(EO/MEEGE =  $x/y$ ).

copolymers was evaluated from the ratio of the experimentally determined  $\Delta H_m$  to the heat of fusion of 100% crystalline PEO (203 J g<sup>-1</sup>).

The polymer electrolytes were prepared by dissolving pre-weighed amounts of P(EO/MEEGE) copolymers and a lithium salt, either LiClO<sub>4</sub> or LiTFSI [lithium bis(trifluoromethylsulfonyl)imide], in dehydrated acetonitrile, and the solutions were cast on Teflon plates, followed by evaporating the solvent in an argon-filled glove box (VAC, [O<sub>2</sub>] < 1 ppm, [H<sub>2</sub>O] < 1 ppm) and further under high vacuum for over 12 h. The concentration of the lithium salts in the polymer electrolytes was represented by the molar ratio of lithium atoms to ether oxygen atoms in the polyether ([Li]/[O]). Ionic conductivity of the polymer electrolytes was determined by means of complex impedance measurements with stainless-steel electrodes and a dimensionally stable Teflon ring spacer, using a computer controlled impedance analyzer over a frequency range from 5 Hz to 13 MHz during cooling cycle. The interfacial resistance ( $R_i$ ) at the lithium electrode interface was estimated by impedance measurement under a 10 mV ac perturbation using completely sealed Li/polymer electrolyte/Li cells.

Composite cathode consisted of 66 wt.% of LiCoO<sub>2</sub> (Honjo FMC Energy System), 13 wt.% of graphite (KS-15, Timcal) as an electronic conductor and 21 wt.% of P(EO/MEEGE = 91/9)-LiClO<sub>4</sub> as an ion-conductive binder. Cathode films were prepared by casting the appropriate acetonitrile slurry on an aluminum foil current collector by using a doctor blade, and then dried under high vacuum. Lithium polymer batteries using lithium anode, a solid polymer electrolyte film with a thickness of 40 μm, and the LiCoO<sub>2</sub> composite cathode were assembled in a dry argon-filled glove box. The charge–discharge test of this battery was performed in 2.5–4.3 V range under a galvanostatic condition (0.1 mA/cm<sup>2</sup>) at 60°C, using a charge–discharge controller BTS-2004W (Nagano). The cell impedance at open circuit equilibrium states was determined by complex impedance measurements at several cathode potentials vs. Li/Li<sup>+</sup>.

### 3. Results and discussion

Fig. 1 shows the effects of the MEEGE composition in P(EO/MEEGE) copolymers on the ionic conductivity  $\sigma$  of the polymer electrolytes at 30°C and 60°C and on the degree of crystallinity of the base polymers. With increasing the MEEGE composition, the conductivity appreciably

increases and takes a maximum at MEEGE compositions of 0.2–0.3. The decrease in the degree of crystallinity of the copolymers with increasing the MEEGE composition might be a reason for the conductivity increase. However, we assign that the introduction of highly mobile ether side chains (the introduction of MEEGE), which can coordinate with lithium ions, contributes predominantly to the increase in the ionic conductivity [7], because of the following reasons. Even for salt-free P(EO/MEEGE) copolymers, their  $T_m$  were lower than 50°C, and with increasing the salt concentrations,  $T_m$  and the degree of crystallinity decreased considerably. These facts indicate that the ionic conductivity at 30°C might be influenced by the crystallinity but the conductivity at 60°C is that of completely amorphous P(EO/MEEGE) polymer electrolytes. The conductivity maxima are similarly observed both at 30°C and 60°C. The high ionic conductivity of the polymer electrolytes may be realized by the fast ion transport assisted by the fast side chain motion, especially at the optimum MEEGE compositions in the copolymers in terms of ion-coordination and ion-transport. A polymer electrolyte, P(EO/MEEGE) containing 27 mol% of MEEGE complexed with LiTFSI, exhibited high ionic conductivities of  $1.4 \times 10^{-3}$  S cm<sup>-1</sup> at 60°C and  $3.3 \times 10^{-4}$  S cm<sup>-1</sup> even at 30°C, without incorporating any low molecular weight plasticizers. The magnitude of the conductivities is the highest in the polyether-based polymer electrolytes ever reported. Structurally similar polymer electrolytes reported before [9] showed a little lower conductivity than the present polymer electrolytes, but this seems to be due to the difference in doped salt species.

Fig. 2 shows the Arrhenius plots of ionic conductivity  $\sigma$  and interfacial resistance  $R_i$  at the lithium electrode interface for P(EO/MEEGE) electrolytes containing either LiTFSI or LiClO<sub>4</sub>. It is interesting to note that the Arrhe-

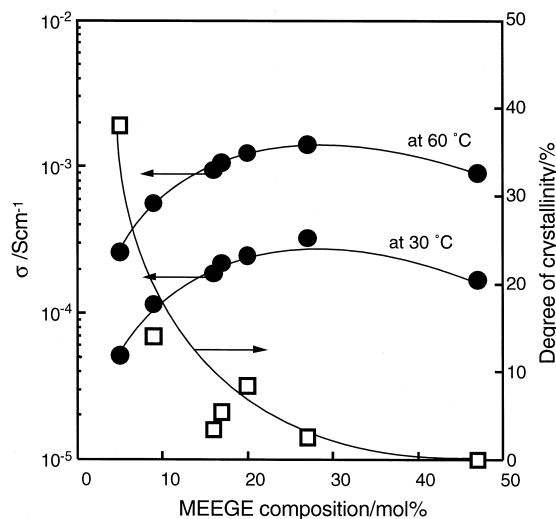


Fig. 1. Effects of MEEGE composition on the ionic conductivity of P(EO/MEEGE)-LiTFSI complexes ([Li]/[O] = 0.06) and on the degree of crystallinity of the salt-free copolymers.

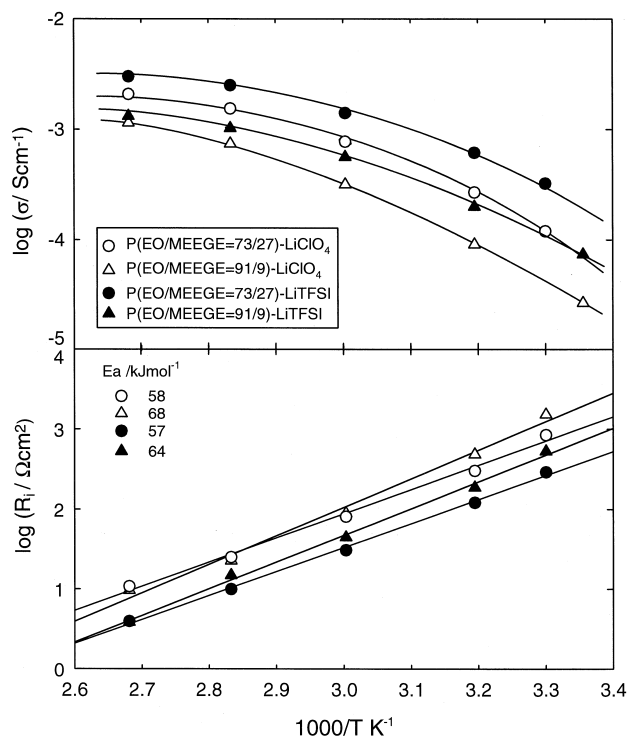


Fig. 2. Arrhenius plots of ionic conductivity (top), and interfacial resistance ( $R_i$ ) at the lithium electrode interface (bottom) for P(EO/MEEGE) electrolytes ( $[\text{Li}]/[\text{O}] = 0.06$ ).

nus plots of  $R_i$  give straight lines, indicating thermally activated processes for the interfacial reactions, whereas those of  $\sigma$  give positively curved profiles, which fit Vogel–Tamman–Fulcher eq.  $R_i$  at the lithium interface decreases with increasing the ionic conductivity of the polymer electrolytes, which is affected by the composition of MEEGE and lithium salt species. It is found that the introduction of highly mobile side chains (MEEGE) to the polymer electrolytes brings about not only high ionic conductivity but also fast charge transfer reaction at the lithium electrode interface. However, the activation ener-

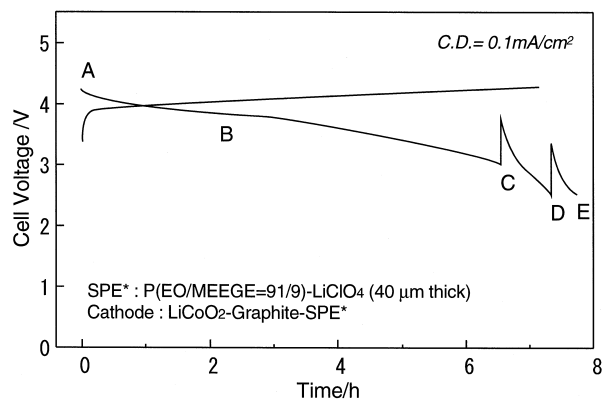


Fig. 3. Galvanostatic (0.1 mA/cm<sup>2</sup>) charge and discharge curves obtained for an all-solid Li/SPE/LiCoO<sub>2</sub> composite cathode cell at 60°C.

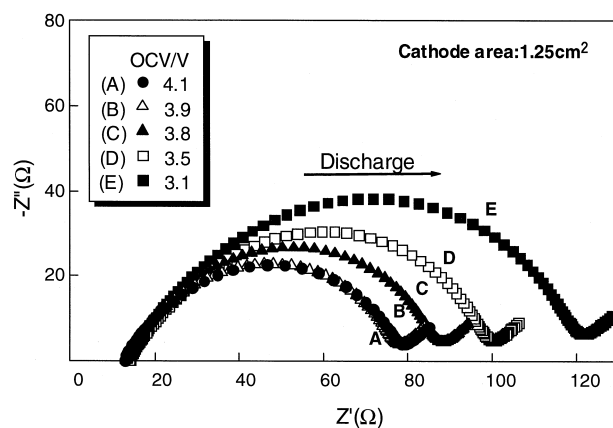


Fig. 4. Impedance spectra of a Li/SPE/LiCoO<sub>2</sub> composite cathode cell as a function of cathode potential vs. Li/Li<sup>+</sup> at 60°C.

gies calculated from slopes of the Arrhenius plots are 57–68 kJ/mol, which are almost independent of the MEEGE compositions and the kind of lithium salts used in this experiment.

In liquid electrolytes, as indicated by several authors [10–12], growth of passivation films on lithium electrodes, as so-called solid electrolyte interface (SEI), proceeds with contact time; thus  $R_i$  accordingly increases. In contrast, the interface between metallic lithium and P(EO/MEEGE) polymer electrolytes complexed with either LiClO<sub>4</sub> or LiTFSI was rather stable. At room temperature and at 60°C,  $R_i$  did not change with time and was constant over 600 h. Furthermore, even after cycling the potential of a symmetrical lithium electrode cell between  $\pm 0.3$  V at

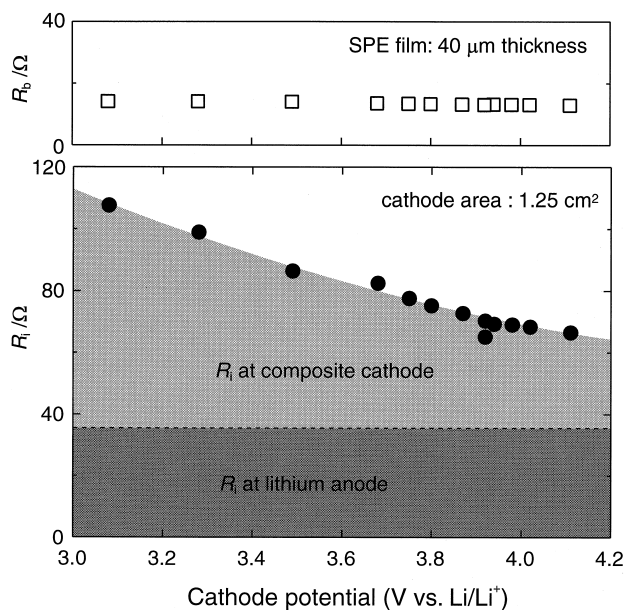


Fig. 5. Variation of interfacial resistance ( $R_i$ ) and bulk resistance ( $R_b$ ) for a Li/SPE/LiCoO<sub>2</sub> composite cathode cell as a function of cathode potential vs. Li/Li<sup>+</sup> at 60°C.

1 mV/s for several times during storage of the cell, the change in  $R_i$  was negligible. These results indicate that the interface between metallic lithium and the P(EO/MEEGE) polymer electrolytes is stable, and that formation of pronounced passivation films, as seen in liquid electrolytes, is hard to occur. However, for conclusive remarks more detailed study is required and now in progress in our group.

In order to explore composite cathode interface properties, a lithium polymer battery was constructed by using P(EO/MEEGE = 91/9) copolymer as a matrix of solid polymer electrolyte films and as an ion-conductive binder for the composite cathode. As shown in Fig. 3, a solvent-free all-solid lithium-polymer-battery, Li/P(EO/MEEGE = 91/9)-LiClO<sub>4</sub>/LiCoO<sub>2</sub> composite cathode cell, exhibits high discharge voltages and a long discharging life of over 7 h at a rate of 0.1 mA/cm<sup>2</sup>. It is seen that polarization is pronounced with discharging the cell at this current density. A P(EO/MEEGE = 91/9) electrolyte film having 40 μm thickness, without chemically cross-linked structure, was found to keep separate between lithium anode and the composite cathode under a contact pressure of 5 kg/cm<sup>2</sup> even at 60°C. Fig. 4 shows the impedance plots of this cell as a function of cathode potentials vs. Li/Li<sup>+</sup> at equilibrium states. The total cell impedance (summation of electrolyte bulk resistance,  $R_b$ , and  $R_i$ ) after full charge is considerably low, i.e., 80 Ω at 60°C when the cathode area is 1.25 cm<sup>2</sup>, and the electrode interfacial resistance apparently increases as the battery is discharged. Fig. 5 shows the variation of interfacial resistance  $R_i$  and bulk resistance  $R_b$  as a function of cathode potentials vs. Li/Li<sup>+</sup> for the Li/SPE/LiCoO<sub>2</sub> composite cathode cell at 60°C. The contact area between electrode active materials and polymer electrolyte does not change through the charge-discharge processes, because of the constant value of  $R_b$  independent of cathode potential, as shown in Fig. 5.  $R_i$  is separated into anode and cathode components by assuming that  $R_i$  at the lithium interface is unchanged during the discharging. The interfacial resistance at the composite cathode containing the polymer electrolyte increases with decreasing cathode potential, if the above assumption is valid. It is implicated that such a increase in  $R_i$  would be caused by the decrease in the conductivity of LiCoO<sub>2</sub>-active material and by the increase in charge-transfer resistance at the cathode interface with discharging.

#### 4. Conclusion

High-molecular-weight comb-shaped polyethers, P(EO/MEEGE), have been used as matrixes of polymer electrolytes. With increasing MEEGE composition, the bulk ionic conductivity increases and charge-transfer resistance at lithium interface decreases. A P(EO/MEEGE = 73/27) electrolyte containing LiTFSI, exhibits a high ionic conductivity of  $1.4 \times 10^{-3}$  S cm<sup>-1</sup> and a low and stable interfacial resistance of 31 Ω cm<sup>2</sup> at the lithium electrode interface at 60°C. An all solid Li/P(EO/MEEGE)/LiCoO<sub>2</sub> cell can be discharged at 0.1 mA/cm<sup>2</sup>, and a summation of the bulk electrolyte resistance and the total interfacial resistance is 96 Ω cm<sup>2</sup> after full charge, at 60°C. The charge-discharge cycle performance of the lithium polymer batteries is now under investigation.

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