

Electrochemical properties of composite polymer electrolyte applied to rechargeable lithium polymer battery

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Received 13 April 2004; accepted 24 May 2004

Available online 30 July 2004

Abstract

High-molecular-weight comb-shaped polyethers, poly(ethylene oxide-co-2-(2-methoxyethoxy) ethyl glycidyl ether-co-allyl glycidyl ether) (P(EO/EM/AGE)) and poly(ethylene oxide-co-2-(2-methoxyethoxy)ethyl glycidyl ether) (P(EO/EM)), were synthesized and used for the preparation of the all solid polymer electrolyte and the composite polymer electrolyte combined with a plasticizer Star-EO-OMe, pentaerythritol tetrakis(2-methoxyethyl ether), which shows low vapor pressure, respectively. Some electrochemical properties of the polymer electrolytes and performances of the cell consisting of lithium/polymer electrolyte/LiCoO₂ were studied. The addition of Star-EO-OMe to polymer electrolyte brought about a large increase in ionic conductivity. The composite electrolyte containing 50 wt.% of Star-EO-OMe complexed with LiTFSI, lithium bis(trifluoromethylsulfonyl)imide, exhibited high ionic conductivity in the order of 10⁻⁴ S cm⁻¹ at 10 °C and approximately 10⁻⁵ S cm⁻¹ at -20 °C. The cell performance was also improved by the addition of Star-EO-OMe.
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Keywords: Polymer battery; Comb polymer; Composite polymer electrolyte; Lithium electrode

1. Introduction

Battery systems based on solid polymer electrolytes combined with a metallic lithium anode have been expected as new generation high-energy storage devices, in particular for electric vehicles and load leveling applications.

Polymer electrolytes have been studied for more than two decades since the first investigation reported by Armand et al. in 1979 [1].

Polyethylene oxide (PEO) has been regarded to show the good performance as a polymer solid electrolyte and many studies using PEO complexed with various lithium salts were reported [2–4]. However, a big disadvantage of PEO is its crystallinity. The crystalline part does not contribute to ionic conduction at all, which causes a decrease of ionic conduction. One of the useful method to decrease the crystallization of oxyethylene segments is the introduction of a side chain to the PEO main chain. Based on the concept described above, we have already reported the high-molecular-weight comb-shaped polyethers consisting of oxyethylene units both in the main chain and the side chains, P(EO/EM), that is quite sufficient for battery applications. P(EO/EM),

poly(ethylene oxide-co-2-(2-methoxyethoxy)ethyl glycidyl ether), shows high ionic conductivity of 10⁻⁴ S cm⁻¹ at 30 °C. The liquid-free rechargeable lithium polymer battery showed excellent cell performance at low discharge rate and high temperature [5–8].

We studied electrochemical properties of the composite polymer electrolyte comprising P(EO/EM) and a plasticizer Star-EO-OMe, pentaerythritol tetrakis(2-methoxyethyl ether), and performance of the polymer battery using the electrolyte for room temperature use. Star-EO-OMe has been chosen as a plasticizer since it has very low vapor pressure that minimizes the ruin of strong points of the polymer electrolyte.

2. Experimental

2.1. Synthesis of polyethers and plasticizer

High-molecular-weight polyethers, P(EO/EM/AGE) and P(EO/EM)s, are synthesized by coordination anionic polymerization of ethylene oxide (EO) with 2-(2-methoxyethoxy)ethyl glycidyl ether (EM) and with or without allyl glycidyl ether (AGE) in hexane using a catalyst of condensation product of dibutyltin oxide and tributylphos-

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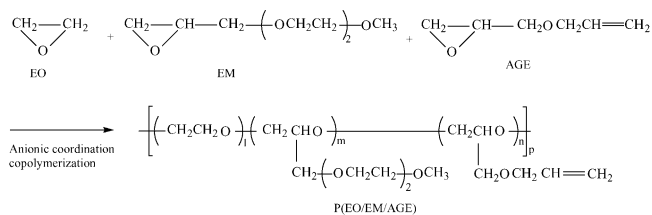


Fig. 1. Synthesis of P(EO/EM/AGE).

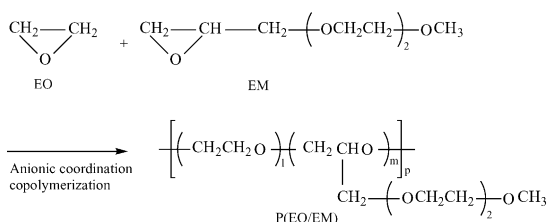


Fig. 2. Synthesis of P(EO/EM).

phate at 20 °C [9] as shown in Figs. 1 and 2. The composition in the polyethers was determined by ¹H NMR measurement on a Nihon Denshi JEOL-JNM-GSX-270 in deuterated benzene. The weight-average molecular weight (M_w) and the index of polydispersity (M_w/M_n) were evaluated by a size exclusion chromatography (SEC) on a Shimadzu C-R4A/LC6AD/RID-6A, and are summarized in Table 1. The SEC measurement was carried out using *N,N*-dimethylformamide with 0.1 mmol/L of LiBr at 60 °C. The contents of ETU-2 were 20, 22 and 12 mol% for P(EO/EM/AGE)-20, P(EO/EM)-22 and P(EO/EM)-12, respectively. M_w and M_w/M_n were calculated using the calibration of polystyrene standards. M_w and M_w/M_n of P(EO/EM/AGE) and P(EO/EM) were in the order of 10^6 g mol⁻¹ and 4.5–7.3.

Star-EO-OMe was prepared by the reaction of pentaerythritol with 2-chloroethyl methyl ether in dimethyl sulfoxide at 60 °C. Fig. 3 shows the structure of Star-EO-OMe. The boiling point was 137 °C at 0.2 mmHg.

Table 1
Characteristics of polyethers

Sample code	Composition (mol%)			M_w ($\times 10^6$)	M_w/M_n
	[EO]	[ETU-2]	[AGE]		
P(EO/EM/AGE)-20	80	20	1.7	1.6	5.1
P(EO/EM)-22	78	22	–	1.3	4.5
P(EO/EM)-12	88	12	–	3.2	7.3

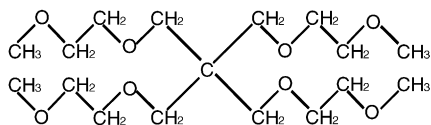


Fig. 3. Structure of Star-EO-OMe.

2.2. Preparation of polymer electrolyte films

All solid polymer electrolyte film was prepared by solution casting, i.e., the viscous acetonitril solution, which was prepared by mixing a P(EO/EM/AGE)-20, benzoyl-*m*-toluoyl peroxide as a free radical generator and LiTFSI, lithium bis(trifluoromethylsulfonyl) imide made by Minnesota Mining and Manufacturing Company in dehydrated acetonitrile, was poured on a silicone-treated PET film, dried and crosslinked at 100 °C for 3 h under an inert atmosphere. The optimum concentration of the lithium salt in the electrolyte was [Li]/[O] = 0.06 (the ratio of Li atoms to all the ether oxygen atoms in the electrolyte) as previously reported [6]. The thickness of the film was 50 μm.

The composite polymer electrolyte film was also prepared by solution casting. P(EO/EM)-22 dissolved together with Star-EO-OMe and LiTFSI in dehydrated acetonitrile was impregnated into the separator of 16 μm thickness (Tonon Chemical Co. Ltd.), and dried at 70 °C for 3 h under inert atmosphere. The optimum concentration of the lithium salt in the electrolyte was [Li]/[O] = 0.04.

2.3. Electrochemical measurement

The bulk resistance of the polymer electrolyte and the interfacial resistance between the electrolyte and metallic lithium were determined by complex impedance measurement using a computer-controlled Solartron SI 1260 impedance analyzer with a temperature-controlled box. An alternating current over the frequency range 0.1 Hz to 10 MHz was used and the applied voltage was 0.5 V.

2.4. Preparation of cathode films

The composite cathode for all solid polymer electrolyte consisted of 82 wt.% of LiCoO₂ (Honjo FMC Energy Systems), 5 wt.% of conductive carbon material and 13 wt.% of the mixture of P(EO/EM)-12 and LiBF₄ as an ion-conductive binder. The cathode film, of which thickness was approximately 20 μm, was prepared by a doctor blade casting process on an aluminum foil current collector. After drying, the film was roll-compressed in order to increase the packing density which lead to improved electrical conductivity.

The composite cathode for composite polymer electrolyte consisted of 90 wt.% of LiCoO₂, 6 wt.% of acetylene black, 4 wt.% of PVDF as a binder that was impregnated with 15 wt.% of the mixture of P(EO/EM)-12, Star-EO-OMe and LiTFSI, as an ion-conductor.

2.5. Cell assembly

A monolayer coin-type cell (CR2032), constructed from lithium anode (0.3 mm thickness; Honjo Metal Co. Ltd.), the all solid polymer electrolyte or the composite polymer electrolyte with a separator and the composite cathode, was

assembled in a dry argon-filled glove box ($[O_2] < 1$ ppm, $[H_2O] < 1$ ppm).

2.6. Cell characterization

Cell performances were evaluated by BTS-2004W (Nagano) charge–discharge controller in the range of 3.0–4.2 V. Charging and discharging were carried out with CC–CV (constant current–constant voltage) and CC, respectively.

3. Results and discussion

3.1. Ionic conductivity

The Arrhenius plots are shown for all solid polymer electrolyte consisting of P(EO/EM/AGE)-20 and LiTFSI and the composite polymer electrolyte consisting of P(EO/EM)-22, Star-EO-OMe, and LiTFSI in Fig. 4. The weight ratio of P(EO/EM)-22 and Star-EO-OMe was 50:50. In Fig. 4, the experimental points of the ionic conductivity exhibited convexly curved profiles, as can be expressed by WLF or VTF equations. The addition of Star-EO-OMe to polymer electrolyte brought about a large increase in the ionic conductivity which was attributable to decrease in glass transition temperature, -70°C for P(EO/EM/AGE) and -86°C for the plasticized polymer consisting of P(EO/EM)-22 and Star-EO-OMe (50:50) weight ratio. The composite polymer electrolyte exhibited high ionic conductivity of more than $10^{-4} \text{ S cm}^{-1}$ at 10°C and approximately $10^{-5} \text{ S cm}^{-1}$ at -20°C .

3.2. Bulk resistance and interfacial resistance

The results of R_b and R_i of the composite polymer electrolyte with the separator at lithium electrode interface are shown in Fig. 5. The composite polymer electrolyte exhibited low and stable bulk resistance of $15 \Omega \text{ cm}^2$ and interfacial resistance of $170 \Omega \text{ cm}^2$ at 60°C . It was confirmed that the electrolyte was stable with metallic lithium.

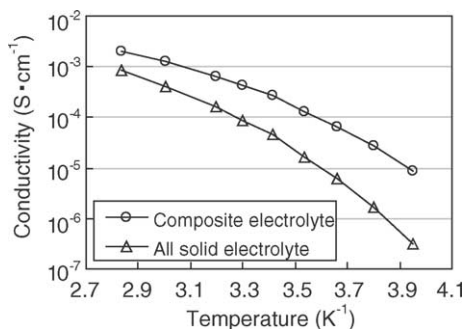


Fig. 4. Arrhenius plots of ionic conductivity of all solid polymer electrolyte and composite electrolyte.

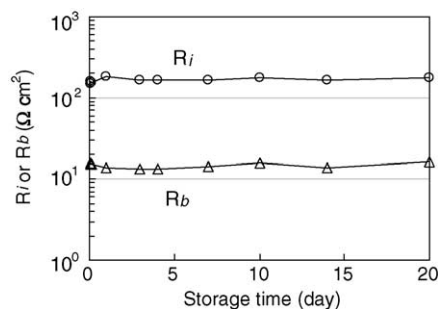


Fig. 5. Variation of R_b and R_i at lithium electrode interface for composite polymer electrolyte at 60°C .

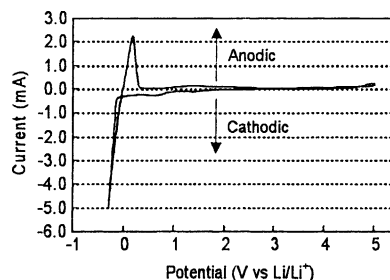


Fig. 6. Cyclic voltammograms for Li/composite polymer electrolyte/SUS316L cell at 60°C ; scan rate: 10 mV s^{-1} ; effective surface area of electrodes: 1.54 cm^2 .

3.3. Electrochemical stability

Electrochemical stability of the composite polymer electrolyte has been investigated by using cyclic voltammetry. Fig. 6 shows a voltammogram of the electrolyte at 60°C . The voltammogram clearly showed the deposition of metallic lithium at the cathodic limit and stripping of lithium in the returning anodic scan. In the anodic scan, irreversible oxidation appeared at 5 V versus Li/Li⁺. Consequently, the composite polymer electrolyte was stable up to 5 V.

3.4. Cell characterization

The cycleability of the cell using the composite polymer electrolyte was measured at 0.2 C and 60°C . As clearly explained by the result in Fig. 7, the discharge capacity grad-

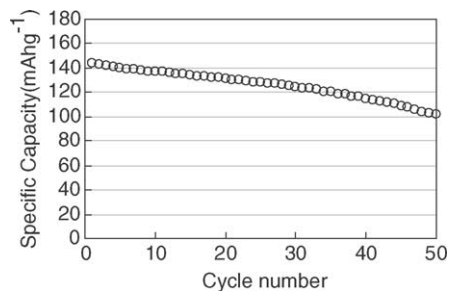


Fig. 7. Specific discharge capacity of Li/composite polymer electrolyte/LiCoO₂ cell with the voltage range of 3.0–4.2 V according to cycles.

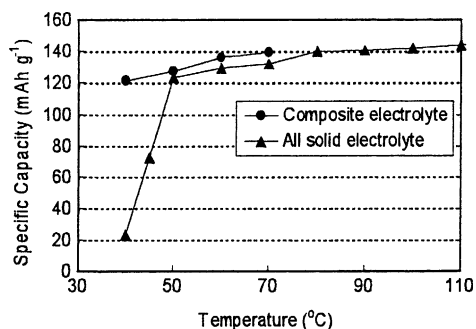


Fig. 8. Temperature dependence of discharge capacity.

ually decreased at the rate of about 0.6% per cycle with the number of discharge cycles. At the 50th cycle, the capacity declined to 70% of the initial value of 142 mAh g⁻¹.

Temperature dependence of the discharge capacity was measured. The cell was charged at the rate of 0.2 C at 60 °C and discharged at various temperatures from 40 to 110 °C at 0.2 C. The discharge capacities at various temperatures are shown in Fig. 8. A significant decrease in the capacity of the cell using the all solid polymer electrolyte was observed below 50 °C. The capacity at 40 °C went down to 17% of that at 50 °C. On the other hand, the value of the discharge capacity of the cell using the composite polymer electrolyte was more than 120 mAh g⁻¹ at 40 °C. The cell performance at near room temperature was improved by adding a plasticizer Star-EO-OMe.

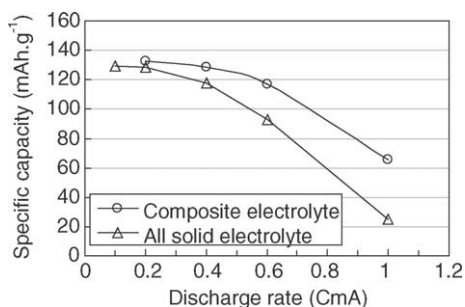


Fig. 9. Current rate dependency on discharge capacity from 0.1 to 1 C mA.

The cell also left a problem in high-rate discharging performance. As shown in Fig. 9, the discharge capacity of cell using the all solid polymer electrolyte at 1 C remarkably decreased to below 30 mAh g⁻¹, while the values of the discharge capacities of the cell using a composite polymer electrolyte were more than 60 mAh g⁻¹ at 1 C. The good high-rate characteristics of the cell using the composite polymer electrolyte may be attributed to the high diffusion rate of lithium ions inside the cathode.

4. Conclusion

The composite polymer electrolyte containing 50 wt.% of Star-EO-OMe complexed with LiTFSI exhibited high ionic conductivity of more than 10⁻⁴ S cm⁻¹ at 10 °C. The lithium polymer battery using the composite polymer electrolyte showed excellent discharge capacity, the value of which was more than 120 mAh g⁻¹ at 40 °C. The cell also showed good high-rate characteristics. The discharge capacity was more than 60 mAh g⁻¹ at 1 C.

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