

Rechargeable Lithium Polymer Battery

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With the aim of improving electrochemical properties at lower temperature, we prepared the composite polymer electrolyte comprising high molecular weight comb polymer P(EO/EM), poly[ethylene oxide-co-2-(2-methoxyethoxy)ethyl glycidyl ether] and a plasticizer Star-EO-OMe, pentaerythritol tetrakis(2-methoxyethyl ether) which shows low vapor pressure. Some electrochemical properties of the composite polymer electrolyte and performance of the cell consist of lithium/composite electrolyte/LiCoO₂ has been 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 of more than 10⁻⁴ S cm⁻¹ at 10 °C and approximately 10⁻⁵ S cm⁻¹ at -20 °C. The cell performance was improved by the addition of Star-EO-OMe.

Key words: Polymer battery, Comb polymer, Composite polymer electrolyte, Lithium electrode

1. INTRODUCTION

Battery systems based on solid polymer electrolytes combined with a metallic lithium anode are 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 in 1979[1].

Although polyethylene oxide (PEO), which is the most popular material for solid polymer electrolytes and many investigations on the polymer complexed with various lithium salts, have been published [2-4], its conductivity is quite insufficient for battery applications.

We have already reported that a high molecular weight comb polymer P(EO/EM), poly[ethylene oxide-co-2-(2-methoxyethoxy)ethyl glycidyl ether], which shows a high ionic conductivity, 10⁻⁴ S cm⁻¹ at 30 °C, and a liquid-free rechargeable lithium polymer battery showed excellent cell performance at low discharge rates and high temperatures [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.

2. EXPERIMENTAL

2.1 Synthesis of polymers

P(EO/EM (=78/22 molar ratio)) and P(EO/EM/AGE (=80/20/1.7)) were prepared by the ring-opening copolymerization of ethylene oxide (EO) with

2-(2-methoxyethoxy)ethyl glycidyl ether (EM) and with or without allyl glycidyl ether (AGE) in hexane at 20 °C [9]. Fig. 1 and 2 show the structures of these polymers. The Mw and Mw/Mn values of P(EO/EM) and P(EO/EM/AGE) were of the order 10⁶ g mol⁻¹ and about 4.5-5.1, respectively.

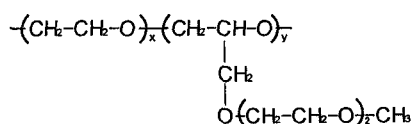


Fig. 1. Structure of P(EO/EM)

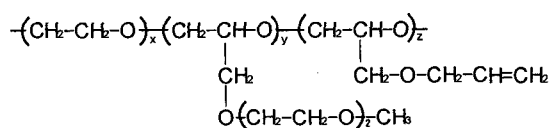


Fig. 2. Structure of P(EO/EM/AGE)

2.2 Synthesis of plasticizer

Star-EO-OMe was prepared by the reaction of pentaerythritol with 2-chloromethyl 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.

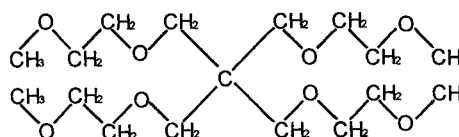


Fig.3. Structure of Star-EO-OMe

2.3 Preparation of all solid polymer electrolyte films

Polymer P(EO/EM/AGE) dissolved together with an organic peroxide and LiTFSI, lithium bis(trifluoromethylsulfonyl) imide made by Minnesota Mining and Manufacturing Company, in dehydrated acetonitrile was cast on a silicone-treated PET film, dried and crosslinked at 100 °C for 3 hours under an inert atmosphere. The optimum concentration of the lithium salts in the electrolytes was [Li]/[O]=0.06 (the ratio of Li atoms to all the ether oxygen atoms in the polymer) as previously reported [6]. The thickness of the film was 50 microns.

2.4 Preparation of composite polymer electrolyte films

Polymer P(EO/EM) dissolved together with Star-EO-OMe and LiTFSI in dehydrated acetonitrile was impregnated into the separator of 16 microns thickness (TONEN CHEMICAL CO. LTD), and dried at 70 °C for 3 hours under an inert atmosphere. The optimum concentration of the lithium salts in the electrolytes was [Li]/[O]=0.04.

2.5 Electrochemical measurement

The bulk resistance of the polymer electrolyte and the interfacial resistance between the electrolyte and metallic lithium were measured by the AC impedance method using an impedance analyzer (Solartron SI 1260) over a frequency range from 0.1 Hz to 10 MHz.

2.6 Preparation of cathode films for all solid polymer electrolyte

Composite cathodes consisted of 82 wt.% of LiCoO₂ (Honjo FMC Energy Systems), 5 wt.% of conductive carbon material and 13 wt.% of P(EO/EM(=88/12))-LiBF₄ as an ion-conductive binder. Cathode films, of which thicknesses were approximately 20 microns, were 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 read to improved electrical conductivity.

2.7 Preparation of cathode films for composite polymer electrolyte

Composite cathodes 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), Star-EO-OMe and LiTFSI, as an ion-conductor.

2.8 Cell assembly

A monolayer coin type cell (CR2032), constructed from lithium anode (HONJO METAL CO. LTD.; 0.3 mm thickness), 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 ([O₂] < 1 ppm, [H₂O] < 1 ppm).

2.9 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 C.C.C.V. (constant current–constant voltage) and C.C., respectively.

3. RESULTS AND DISCUSSION

3.1 Ionic conductivity

Fig.4 shows the temperature dependences of ionic conductivity for all solid polymer electrolyte consist of P(EO/EM/AGE) and LiTFSI and the composite polymer electrolyte consist of P(EO/EM), Star-EO-OMe, and LiTFSI. The weight ratio of P(EO/EM) and Star-EO-OMe was 50:50. The Arrhenius plots of the ionic conductivity exhibited positively 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 ionic conductivity due to decrease in glass transition temperature, -55°C for the all solid polymer electrolyte and -72°C for the composite polymer electrolyte. The composite polymer electrolyte exhibited high ionic conductivity of more than 10⁻⁴ S cm⁻¹ at 10 °C and approximately 10⁻⁵ S cm⁻¹ at -20 °C.

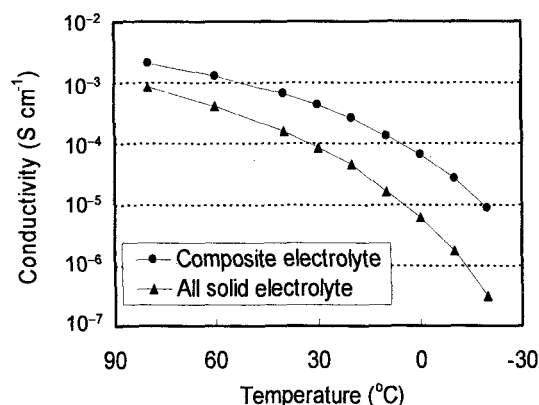


Fig.4. Ionic conductivity of all solid polymer electrolyte and composite electrolyte

3.2 Bulk resistance and interfacial resistance

Fig.5 shows the results of the bulk resistance (R_b) and the interfacial resistance (R_i) of the composite polymer electrolyte with the separator at lithium electrode

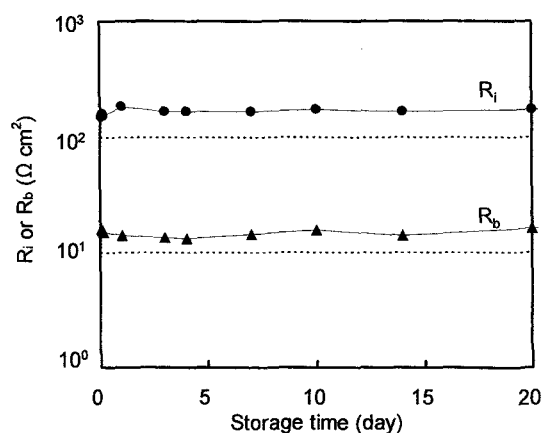


Fig.5. Variation of R_b and R_i at lithium electrode interface for composite polymer electrolyte at 60 °C

interface. 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.

3.3 Electrochemical stability

Fig.6 shows the cyclic voltamograms for the composite electrolyte. These current-voltage curves followed almost the same line through 20 cycles. The result indicated the composite polymer electrolyte possessed high stability at lithium electrode interface, even at high temperature.

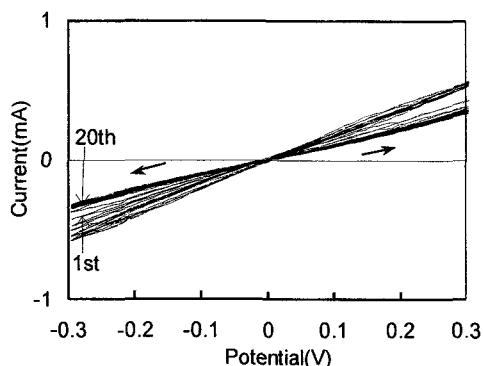


Fig.6. Cyclic voltamograms of Li/Composite polymer electrolyte/Li cell from 1st to 20th cycles at 60°C at a scan rate of 1 mV s^{-1}

Electrochemical stability of the composite polymer electrolyte has been investigated by using cyclic voltammetry. Fig.7 shows a voltamogram of the electrolyte at 60°C . The voltamogram 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.

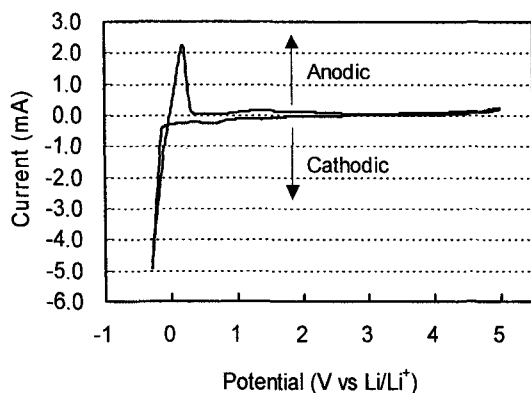


Fig.7. Cyclic voltamograms for Li/Composite polymer electrolyte/SUS316L cell at 60°C .
Scan rate= 10 mV s^{-1}
Effective surface area of electrodes = 1.54 cm^2

3.4 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.8, the discharge capacity gradually 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} .

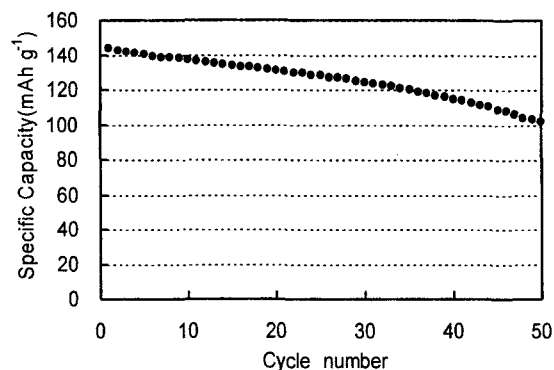


Fig.8. Specific discharge capacity of Li/Composite polymer electrolyte/ LiCoO_2 cell with the voltage range of 3.0–4.2 V according to cycles.

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.9. 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 . But 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.

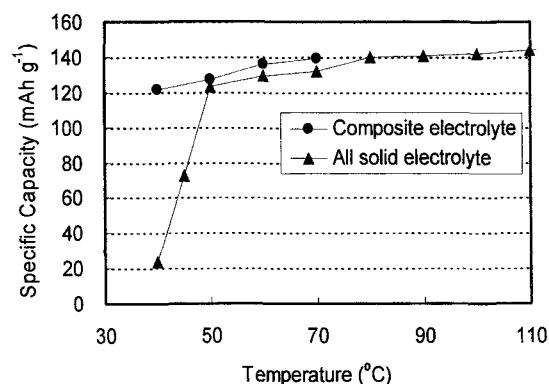


Fig.9. Temperature dependence of discharge capacity.

The cell also left a problem in high-rate discharging performance. As shown in Fig.10, the discharge capacity of cell using the all solid polymer electrolyte at 1 C remarkably decreased to below 30 mAh g^{-1} . But 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.

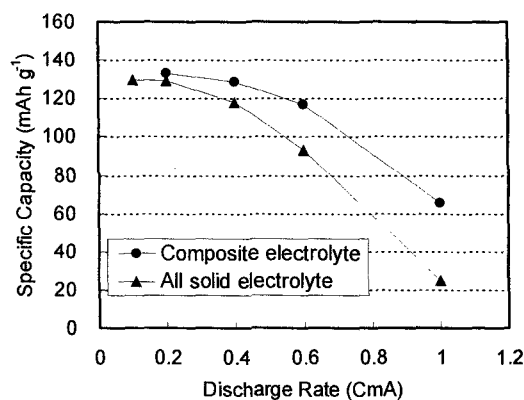


Fig.10. Current rate dependency on discharge capacity from 0.1 to 1 CmA.

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

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