

Notes

Characterization of a Cross-linked Polymer Electrolyte Prepared from Oligo(ethylene glycol) methacrylates-Acrylonitrile

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Abstract : A cross-linked solid polymer electrolyte was prepared by copolymerizing photochemically acrylonitrile (AN), oligo(ethylene glycol ethyl ether) methacrylate, oligo(ethylene glycol) dimethacrylate in the presence of lithium perchlorate as a lithium salt, ethylene carbonate-propylene carbonate as a mixed plasticizer, and poly(ethylene oxide) as a polymer matrix. The maximum ionic conductivity of the polymer electrolyte was 2.35×10^{-3} S/cm. The interface resistance of the polymer electrolyte was very low compared to that of the polymer electrolyte without AN. The former electrolyte was stable up to 4.3 V and the Ah efficiency was nearly 100% during the charge-discharge cycle.

Introduction

Since the first solid polymer electrolyte (SPE) consisting of complexes of poly(ethylene oxide) (PEO) and lithium salts was studied,¹ many researches have been conducted on SPEs. As linear PEO electrolytes showed low ionic conductivities owing to their high crystallinity, many researches have focused on increasing ionic conductivity by destroying crystallization regions of the PEOs. For example, copolymers containing ethylene oxide units or acrylate derivative polymers with the units as side chains have been proposed.^{2,3} However, the ionic conductivities of all these polymers are too low to be applied to any practical use. An ionic conductivity of 10^3 S/cm is required to apply solid polymer electrolytes to lithium polymer batteries.

Plasticized polymer electrolytes were proposed and they exhibited ionic conductivities of 10^3 S/cm.^{4,7} However, their mechanical properties were weak and the plasticizers leaked out from the polymer electrolytes. To overcome these problems, cross-

linked acrylate polymers with both lithium salts and plasticizers have been prepared.⁸⁻¹¹ Their interface resistance was found to be high due to low adhesion to metal electrodes.¹² In addition, they caused bad charge and discharge characteristics and their Ah efficiency and utilization were very low. On the other hand, the interface resistances of polyelectrolytes based on acrylonitrile (AN) were reported to be low.¹³

In this work, a cross-linked acrylate polymer electrolyte was prepared by copolymerizing photochemically oligo(ethylene glycol ethyl ether) methacrylate (OEGEEM), oligo(ethylene glycol) dimethacrylate (OEGDMA), and AN in the presence of lithium perchlorate as a lithium salt, ethylene carbonate (EC)-propylene carbonate (PC) as a mixed plasticizer, and PEO as a polymer matrix. Its ionic conductivity, interface resistance, and charge and discharge characteristics were investigated.

Experimental

Materials. OEGDMA (Polyscience), OEGEEM (Polyscience), AN (Aldrich), lithium perchlorate

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(Aldrich; purity, 95%), PEO with a molecular weight of 2,000,000 (Aldrich), and methylbenzylformate (Aldrich) (MBF) as a photoinitiator were used as received. EC (Aldrich; purity, 98%) and PC (Aldrich; purity, 98%) were used after eliminating moisture using a molecular sieve. Stainless steel (thickness : 100 μm) (SUS) and lithium foil (FMC; thickness, 100 μm) were also used for electrodes. Moreover, TiS_2 (Aldrich) and acetylene black (Gulf oil) were used for the composite cathode.

Preparation of the Cross-linked Polymer Electrolyte. The lithium perchlorate (0.57 g) was dissolved in a mixed plasticizer (4.5 g) of EC-PC (molar ratio 1 : 1). Next, OEGDMA, OEGEEM, and AN were added to the solution. The molar ratio of OEGEEM and OEGDMA was 2 : 1. The AN content was 20% (0.6 g) of the total monomer weight (3 g). Also, 5% (0.15 g) of PEO of the total monomer weight was added to improve the mechanical properties.¹¹ The mixture was then stirred for 6 h. To this solution, MBF of 1.5% (4.5×10^{-2} g) of the total monomer weight was finally added. This solution was then poured onto a glass plate and photopolymerized in an argon atmosphere using a high-pressure mercury lamp for 5 min (Scheme I). Composite cathode was prepared by blending TiS_2 , acetylene black, and PEO. With the exception of UV irradiation, the entire experiment was done in the glove box.

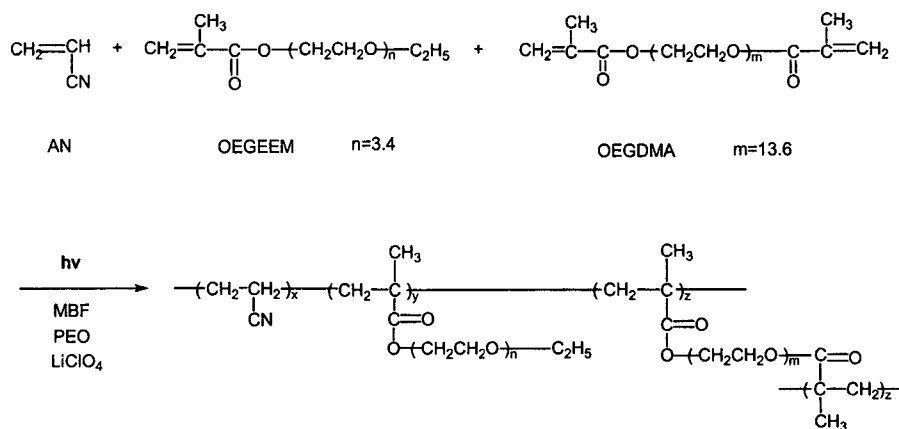
The resulting cross-linked polymer electrolyte was a film with a thickness of approximately 150 μm .

Measurements. AC impedances of a cell (2×2 cm) fabricated with SUS and the film were measured with an IM6 impedance measurement system (Zahner electric). The amplitude was varied from 1 to 10 mV and the frequency was ranged between 100 Hz and 100 MHz. The ionic conductivities were then calculated from the impedance values. To estimate electrochemical stability of the SPE, a SUS/SPE/Li cell (2×2 cm) was fabricated. SUS was used as the working electrode and Li metal was used as both the counter electrode and reference electrode. Cyclic voltamograms were measured in the range of 1 to 5.5 V at 1 mV/sec scan rate with an IM6 potentiostat/galvanostat.

To evaluate charge and discharge characteristics of the SPE, a TiS_2 /SPE/Li cell was fabricated. TiS_2 and Li foil were used for the cathode and the anode, respectively. Charge and discharge experiment was performed in the range of 1.6 to 2.6 V at room temperature with a multicycle charger/discharger system (Maccor).

Results and Discussion

The resulting film was sticky and transparent in visible region. In addition, the film exhibited a tensile strength of a cell component level. The impedance spectra of the cell are given in Figure 1. The ionic conductivity calculated from the spectrum at 20 $^\circ\text{C}$ was 2.35×10^{-3} S/cm. The interface resistances of the Li/SPE/Li cell obtained from the impedance analysis are given as a function of



Scheme I. Preparation of the cross-linked polymer electrolyte (film).

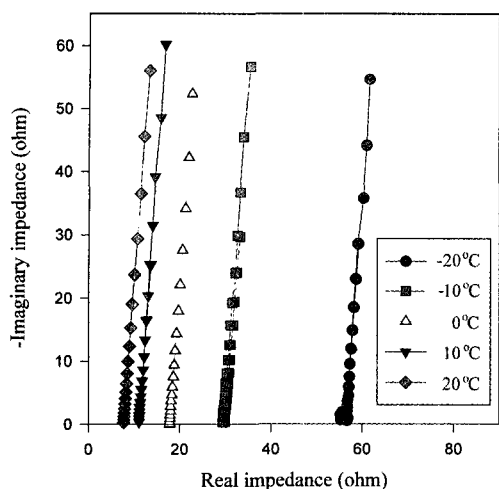


Figure 1. Nyquist plots of the SUS/SPE/SUS cell.

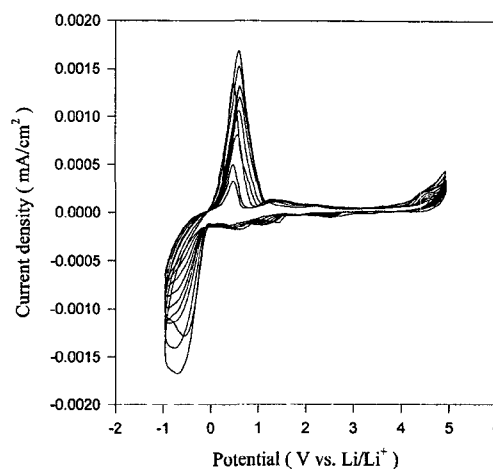


Figure 3. Electrochemical stability windows of the SUS/SPE/Li cell.

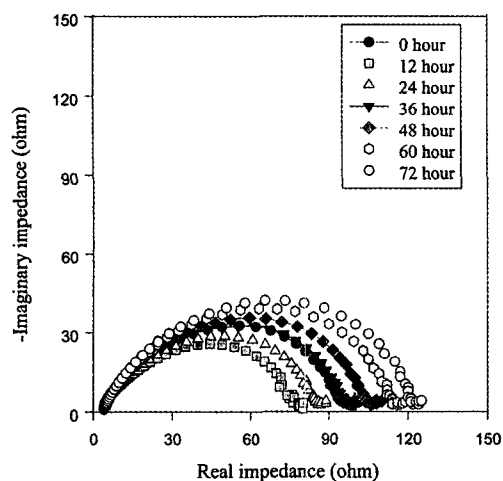


Figure 2. Changes in impedance spectra of the Li/SPE/Li cell with a function of time.

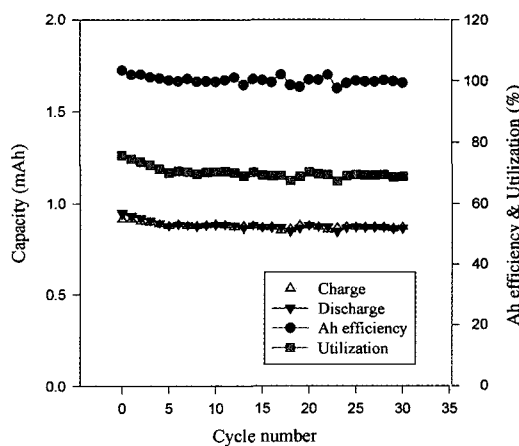


Figure 4. Variations of the charge and discharge capacity and the Ah efficiency of the TiS₂/SPE/Li cell with cycling at room temperature : current density, 0.05 mA/cm² ; voltage range, 1.6 - 2.6 V.

time in Figure 2. The interface resistances were found to be higher than the bulk resistances of the polymer electrolyte. The former resistances can be due to the passivation layer between the Li electrode and the polymer electrolyte.^{14,15} However, the interface resistance of the Li/SPE/Li cell was 78 ohm for 4 h storage and 125 ohm for 72 h storage as shown in Figure 2. On the other hand, the interface resistance of the cell of the SPE without AN was 750 ohm for 4 h storage and 1400 ohm for 48 h storage.¹² The former result indicates that the SPE with AN units enhances the

contact with the Li electrode. Figure 3 exhibits cyclic voltamograms of the SUS/SPE/Li cell. In Figure 3, anodic and cathodic peaks due to reversible Li plating and stripping were observed around 0 V vs Li/Li⁺. In addition, the SPE was stable up to 4.3 V, indicating that the SPE is suitable for applications in lithium polymer batteries. Figure 4 shows the charge and discharge profiles of the TiS₂/SPE/Li cell in the range of 1.6 to 2.6 V at 0.05 mA/cm² current density. In Figure 4, the utilization was 70% and the Ah efficiency was

almost 100% during the charge-discharge cycle. Therefore, these results suggest that the SPE can be a good candidate for applications in secondary lithium polymer batteries.

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