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Uv-Curable Polymer Electrolyte

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UV-CURABLE POLYMER ELECTROLYTE

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Abstract UV-cured polymer electrolytes were prepared based on polyethylene glycol diacrylate (PEGDA). A series of PEGDA was complexed with lithium triflate salt and the effect of chain length of PEG on the ionic conductivity was studied at various salt concentration. The highest ionic conductivity at room temperature was 1.7×10^{-5} S/cm for 14 EGDA at the [EO]/[Li⁺] mole ratio of 8 which resulted from the balance between the number of total charge carriers and hindered mobility of polymer chain. Cyclic voltammogram for polypyrrole/PEGDA electrolyte/Li foil cell showed a pair of sharp redox peaks even at room temperature.

INTRODUCTION

To develop rechargeable lithium polymer batteries which have high power and energy density the solid polymer electrolytes are required to be highly conductive, electrochemically stable, mechanically strong and flexible. In this respect UV-curable polymer electrolytes based on PEGDA may be considered as one of the best candidates due to their additional easy processibility and high transparency. We investigated the effect of PEG size on the ionic conductivity and optimized the salt concentration. Also its performance was tested using the cell composed of polypyrrole and Li foil as electrodes.

EXPERIMENTAL

PEG diacrylate was mechanically mixed with lithium triflate under N₂ atmosphere and

then initiator (1 ~ 10wt%, Darocure 1173) and accelerator (1 ~ 10 wt%, triethyl amine) were added prior to UV irradiation. The mixture was coated on a glass plate using Doctor blade and cured with UV irradiator (Fusion F-450). The cured film was peeled off, dried at 80 °C in vacuum oven and stored in glove box for later use. Ionic conductivity was measured using impedance analyzer (HP 4192A) and the degree of ion dissociation was characterized by the deconvolution of FTIR (Midac Prospect) spectra.

The electrochemical cell was assembled in a glove box by using Li foil, polymer electrolyte and polypyrrole. The polypyrrole was electrochemically polymerized on platinum disc in an aqueous lithium dodecylsulfate solution containing polyethylene oxide. Cyclic voltammogram was obtained using potentiostat (EG & G 362) interfaced with IBM PC.

RESULTS AND DISCUSSION

Ionic conductivities of UV-cured polymer electrolytes are shown in FIGURE 1 as a function of mole ratio of ethylene glycol (EG) to lithium salt. The number indicates that of EG unit in PEG. The conductivities ranged from 10^{-7} to 10^{-5} S/cm depending on EG unit in the polymer electrolytes. The maximum conductivity appears at a salt concentration of 8 and 10 for 9 EG and 14 EG, respectively, which may result from the balance between the number of charge carriers and hindered mobility of the polymer chain with increasing salt concentration. The highest conductivity of 1.7×10^{-5} S/cm was obtained for 14 EG at the mole ratio of 8.

The ion dissociation in the films was investigated by deconvoluting SO_3^- symmetric peak. The frequency window was in the range of 1010 to 1050 cm^{-1} . Typical FTIR spectra shown in FIGURE 2 are for 14 EG films at different salt ratios. The two peaks at 1030 and 1040 cm^{-1} are assigned to free ion and ion pair, respectively. The deconvoluted result is tabulated in TABLE 1 along with its conductivity. As the salt ratio increases, relative percentage of free ion decreases but total number of free charge carriers increases. Also the increased ion-polymer chain interaction reduces the chain mobility, which is essential for high ionic conductivity. Therefore, the salt ratio should be

optimized to obtain the highest conductivity.

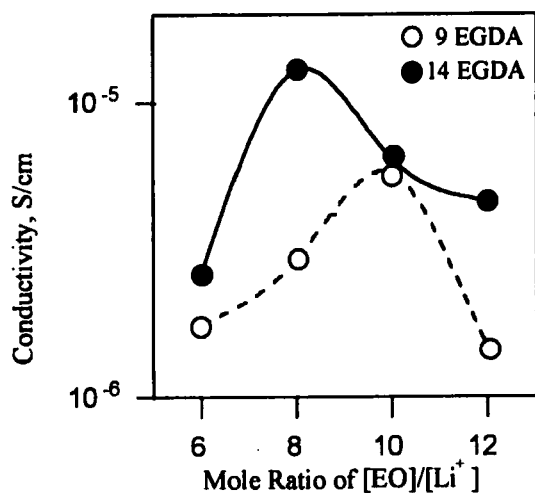


FIGURE 1 Ionic conductivity of polymer electrolyte films as a function of $[\text{EO}]/[\text{Li}^+]$.

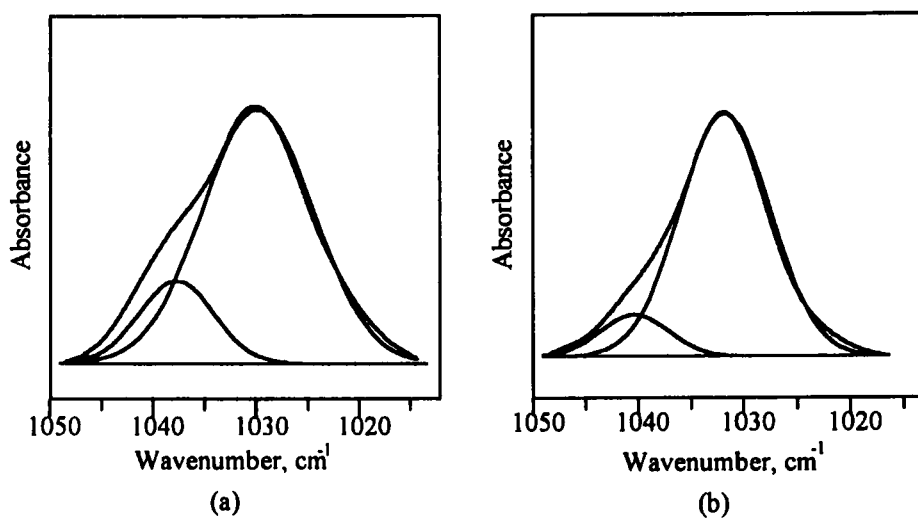


FIGURE 2 Deconvoluted FTIR spectra of 14EGDA/LiCF₃SO₃ films: (a) $[\text{EO}]/[\text{Li}^+] = 6$ and (b) $[\text{EO}]/[\text{Li}^+] = 12$.

FIGURE 3 shows cyclic voltammogram at a scan rate of 20 mV/s for the all solid state cell which was made with 14 EG. A pair of sharp current peaks occurs around 3.0 V due to redox reaction of polypyrrole. The peak separation between redox peaks is very small and the ratio of anodic peak to cathodic peak is close to 1, implying that redox reaction in the cell is quite reversible. The rising peak above 3.5 V may be due to the decomposition of the triflate ion.

TABLE 1 Result of Peak Deconvolution as a Function of Salt Concentration.

Salt Concentration [EO]/[Li ⁺]	Free Ion / Ion Pair (%) / (%)	Conductivity (S/cm)
6	67.3 / 32.7	2.6×10^{-6}
8	80.5 / 19.5	1.7×10^{-5}
10	87.0 / 13.0	6.5×10^{-6}
12	88.4 / 11.6	4.6×10^{-6}

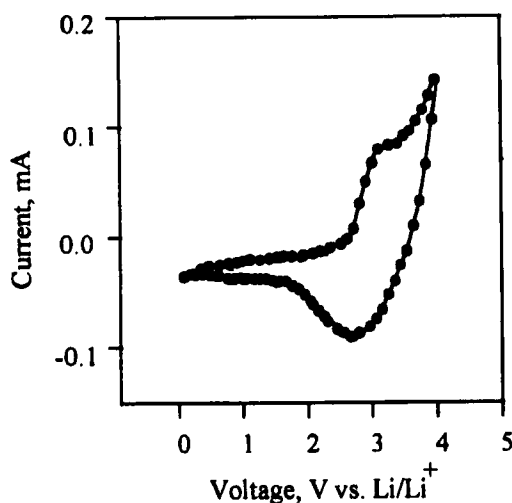


FIGURE 3 Cyclic voltammogram of Li/14 PEGDA/polypyrrole cell.

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