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Articles

Effect of Poly(ethylene glycol) dimethyl ether Plasticizer on Ionic Conductivity of Cross-Linked Poly[siloxane-*g*-oligo(ethylene oxide)] Solid Polymer Electrolytes

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Abstract: Cross-linked network solid polymer electrolytes were prepared by means of *in situ* hydrosilylation between poly[hydromethylslioxane-*g*-oligo(ethylene oxide)] and diallyl or triallyl group-containing poly(ethylene glycols). The conductivities of the resulting polymer electrolytes were greatly enhanced upon the addition of poly(ethylene glycol) dimethyl ether (PEGDME) as an ion-conducting plasticizer. Conductivities of the cross-linked polymer electrolytes were more dependent on the molecular weight of PEGDME than on the cross-linkers. The maximum conductivity was found to be 5.6×10^{-4} S/cm at 30 °C for the sample containing 75 wt% of PEGDME ($M_n = 400$). These electrolytes exhibited electrochemical stability up to 4.5 V against the lithium reference electrode. We observed reversible electrochemical plating/stripping of lithium on the nickel electrode.

Keywords: polymer electrolytes, lithium battery, PEO, polysiloxane, hydrosilyation.

Introduction

A solid polymer electrolyte (SPE) based on polyethylene oxide (PEO) has drawn more attention because decomposition of liquid electrolyte such as ethylene carbonate and propylene carbonate at the highly reactive lithium metal electrode limits their use in the high energy density secondary batteries such as lithium-sulfur and lithium metal batteries.[1,2] However, the ionic conductivity of these solid polymer electrolytes at ambient temperature needs to be improved for practical use.

The ionic conductivity of the SPE is strongly correlated to the segmental motion of the polymer chain and, thus, amorphous polymers with low glass transition temperature (T_g) are preferred for SPE. Oligo(ethylene oxide) grafted comb-shaped and network polymers have been known as an efficient way to prepare amorphous polymer, and have been extensively studied for SPEs using different polymer backbones such as polyphospazene,[3,4] polyacrylate[5-7] and polysiloxane.[8-12]

Among them, polysiloxanes are a good candidate for the SPE backbone because of its low T_g (-123 °C for poly(dimethylsiloxanes)) and chemical inertness. Different oligo(ethylene oxide) grafted comb-shaped polysiloxanes have been tested for the SPE and shown some promises.[8,9,12-14] The maximum conductivity of polysiloxane based SPE was reported to be 4.5×10^{-4} S/cm.[14] The conductivity of these

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polymers was near the conductivity of the practical use (~ 10^{-3} S/cm). However, these materials suffered from the poor dimensional stability as most low T_g polymers did, thus cross-linking was necessary.

The dimensional stability of polysiloxane can be improved by cross-linking. Cross-linking oligo(ethylene oxide) grafted polysiloxane has been previously investigated for the hydroxy fuctionalized prepolymer with toluene diisocyanate[11] and the epoxy functional group grafted poly(methylsiloxane) with amine terminated poly(propylene oxide).[15] However, these cross-linking methods produced reactive functional group such as urethane or hydroxyl group to the lithium electrode, which resulted on the increase of the interfacial resistance between lithium electrode and SPE. Since the acryl functional group can be easily cross-linked with a radical initiator and does not produce any active group that can react with lithium, we synthesized an oligo(ethylene oxide) grafted polysiloxane with acryl groups and tested for SPE.[16] The cross-linked SPE showed good film-forming properties and dimensional stability. Moreover, the ionic conductivity was greatly enhanced by adding ion conducting plasticizer, low molecular weight poly(ethylene glycol) dimethyl ether (PEGDME). The maximum conductivity was as high as 8×10^{-4} S/cm at ambient temperature.

Although acryl functional group was excellent for the cross-linking, it required extra synthetic steps, and we were interested in the use of hydrosilylation for cross-linking of partially modified poly(hydromethylsiloxnae) (PHMS). During our evaluation of the technical merits of the cross-linked polysiloxanes by hydrosilylation reaction for SPE,[17] a similar approach was reported by Zhang *et al.*[18] We were prompted to report our results because we used two different kinds of cross-linkers such as diallyl and triallyl pendent poly(ethylene glycol) and added PEGDME as an ion conducting plasticizer. In this paper, we report the effects of cross-linkers and added ion conducting plasticizers on the ionic conductivity at various temperatures along with the electrochemical stability of the prepared SPE at the ambient temperature.

Experimental

Materials. Poly(ethylene glycol) dimetyl ether (PEGDME, M_n = 250, 400, 500, 1,000, Aldrich and Polysciences), poly (ethylene glycol) monometyl ether (PEGME, M_n = 350, Aldrich), triethylene glycol (Aldrich), glycerol ethoxylate-*co*-propoxylate triol (GEPTO, M_n = 2,600, Aldrich), poly (hydromethylsiloxane) (PHMS, Aldrich) and $LiCF_3SO_3$ (Aldrich) were dried in vacuum before use. Platinium divinyl tetramethyldisiloxane (3 wt% in xylene, Aldrich) was used as received. All other reagents used for synthesis were purified by conventional methods.

Synthesis of Cross-linkers.

Triethylene glycol diallyl ether (TEGDAE): Into a 1,000 mL of 3 necked round bottomed flask fitted with a condenser was charged with triethylene glycol (17.8 g), NaOH (12 g) and anhydrous THF (500 mL). After addition of allyl bromide (36.3 g), the resulting solution was refluxed for 12 hrs and then filtered out to remove the generated salts and excess NaOH. The filtrate was concentrated by rotary evaporation to give a viscous liquid. The residue was dissolved in CH_2Cl_2 and extracted 3 times with 5 wt% NaOH aqueous solution. After drying over anhydrous $MgSO_4$, concentration of CH_2Cl_2 solution and purification by flash column chromatography yielded the desired TEGDAE in 92% as pale yellow liquid.

^{1}H-NMR (300 MHz, $CDCl_3$): δ (ppm) 5.80-5.90 (m, 2H), 5.25-5.08 (m, 4H), 3.94-3.97 (m, 4H), 3.51-3.62 (m, 8H)

Glycerol (ethoxylate-co-propoxylate) triallyl ether (GEPTAE): The similar procedure as described above was employed, using glycerol ethoylate-*co*-propoxylate triol (GEPTO, M_n = 2,600) instead of triethylene glycol to yield g (93 %) of the triallyl derivatives as pale yellow liquid.

^{1}H-NMR (300 MHz, $CDCl_3$): δ (ppm) 5.98-5.84 (m, 3H), 5.31-5.15 (m, 6H), 4.03-3.98(d, 6H), 3.75-3.51 (m, 168H), 1.18-1.13 (d, 35H)

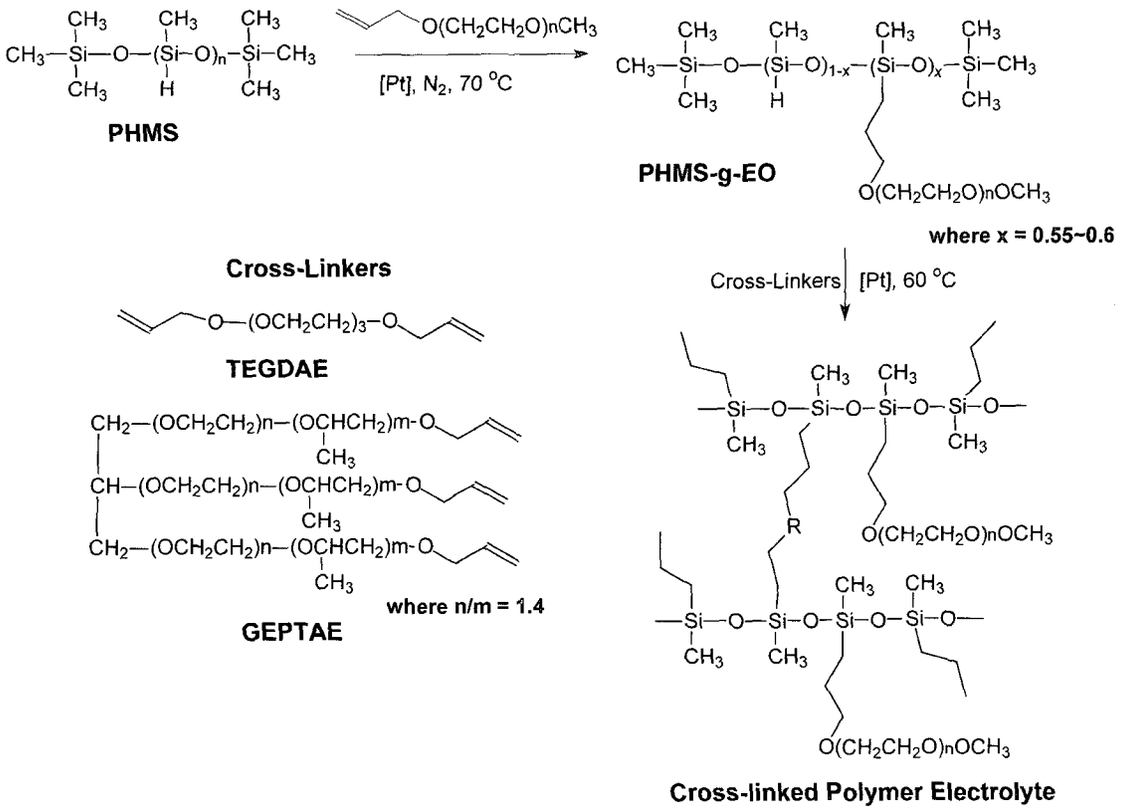
Synthesis of Oligo(ethylene oxide) Grafted Poly(hydromethylsiloxane). The poly[hydromethylsiloxanes-*g*-oligo(ethylene oxide)] (PHMS-*g*-EO) was synthesized by partial hydrosilylation of poly(hydromethylsiloxane) (PHMS) and poly ethylene glycol allyl methyl ether (PEGAME) as shown in Scheme I.

Poly ethylene glycol allyl methyl ether (PEGAME): The similar procedure for synthesis of TEGDAE as described above was employed using poly(ethylene glycol) monometyl ether (PEGME, M_n = 350) instead of triethylene glycol (95% yield).

^{1}H-NMR (300 MHz, $CDCl_3$): δ (ppm) 5.95~6.15 (m, 2H), 5.25~5.50 (m, 1H), 4.14~4.18 (m, 2H), 3.66~3.86 (m, 28.8H), 3.52 (S, 3H)

Poly[hydromethylsiloxanes-g-oligo(ethylene oxide)] (PHMS-g-EO): Into a 100 mL of 3 necked round bottom flask fitted with a condenser and a drying tube was placed a solution of PHMS (2.0 g) in 20 mL of dried toluene and was added 100 μL of platinium divinyl tetramethyldisiloxane (3 wt% in xylene). PEGAME (10.4 g) was added to the stirred solution and the solution was warmed to 50 °C for 4 hrs under nitrogen atmosphere. All volatile solvents were removed by rotary evaporation to yield a viscous liquid. This viscous liquid was dissolved in diethyl ether and stored at -20 °C for overnight and the bottom viscous liquid was collected by decanting the supernant solution. The polymer was purified by repeated fractionation over a cold (-20 °C) diethyl ether and dried in vacuum. Figure 1 shows the ^{1}H-NMR spectrum of the synthesized PHMS-*g*-EO. The mole fraction (x) of the grafted oligo(ethylene oxide) was determined to be 0.55 ~ 0.6 by the ^{1}H-NMR analysis.

Preparation of Cross-linked SPE. Cross-linked solid



Scheme I. Synthetic scheme of the cross-linked polymer electrolyte using oligo(ethylene oxide) grafted polysiloxane.

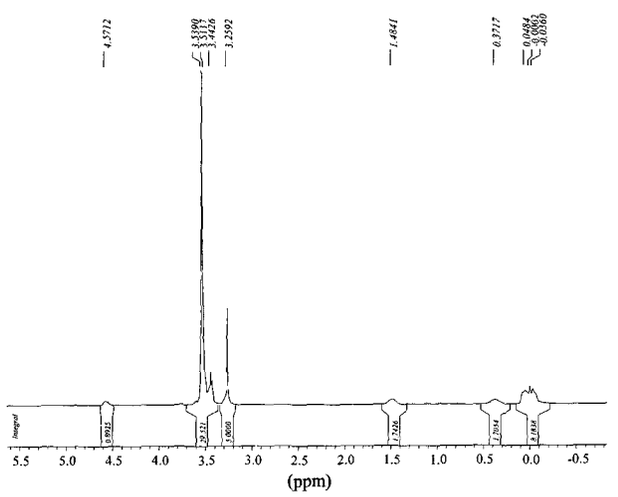


Figure 1. ^{1}H-NMR spectrum of PHMS-*g*-EO.

polymer electrolytes were prepared by in-situ thermal curing using a homogeneous precursor solution of PHMS-*g*-EO, cross-linker (TEGDAE or GEPTAE), PEGDME, a lithium salt ($LiCF_3SO_3$) and a platinium divinyl tetramethyldisiloxane catalyst. The mole ratio between Si-H in PHMS-*g*-EO and allyl group in cross-linker was adjusted as the same. The amount of Pt catalyst was about 10 μL in a 0.1 g of precursor mixture and the residual solvents were removed under dynamic vacuum for 2 hrs. The homogeneous solution was filled in a small gap between the desired substrates such as ITO glass, lithium and nickel. The gap of substrate was maintained about 100 μm by using polyimide tape spacer. The cell was sealed with metallized polyethylene bag in a glove box under argon atmosphere and was cured in convection oven at 60 °C for 10 hrs.

Conductivity and Electrochemical Stability. The conductivity measurement was carried out by curing the polysiloxane mixtures directly onto the pre-patterned ITO cell that has been developed by our laboratory.[7,19,20] The thickness of the polymer layer was about 100 μm. The AC impedance was recorded using an impedance analyzer (Zahner Elektrik, model IM6) in the frequency range of 1 Hz to 1 MHz. The temperature of the sample was controlled by means of the programmable hot plate (Mettler, model FP82HT). The electrochemical stability of the solid polymer electrolytes was examined by means of cyclic voltammetry using an EG&G model 270 potentiostat. The electrochemical cell was a typical two-electrode system using a nickel working electrode and a lithium foil electrode for a counter and reference electrode.

Thermal Property. The T_g of the cured polymer electrolytes was determined by using a differential scanning calori-

meter (TA Instruments, model Universal V2.5H). The measurements were performed with hermitically sealed aluminum pan over the temperature range of 120-0 °C under nitrogen atmosphere. The temperature scan rate was 10 °C/min.

Results and Discussion

Preparation of Polymer Electrolytes. The synthesis of partially grafted PHMS was straightforward although removal of the unreacted PEGAME and some side products was not easy. By repetitive fractionation over cold diethyl ether solution, most of the impurities could be removed. The grafting ratio of PEGAME was estimated from the ^{1}H-NMR peak ratio of Si-H at 4.6 ppm and Si-CH_3 at 0 ppm. The grafting ratio was consistently obtained to be 0.55~0.6 in several different runs. The course of cross-linking reaction of the polymer electrolyte precursor was followed by FT-IR. Figure 2 shows FT-IR spectra of precursor mixture before and after thermal curing. The peaks corresponding to the Si-H vibration (912, 2182 cm^{-1}) are almost completely disappeared after curing. The resulting polymer electrolyte showed elastic characteristics and can be formed as thin film on the different electrodes such as nickel, ITO and Li without generating bubbles. The cross-linked polymer electrolyte was transparent and showed single T_g by DSC study. It is concluded that the cross-linked polymer electrolyte is miscible with the PEGDME within the range of concentration used in the experiment.

Ionic Conductivities. To optimize the salt concentration, ionic conductivity was measured as a function of [EO]/[Li] ratio (Figure 3). The polymer electrolyte complexed with $LiCF_3SO_3$ was prepared by using TEGDAE as a cross-linker and containing 60 wt% of PEGDME (M_n = 400). A typical bell shape of conductivity curve was observed with a maximum. The T_g decreased as increasing the [EO]/[Li] ratio. The increase of T_g with increasing lithium salt concentration can be ascribed to the inter- and intra-molecular coordination of ether dipoles with the lithium ions, which may act as transient cross-linking points in the polymer electrolytes. The increase in the T_g may decrease the segmental motion of the host polymer which is directly related to the decrease of the ionic mobility.[21] In contrast, the number of charge carriers, lithium ions, increases with increasing the salt concentration. The maximum in the conductivity is attributed to a balance between the increase of charge carrier density and the decrease of chain flexibility. The maximum conductivity was found when [EO]/[Li] ratio was 15. This value was rather lower than that reported by Zhang *et al.*[18] We assumed that the difference was from the use of different lithium salt and the added ion conducting plasticizer. Hereafter, the [EO]/[Li] ratio of SPE was fixed to be 15 in this study.

Figure 4 shows the changes of isothermal conductivity and T_g with the variation molecular weight of PEGDME used as a plasticizer. In this case, the TEGDAE was used as a cross-linker and the content of plasticizer was 60 wt%. At 30 °C, the ionic conductivity was strongly dependent on the

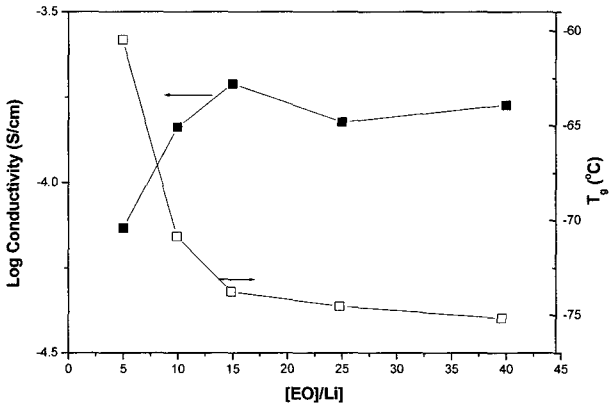


Figure 3. Dependence of conductivity and T_g as a function of [EO]/[Li] ratio (Cross-linker: TEGDAE).

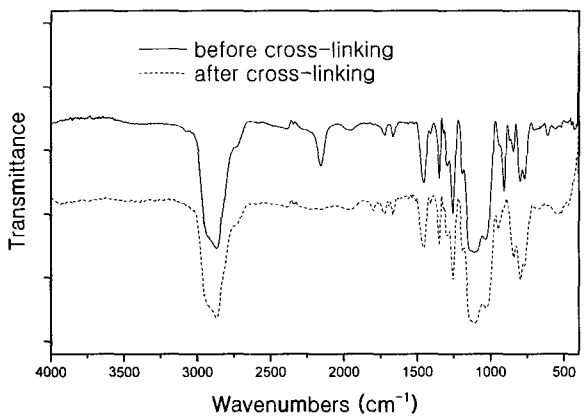


Figure 2. FT-IR spectra of PHMS-*g*-EO before and after thermal curing with using TEGDAE as cross-linker.

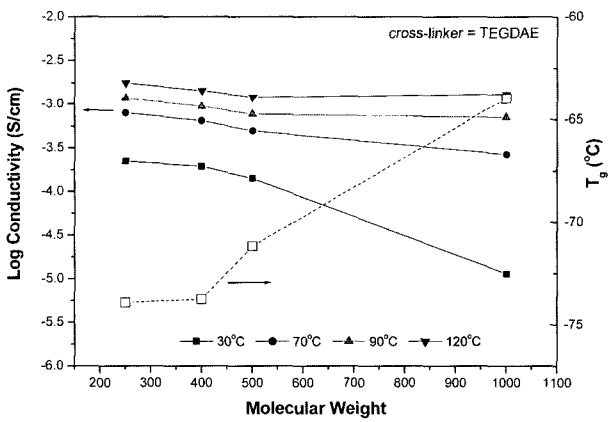


Figure 4. Dependence of isothermal conductivity and T_g as a function of PEGDME molecular weight.

molecular weight of PEGDME. The ionic conductivity decreased with increasing the molecular weight of PEGDME. The decrease of ionic conductivity corresponded to the increased of T_g. The ionic conductivity showed a monotonous decrease with increasing the molecular weight of PEGDME and drastic decrease in the ionic conductivity due to phase transition such as the crystallization was not observed over the temperature range of 30-120 °C.

The change of the measured conductivity and T_g as a function of the PEGDME (M_n = 400) content is shown in Figure 5. Ionic conductivities of polymer electrolyte without plasticizer were measured to be 5.5×10^{-5} S/cm for TEGDAE and 2.4×10^{-5} S/cm for GEPTAE. From this result, it seemed that the effect of cross-linkers was minimal for this type of SPE. The measured ionic conductivity had similar order of magnitude with the reported value for cross-linked polysiloxane with acrylate functional group.[16] However, the ionic conductivity was slightly lower than that of cross-linked polysiloxane reported by Zhang *et al.*,[18] The lower conductivity may be attributed to the difference of lithium salt since the polymer electrolyte complexed by $LiN(CF_3SO_2)_2$ which was used by Zhang *et al.*, usually gave higher conductivity compared to that complexed by $LiCF_3SO_3$ used in this study.[22] As the content of the PEGDME increased, the conductivity gradually increased but the T_g of the polymer decreased. The similar increase of the conductivity has been reported for the PVDF-HFP[23] and cross-linked polymer electrolyte[7,16] plasticized with PEGDME. The plasticizing effect of PEGDME is clearly seen by the decreasing of T_g of the polymer electrolytes. The maximum conductivity at 30 °C was measured to be 5.6×10^{-4} S/cm containing 75 wt% of PEGDME (M_n = 400).

In Figure 6, the temperature dependence of conductivity (σ) is shown for the polymer electrolyte prepared from TEGDAE and GEPTAE containing different amount of PEGDME. The ionic conductivity was increased as the ion mobility was enhanced with the increased segmental motion of the siloxane main chain and the PEO side chain at the elevated temperature. Conductivity-temperature (σ-T) curves are deviated from Arrhenius behavior. These curves show a typical Vogel-Tamman-Fulcher (VTF) relationship (eq. 1) in the temperature range from 30 to 120 °C.

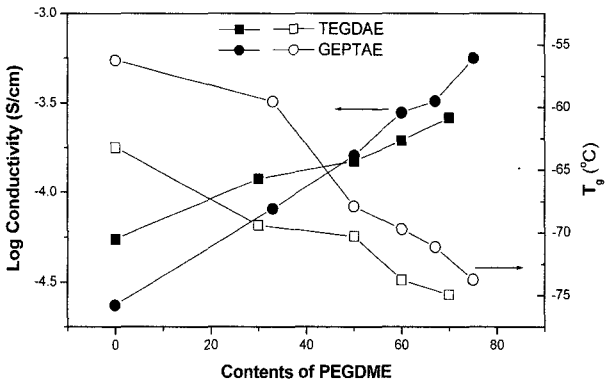


Figure 5. Dependence of conductivity and T_g as a function of PEGDME content.

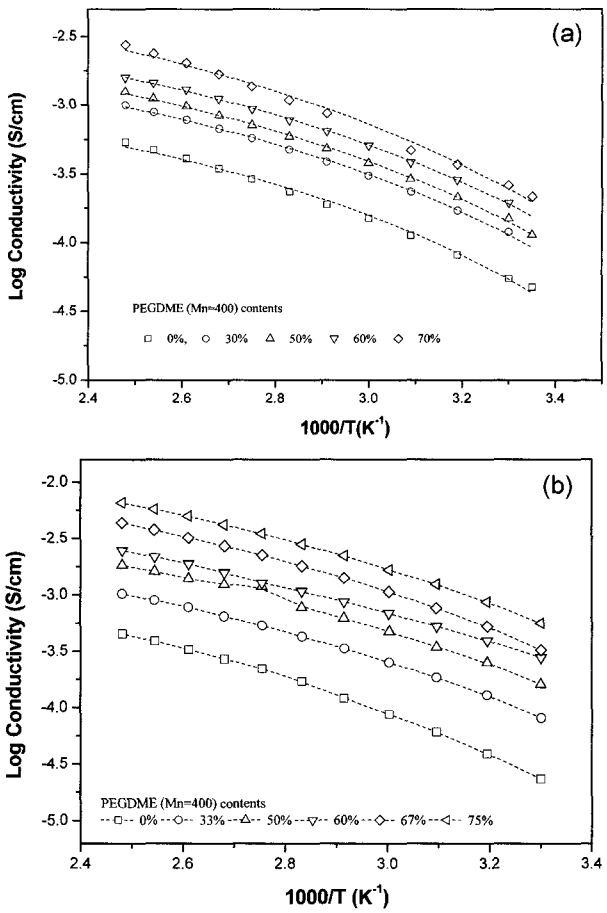


Figure 6. Temperature dependence of conductivity for various PEGDME (M_n = 400) contents with different cross-linkers of (a) TEGDAE and (b) GEPTAE.

$$\sigma = AT^{-\frac{1}{2}}\exp\left(-\frac{E_a}{R(T-T_o)}\right) \quad (1)$$

where A, E_a, R and T_o are fitted parameters which are related to the carrier density, pseudo activation energy, gas constant and zero configuration entropy of the polymer chain, respectively. The VTF expression implies that the main mechanism of ion conduction may be related to the free volume theory.[1,24]

The E_a of the polymer electrolyte was calculated to be 7.0 ~8.3 kJ/mol, which was similar to the reported value of the cross-linked oligo(ethylene oxide) grafted polysiloxane polymer electrolyte.[16,18]

Electrochemical Properties. Figure 7 shows cyclic voltammograms of polymer electrolyte which containing 75% PEGDME at 30 °C as a typical example. In anodic scan,

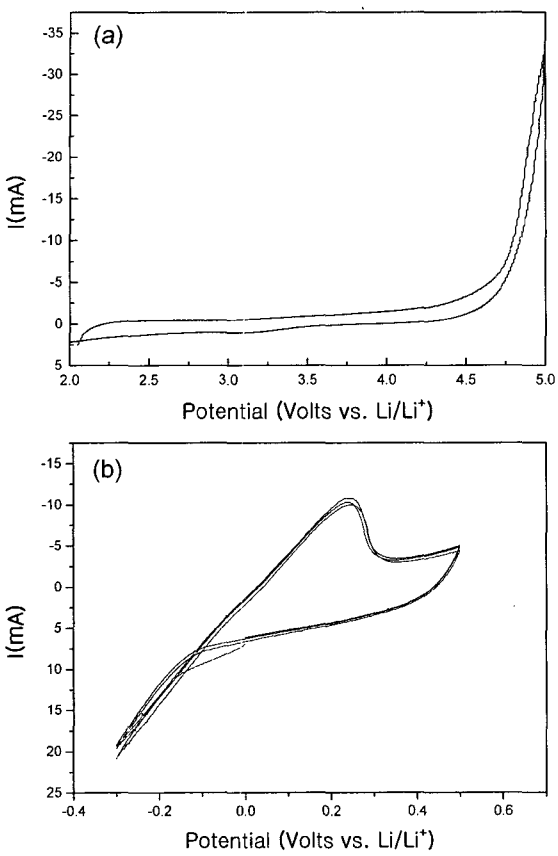


Figure 7. Cyclic voltammogram of the polymer electrolyte containing 75 wt% PEGDME (M_n = 400) (Cross-linker: GEPTAE).

irreversible anodic degradation of the polymer electrolyte was starting ca. 4.5 V against lithium reference electrode. In cathodic scan, we observed the reversible plating/stripping of lithium on the nickel electrode in potential range of -0.3 to 0.5 V. The deposition of the lithium is starting ca. -0.05 V and maximum anodic peak is found to be ca. 0.2 V. Although the cyclic voltammetric study cannot directly related to the long-term stability of polymer electrolytes, the resulting polymer electrolyte which showed stable potential window up to 4.5 V may be acceptable for practical lithium-polymer battery.

Summary

In this paper, a solid polymer electrolyte based on cross-linked poly[siloxanes-*g*-oligo(ethylene oxide)] plasticized with low molecular weight PEGDME was prepared, and the ionic conductivity and electrochemical stability of the resulting polymer electrolyte were studied. The ionic conductivity of the cross-linked polymer electrolytes without plasticizer was $5.5\times 10^{-5}\sim 2.4\times 10^{-5}$ S/cm. The conductivity increased as the content of the ion conducting plasticizer, PEGDME, increased. The maximum conductivity was 5.6×10^{-4} S/cm containing 75 wt% of PEGDME (M_n = 400). Stable potential window of the polymer electrolyte was measured to be 4.5 V which may be acceptable for practical lithium-polymer batteries.

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