

# Poly(ethylene glycol) Electrolyte Gels Prepared by Condensation Reaction

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**ABSTRACT:** Poly(ethylene glycol) electrolyte gels were prepared by condensation reaction in the presence of tetraethoxysilane. Differential scanning calorimetry and X-ray diffraction spectroscopy were used to investigate the thermal transition behavior and crystalline structure of polymer gels prepared. Both formation of crosslinks and incorporation of salts or plasticizers reduced the development of crystalline structure of poly(ethylene glycol)s. Cyclic voltammetric and ion-conducting behaviors of polymer gels were analyzed using potentiostat and impedance spectroscopy, and those

were also considerably affected by the crosslinking density of polymers and the concentration of electrolyte salt or plasticizers incorporated. Poly(ethylene glycol) gels possessing certain levels of electrolyte salt and plasticizer were expected to have applications of solid electrolytes for lithium polymer secondary batteries. © 2002 Wiley Periodicals, Inc. *J Appl Polym Sci* 86: 948–956, 2002

**Key words:** polymer electrolytes; crosslinking; poly(ethylene glycol); gels; secondary batteries

## INTRODUCTION

Lithium secondary batteries are classified into lithium ion batteries (LIB) and lithium polymer batteries (LPB) according to the types of electrolyte materials.<sup>1</sup> Because LIB has safety problems associated with the leakage and explosion of liquid electrolytes in severe working conditions, the replacement of LIB with LPB has been actively considered. LPB does not need a safety device to prevent overcharge and also can be fabricated into a light and flexible shape.<sup>2–5</sup>

Polymer electrolyte is one of the most important components in the fabrication of LPB. Polymer electrolytes must be either solid or gel-type materials with ion conductivity of  $10^{-8}$  to  $10^{-3}$  S/cm.<sup>6–8</sup> Nevertheless, the polymer electrolytes developed so far have some problems associated with their inherent properties. It was reported that the gel-type polymer electrolytes not only have much lower mechanical strength than that of the separator but also have much lower ion conductivity than that of liquid electrolytes.<sup>9,10</sup>

For these reasons, many studies have been conducted regarding the development of new polymer electrolyte systems.<sup>11,12</sup> The two polymer electrolyte types, hybrid solid and intrinsic solid, were generally the focus of the research. The hybrid solid type was usually prepared by impregnating liquid electrolytes

into polymer films with fixation of electrolyte salts. Organic solvents such as ethylene carbonate, propylene carbonate, dimethyl carbonate, and diethyl carbonate were used. Impregnation of the electrolyte salt-dissolved liquids in polymer matrices generated an ion conductivity of about  $10^{-3}$  S/cm. However, because the actual medium for ion transport was liquid and there was no compatibility between polymer and liquid, those hybrid electrolyte systems hardly eliminated the drawbacks associated with LIB. To overcome this, low molecular weight poly(ethylene oxide)s (PEO) or poly(ethylene glycol)s (PEG) were used to replace electrolyte liquids.<sup>13–19</sup> Low molecular weight PEOs were melt compounded with poly(vinylidene fluoride)–hexafluorophenylene (PVDF–HFP) copolymers into composites, and showed rather good ion-conducting results.

Intrinsic solid types are usually prepared by fixing electrolyte salts in the polymers generally composed of heterogeneous atoms such as O, N, or S. Ion conductivity is attained by the movement of dissociated ions in an electric field. High molecular weight poly(ethylene oxide) (PEO) was one of most widely studied intrinsic solid polymers.<sup>20–24</sup> The movement of lithium ions was triggered by active segmental motion of amorphous polymer chains.<sup>25</sup> However, a major problem associated with PEO was the presence of crystalline structure. PEO in the number-average molecular weight of around  $10^6$  g/gmol contains about 80% of crystallinity. The ion conductivity decreased rapidly to around  $10^{-9}$  to  $10^{-8}$  S/cm when the crystalline structure was developed. Amorphous polymers such as poly(methyl methacrylate) or poly(di-

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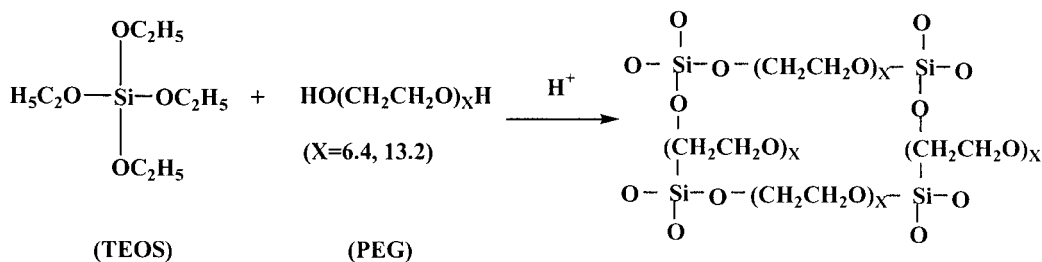


Figure 1 Schematic reaction mode for the synthesis of XPEG by sol-gel condensation.

methyl siloxane) were copolymerized or grafted with/on PEO to prevent crystallization, but their ion conductivities were not just satisfied.<sup>26,27</sup> On the other hand, more mechanically stable intrinsic solid polymer electrolytes such as high molecular weight PEO generally did not demonstrate high ion conductivity because of much lower molecular mobility.

In this study, relatively low molecular weight PEGs were crosslinked in the presence of tetraethoxysilane (TEOS) by sol-gel condensation reaction, not only to prevent the formation of crystalline structure but also to attain high mechanical strength. Effects of electrolyte salts and plasticizers on the thermal, mechanical, and electrochemical properties of the crosslinked PEG (XPEG) were investigated for the consideration of novel solid electrolyte systems for lithium polymer secondary batteries.

## EXPERIMENTAL

### Raw materials

PEGs with molecular weights of 300 and 600 g/gmol were purchased from Aldrich Chemical Co. (Milwaukee, WI), which were then dried in a vacuum oven for 1 week to eliminate humidity, and then stored in a desiccator before use. Tetraethoxysilane (TEOS), a crosslinking agent, was purchased from KC Technology (Seoul, South Korea). Ethylene carbonate (EC), propylene carbonate (PC), and other plasticizers and solvents were purchased from Aldrich.  $\text{LiClO}_4$  (purity > 99%; Acros Organics, Morris Plains, NJ) was used as the electrolyte salt. Lithium (Li, purity > 99.9%; Aldrich) was used as the electrode material.

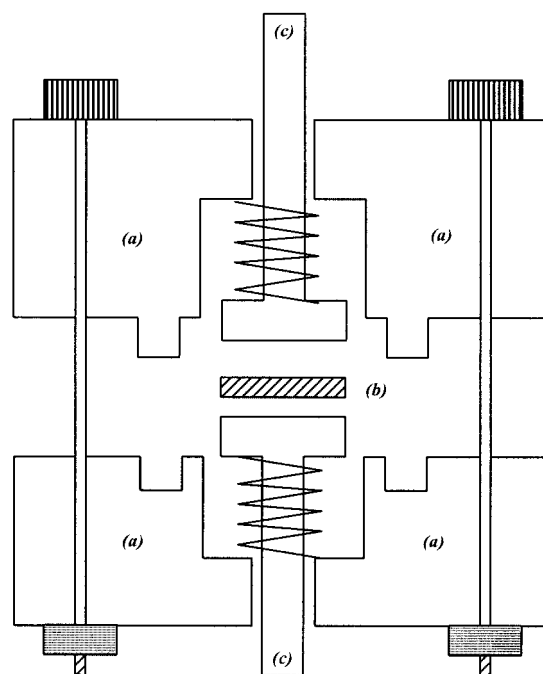
### Preparation of PEG electrolyte gels

Crosslinked PEG (XPEG) was prepared by condensation reaction. PEG (0.025 mol) and TEOS (0.0125 mol) were dissolved in acetonitrile at room temperature. The crosslinking reaction was conducted in a three-neck flask at 120°C for 3 h. Nitrogen gas was continuously purged to prevent oxidation. The products were placed in a vacuum oven at 100°C for 1 h for complete reaction. The reaction mode is schematically represented in Figure 1.  $\text{LiClO}_4$  was mixed with

EC/PC solvent and then the solution was mixed with PEG to have a different concentration at the beginning of the reaction. To prepare polymer gels in film shape, the reactants were withdrawn just before gelation occurred, and then coated on the aluminum foil using doctor blades. The crosslinking reaction was completed at the same condition after the desired thickness of coated film was achieved. After completion of the curing reaction, the products were dried in a vacuum oven to remove residual reactants and solvents.

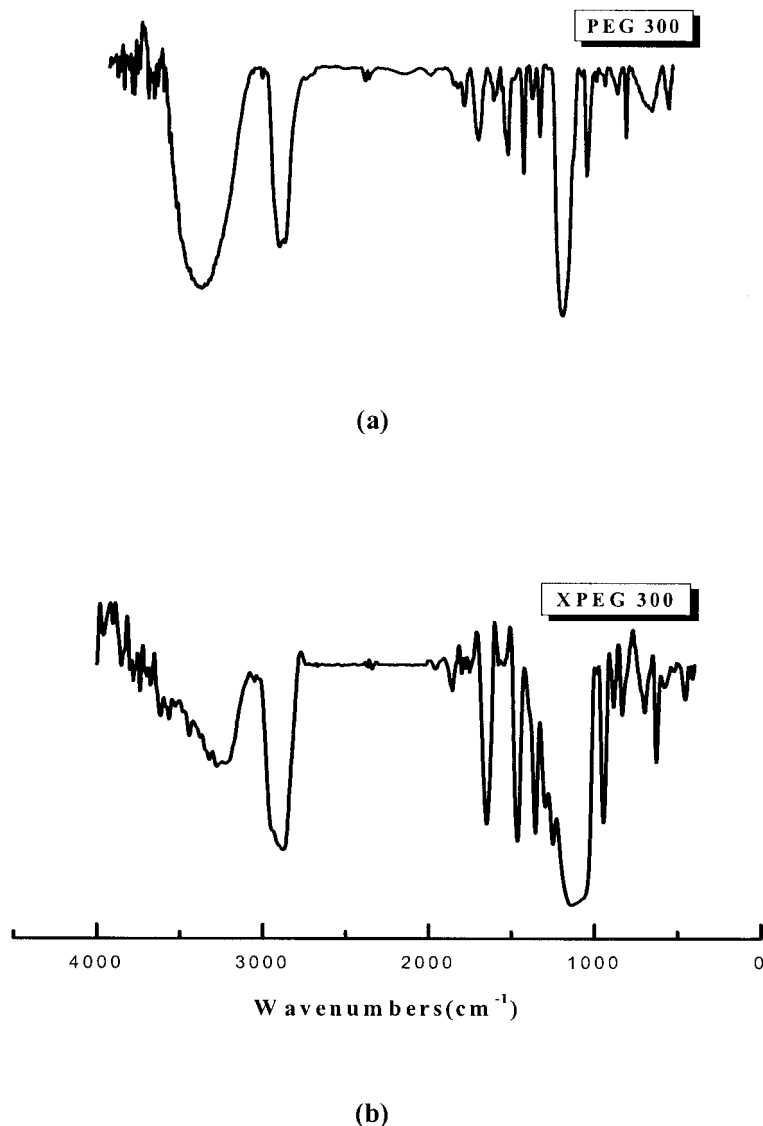
### Characterization of XPEG

Fourier transform infrared spectroscopy (FTIR, Unicam, Mattson 1000) was used to investigate the presence of crosslinks (siloxane groups) in the synthesized



(a) : Teflon body  
 (b) : Polymer electrolyte  
 (c) : Stainless steel electrode :

Figure 2 Typical membrane electrode assembly of lithium polymer batteries.



**Figure 3** FTIR spectra of (a) PEG300 and (b) XPEG300 polymer electrolyte systems.

polymer products.  $^1\text{H}$ -Fourier transform nuclear magnetic resonance spectroscopy (FT-NMR, Unity Inova 500; Varian Associates, Palo Alto, CA) was also used to analyze the chemical structure of synthesized polymer molecules.

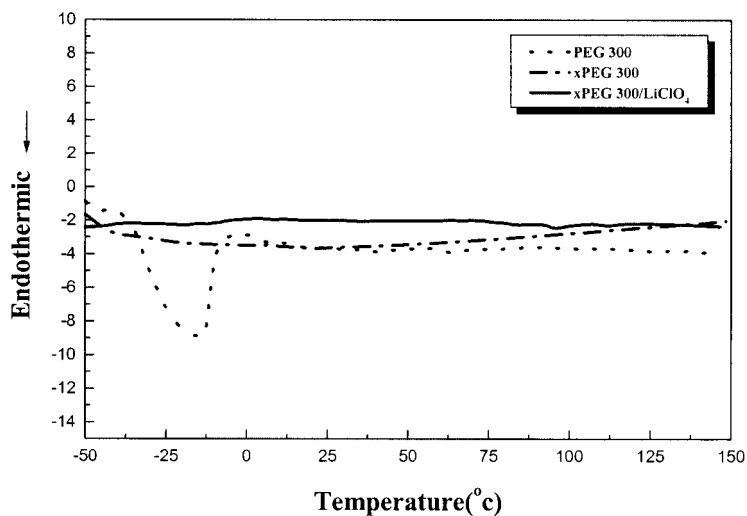
Thermal properties were investigated using a DSC7 differential scanning calorimeter (Perkin Elmer Cetus Instruments, Norwalk, CT) and a TGA7 thermogravimetric analyzer (Perkin Elmer Cetus Instruments). In DSC measurement, 6 to 9 mg of polymer sample was heated from  $-50$  to  $150^\circ\text{C}$  with a scanning rate of  $10^\circ\text{C}/\text{min}$  in the presence of nitrogen gas. The second heating scan was obtained after cooling the first heated sample at a cooling rate of  $30^\circ\text{C}/\text{min}$ . Glass- and melting-transition temperatures, and crystallization temperatures were determined from DSC experiments. Decomposition temperatures of synthesized copolymers were determined from TGA measure-

ments. A 10-mg polymer sample was heated from  $25$  to  $450^\circ\text{C}$  with the scanning rate of  $10^\circ\text{C}/\text{min}$  in the presence of nitrogen gas.

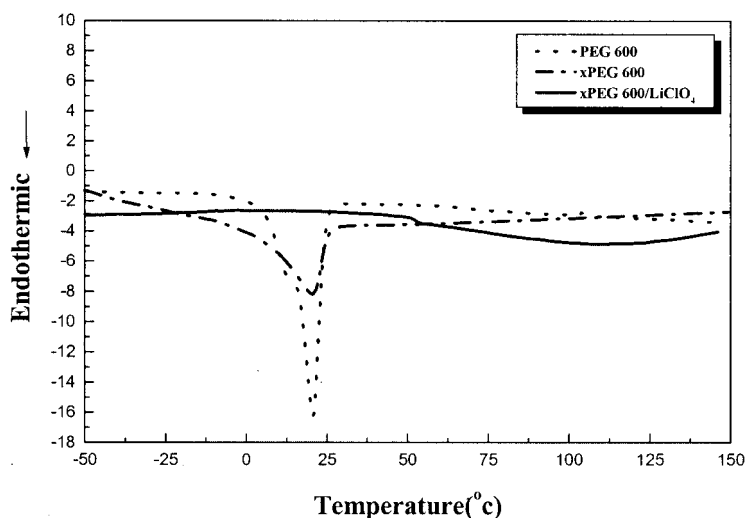
X-ray diffraction spectroscopy was used to investigate the presence of crystalline structure. Scanning was conducted in the range of  $10^\circ < 2\theta < 60^\circ$  at the rate of  $10^\circ/\text{min}$ , and the output power was  $30\text{ kV}/100$ . Both the pure and salt-incorporated XPEGs were sampled for analyzing their crystalline structures.

#### Electrochemical property measurement

SS/polymer electrolyte/Li/SS cells, in which polymer electrolytes were sandwiched between stainless steel (SS) working and lithium (Li) counter electrodes, were prepared to measure the cyclic voltammetric behavior. The area of working electrode



(a)



(b)

Figure 4 DSC thermograms of (a) XPEG300 and (b) XPEG600 polymer electrolyte systems.

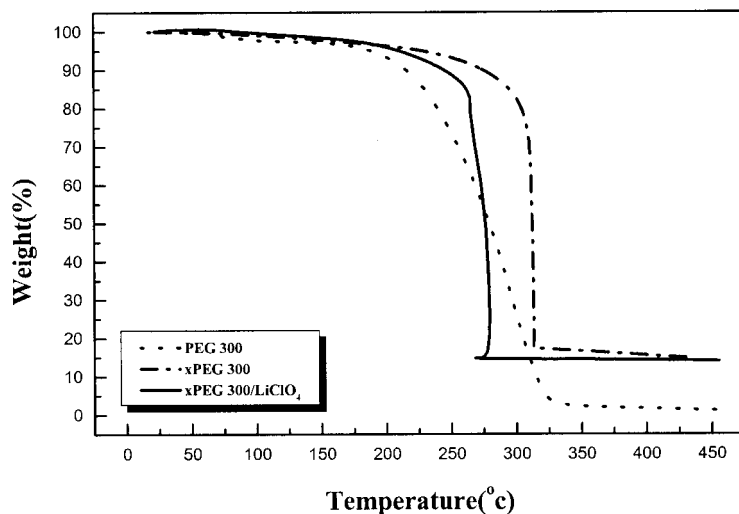
was  $0.785 \text{ cm}^2$ . Measurements were conducted using a PAR 175 potentiostat/galvanostat with PAR 175 Universal Programmer at the potential scanning rate of  $10 \text{ mV/s}$ .

Measurement of the ion conductivity of the prepared polymer electrolytes was by ac-impedance spectroscopy. The measurement system was composed of the Solartron 1260 frequency response analyzer and Solartron 1287 electrochemical interface controlled by an electrochemical impedance system software. Membrane electrode assembly (MEA) was fabricated as shown in Figure 2.

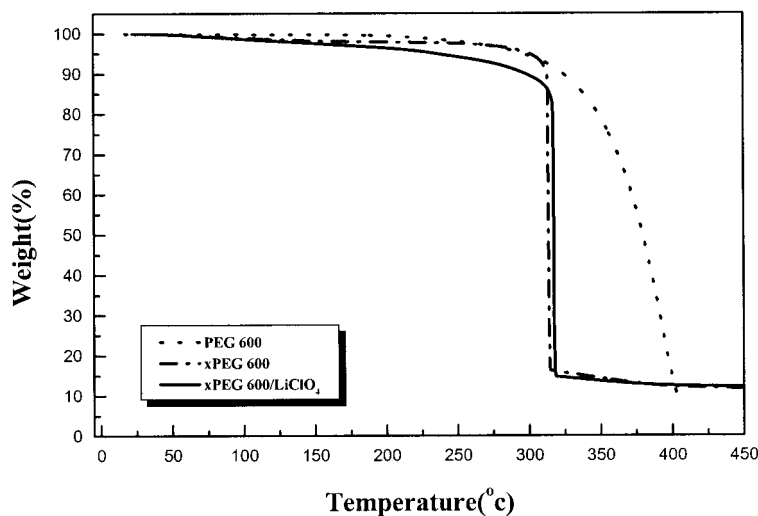
## RESULTS AND DISCUSSION

### Chemical structure of XPEGs

The crosslinking reaction illustrated in Figure 1 produced XPEGs with the two different number-average molecular weights between consecutive crosslinks ( $\bar{M}_c$ ) of 300 and 600 g/gmol. Figure 3 shows the FTIR spectrum of XPEG300; the  $\bar{M}_c$  value of XPEG was 300 g/gmol. The IR bands around the wavenumbers of  $3400$  and  $1100 \text{ cm}^{-1}$  were attributed to the  $-\text{OH}$  and  $\text{Si}-\text{O}$  groups, respectively. Because no liquid TEOS was present in the final solid film product, the de-



(a)



(b)

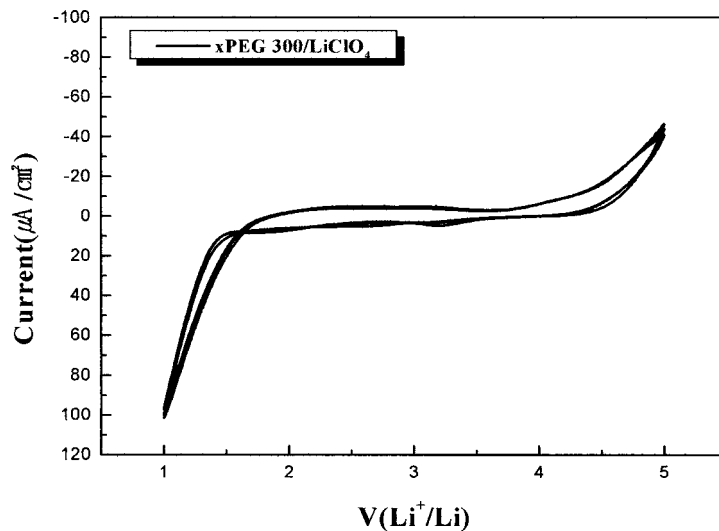
Figure 5 TGA thermograms of (a) XPEG300 and (b) PEG600 polymer electrolyte systems.

creased band intensity at  $3400\text{ cm}^{-1}$ , but increased one at  $1100\text{ cm}^{-1}$  after sol-gel reaction, implied that crosslinks were formed during reaction. The IR spectrum of the XPEG600 system was similar to that of the XPEG300 system.

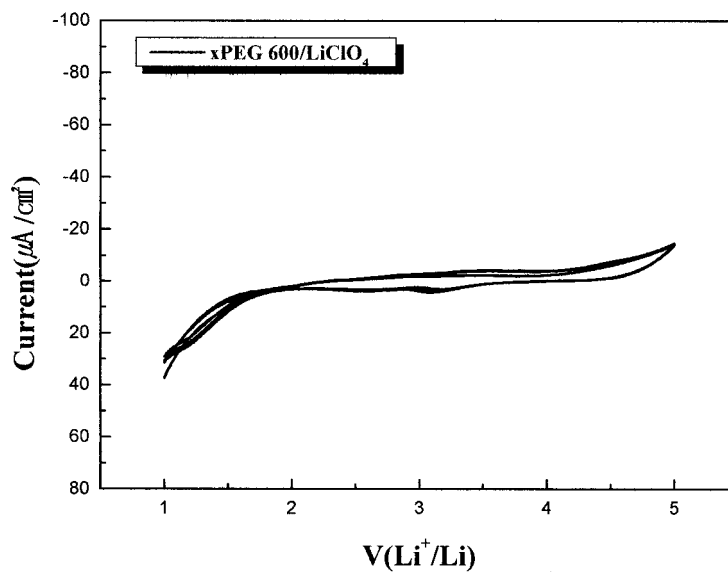
#### Thermal properties and crystallinity of XPEG

Figure 4 (a) and (b) show the DSC thermograms of the XPEG300 and the XPEG600 systems, respectively. Both the melting-transition temperature ( $T_m$ ) and heat

of fusion ( $\Delta H_f$ ) of uncrosslinked PEG increased with increasing number-average molecular weight,  $\bar{M}_n$ . The  $T_m$  value of PEG300 was lower than room temperature, but that of PEG600 was around  $20^\circ\text{C}$ . Crosslinking of PEG600 resulted in quite an observable decrease of  $\Delta H_f$ , attributed to the more difficult molecular orientation associated with the less mobile crosslinked molecular structure. No crystalline structure was formed for XPEG300 because of the limitations in molecular orientation. Addition of salts in the XPEG series eliminated the crystalline structures completely



(a)



(b)

Figure 6 Cyclic voltammograms of (a) XPEG300 and (b) XPEG600 polymer electrolyte systems.

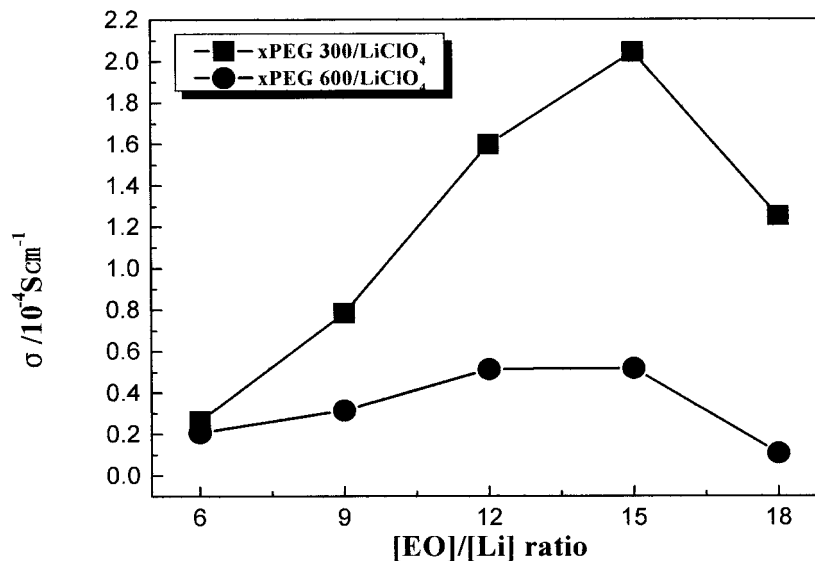
by disrupting molecular orientation. X-ray diffraction patterns complemented the DSC results. No crystalline structures were observed at room temperature for either the XPEG300 or the XPEG600 system, regardless of the presence of dissolved electrolytes. The crystalline phase of XPEG600 was not observed in X-ray diffraction because this XRD measurement was conducted at room temperature, at which almost all crystals were melted.

The thermal stability of XPEG systems is shown in Figure 5. The XPEG300 system was much more ther-

mally stable than the PEG300 system. XPEG systems were thermally stable up to 300°C and incorporation of salt into XPEG systems had no significant effect on its behavior. No noticeable effect of crosslink density was observed on thermal stability.

#### Electrochemical properties of XPEGs

Figure 6(a) and (b) show the cyclic voltammograms of the XPEG300 and XPEG600 polymer electrolyte sys-

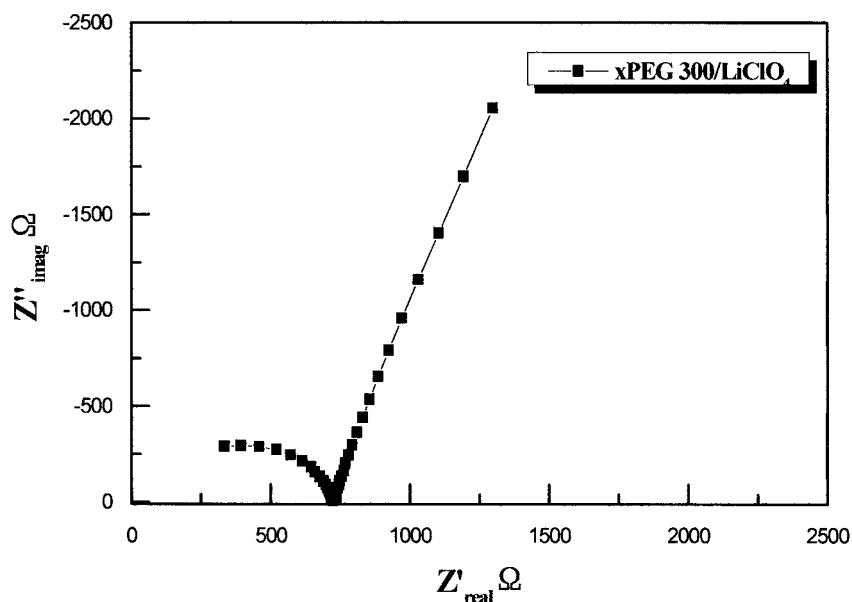


**Figure 7** Salt concentration dependency of ionic conductivity of XPEG300 and XPEG600 polymer electrolyte systems at room temperature.

tems, respectively. All XPEGs were electrochemically stable up to 4.5 V, above which an increase in current was observed, attributed to the oxidation of the polymer electrolytes. There was no clear difference in the voltammetric behavior between the two present XPEG systems.

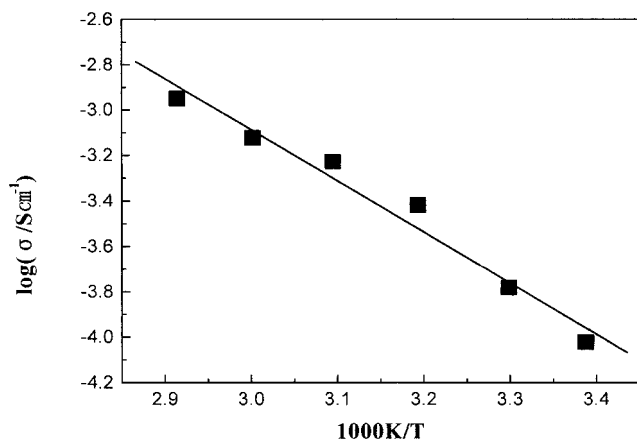
In Figure 7, the salt concentration effect on the room-temperature ion conductivities of XPEG electrolyte systems is represented. Each conductivity value was obtained from the intercept on the real axis of a typical Nyquist plot. An example of ac-impedance measurement for the ss//XPEG300/LiClO<sub>4</sub>//ss cell is represented in Figure 8. The ionic conductivities of the

XPEG300 system were higher than those of the XPEG600 system for all salt concentrations in the present experimental range. This trend was probably the result of more mobile molecular motion associated with amorphous molecular structure. Incorporation of electrolyte salt in the [O]/[Li] ratio of 15 led to the highest ionic conductivities for both systems. In the XPEG300 system, the ion conductivity increased by more than 7 times by addition of salt in the [O]/[Li] ratio of 15. Incorporation of salt up to a certain concentration, [O]/[Li] ratio of 15, enhanced the ion transport monotonically, but beyond that the molecular motion was too restricted to attain high Li ion transport.



**Figure 8** Nyquist plot of the ss//xPEG300/LiClO<sub>4</sub>//ss cell.





**Figure 9** Temperature dependency of ion conductivity of XPEG300 polymer electrolyte systems possessing  $\text{LiClO}_4$  in the  $[\text{O}]/[\text{Li}]$  ratio of 15.

Figure 9 shows the temperature dependency of ionic conductivity for the XPEG300 system possessing electrolyte salt in the  $[\text{O}]/[\text{Li}]$  ratio of 15. The ionic conductivity increased with increasing temperature. There was an Arrhenius relationship between ionic conductivity and temperature. The order of ion conductivity was about  $10^{-4}$  S/cm at room temperature but was about  $10^{-3}$  S/cm at  $70^\circ\text{C}$ .

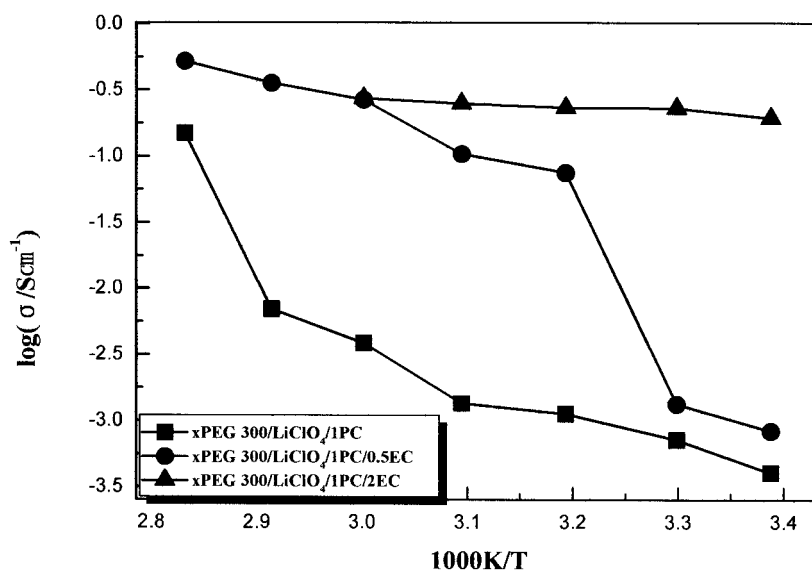
Figure 10 shows the plasticizer effect on the ionic conductivity of the XPEG300 system possessing the salt in the  $[\text{O}]/[\text{Li}]$  ratio of 15. The addition of solvents (plasticizer) led to another order of magnitude increase in the ionic conductivity compared with that of the pure polymer electrolyte systems because of increased molecular mobility. The room-

temperature conductivities of all plasticizer-incorporated XPEGs in this study were even higher than  $10^{-3}$  S/cm, the typical value of ion conductivity commercially available. Addition of more EC plasticizer induced an even greater increase of ion conductivity. More incorporation of plasticizer than the highest amount shown in this figure resulted in the loss of mechanical strength of polymer films, such that any further application would be of no importance.

## CONCLUSIONS

Low molecular weight PEGs were crosslinked with TEOS through a sol-gel condensation reaction. Crystallinity of poly(ethylene glycol) reduced significantly by the formation of crosslinks, and was completely eliminated by incorporation of salts and plasticizers. The room-temperature conductivity of the prepared XPEGs increased to higher than  $10^{-3}$  S/cm by incorporation of plasticizers. Cyclic voltammograms illustrated electrochemical stability up to 4.5 V, regardless of polymer molecular weight. The prepared polymer gels also illustrated thermal and mechanical stability, even with incorporation of plasticizer. These excellent electrochemical and bulk properties of the XPEGs led us to optimistic expectations concerning their application as novel solid electrolyte materials in the fabrication of lithium polymer secondary batteries.

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**Figure 10** Plasticizer concentration effect on the temperature-dependent ion conductivity of XPEG300 polymer electrolyte systems possessing  $\text{LiClO}_4$  in the  $[\text{O}]/[\text{Li}]$  ratio of 15.



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