

# Ionic Conductivity and Physical Stability Study of Gel Network Polymer Electrolytes

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**ABSTRACT:** Gel polymer electrolytes (GPE) were prepared by a crosslinking reaction between poly(ethylene glycol) and a crosslinking agent with three isocyanate groups in the presence of propylene carbonate (PC) and ethylene carbonate (EC) or their mixture, and their ionic conducting behavior was carefully investigated. When the plasticizer amount was fixed, the ionic conductivity was greatly influenced by the nature of plasticizers. It was found that the conductivity data followed the Arrhenius equation in the GPE. Whatever plasticizer was used, a maximum ambient conductivity was found at a salt concentration near  $[Li^+]/[EO]$  equal to 0.20. The physical stability of GPE was studied qualitatively by weight loss of GPE under pressure. It was shown that the stability was greatly affected by the network structure of the GPE and the most stable one in our research was the GPE containing the PEO<sub>1000</sub> segment, which has a strong interaction between network and plasticizers. © 2000 John Wiley & Sons, Inc. *J Appl Polym Sci* 77: 2957–2962, 2000

**Key words:** gels; network polymer electrolytes; ionic conductivity; arrhenius equation; stability

## INTRODUCTION

Solid polymer electrolytes (SPE) have been quickly developed since the pioneering investigations were carried out by Wright et al.<sup>1</sup> and Armand et al.<sup>2</sup> in 1970s. Due to good mechanical strength, easy packaging, and high energy densities, applications of solid polymer electrolytes as separators for lithium batteries have been given a great deal of attention in recent years. For example, electric vehicles powered by solid-state batteries are becoming “new generation” traffic tools because of their ability to meet environmental requirement, so developing an appropriate polymer electrolyte is becoming an urgent task.

The widely investigated poly(ethylene oxide) (PEO)/alkali metal salt complexes exhibit very low ambient ionic conductivity, typically  $10^{-7}$   $Scm^{-1}$  because of the severe crystallinity of PEO. To hinder the crystallinity of PEO, various approaches such as copolymerization,<sup>3</sup> grafting,<sup>4</sup> and crosslinking<sup>5</sup> have been employed to prepare polymer hosts consisting mainly of amorphous PEO.

In our previous work,<sup>6</sup> network polymer electrolytes containing PEO chains were synthesized by a crosslinking reaction. Effects of various factors, such as crosslinking density and size of network on ionic conductivity of this system, were explored in detail. Although the resultant network polymer electrolytes were completely amorphous, as indicated by X-ray diffraction measurement, their ambient ionic conductivities were still rather low—only in the range of  $10^{-5}$   $Scm^{-1}$  or lower.

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Therefore, the focus of our investigation has been turned to the gel polymer electrolytes (GPE). As is well known, gel polymer electrolytes, which are generally composed of polar polymer, alkali metal salts, and plasticizers, are a new generation of solid polymer electrolytes, and because of their high performance in the practical application to high-energy density lithium batteries, their preparation, electrical, and mechanical properties have been reported on in the last few years.<sup>7-9</sup> However, so far, little has been reported about the physical stability of this kind of electrolyte. This article will present the results on the physical stability as well as ionic conductivity of these gel polymer electrolytes.

## EXPERIMENTAL

### Materials

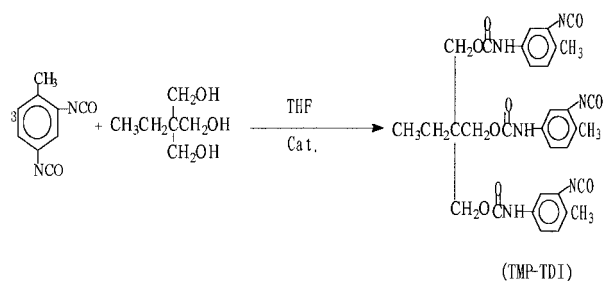
Poly(ethylene oxide) (PEO) with molecular weights of 600, 800, 1000, 1500, or 2000, lithium perchlorate ( $\text{LiClO}_4$ ), and plasticizers including ethylene carbonate (EC), propylene carbonate (PC), dimethyl formide (DMF),  $\gamma$ -butyrolactone ( $\gamma$ -BL), diethylene carbonate (DEC), and dimethyl ethyleneglycol (DME) were all purchased from Aldrich Chemical Company. PEO and  $\text{LiClO}_4$  were desiccated under vacuum at 120 and 170°C, respectively for 24 h prior to use. The plasticizers were distilled under vacuum and then stored with 4 Å molecular sieves. 1,1,1-Tri(hydroxy methyl) propane (TMP) was recrystallized using methanol, and toluene 2,4-diisocyanate (TDI) was used as received.

### Synthesis of the Crosslinking Agent of Gel Network Polymer Electrolytes

The detailed synthesis procedure of the crosslinking agent (TMP-TDI) was reported in our previous work.<sup>6</sup> Its reaction equation is shown in Figure 1.

### Preparation of Gel Network Polymer Electrolytes

PEO, TMP-TDI, and catalyst dibutyltin dilaurate (DBTDL),  $\text{LiClO}_4$  were mixed together with a plasticizer and anhydrous tetrahydrofuran (THF) (not used sometimes). Stirring vigorously, the mixture was heated to 80°C under nitrogen atmosphere and kept at this temperature for 1 h to form a viscous liquid, which was then cast in a



**Figure 1** Synthesis of the crosslinking agent (TMP-TDI).

self-made polytetrafluoroethylene mold. After heating in the vacuum oven at 70°C for 48 h for curing, the final products were semitransparent films with good elasticity.

### Measurement

The ionic conductivity was measured using an HIOKI LCR 3520 Hi TESTER at 1 kHz. The experimental procedure was the following: a disk of known area was cut from the parent electrolytes film. The disk was placed in the center of a Teflon spacer ring and compressed between two stainless rods inserted into opposite ends of the Teflon spacer ring. The thickness of the samples was taken to be the Teflon spacer thickness for relatively thin and compressible samples, while the electrolyte thickness was measured with calipers for thicker and more rigid samples.

To estimate the gel fraction of the synthesized network polymers, weighed amounts of network polymers were extracted using tetrahydrofuran (THF) as the extracting solvent for 24 h on Soxhlet's extractors. After extraction, the gelled polymer was placed in a vacuum oven at 100°C for 24 h to get rid of the solvent, and the weight of the polymer was measured again. The gel fraction was calculated according to the following equation:

$$\text{Gel\%} = 100B/A$$

where  $A$  and  $B$  are weights of the network polymers before and after the extraction, respectively.

To study the physical stability of gel polymer electrolytes, a simple experiment was carried out on various systems. The samples were subjected to a fixed downward pressure (the weight of the downward object was fixed at 10 kg, and the areas of various samples were fixed at 4 cm<sup>2</sup>). For var-

**Table I** Gel Fraction of the Network Polymers Containing Various PEO Segments

Samples	PEO Molecular Weight ( $M_w$ )	Gel Fraction <sup>a</sup> (%)
NT-PEO <sub>600</sub>	600	98.3
NT-PEO <sub>1000</sub>	1000	97.5
NT-PEO <sub>1500</sub>	1500	95.6
NT-PEO <sub>2000</sub>	2000	94.0

<sup>a</sup> Tetrahydrofuran (THF) as the extracting solvent for 24 h on Soxhlet's extractor.

ious time intervals, the weight of each GPE sample were measured. The percent of weight loss is calculated according to the following equation:

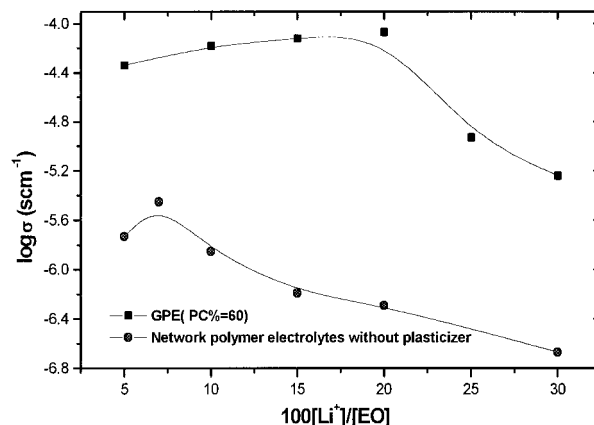
$$\text{Weight loss \%} = 100B/A$$

where  $A$  is the sample weight before exerted pressure,  $B$  is the sample weight after exerted pressure for different time intervals.

## RESULTS AND DISCUSSION

Table I lists the gel fraction of the network polymers containing various PEO segments. It can be seen from Table I that, with increasing of molecular weight of the PEO segment, the gel fraction is decreased proportionally from 98.3 to 94.0%. The results are relevant to the reactivity of poly(ethylene glycol) in the crosslinking reaction. The terminal hydroxy ( $\mu\text{OH}$ ) on the longer PEO<sub>2000</sub> segment is less active in the crosslinking reaction compared to that on the shorter PEO<sub>600</sub> segment. The 97.5% gel fraction of the network polymer containing the PEO<sub>1000</sub> segment is high enough to prepare gel network polymer electrolytes.

All gel polymer electrolytes showed a great enhancement of ambient conductivity compared to the electrolytes without plasticizers. Figure 2 offers a clear example of the above-mentioned difference. The ionic conductivity of GPE is nearly 2–3 orders of magnitude higher than that of the conventional electrolytes, as indicated in Figure 2, and the maximum conductivity of GPE appeared at  $[\text{Li}^+]/[\text{EO}]$  equal to 20%, which is much higher compared to the 10% of the conventional electrolytes. This phenomena is ascribed to the permittivity increasing of the whole GPE system, because the introduced PC plasticizer has a high

**Figure 2** Ambient ionic conductivity of GPE and the unplasticized network polymer electrolytes containing the PEO<sub>1000</sub> segment.

relative permittivity ( $\epsilon = 64.4$  at  $25^\circ\text{C}$ ), which will contribute to the enhancement of the dissociation of ion pairs or ion clusters. At the same time, the apparent softer GPE films, relating to the plasticizing effect of PC, exhibit a much lower glass transition temperature ( $T_g = -60.2^\circ\text{C}$ ) than that of the unplasticized one ( $T_g = 23.7^\circ\text{C}$ ).

The effect of plasticizers on the polymer mobility and conductivity depends on the specific nature of the plasticizers, including viscosity, dielectric constants, polymer–plasticizer interaction, and ion–plasticizer coordination. Table II lists the ambient conductivity data of the GPE with various plasticizers.

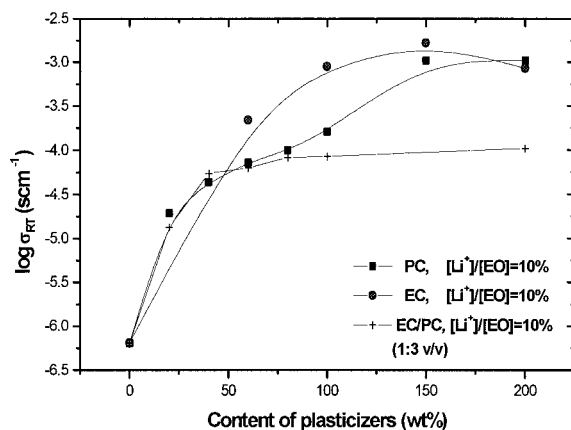
Ionic conductivity of GPE films containing PC, EC, and EC/PC mixed plasticizers, as a function

**Table II** Effect of Plasticizer on Ionic Conductivity of Gel Polymer Electrolytes<sup>a</sup>

Plasticizer <sup>b</sup>	$[\text{Li}^+]/[\text{EO}]$ (%)	Ambient Conductivity ( $\sigma$ , $\text{Scm}^{-1}$ )
no	10	$6.38 \times 10^{-7}$
DME	10	$9.70 \times 10^{-7}$
DEC	10	$1.14 \times 10^{-6}$
EC	10	$3.75 \times 10^{-5}$
EC/PC (1 : 3 v/v)	10	$5.48 \times 10^{-5}$
PC	10	$6.68 \times 10^{-5}$
EC/PC (3 : 1 v/v)	10	$4.25 \times 10^{-4}$
DMF	10	$3.71 \times 10^{-5}$
$\gamma$ -BL	10	$1.06 \times 10^{-4}$

<sup>a</sup> GPE containing the PEO<sub>1000</sub> segment;

<sup>b</sup> Weight of all kinds of plasticizers was fixed at 60%.

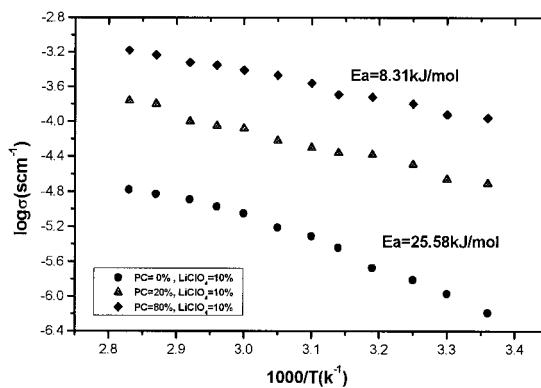


**Figure 3** Effect of the content of the plasticizers on room temperature conductivity for the GPE containing the PEO<sub>1000</sub> segment.

of the amount, is shown in Figure 3 for the series of the GPE system in which the PEO molecular weight is 1000. A maximum conductivity equal to  $1.1 \times 10^{-3} \text{ Scm}^{-1}$  at room temperature is observed in the GPE containing 200%(weight) PC plasticizer. No significant increase in the conductivity values are found when the amount of PC or EC/PC(1 : 3 v/v) plasticizer is increased from 20 to 100%; however, the conductivity for EC plasticized GPE showed substantial variation. For EC plasticized GPE, ionic conductivity was increased when EC increased from 50 to 150%. Above 150%, the conductivity dropped slightly, probably due to the tendency of EC to crystallize at room temperature. Although the dissolved EC was combined with the network skeleton intimately, and acted as an ionic conducting channel, at high enough levels, EC will crystallize, reducing ion migration.

The conductivity results for GPE with mixed plasticizers are also shown in Figure 3. The mixture of plasticizers was chosen with the ratio EC/PC = 1 : 3, where the EC/PC ratio refers to the volume ratio of the plasticizers EC and PC. With a 1 : 3 mixture of plasticizers EC and PC, the GPE shows conductivity values lower than those for samples with pure PC or pure EC at all temperatures studied.<sup>7</sup>

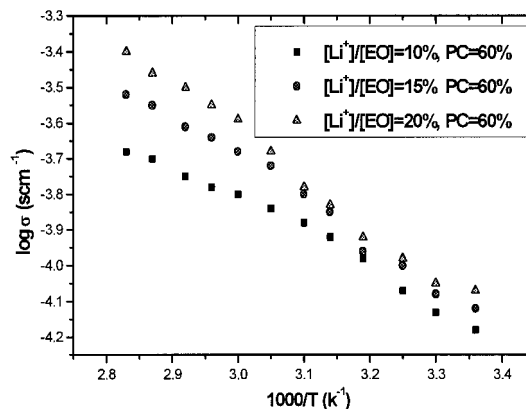
Arrhenius plots for GPE and unplasticized network polymer electrolytes are depicted in Figure 4 for different plasticizer levels, and in Figure 5 for different salt levels. As shown in Figure 4, the Arrhenius plots of all the plasticized electrolytes are almost linear, which is different from the curved line of the unplasticized network polymer



**Figure 4** Arrhenius plots for the GPEs with the PC plasticizer.

electrolytes. The calculated activation energy for the investigated PC plasticized GPE is 8.31 kJ/mol, which is much lower than that of the unplasticized network polymer electrolytes (25.58 kJ/mol, calculated from the VTF equation). Ion migration in the network polymer electrolytes follows the VTF equation, and is probably due to the segmental movement of the polymer. In the GPEs, the network polymer matrix offers little contribution to ion conduction, and the plasticizers act as the main channel for ion migration.

A different effect of temperature on ionic conductivity is shown in Figure 5. In the low temperature range, the ionic conductivities of the three GPEs with different LiClO<sub>4</sub> concentrations exhibit no significant difference, but at higher temperatures, the difference is extremely large. One interpretation is that the dissociation of LiClO<sub>4</sub> becomes easier with increasing temperature.

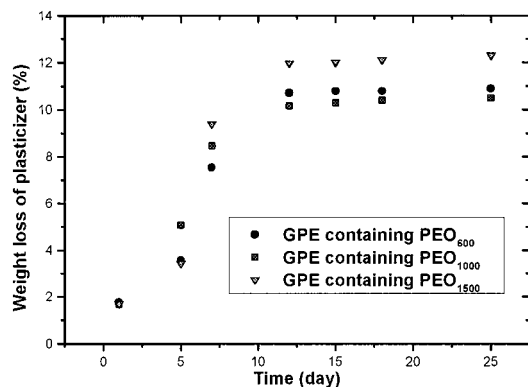


**Figure 5** Effect of temperature on the GPE containing the PEO<sub>1000</sub> segment.

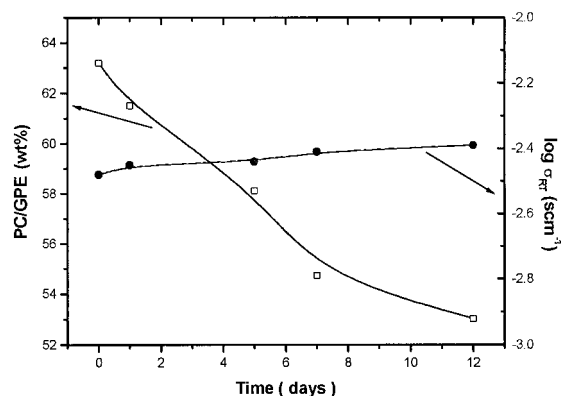
Successful gel polymer electrolytes call for both dimensional stability and ambient high ionic conductivity. The leakage of plasticizers from the polymer matrix will result in an unstable electrolytes/electrode interface caused by the reaction with the active electrode. A simple experiment was carried out to investigate this aspect on our synthesized GPEs. The subject GPE had the same plasticizer PC, where the amount was fixed at 200% of the network polymer host. The results are depicted in Figure 6.

The weight loss directly relates to the interaction between the network polymer and the plasticizers. This interaction alters with the plasticizer nature and the network structure. When the plasticizer and its amount are fixed, the interaction will be influenced only by the network structure. After a fixed pressure for 1 day, the weight loss percent of GPEs with different structures was identical, about 2% (weight). Five days later, the GPE containing the PEO<sub>1500</sub> segments had a relatively higher weight loss compared to that of the GPEs containing the PEO<sub>1000</sub> and PEO<sub>600</sub> segments. After 12 days or longer, the weight loss of any GPEs was not altered, and kept the same order: GPE(PEO<sub>1500</sub>) > GPE (PEO<sub>600</sub>) > GPE(PEO<sub>1000</sub>).

It is clear that the GPE containing PEO<sub>1000</sub> is the best candidate electrolyte due to its good dimensional stability. Too large or too small a network size is detrimental to the dimensional stability of GPE. So we made a further investigation on the ambient conductivity of GPE containing the PEO<sub>1000</sub> segment. Figure 7 is the relationship between the plasticizer weight loss and the ambient ionic conductivity. It can be observed from



**Figure 6** Weight loss of different GPEs with the same plasticizer content (200%) as a function of time.



**Figure 7** Relationship between weight loss and ambient conductivity for GPEs containing the PEO<sub>1000</sub> segment.

Figure 7 that although the PC content is decreased from 63.7 to 53.7% after 12 days, the GPE has no significant deterioration in ambient ionic conductivity, which is consistent with the results obtained from Figure 3.

## CONCLUSIONS

The gel network polymer electrolytes exhibit ambient conductivities of nearly three orders of magnitude higher than those of unplasticized electrolytes. The effect of LiClO<sub>4</sub> concentration on ionic conductivity is slightly different from the conventional one, except for the appearance of a maximum ionic conductivity. Different plasticizers will affect ionic conductivity due to different variability in characteristics such as permittivity and viscosity. The GPEs investigated in our study followed the Arrhenius plots, not the VTF type, which indicated that ionic migration in the GPE mainly takes place in channels existing in the plasticizers. GPEs with different network structure have different physical stability, among which the GPE containing the PEO<sub>1000</sub> segment gave the best stability after a long time pressure, mainly due to the stronger interaction between the plasticizer and the networks. In the GPE containing the PEO<sub>1000</sub> segment, the ambient conductivity showed no significant alteration when the plasticizers escaped from the networks under pressure.

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