

# A study of cross-linked PEO gel polymer electrolytes using bisphenol A ethoxylate diacrylate: ionic conductivity and mechanical properties

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## Abstract

Ionic conductivity, mechanical stability and electrochemical property were examined on the poly ethyleneoxide (PEO) based cross-linked gel polymer electrolyte. Bisphenol A ethoxylate diacrylates (BPAEDA) with different numbers of ethylene oxide units ( $n = 4, 15$ ) were used as cross-linkers. The curing kinetics of the cross-linker was examined by an FT-IR study with two types of initiators and at different curing temperatures. Higher conductivity was observed for the longer ethylene oxide unit. Conductivity of the polymer electrolyte prepared from BPAEDA ( $n = 15$ ) and liquid electrolyte (70 wt.%) was  $3.47 \times 10^{-3}$  S/cm at 30 °C. Improved tensile strength and elongation at break were realized from the polymer electrolyte using BPAEDA as a cross-linker. Electrolyte having higher cross-linking density showed higher tensile strength, but showed decreased flexibility. The stability of the polymer electrolyte against electrochemical oxidation could be extended to larger than 4.5 V (versus Li/Li<sup>+</sup>). Lithium cycling efficiency of the polymer electrolyte was about 80%.

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**Keywords:** Polymer electrolytes; Lithium battery; Bisphenol A ethoxylate diacrylate

## 1. Introduction

Many researches have been carried out for lithium-polymer batteries using gel polymer electrolyte which contains polar organic solvents such as propylene carbonate (PC) and ethylene carbonate (EC). The issue of the gel polymer electrolytes is providing as high conductivity as the liquid electrolyte with improved safety. Thermoplastics such as poly(vinylidene fluoride) (PVdF) [1,2], poly(vinylidene fluoride-co-hexafluoropropylene) (PVdF-HFP) [3,4] poly(acrylonitrile) (PAN) [5,6] and poly(methyl methacrylate) (PMMA) [7] were examples of the widely used polymer matrices for gel electrolytes. However, dimensional stability and mechanical properties of these polymer electrolytes became poor with increasing content of liquid electrolyte, especially at the elevated temperature. Another drawback of these polymer electrolytes was that the interaction between polymer matrices and polar solvents was not strong enough to form stable gel electrolytes. Thus, the conductivity decreased with time due to the loss of organic solvent or phase separation.

The cross-linked poly ethyleneoxide (PEO) polymer network was used to form a stable gel electrolyte without losing the organic solvent as well as improved mechanical

stability [8–10]. It was reported that the cross-linked PEO polymer network could entrap organic solvent as high as 80 wt.%, and the conductivity showed satisfactory values, on the order of  $10^{-3}$  S/cm, for the lithium-polymer battery application. However, the mechanical stability was not good enough to withstand the battery manufacturing process. Thus, inorganic fillers and porous membranes were co-employed to enhance the mechanical stability [11,12].

Previously, we reported pure solid polymer electrolytes using bisphenol A ethoxylate diacrylate (BPAEDA) as a cross-linker [13]. By using BPAEDA, improvements of mechanical properties for the intrinsic solid polymer electrolyte have been observed. The relatively good mechanical stability could be attributed by the introduction of the aromatic ring between the ethoxylate acrylates.

In this study, we prepared cross-linked gel polymer electrolyte using bisphenol A ethoxylate diacrylate ( $n = 4, 15$ ) (BPAEDA). The characteristics of ionic conductivity, mechanical properties and electrochemical properties of cross-linked PEO gel electrolytes were studied.

## 2. Experimental

The chemical structure of BPAEDA used for the cross-linker is shown in Fig. 1. The BPAEDA ( $n = 4$ ) was

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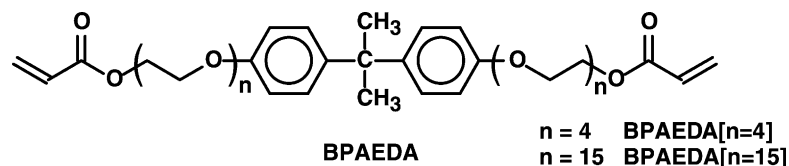


Fig. 1. Chemical structure of the cross-linker, bisphenol A ethoxylate diacrylate (BPAEDA).

purchased from Aldrich and purified by using a silica-gel column to remove low molecular weight impurities. The BPAEDA ( $n = 15$ ) was synthesized by the reaction of the bisphenol A ethoxylate ( $n = 15$ , Aldrich) and acryloyl chloride (Aldrich) in the presence of tributylamine according to the previously reported method [13]. The cross-linkers were purified by using silica-gel column chromatography and dried in vacuum at 40 °C for 24 h before use to remove the residual water.

Propylene carbonate (PC, Merck), ethylene carbonate (EC, Merck) and 1 M LiPF<sub>6</sub> in PC + EC (1:1 (v/v), Merck) were used as received. Battery grade LiAsF<sub>6</sub> and LiPF<sub>6</sub>, were purchased from Merck, and dried in vacuum at 80 °C for 24 h.

Gel polymer electrolytes were prepared by radical initiated cross-linking reaction of a homogeneous solution composed of BPAEDA, liquid electrolyte (EC:PC = 1:1 (v/v)), Li salt and radical initiator. 2, 2'-Azobis(isobutyronitrile) (AIBN, Junsei chemical) or benzoyl peroxide (BPO, Aldrich) was used as a radical initiator. The amount of radical initiator was 1 wt.% of the used cross-linker. The homogeneous solution mixture was filled into a small gap between the desired substrates such as glass, lithium and nickel. The gap of substrate was maintained by using 100 μm polyimide tape. The cell was sealed with metallized polyethylene bag in a glove box under argon atmosphere and was cured in a convection oven at the desired temperature (80–100 °C) for 15 min. The samples for FT-IR studies were prepared by sandwiching the homogeneous electrolyte mixture between two silicone (1 1 1) wafers, which were transparent to IR.

The  $T_g$  of the cured polymer electrolytes was determined by using a differential scanning calorimeter (TA Instruments, model Universal V2.5H). The measurements were performed with hermitically sealed aluminum pan over the temperature range of –120 to 0 °C under nitrogen atmosphere. The temperature scan rate was 10 °C/min.

Tensile properties of cross-linked polymer gel electrolytes were measured according to the ASTM-638 using universal tensile meter (Instron 4482). The crosshead speed was 10 mm/min with the 1 kg force load.

The ionic conductivity of the electrolytes was measured with a complex impedance analyzer (Zahner Elektrik, model IM6) coupled to an IBM-PC compatible computer over a frequency range from 1 Hz to 1 MHz. An ac perturbation of 10 mV was applied to the cell. The conductivity value was calculated from the bulk resistance in the complex impedance diagram. During the test, the temperature was

controlled by means of a programmable hot plate (Mettler, model FP82HT).

The electrochemical stability window of the gel polymer electrolyte was determined by cyclic voltammetry at a scanning rate of 10 mV/s using an EG&G model 273 potentiostat/galvanostat. A nickel plate was used as a working electrode and a lithium metal foil (FMC) as a counter and reference electrode. The lithium plating/stripping cycling efficiency was studied by means of chronopotentiometry using TOSCAT-2000 battery tester (Toyo, Japan). The plating/stripping current density of 0.1 mA/cm<sup>2</sup> and total plating electricity of 0.1 C/cm<sup>2</sup> were used. The stripping of lithium proceeded until the voltage reached the cut-off potential of 1.0 V (versus Li/Li<sup>+</sup>). The lithium cycling efficiency at each cycle was calculated according to Eq. (1).

$$\text{Efficiency (\%)} = \frac{Q_s}{Q_p} \times 100 \quad (1)$$

where  $Q_p$  and  $Q_s$  correspond to the electrical charge for plating and stripping, respectively.

### 3. Results and discussion

#### 3.1. Preparation of electrolytes

Usually, gel polymer electrolytes were prepared by soaking the polymer matrices in the liquid electrolyte. This process was time consuming and the content of liquid electrolyte in the gel polymer electrolyte may not be easily controlled. Thus, the process is not suitable for mass production of battery process. The gel polymer electrolyte in this study was prepared by in situ thermal curing with a homogeneous solution of cross-linker and liquid electrolyte, which was more favorable for battery manufacturing process.

Before engaging a series of experiment, two different initiators were tested for the cross-linking behavior. The cross-linking reaction was estimated by FT-IR. Fig. 2(a) shows the FT-IR spectra of the gel polymer electrolyte at different curing times. The peaks corresponding to the C=C vibration (1636 and 1408 cm<sup>-1</sup>) decreased gradually with the curing time. After 30 min of curing, the peaks at 1636 and 1408 cm<sup>-1</sup> were almost completely disappeared. The conversion of cross-linking reaction of electrolytes was estimated by comparing the relative peak area of C=C vibration at 1636 cm<sup>-1</sup> with that of C=O vibration. The peak corresponding to the C=O vibration appeared at

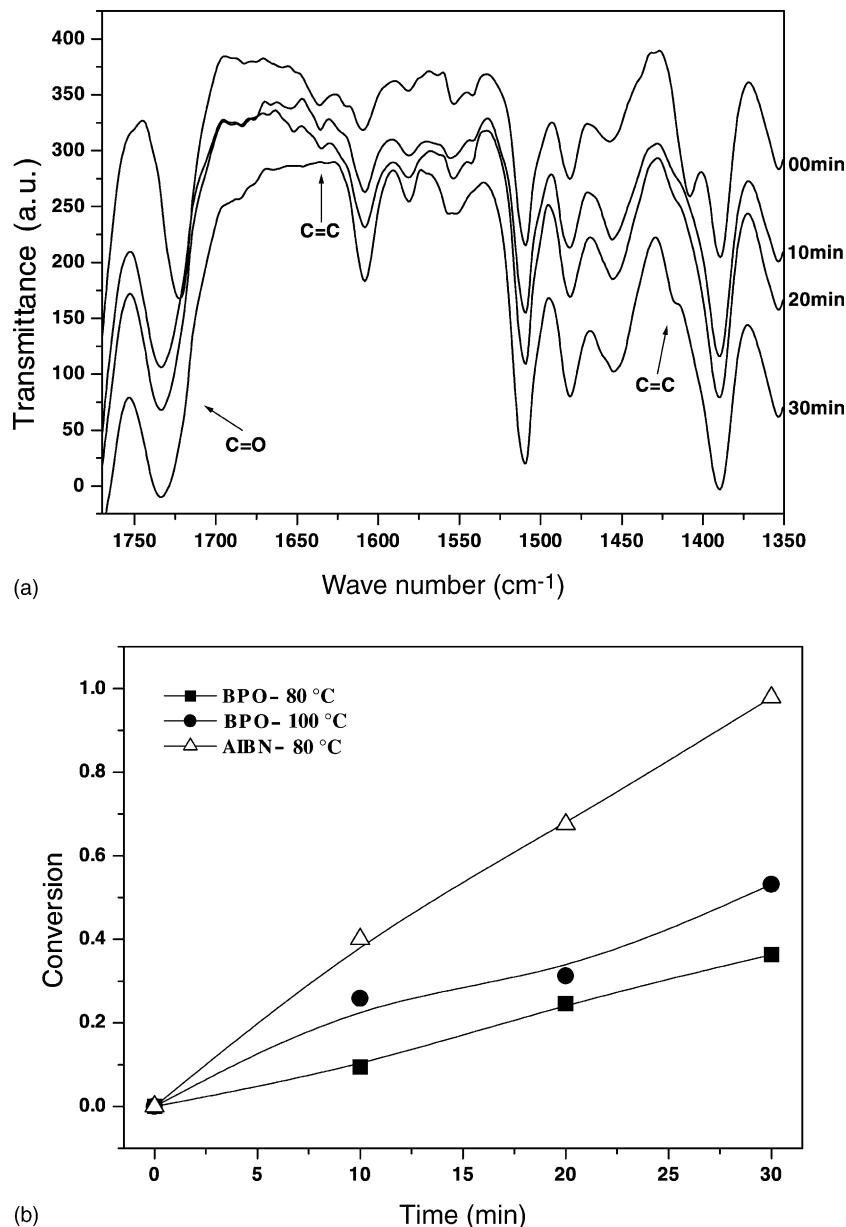


Fig. 2. (a) FT-IR spectra of electrolytes composed of BPAEDA ( $n = 4$ ) and 50 wt.% of 1 M LiPF<sub>6</sub> in EC + PC at the different curing time and (b) the degree of conversion for the different initiators and temperatures as a function of curing time.

1722 cm<sup>-1</sup> before curing, and it shifted to 1733 cm<sup>-1</sup> after curing. This peak shift was related to the change of conjugated C=O to unconjugated C=O by curing. Assuming that the difference of the extinction coefficients of the two C=O vibrations is negligible, the peak area of C=O vibration around 1722–1733 cm<sup>-1</sup> was used as an internal standard.

In Fig. 2(b) the degree of the conversion during cross-linking reaction is plotted along with curing time for different initiators and curing temperatures. When BPO was used as a radical initiator, the degree of conversion after 30 min was calculated to be 0.36 at 80 °C and 0.56 at 100 °C. When AIBN was used instead, a faster cross-linking reaction was observed, and the degree of conversion after 30 min was

calculated to be 0.98 at 80 °C. The faster curing reaction for the AIBN compared to that of BPO is due to the lower decomposition temperature of AIBN than that of BPO. When AIBN was used as an initiator almost complete conversion for curing was found at 100 °C after 15 min. Thus, the rest of curing was conducted at 100 °C for 15 min using AIBN as an initiator.

### 3.2. Ionic conductivity

In Fig. 3, the temperature dependence of conductivity ( $\sigma$ ) is shown for the polymer electrolyte prepared from BPAEDA ( $n = 4$ ) (GPE4) and BPAEDA ( $n = 15$ ) (GPE15) containing different amount of liquid electrolyte. The curves

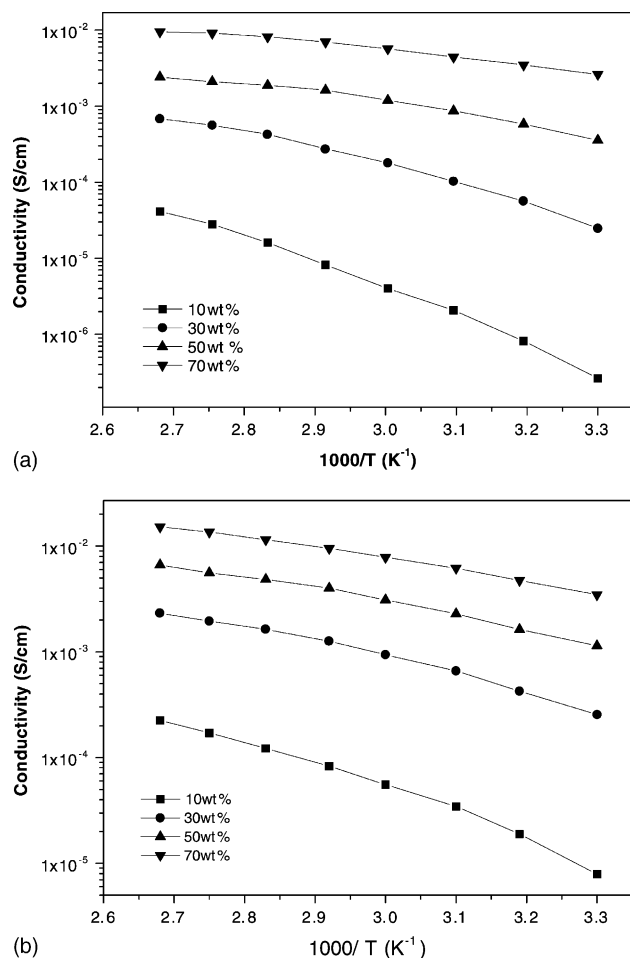


Fig. 3. Temperature dependence of conductivity of polymer electrolytes at various contents of liquid electrolyte (1 M LiPF<sub>6</sub> in EC + PC) for (a) GPE4 and (b) GPE15.

show a typical Vogel–Tamman–Fulcher (VTF) relationship (Eq. (2)) in the temperature range of 30–120 °C, i.e.

$$\sigma = AT^{1/2} \exp\left(\frac{-E_a}{R(T - T_0)}\right) \quad (2)$$

where  $A$ ,  $E_a$  and  $T_0$  are fitted parameters which are related to the charge carrier density, pseudo activation energy and the temperature at which the segmental mobility of polymer backbone ceases, respectively. The VTF expression implies that the main mechanism of ion conduction can be related to the free volume theory [14]. The fitted parameters,  $A$ ,  $E_a$  and

$T_0$ , at the different contents of liquid electrolyte are listed in Table 1. The fitted parameters were comparable to those of other gel polymer electrolytes such as PVdF-HFP [3] and cross-linked PEO [15]. When the content of the liquid electrolyte increased,  $E_a$  and  $T_0$  decreased, but the  $A$  parameter remained almost constant. Increasing the contents of liquid electrolyte resulted in the increase of the effective ion conduction pathway in the polymer, thus the  $E_a$  and  $T_0$  decreased.

The changes of conductivity at 30 °C and glass transition temperature ( $T_g$ ) as a function of liquid electrolyte (1 M LiPF<sub>6</sub> in EC + PC) content are shown in Fig. 4. The ionic conductivity increased, but  $T_g$  decreased with increasing the EC + PC contents. The conductivities of electrolyte at 30 °C containing 70 wt.% of PC + EC were  $3.47 \times 10^{-3}$  S/cm for GPE15 and  $2.47 \times 10^{-3}$  S/cm for GPE4. The GPE15 showed higher ionic conductivity compared to that of the GPE4. However,  $T_g$ 's of the GPE4 were lower than that of the GPE15 except for 70 wt.% liquid electrolyte content.

### 3.3. Mechanical properties

In Fig. 5, tensile strength and maximum elongation at break of polymer electrolytes as a function of the liquid electrolyte content are shown. The tensile strength decreased as increasing the liquid electrolyte content in the polymer electrolytes. Tensile strength of the resulting polymer electrolytes containing 70 wt.% liquid electrolyte was 0.5 MPa for GPE4 and 0.3 MPa for GPE15. The elongation at break of the films of  $n = 15$  increased as increasing the content of liquid electrolyte due to the plasticizing effect on the polymer chain. But for the GPE4 film, plasticizing effect of the liquid electrolyte seemed to have little effect on the elongation because of the high cross-linking density. Maximum elongation at break was measured to be in the range of 30–80% for the GPE15 and 46–25% for the GPE4. Mechanical stability of the UV cross-linked poly(ethyleneglycol dimethacrylate) (PEGDA) polymer electrolytes, which have only a aliphatic polymer backbone, was reported to be very poor, and their tensile elongation has been reported to be near zero [16]. The tensile property can be improved by blending PEGDA with PVdF. Maximum elongation was increased to 60% by a PEGDA/PVdF (1:1) blend film [16]. However, when BPAEDA was used as a cross-linker, the tensile elongation property was almost same as that of the PEGDA/PVdF (1:1) blend film. This improved tensile

Table 1  
The VTF fitting parameters for different contents of liquid electrolyte

EC + PC content (wt.%)	GPE4			GPE15		
	$A$ (S cm <sup>-1</sup> K <sup>1/2</sup> )	$E_a$ (kJ mol <sup>-1</sup> )	$T_0$ (K)	$A$ (S cm <sup>-1</sup> K <sup>1/2</sup> )	$E_a$ (kJ mol <sup>-1</sup> )	$T_0$ (K)
10	0.22	13.3	185	0.18	12.2	151
30	0.40	10.31	173	0.35	9.69	137
50	0.32	9.57	130	0.59	9.29	121
70	0.38	6.98	126	0.51	6.83	136

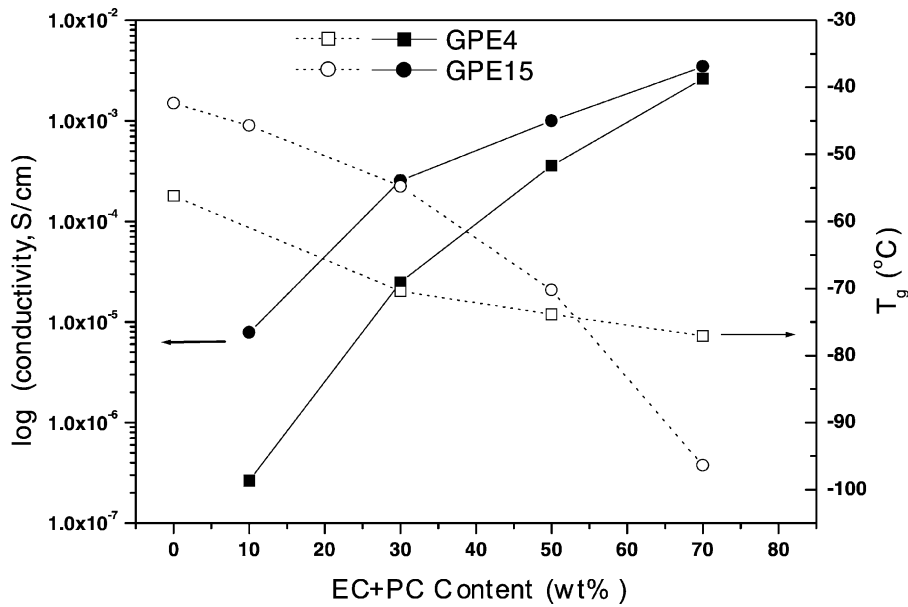
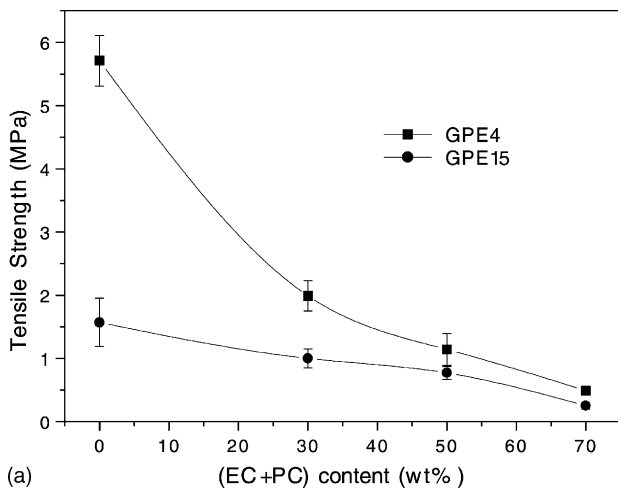
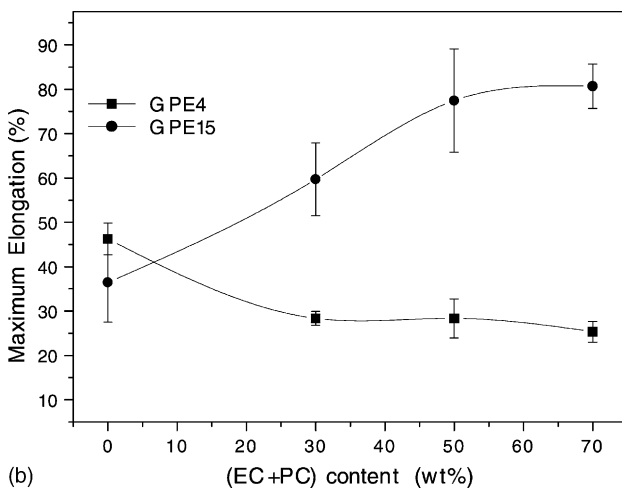


Fig. 4. Ionic conductivity at 30 °C (closed symbol) and glass transition temperature (open symbol) as a function of liquid electrolyte content: (□, ■) GPE4; and (○, ●) GPE15.



(a)



(b)

Fig. 5. (a) Tensile strength and (b) maximum elongation as a function liquid electrolyte contents: (■) GPE4; and (●) GPE15.

elongation of the resulting polymer electrolytes may be due to the rigid aromatic rings in the cross-linker.

For the cross-linked polymer, the degree of cross-linking density strongly affected the mechanical properties such as tensile strength and maximum elongation. In general, the polymer with the high degree of cross-linking density has high mechanical strength but, low extensibility. The degree of cross-linking density of the GPE4 expected to be high compared to that of the GPE15. Thus, the GPE4 have higher tensile strength, but lower maximum elongation at break than the GPE15.

### 3.4. Electrochemical properties

Electrochemical stability of the electrolyte was studied by means of cyclic voltammogram at room temperature with potential sweep rate of 10 mV/s. Fig. 6 shows the cyclic

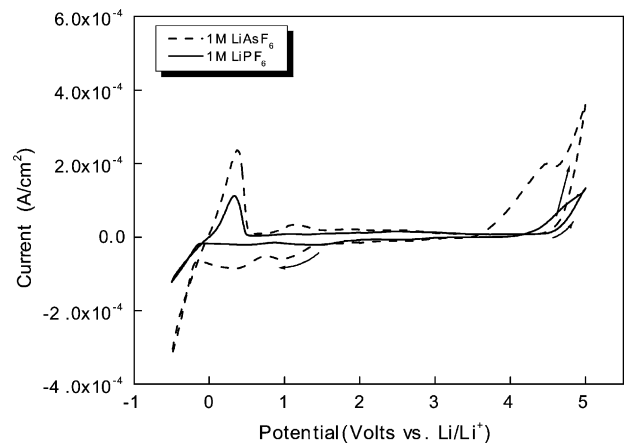


Fig. 6. Cyclic voltammograms of GPE4 containing 70 wt.% EC + PC. Working electrode = nickel and sweep rate = 10 mV/s.

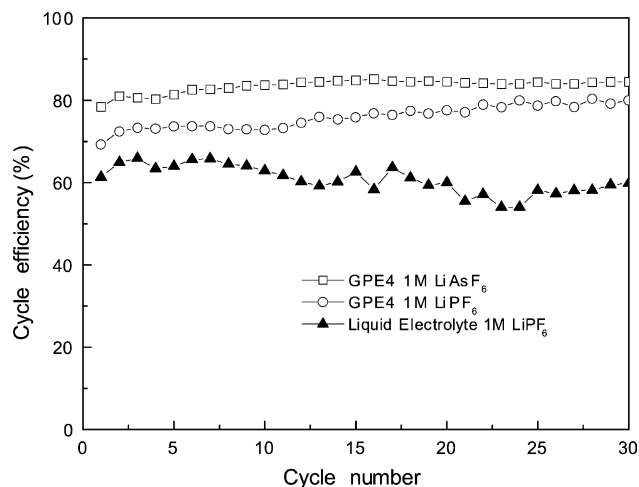


Fig. 7. Cycling efficiencies of Li on the nickel electrode with repeated cycles for the GPE4 containing 70 wt.% EC + PC (open symbol) and in liquid electrolyte (1 M LiPF<sub>6</sub> in EC + PC, closed symbol). Current density = 0.1 mA/cm<sup>2</sup>.

voltammograms of the GPE4 containing 70 wt.% of liquid electrolyte with different lithium salts, LiPF<sub>6</sub> and LiAsF<sub>6</sub>. On cathodic sweeping, the plating of Li on the nickel electrode took place at  $-0.1$  V (versus Li/Li<sup>+</sup>). On the reverse scan, Li stripping took place at a peak potential of 0.32 V (versus Li/Li<sup>+</sup>). The oxidative degradation of gel polymer electrolyte started to occur around 4.5 V (versus Li<sup>+</sup>/Li), thus the electrochemical stability window of the prepared polymer electrolytes was acceptable for lithium battery applications.

Lithium plating/stripping cycling efficiency on the Ni electrode for the polymer electrolytes was investigated and compared to that of the liquid electrolytes. Fig. 7 shows cycling efficiencies of Li on the Ni substrate with repeated cycles for different electrolytes. Liquid electrolyte performance (1 M LiPF<sub>6</sub> in EC + PC) was also given for comparison with the gel polymer electrolyte. The lithium cycling efficiency for gel polymer electrolytes showed a remarkable improvement. About 80% of cycling efficiency was sustained after more than 30th cycle of the polymer electrolytes, whereas about 60% of cycling efficiency was observed for the liquid electrolyte. Lithium cycling efficiency after the third cycle changed very little with cycle number. The lithium cycling efficiency was about the same value of the reported PVdF based gel polymer electrolyte [17]. The improved efficiency may be due to the mechanical suppression of the polymer electrolyte on the lithium/electrolyte interface as the previous report in the inhibition of lithium dendrite formation by the polymer electrolyte [18,19].

#### 4. Summary

In this paper, cross-linked gel polymer electrolytes were prepared using BPAEDA as a cross-linker, and the conductivity, mechanical property and electrochemical stability of the resulting polymer electrolyte were studied.

The conductivity increased as the content of the liquid electrolyte increased and as the repeating ethylene oxide unit in the cross-linker became longer. The maximum conductivity for the GPE15 containing 70 wt.% liquid electrolyte (1 M LiPF<sub>6</sub> in EC + PC) was  $3.47 \times 10^{-3}$  S/cm at 30 °C, which was comparable to the reported conductivity of other gel polymer electrolytes.

The tensile strength and maximum elongation of the resulting polymer electrolytes were in the range of 0.3–5.7 MPa and 25–80%, respectively. Aromatic ring and acrylate group that are introduced to the cross-linker impart improved mechanical strength, while sustaining high ion conductivity. The oxidation stability of the polymer electrolyte could be extended to larger than 4.5 V (versus Li/Li<sup>+</sup>). Lithium cycling efficiency of the polymer electrolyte was about 80%.

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