Preparation of UV Curable Gel Polymer Electrolytes and Their Electrochemical Properties

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We have investigated the effect of the number of ethylene oxide (EO) units inside poly(ethylene glycol) dimethacrylate (PEGDMA) on the ionic conductivity of its gelled polymer electrolyte, whose content ranges from 50 to 80 wt%. PEGDMA gelled polymer electrolytes, a crosslinked structure, were prepared using simple photo-induced radical polymerization by ultraviolet light. The effect of the number of EO on the ionic conductivity was clearly shown in samples of lower liquid electrolyte content. We have concluded that the ionic conductivity increased in proportion to both the number of EO units and the plasticizer content. We have also studied the electrochemical properties of 13PEGDMA (number of EO units is 13) gelled polymer electrolyte.

Keywords : Polyethylene glycol dimethacrylate, Ionic conductivity, Chain length of ethylene oxide.

Introduction

Lithium polymer batteries using solid polymer electrolytes (SPEs) generally have high energy densities, high voltage and are light weight, making them outstanding candidates for portable applications, such as cellular phones and notebook computers. Because of these features, they are in increasing demand. The energy characteristics of lithium secondary batteries might make them quite attractive as an electric vehicle for erasing environmental pollution. They could also resolve the defects of lithium ion batteries using liquid electrolyte, such as instability and the difficulty encountered when manufacturing large flat type batteries made of this material.

Poly(ethylene oxide) (PEO) has been the typical material for polymer electrolyte since the 1970s, and a lot of studies have been done on PEO, including basic characterization and application research. PEO as a polymer solvent can strongly coordinate cations to form electrolytes such as low molecular weight solvents, *e.g.* tetrahydrofuran, and the $-(CH_2CH_2O)_n-$ provides just the right spacing for maximum solvation. PEO has been studied as a polymer solvent to dissociate lithium salt because of its polarity and flexibility, which allows conformational changes that increase the interactions of PEO units with partially dissociated salt, decrease the energy of coordination and increase its stability.[1,2] Much research has focused on the phenomena of the dissociation of lithium salts in PEO,[3,4] and the diffusion or migration of lithium ion.[5,6] Many studies have been conducted on the improvement of ionic conductivity of polymer electrolytes based on PEO, *i.e.* 1) minimization of the crystallinity of PEO to make a fully amorphous polymer,[7-10] 2) investigation of the effect of the mixing of nano-sized inorganic filler on the ionic conductivity of PEO composite,[11-13] 3) addition of liquid plasticizer to prepare PEO gel electrolyte,[14,15] to name a few.

One key material based on PEO for polymer electrolyte is polyethylene glycol dimethacrylate (PEGDMA), which has been widely used as a polymer solvent as well as a crosslinking agent. Several papers have been published on polymer electrolytes having PEGDMA as a crosslinking agent. PEGDMA was more frequently used in gelled polymer electrolyte than solid polymer electrolyte because its use gives several important properties to polymer electrolytes, such as chemical resistance, electrochemical stability, thermal stability and dimensional stability.[16-23]

Although PEGDMA is widely used in gelled polymer electrolytes, only recently has is found use as a crosslinking agent incorporating other monomers to fabricate a crosslinked gelled polymer electrolyte without focusing on the detailed study regarding the effect of the number of ethylene oxide in PEGDMA and the content of plasticizer on the ionic conductivity. Since the ionic conductivity of gelled polymer electrolyte based on PEGDMA will not be affected by the number of ethylene oxide, nor by the content of plasticizer, the result of ionic conductivity related to the chain length of ethylene oxide has to be discussed in context of the content of plasticizer. In the present study, several crosslinked gelled polymer electrolytes based on PEGDMA were prepared by using UV based photo-polymerization. The ionic conductivity was measured according to two major factors, the number of ethylene oxide and the content of plasticizer. We investigated the effect of these two major factors on the ionic conductivity of PEGDMA based gelled polymer electrolyte. Ionic conductivity dependence on temperature and storage time was also studied.

Experimental Section

Reagents and materials. Three kinds of PEGDMA were

Table 1. Designation of poly(ethylene glycol) dimethacrylate used in this study

Chemical structure	Number of ethylene oxide, *n*	Sample code	Supplier
$H_2C=C-C\left(O\,CH_2\,CH_2\right)_n O-C-C=CH_2$ with CH_3 groups	3	3PEGDMA	Polysciences, Inc.
	4	4PEGDMA	Aldrich Chem.
	9	9PEGDMA	Aldrich Chem.
	13	13PEGDMA	Polysciences, Inc.

used for gelled polymer electrolytes (See Table 1). Lithium triflate (LiCF$_3$SO$_3$) and lithium perchlorate (LiClO$_4$) were used as lithium salt. They were purchased from Aldrich Chem. Co. Ethylene carbonate and propylene carbonate (high purity grade, Aldrich Chem. Co.) were used as received. Carbonate solvents were used as a solvent to dissolve lithium salts as well as a plasticizer for gelled polymer electrolytes. Darocur1173 (2-hydroxy-2-methyl-1-phenyl-propan-1-one), a photo-initiator, was purchased from Ciba Specialty Chemicals and triethylamine (TEA, Junsei Chem. Co.) was used as an accelerator for photo-polymerization.
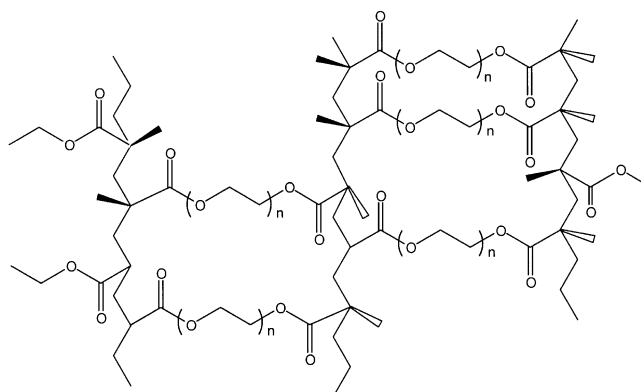
Preparation of PEGDMA-based crosslinked gelled polymer electrolyte. A lithium salt was mixed with PEGDMA and carbonate solvent for 5 hrs to prepare a homogeneous solution (total 20 g-base) in a 50-mL Erlenmeyer flask. Darocur 1173 and TEA were added to the homogeneous solution . Darocur 1173 is a highly efficient liquid photo-initiator that is used to initiate the photo-induced radical polymerization of chemically unsaturated prepolymer like PEGDMA. A recommended concentration of Darocur 1173 was 1-3 wt% vs. the total weight of unsaturated compounds for a resulting film thickness of 20-200 μm. 3 wt% of Darocur 1173 was used in this study. The final solution was cast onto a glass plate and transferred to a UV chamber whose temperature was adjusted to 25 ^{o}C. The solution was irradiated by UV (365 nm, 30W) for more than 30 minutes to prepare a fully crosslinked gelled polymer electrolyte. The photo-initiator makes a reactive radical by UV irradi-ation after which a typical radical polymerization is process-ed. The thickness of the crosslinked gelled polymer electro-lytes in this study was controlled at around 150 μm. The crosslinked gelled polymer electrolytes were flexible and free standing in the 50-80% range of the content of plasticiz-er *vs.* the content of PEGDMA. The lower the content of liquid electrolyte the stronger the film. The crosslinked PEGDMA gelled polymer electrolyte was stored in a dry box for 2 days before it was analyzed.

Electrochemical evaluation and thermal analysis. The ionic conductivities of the crosslinked PEGDMA gelled polymer electrolytes at temperatures ranging from -20 to 60 ^{o}C were measured from the AC impedance spectra of cells assembled by sandwiching the gelled polymer electrolyte between two stainless steel (SS) blocking electrodes and packaging them with a plastic pouch (the area of SS elec-trode was 4 cm^2). All test cells were assembled in a glove box. The AC impedance of the cells was measured by using Impedance Spectrum Analyzer, IM6 (Zahner Co.). 10 mV AC amplitude was applied with a frequency sweep from 0.1

Hz to 1 MHz. The cells were placed in a low temperature thermostat chamber (Lauda RM 20 S) to investigate the temperature dependency of the ionic conductivity of the sample. Impedance spectroscopy measures the alternating current resistance (the impedance) of the sample as a func-tion of frequency. From the measured resistance the bulk ionic conductivity is calculated from the equation $\sigma = (1/R)$ x (l/A), where σ is the ionic conductivity, R is the bulk resistance, l is the thickness of the sample and A is the effective measurement area of the cell. A linear sweep voltammetry (LSV) experiment was carried out on Li metal/gelled polymer electrolyte/SUS cell at scanning rates of 0.5, 1.0 and 5 mV/s to measure the electrochemical stability window. IM6 was also used for LSV measurement of the cells. Differential Scanning Calorimetry (DSC, DuPont TA9900) was carried out to find the glass transition temperature of crosslinked polymer electrolytes with a temperature range of -80~100 ^{o}C and scan rate of 20 ^{o}C/min.

Results and Discussion

Glass transition temperatures of crosslinked PEGDMA polymers. Individual PEGDMA compounds are well bonded together to makes three dimensional network polymers by photo-induced radical polymerization.[23] Their typical struc-tures are shown in Scheme 1. The chain length of ethylene oxide (EO) determines the inter chain length between two PEGMDA polymers, and the mobility of the network poly-mer is decided by EO chain length. A longer chain length of EO could, in general, give more flexible chain motion, which could contribute the increase of lithium ion transport. To study the chain flexibility of the crosslinked polymer electrolyte itself as a function of EO chain length through

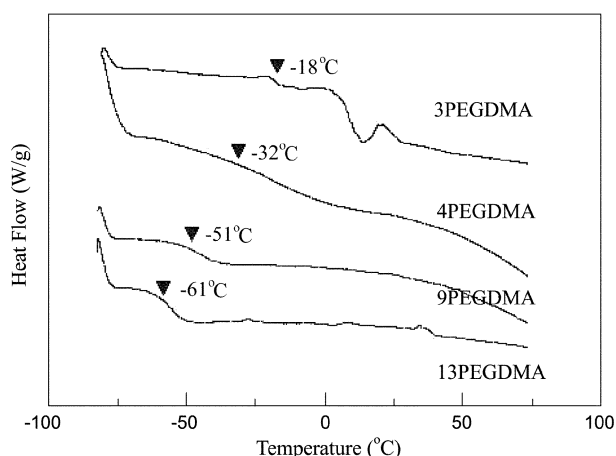**Scheme 1**. Estimated network structure of PEGDMA polymers.

Figure 1. DSC profiles of PEGDMA/LiCF$_3$SO$_3$ films: Ratio of [EO]/[Li$^+$] was 8 and the marked points are on-set point of glass transition zone.

DSC experiment, we prepared PEGDMA/LiCF$_3$SO$_3$ films without any plasticizer to get rid of any other effects on the chain flexibility. The ratio of [EO]/[Li$^+$] was 8. The marked points in Figure 1 are on-set points of the glass transition zone. We found that crosslinked polymer electrolytes having the repeating unit of EO of 4-13 showed only glass transition temperature, which indicated that these polymer electrolytes were fully amorphous.[10,24] The longer the chain length in the crosslinked polymer electrolyte the lower T$_g$ was because of the easy segmental motion of the EO unit in longer chain PEGDMA. Although T$_g$ of a gelled polymer electrolyte is affected mainly by the content of liquid electrolyte, the EO chain length of PEGDMA is also considered to be a factor that may contribute to the ionic conductivity of the cross-linked gelled polymer electrolyte, according to the DSC result.

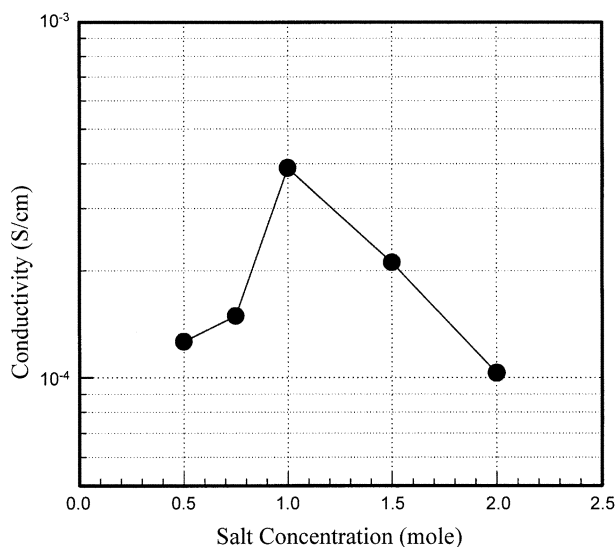**Ionic conductivities of the PEGDMA gelled polymer electrolytes**. Ionic conductivity in this case is commonly affected by the molar concentration of lithium salt. We investigated the effect of salt concentration on ionic conductivity with 13PEGDMA/LiCF$_3$SO$_3$/PC films, and the result is shown in Figure 2. The content of plasticizer, PC, was 50 wt%. In general, the higher the molar concentration of lithium salt in an electrolyte system the higher the ionic conductivity. This is due to the fact that the ionic conductivity depends on the number of free ions in the electrolyte system. The ionic conductivity, however, decreases at a point where the molar concentration exceeds a certain value due to the hindrance of transport of free ions by ion aggregation or association. We found that the maximum ionic conductivity was acquired at a salt concentration of *ca.* 1.0 M in the 13PEGDMA/LiCF$_3$SO$_3$/ PC gelled electrolyte film, and the molar concentration was fixed at 1.0 M in all the other electrolyte systems.

Figure 3 shows the change in the ionic conductivity of PEGDMA/LiCF$_3$SO$_3$/PC gelled electrolyte films as a function of EO chain length and content of plasticizer, PC. We found that overall ionic conductivity increases in proportion to the EO chain length and the content of plasticizer. The gelled polymer electrolyte films having a content of plasticizer of more that 75 wt% did not show significant dependency of EO chain length on ionic conductivities. In other cases, however, ionic conductivities increased in proportion to the EO chain length, and gelled polymer electrolyte based on 13PEGDMA having the longest EO chain length showed the highest ionic conductivities regardless of the content of plasticizer. The ionic conductivity, in fact, is strongly dependent upon the content of plasticizer in most gelled polymer electrolytes. Of great importance is preparing a gelled polymer electrolyte having the homogeneous conducting channel for lithium ion. This is achieved by using the proper level of the content of plasticizer.[25-26] In this context, the gelled polymer electrolytes with a plasticizer content of
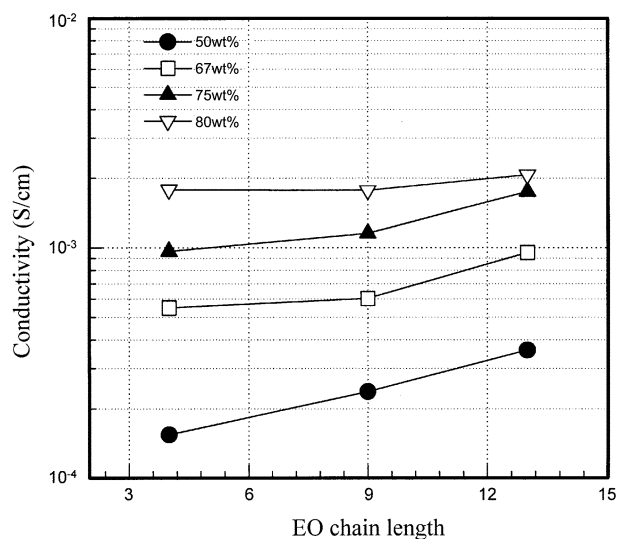

Figure 2. Ionic conductivity of 13PEGDMA/LiCF$_3$SO$_3$/PC gelled polymer electrolyte films as a function of salt concentration at 25 °C.

Figure 3. Ionic conductivities of PEGDMA/LiCF$_3$SO$_3$/PC gelled polymer electrolyte films as a function of ethylene oxide (EO) chain length inside of PEGDMA and content of plasticizer at 25 °C. The concentration of LiCF$_3$SO$_3$ in PC was 1 M.
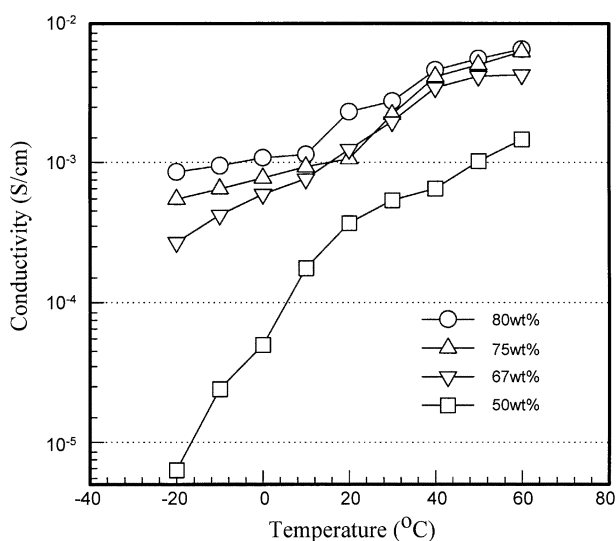
Table 2. Result of ionic conductivities of (PEG)13DMA gelled polymer electrolyte according to sort of lithium salt and content of plasticizer [$\times 10^{-3}$ S/cm]

Content of plasticizer (wt%)	1 M of LiCF$_3$SO$_3$			1 M of LiClO$_4$		
	In PC	In EC/PC = 1/1 (by wt.)	In EC/PC = 2/1 (by wt.)	In PC	In EC/PC = 1/1 (by wt.)	In EC/PC = 2/1 (by wt.)
50	0.36	0.40	0.39	0.31	0.73	0.61
67	0.95	1.21	1.23	1.54	1.69	1.88
75	1.75	1.86	1.70	3.48	3.63	3.25
80	2.07	2.48	2.01	4.38	4.40	3.91

more than 75 wt% showed ionic conductivity of more than 10^{-3} S/cm at 25 °C regardless of EO chain length. In the case of plasticizer content of 50 wt %, however, considering that it is a gelled polymer electrolyte system, the ionic conductivity was quite low even in 13PEGDMA system because 50 wt% is not enough content to form a homogeneous conducting path.
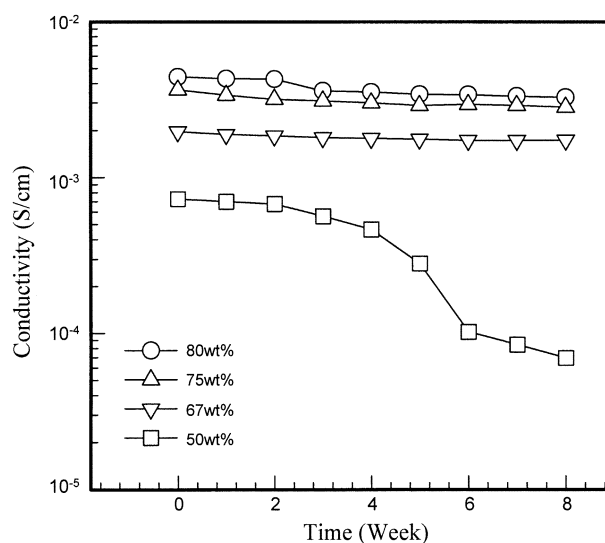
We investigated the ionic conductivities of gelled polymer electrolytes based on 13PEGDMA with different lithium salts, plasticizers (PC and EC/PC mixture) and plasticizer content. As shown in Figure 3, plasticizer content is an important factor that firmly affects the ionic conductivities of 13PEGDMA gelled polymer electrolytes, and the effect stemming from the type of plasticizers (PC, EC/PC mixture) is negligible (see Table 2). LiClO$_4$ has a smaller ion radius than LiCF$_3$SO$_3$, and the molar conductivity of ClO$_4^-$ is slightly larger than that of CF$_3$SO$_3^-$ in a liquid electrolyte system.[27] Table 2 shows a similar result, namely that the ionic conductivities of 13PEGDMA gelled polymer electrolytes with LiClO$_4$ are higher than those with LiCF$_3$SO$_3$ reported for liquid electrolyte systems.

We investigated the temperature dependency of the ionic conductivity of 13PEGDMA/LiClO$_4$/(EC/PC = 1/1 by wt%) films over the range of 20-60 °C (See Figure 4). The ionic conductivity of a polymer electrolyte strongly depends on temperature.[28] Clearly, the ionic conductivities of crosslinked PEGDMA gelled polymer electrolytes in this study were above 1×10^{-3} S/cm above room temperature, except in the case of a plasticizer content of 50 wt%. As shown in Figure 3 and Table 2, 50 wt% is not the content needed to form a homogeneous conducting path, and that is why the ionic conductivity drops sharply at below 20 °C. This behavior of ionic conductivity is similar to that of a solid polymer electrolyte.

Figure 5 shows the long-term stability of the ionic conductivity of 13PEGDMA/LiClO$_4$/(EC/PC = 1/1 by wt%) films. As shown in Figure 4, similar result is shown in Figure 5. The crosslinked gelled polymer electrolyte that has a plasticizer content of 50 wt% among them only shows the decay of ionic conductivity with the storage time. The lack of plasticizer may be the main reason of the disconnection for the conducting path. Another reason could be a slight evaporation of some plasticizer to other spaces inside of plastic pouch used for the packaging of the SS/gelled polymer electrolyte/SS cell. The results in Figure 5 are more proof that 50 wt% is not enough plasticizer content to make a stable crosslinked gelled polymer electrolyte. Other results show stable ionic conductivities of more than 1×10^{-3} S/cm regardless of the storage time. That means there are no phase separation and loss of liquid electrolyte.

Figure 4. Effect of temperature on the ionic conductivities of 13PEGDMA/LiClO$_4$/(EC/PC = 1/1 by wt%) gelled polymer electrolyte films: salt concentration was 1 M.

Figure 5. Long term stability of the ionic conductivity of 13PEGDMA/LiClO$_4$/(EC/PC = 1/1 by wt%) gelled polymer electrolyte films.
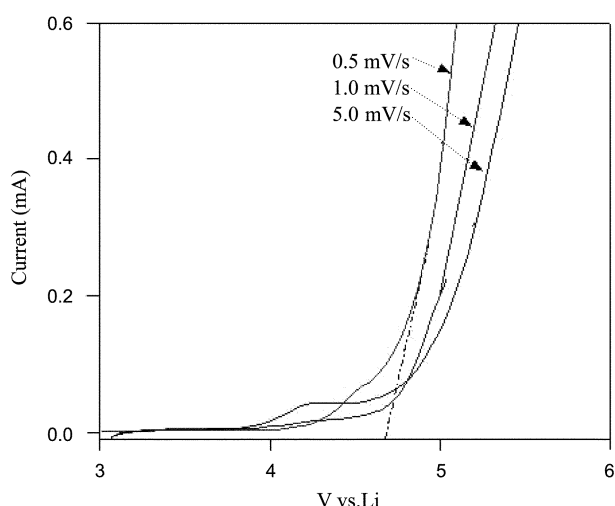
Figure 6. Electrochemical stability window of 13PEGDMA/LiClO$_4$/(EC/PC = 1/1 by wt%) gelled polymer electrolyte film at room temperature. The cell configuration for measurement was Li metal/polymer electrolyte/SS. The content of plasticizer was 75 wt%.

We have investigated the electrochemical stability window of 13PEGDMA/LiClO$_4$/(EC/PC = 1/1 by wt%) film, by using the LSV technique with different voltage sweep rates. Polymer electrolyte for lithium polymer batteries must be stable within the range of its operating voltage, usually above 4.5 V, and show no degradation peak over the voltage range. Figure 6 shows the result of the electrochemical stability window of 13PEGDMA/LiClO$_4$/(EC/PC = 1/1 by wt%) film in a Li metal/polymer electrolyte/SUS cell at room temperature. It shows a wide electrochemical window above 4.5 V (*vs.* Li$^+$/Li), which is sufficient for a common lithium battery system. LSV does not give information regarding an oxidation reaction between a polymer electrolyte and cathode material. For a detailed study of the electrochemical phenomenon, the oxidation resistance of a polymer electrolyte against a lithium metal oxide cathode has to be checked before applying it in a lithium rechargeable battery by use of DSC and accelerated rate calorimeter (ARC).

Conclusions

We prepared crosslinked gelled polymer electrolytes based on PEGDMA plasticized by carbonate solvent, and studied the effect of EO chain length in PEGDMA and the plasticizer content on the ionic conductivity. Although the ionic conductivity was, in general, strongly dependent upon plasticizer content in the gelled polymer electrolyte system, we found that the longer chain length of EO gave more flexible chain motion and contributed to an increase in the ionic conductivity. Its effect was obvious in the gelled polymer electrolyte having low plasticizer content below 67 wt %.

One of the important things that give a gelled polymer electrolyte having a homogeneous conducting channel for lithium ion transport is the proper amount of plasticizer. In this study, plasticizer content of more than 67 wt % was sufficient to prepare stable crosslinked gelled polymer electrolyte that could give ionic conductivity above 1×10^{-3} S/cm above room temperature.

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