

Fabrication of Li-polymer/silica aerogel nanocomposite electrolyte for an all-solid-state lithium battery

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Abstract

Nanocomposite solid-polymer electrolytes were fabricated using polyethylene oxide (PEO), polyvinylidene fluoride (PVDF), LiClO₄ and silica aerogel, with the aim of improving lithium ion conductivity and thermal stability. The effects of the PEO:PVDF ratio, polymer:Li-salt ratio, and silica aerogel content on the electrical conductivity of the solid-polymer electrolytes were examined. Highest lithium ion conductivity of 1.70×10^{-4} S/cm was obtained at 30 °C in the SPE-2 sample with PEO:PVDF=3:1 and polymer:Li-salt=6:1. XRD and FT-IR analysis showed that the observed phenomenon could be explained by the degree of crystallinity of the polymer electrolyte and by the dissociation degree of Li-salt.

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1. Introduction

The demand for solid-state lithium ion electrolytes has increased owing to the safety concerns regarding the use of lithium ion batteries, which contain flammable organic solvent electrolytes [1,2]. The liquid electrolyte can give rise to serious problems such as leakage and gas explosions when the operating temperature rises. The use of an organic or inorganic solid electrolyte not only results in improved safety, but also facilitates the fabrication of miniature batteries using thin films [3,4].

A solid electrolyte is required to have high lithium ion conductivity, mechanical strength, and transference number for lithium ions as well as good thermal/electrochemical stability and compatibility with the electrodes. Recently, polymer-based solid electrolytes have been widely studied for a possible replacement for liquid electrolytes. Various types of polymer-based solid electrolytes for lithium ion batteries exist, such as polyethylene oxide (PEO), polyacrylonitrile (PAN), polymethyl

methacrylate (PMMA), polyvinyl chloride (PVC), and polyvinylidene fluoride (PVDF) [5]. Among them, the PEO-based polymer has attracted considerable attention, owing to its flexible skeleton and good interfacial stability with lithium electrodes. The mechanism of lithium ion conduction in the PEO-based solid-polymer electrolyte involves the coordination of the lithium ion from the Li-salt by the ether oxygen from the PEO, which moves according to the polymer segmental motion [5].

However, at room temperature, the PEO-based solid-polymer electrolytes exhibit low lithium ion conductivity, 10^{-7} – 10^{-6} S/cm. The lithium ion conductivity could be improved by using the lithium salt, which has a large dissociation degree that can increase the concentration of free lithium ions as charge carriers, or by using a polymer with a high dielectric constant, which can allow the lithium ions to be easily dissociated. Further, the addition of inorganic particles such as SiO₂, TiO₂, and Al₂O₃ can reduce the crystallinity of the PEO polymer, thus enhancing the lithium ion mobility [6,7]. It has also been reported that porous rather than nonporous additives increase the dissociation of Li-salt owing to the strong interactions between the Li-salt and porous surfaces [8].

In this study, a polymer blend of PEO and PVDF, containing fluorine as a polar element, was fabricated to improve the

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dissociation degree of the Li-salt. In addition, we anticipate that the addition of ultra-porous silica aerogels, which has a high porosity and specific surface area, would increase the lithium ion conductivity. The silica aerogel was fabricated from water glass using the emulsion polymerization method, as was previously described by our research group [9]. We also investigated the effects of the PEO:PVDF molar ratio, polymer:Li-salt molar ratio, and silica aerogel content on the structural, thermal, and electrical properties.

2. Experimental procedure

2.1. Starting materials

PEO ($M_v=5,000,000$) and PVDF ($M_w=534,000$) were obtained from Sigma-Aldrich. Acetonitrile (ACN, Samchun, 99.8%), lithium perchlorate (LiClO_4 , Sigma-Aldrich, 99.99%), and ethylene carbonate (EC, Sigma-Aldrich, 98%) were used as the solvent, Li-salt, and plasticizer, respectively. Ultra-porous silica aerogel was prepared following a method described in the literature [9].

2.2. Preparation of solid-polymer electrolytes

Various solid-polymer electrolytes with different compositions were fabricated and are listed in Table 1. The PVDF was dissolved in ACN at 100 °C for 2 h, and then PEO was added to the PVDF solution. The resulting solution was then stirred at 100 °C until a homogeneous polymer blend was obtained. To avoid reactions with oxygen and air, EC and LiClO_4 were handled in a glove box and were sequentially added to the polymer blend solution. After the polymer/ LiClO_4 solution was mixed for 24 h at 100 °C, the silica aerogel powder was added to the solution and the mixture was stirred for additional 24 h at 100 °C. Finally, the mixture was cast using a Teflon mold and then dried at room temperature under vacuum conditions.

2.3. Characterization

The crystallinity of the solid-polymer electrolytes was analyzed using X-ray diffraction (XRD, Rigaku, DMAX 2200) with $\text{CuK}\alpha$ radiation. The glass transition temperature (T_g) and the melting temperature (T_m) of the solid-polymer

electrolytes were examined using differential scanning calorimetry (DSC, Perkin Elmer, Jade DSC). The samples were heated and cooled at a rate of 10 °C/min under nitrogen flow from −40 °C to 200 °C. Thermal stability of the solid-polymer electrolyte was tested by heat-treating the samples at 80 °C for 6 h. The chemical bonds were identified using Fourier transform infrared spectroscopy (FT-IR, Bruker, Vertex 80). The resolution and the range were 4 cm^{-1} and 600–3000 cm^{-1} , respectively. The lithium ion conductivities of the solid-polymer electrolytes were evaluated using AC impedance spectroscopy (Zahner, IM6e) with a frequency range from 1 Hz to 1 MHz at 30 °C. Samples were coated with platinum electrodes and sandwiched between two aluminum disks.

3. Results and discussion

Fig. 1 shows the XRD patterns of the solid-polymer electrolytes obtained in this study. As shown in Fig. 1, no characteristic peaks corresponding to the PEO crystalline phase were observed in the SPE-1 sample, thus indicating that SPE-1 is amorphous. On the other hand, small and broad diffraction peaks were identified for PVDF crystalline phases around $2\theta=20^\circ$ in all PVDF samples: SPE-2 to SPE-9 [10]. It appears that the PVDF crystalline peaks are not prominent and its intensity does not increase with increasing the PVDF content. This result indicates that the PVDF crystalline size is small and the PVDF crystallinity is poor for the PEO/PVDF polymer blend.

For the case of the SPE-3, SPE-4, and SPE-5 samples, characteristic peaks corresponding to the LiClO_4 crystalline phase were observed at $2\theta=23.3^\circ$, 31.5° , 33.0° , and 35.6° [11]. Also, their intensities increased with an increase in the PVDF content. For the SPE-5 sample with a large amount of Li-salt, the peaks of the LiClO_4 crystalline phase were distinct. An interesting feature observed in Fig. 1 is that the SPE-2 sample does not show any LiClO_4 crystalline phase, although it contains the same amount of lithium salt but different PVDF contents compared to SPE-3. The absence of the lithium salt diffraction peaks in the SPE-2 sample indicates that the small amount of PVDF does not affect the complexation with lithium

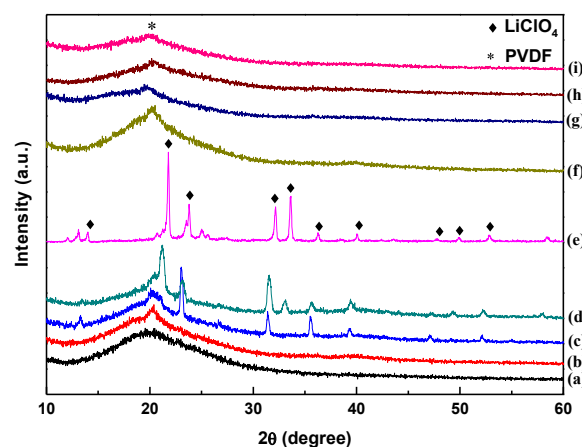


Fig. 1. XRD patterns of the solid polymer electrolytes (a) SPE-1, (b) SPE-2, (c) SPE-3, (d) SPE-4, (e) SPE-5, (f) SPE-6, (g) SPE-7, (h) SPE-8, and (i) SPE-9.

Table 1
Compositions of the solid-polymer electrolytes.

Sample	PEO:PVDF	Polymer:Li-salt	SiO ₂ (wt%)
SPE-1	1:0	6:1	—
SPE-2	3:1	6:1	—
SPE-3	2:1	6:1	—
SPE-4	1:1	6:1	—
SPE-5	3:1	2:1	—
SPE-6	3:1	10:1	—
SPE-7	3:1	6:1	2
SPE-8	3:1	6:1	4
SPE-9	3:1	6:1	8

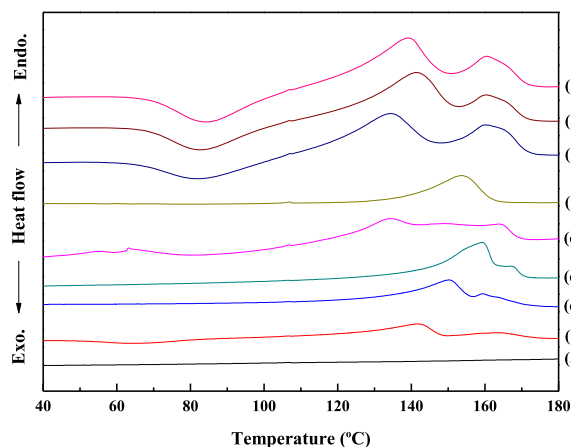


Fig. 2. DSC curves of the solid polymer electrolytes (a) SPE-1, (b) SPE-2, (c) SPE-3, (d) SPE-4, (e) SPE-5, (f) SPE-6, (g) SPE-7, (h) SPE-8, and (i) SPE-9.

negatively. However, it seems that excess PVDF in polymer blend disrupts dissociation of the Li-salt. For the SPE-5 sample containing a large amount of Li-salt, the peaks of the LiClO_4 crystalline phase were distinct. This observed phenomenon suggests that an excess of Li-salt cannot completely form a complex compound with the PEO/PVDF polymer blend.

The SPE-7, SPE-8, and SPE-9 samples contained 2, 4, and 8 wt% silica aerogel powder, respectively, and their PEO:PVDF or polymer:Li-salt ratios were identical. It was found that adding silica aerogel powder to the polymer blend did not affect the diffraction peaks, and the polymer blends containing silica aerogel consisted of an amorphous PEO and some crystalline PVDF phase.

Fig. 2 shows the DSC curves of the solid-polymer electrolyte samples. The glass transition temperatures can be estimated from the derivative of the DSC curve. The transition temperature was found to be approximately -30°C for all samples [12]. No endothermic peaks were found for the SPE-1 sample. This indicates that the added chemicals of the solvent, plasticizer, PEO and Li-salt were homogeneously mixed, thus leading to the formation of an amorphous phase. On the other hand, one or two endothermic peaks were observed between 130 and 160°C for the other samples. These were associated with the melting of the crystalline PVDF, and the endothermic peaks were shifted to higher temperatures with an increase in the PVDF content. This means that bonding strength of the crystalline PVDF becomes stronger and the polymer segmental motion will be slower, thus leading to low lithium ion mobility. For the case of SPE-5 sample, a weak endothermic peak appeared around 60°C . This was attributed to the melting temperature of PEO polymer because the polymer blend was not homogeneously mixed.

Fig. 3 shows the FT-IR spectra obtained for the solid-polymer electrolytes of various compositions. The peak at 2900 cm^{-1} is due to the C–H stretching of the PEO, and its intensity decreased with increasing PVDF content [13]. On the other hand, we observed that the intensity of the C–F stretching peak at 1398 cm^{-1} , which corresponds to the vinylidene group of PVDF, increased with increasing PVDF

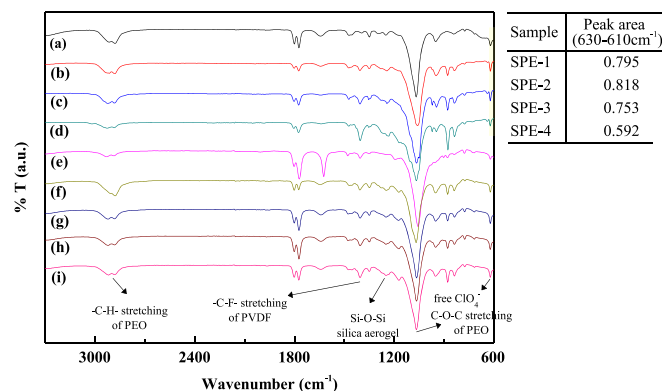


Fig. 3. FT-IR spectra of the solid polymer electrolytes (a) SPE-1, (b) SPE-2, (c) SPE-3, (d) SPE-4, (e) SPE-5, (f) SPE-6, (g) SPE-7, (h) SPE-8, and (i) SPE-9.

content [10]. The C–O–C stretching peak, which is associated with the PEO ether oxygen, was observed at 1150 cm^{-1} [13]. The peak between 610 and 630 cm^{-1} is attributed to the free ClO_4^- and the dissociation degree of Li-salt can be quantitatively speculated from its relative intensity. The ClO_4^- peak area was measured and the values were inserted as shown in Fig. 3. The SPE-2 sample, which the PEO:PVDF ratio is 3:1, showed that the maximum value and peak area decreased with increasing PVDF, thus suggesting that the excess PVDF resulted in the decrease in the degree of dissociation of the Li-salt [12].

On the other hand, the SPE-5 sample with a low polymer to Li-salt ratio, namely the high Li-salt concentration with respect to the polymer blend, exhibited a low intensity for the free ClO_4^- peak. These findings suggest that at a high Li-salt concentration, the ClO_4^- ions tend to re-associate with lithium ions, leading to a decrease in the number of free lithium ions and resulting in the formation of ion–ion pairing [14,15]. It was determined that the peak observed at 1220 cm^{-1} was due to the network structure of silica aerogel, Si–O–Si. The intensity of this peak increased with increasing silica aerogel content [9]. For the samples that contained silica aerogel powder, the peak intensity of the free ClO_4^- ions did not change.

Fig. 4 shows the AC impedance spectra obtained for the solid-polymer electrolytes from various compositions. The equivalent circuit of a symmetrical cell using a blocking electrode is shown in Fig. 4(a). The circuit is composed of R_b and C_b in parallel, connected in series with C_e . Among these circuit elements, the bulk resistance of the solid-polymer electrolyte corresponds to the diameter of the semi-circle in the Nyquist plot shown in Fig. 4(b). The lithium ion conductivities of the solid-polymer electrolytes were calculated from

$$\sigma = \ell / R_b A, \quad (1)$$

and their values are listed in Table 2. Here, ℓ is the thickness of the solid-polymer electrolyte, A is the area of the platinum blocking electrode, and R_b is the bulk resistance of the solid-polymer electrolyte.

In general, the lithium ion conductivity of the solid-polymer electrolyte depends on the concentration and mobility of

lithium ions. As is seen from Table 2, the SPE-2 sample exhibited higher conductivity than SPE-1. This result could be explained by the improved dissociation degree of the Li-salt after the addition of PVDF, as shown by the FT-IR spectra in Fig. 3. However, the further addition of PVDF to PEO resulted in an abrupt decrease in conductivity, suggesting that the

crystalline PVDF leads to a decrease in the mobility of lithium ions and the dissociation degree of Li-salt, as previously described in Fig. 2 and Figs. 1 and 3, respectively. The conductivity of the SPE-3 sample was one order of magnitude lower than that of SPE-2. In this study, the SPE-2 sample with the PEO:PVDF ratio of 3:1 had the maximum lithium ion conductivity of 1.70×10^{-4} S/cm at 30 °C.

In general, the lithium ion conductivity is expected to increase with increasing concentration of Li-salt. However, the conductivity of SPE-2 was higher than that of SPE-5, which has a higher Li-salt concentration. This result is due to the decrease in the number of free lithium ions and the increase in the formation of ion-ion pairs. This behavior has been reported by various researchers [16,17]. Doeffer et al. explained this behavior as a trade-off between increasing numbers of charge carriers and ion aggregation and increased viscosity due to the ionic cross-linking, which lowers the conductivity when the salt concentration exceeds a critical value [18]. In addition, the lithium ion conductivity decreased with increasing silica aerogel powder content. This behavior was attributed to the decrease in the mobility of lithium ions that results from the aggregation of silica aerogel particles.

Thermal stability of the solid-polymer electrolyte is an important property because a lithium ion battery is exposed to a wide range of temperatures, −50 to 80 °C, depending on its operating environment. Fig. 5 shows photographs of the solid-polymer electrolytes before and after the hot oven test at 80 °C for 6 h. The SPE-1 sample became soft and irreversible deformation occurred, while the SPE-2 and 7 samples did not show any shrinkage or shape change at 80 °C. This enhanced thermal stability, observed in the electrolyte samples that contain PVDF and silica aerogel, can be associated with the increased melting temperature by the addition of PVDF and silica aerogel.

4. Conclusions

Lithium-ion-conducting solid-polymer electrolytes consisting of PEO, PVDF and silica aerogel powder were successfully fabricated. The lithium ion conductivities of the solid-polymer

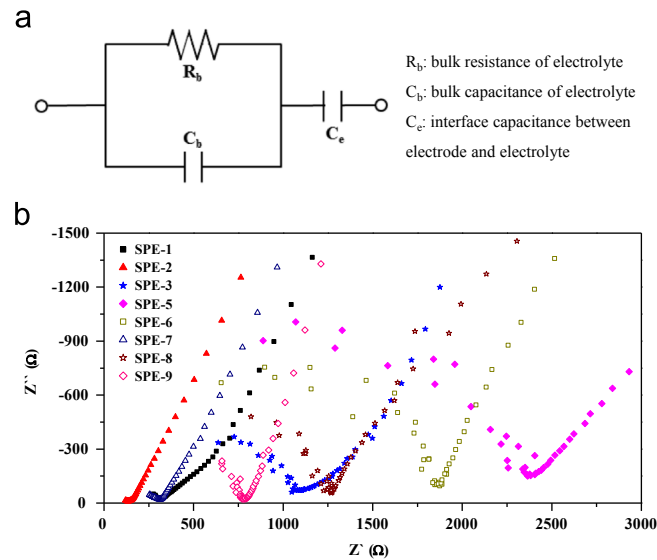


Fig. 4. AC impedance spectra of the solid polymer electrolytes (a) equivalent circuit and (b) Nyquist plot.

Table 2
Lithium ion conductivities of the solid-polymer electrolytes.

Sample	Ionic conductivity (S/cm at 30 °C)
SPE-1	1.39×10^{-4}
SPE-2	1.70×10^{-4}
SPE-3	2.48×10^{-5}
SPE-5	1.12×10^{-5}
SPE-6	1.36×10^{-5}
SPE-7	7.49×10^{-5}
SPE-8	4.07×10^{-5}
SPE-9	3.42×10^{-5}

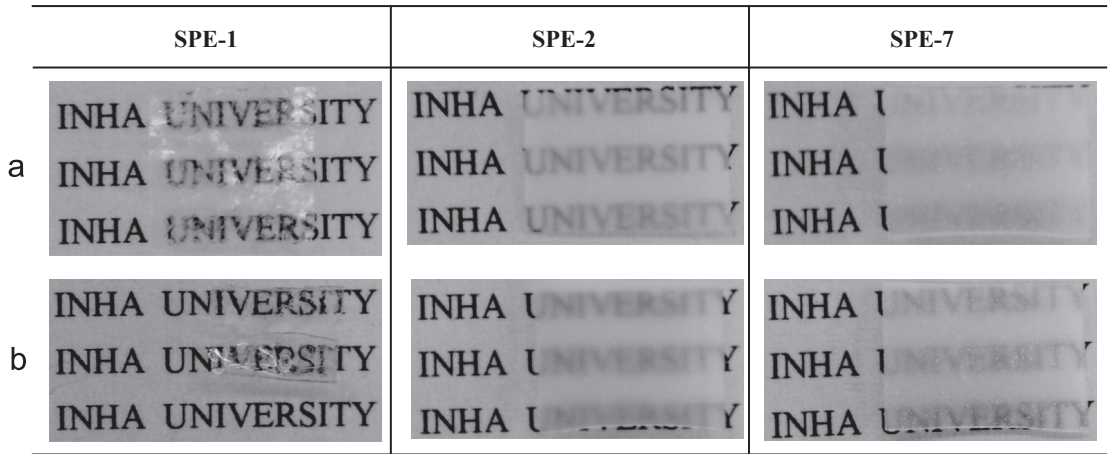


Fig. 5. Photographs of the solid polymer electrolytes (a) before and (b) after hot oven test at 80 °C for 6 h.

electrolytes depend on the PEO:PVDF ratio, polymer:Li-salt ratio and silica aerogel content. The solid-polymer sample with a PEO:PVDF ratio of 3:1 and polymer:Li-salt of 6:1 showed a maximal conductivity of 1.70×10^{-4} S/cm at 30 °C. The addition of PVDF may lead to an increase in the thermal stability and the dissociation degree of the Li-salt and a decrease in the mobility of lithium ions. High Li-salt content resulted in a decrease in the dissociation degree of Li-salt. The conductivity of lithium ions decreased as the content of silica aerogel increased, owing to the mobility degradation caused by the aggregation of silica aerogel particles.

Acknowledgments

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