



Electrochemical stability and conductivity enhancement of composite polymer electrolytes

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Abstract

The electrochemical stability behavior of the composite polymer electrolytes obtained by adding a fine Al₂O₃ powder (activated acidic, neutral, and basic) with a diameter of 5.8 nm to the poly(ethylene oxide) (PEO)–LiClO₄ is described. The strong hydrogen bond between the surface group of Al₂O₃ and lithium salt anion prevents the decomposition of lithium salt anion. An enhancement of the ionic conductivity for the composite polymer electrolytes prepared with Al₂O₃ and BaTiO₃ is described in terms of a reduction of crystallinity and an increase of charge carrier concentration.

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1. Introduction

Development of portable electronic devices has been remarkable in the last decade. A high performance battery with high energy density is indispensable for further development of the portable electronic equipments. A lithium secondary battery using solid polymer electrolyte is an attractive energy source for the portable devices, since the use of solid polymer electrolyte makes the fabrication of safe batteries possible and permits the development of thin batteries with design flexibility. Much of the efforts to date has

focused on poly(ethylene oxide) (PEO) as the host material for solid polymer electrolyte [1–3]. However, PEO-based polymer electrolytes exhibit the poor ambient temperature conductivity and mechanical stability. One point of concern in the development of solid polymer electrolytes lies in the fact that high conductivity is necessarily associated with an amorphous character of the polymer complexes [4]. It is also of importance to improve the mechanical properties of the amorphous polymer electrolytes. Many systems are based on low-molecular-weight PEO which grafted a high T_g polymer backbone that imparts mechanical stability to the material [5–8]. Formation of networks by irradiation or chemical cross-linking can also greatly improve the mechanical properties [9–11], but it may lead to excessive rigidity of the polymer chain with a consequent decay in ionic

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conductivity. Alternatively, the physical approach appears more appropriate in this respect. It is well known that the addition of inert filler is useful to increase the electrical and mechanical properties of solid polymer electrolytes [12,13]. In this paper, we report the electrochemical characteristics of composite polymer electrolytes prepared by addition of Al_2O_3 . The electrochemical stability behavior is discussed in terms of specific interaction between anion and surface group of Al_2O_3 . An improvement of ionic conductivity by addition of ferroelectric BaTiO_3 into composite polymer electrolyte based on (PEO)– LiClO_4 – Al_2O_3 is also reported.

2. Experimental

2.1. Materials

PEO with molecular weight 600,000 and LiClO_4 were supplied by Aldrich and the salt was dried at 100°C in a vacuum oven overnight before use. Three

forms of Al_2O_3 (activated acidic, basic, neutral, 5.8 nm particle size) and BaTiO_3 ($<2\ \mu\text{m}$ particle size) were used after drying according to the literature [13–15]. PEO was dissolved in anhydrous acetonitrile. After the polymer was completely dissolved, a pre-determined amount of LiClO_4 and inorganic fillers were added, and then further mixed using ball mill until homogeneous slurry was achieved. The purpose for using ball milling method is to achieve the homogeneous dispersion of the inorganic filler in the solution. To obtain the reproducible results, the ball milling conditions such as milling duration, rotation speed, container and ball materials were kept being same for all the samples. When the complete homogenization of mixture had occurred, the slurry was cast onto a Teflon plate and left to evaporate solvent slowly at room temperature for 24 h. The films were finally dried under vacuum at 60°C for 24 h. The thickness of composite polymer electrolyte films was about $100\ \mu\text{m}$. All procedures for preparing the composite polymer electrolytes were carried out in a dry room.

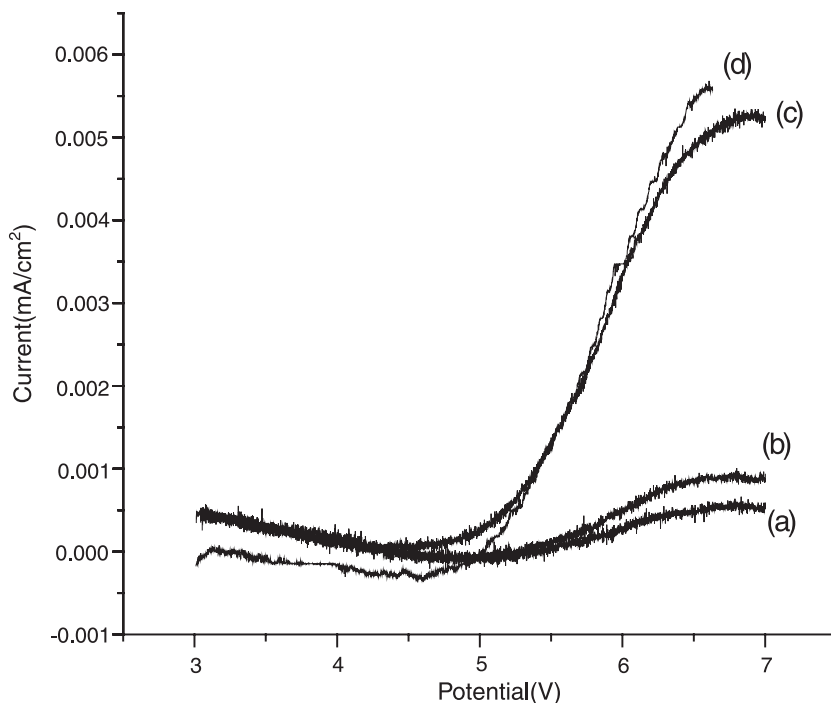


Fig. 1. Linear sweep voltammogram of the PEO-based composite polymer electrolyte at 16°C . Salt content is $[\text{LiClO}_4]/[\text{EO}]=0.1$ and inorganic filler is 10 wt.%. (a) Al_2O_3 activated acidic; (b) Al_2O_3 activated neutral; (c) Al_2O_3 activated basic; (d) filler-free.

2.2. Characterization

Composite polymer electrolyte film was sandwiched between the two disk-like stainless steel (SS) electrodes (15.5 mm in diameter). A.C. impedance measurement was carried out on the cell with a Zahner Elektrik IM6 impedance analyzer over a frequency range from 100 Hz to 1 MHz. The real and imaginary parts of the complex impedance were plotted, and the ionic conductivity could be calculated from the bulk resistance found in complex impedance diagram. Linear sweep voltammetry was performed on an SS working electrode, with counter and reference electrodes of lithium, at a scanning rate of 1 mV/s. DSC studies were carried out to determine the glass transition and melting temperature of the composite polymer electrolytes using a TA instrument DSC 2010. Samples were loaded in aluminum pan and measurements were taken over a temperature range of

– 80 to 120 °C with a heating rate of 10 °C/min. The recorded T_g was taken as the inflection point and T_m was given as the peak point of the melting endotherm. A morphology of the composite polymer electrolyte was observed by scanning electron microscope.

3. Results and discussion

3.1. Effect of inorganic filler on the electrochemical stability

The electrochemical stability of the composite polymer electrolytes prepared with three types of Al_2O_3 was evaluated by linear sweep voltammetric measurement. Experiment was performed by applying an anodic voltage to a cell consisting of a composite polymer electrolyte sandwiched between a lithium electrode and an inert SS electrode. The voltage was

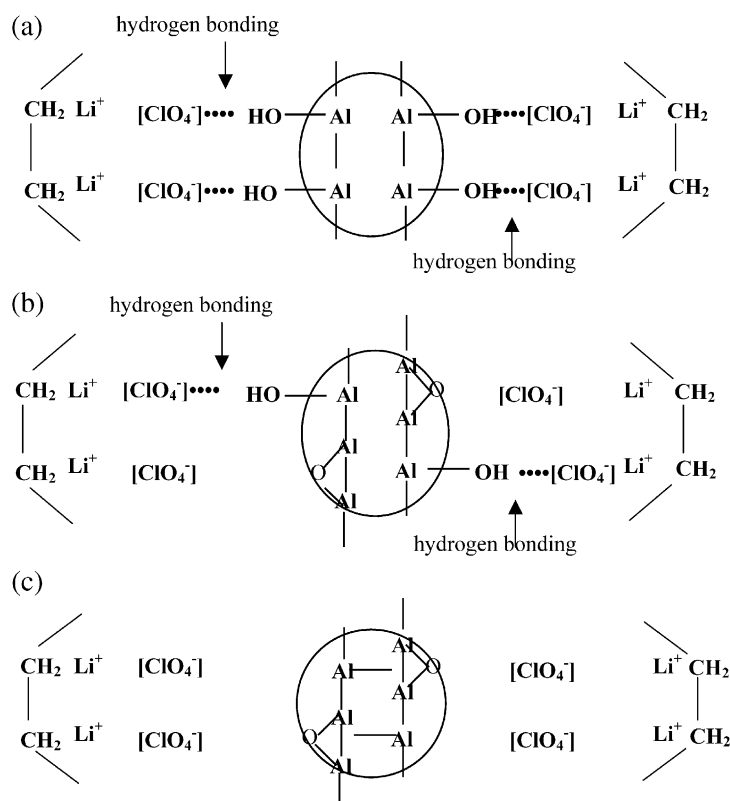


Fig. 2. Pictorial model of the surface interaction between three forms of Al_2O_3 inorganic filler and PEO– LiClO_4 electrolyte complex. (a) Al_2O_3 activated acidic; (b) Al_2O_3 activated neutral; (c) Al_2O_3 activated basic.

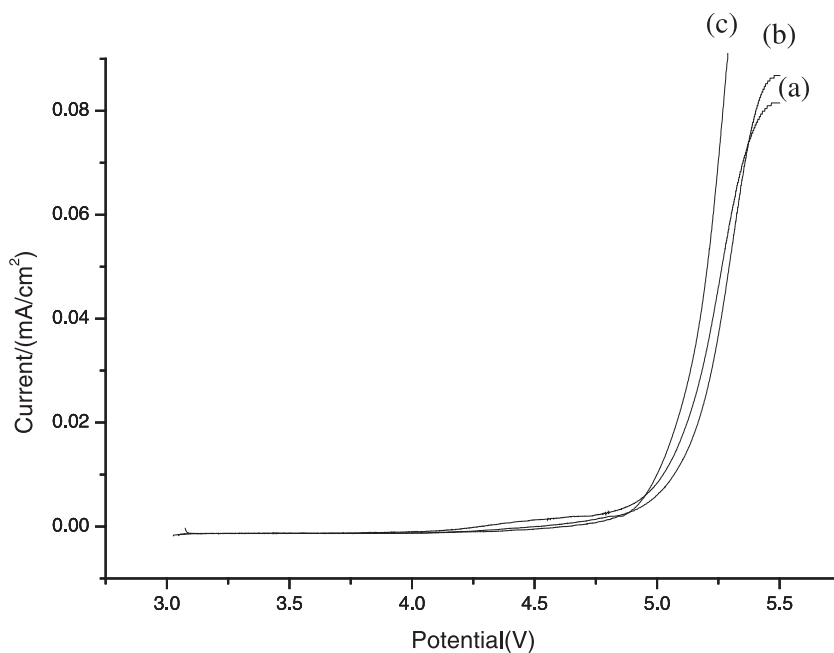


Fig. 3. Linear sweep voltammogram of the PEO-based composite polymer electrolyte at 60 °C. Salt content is $[\text{LiClO}_4]/[\text{EO}]=0.1$ and inorganic filler is 10 wt%. (a) Al_2O_3 activated acid; (b) Al_2O_3 activated neutral; (c) Al_2O_3 activated basic.

swept from the open circuit potential of cell towards more anodic values until a large current due to the electrolyte decomposition at the inert electrode inter-

face occurred. The decomposition voltage limit was defined as the potential at which a rapid rise in current was observed and continued to increase as the poten-

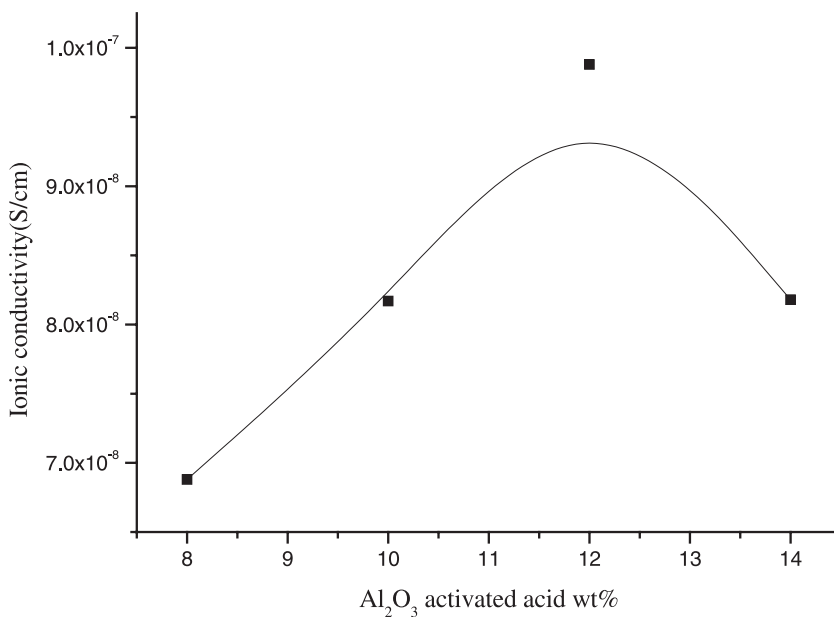


Fig. 4. Variation of ionic conductivity with Al_2O_3 content in the $(\text{PEO})_8\text{-LiClO}_4\text{-Al}_2\text{O}_3$ activated acidic at 16 °C.

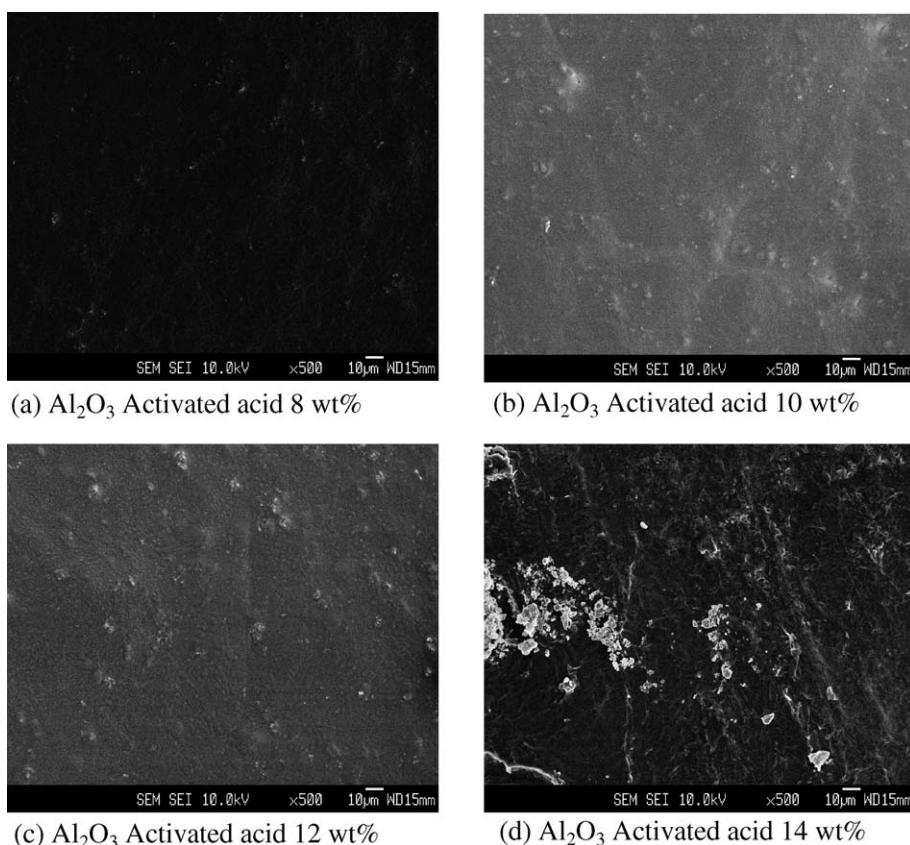
Table 1

DSC result of the composite polymer electrolyte (PEO)₈–LiClO₄–Al₂O₃ activated acid

Al ₂ O ₃ activated acid (wt.%)	<i>T</i> _g (°C)	<i>T</i> _m (°C)	Δ <i>H</i> _m (J/g)	Crystallinity (%)
8	–10.9	81.7	1.18	0.58
10	–24.4	76.6	0.95	0.46
12	–21.5	69.5	0.76	0.37
14	–21.0	73.0	0.98	0.48

tial was swept, since the onset of the current flow may be associated with the decomposition of the given electrolyte. Fig. 1 shows linear sweep voltammetry curves of the cells prepared with composite polymer electrolytes, which are measured at 16 °C. It can be seen that composite polymer electrolyte prepared with Al₂O₃ activated acidic or Al₂O₃ activated neutral exhibits higher electrochemical stability than that prepared with Al₂O₃ activated basic. This result arises

from the difference of surface group arrangements for Al₂O₃ powder, which has been previously proposed by Croce et al. [16]. Fig. 2 illustrates the mechanism of electrochemical stability enhancement. It has been well known that anodic stability window is limited by an irreversible oxidation of the salt anion [4]. In case of Al₂O₃ activated acidic or neutral, the inorganic filler's surface OH is expected to favor interactions (via hydrogen bonding) with ClO₄[–] ion. On the other hand, in composite polymer electrolyte prepared with Al₂O₃ activated basic, no surface OH groups exist, which means no interactions are anticipated between Al₂O₃ and ClO₄[–] ion. On the other hand, the interfacial resistances of the composite polymer electrolytes prepared with three types of Al₂O₃ are less likely to affect their electrochemical stability. From the measurements of interfacial resistances, it is found that the values are little dependent on type Al₂O₃ added into the composite polymer electrolytes. From

Fig. 5. SEM of the (PEO)₈–LiClO₄–Al₂O₃ activated acidic composite polymer electrolyte.

these results, it can be concluded that the electrochemical stability could be enhanced by hydrogen bonding between anion and inorganic filler, which retards the decomposition of lithium salt anion. Fig. 3 shows results of linear sweep voltammetry measurement of the cells prepared with composite polymer electrolytes, which are measured at 60 °C. It is found that decomposition voltages of three composite polymer electrolytes are little dependent on type of Al₂O₃. When compared to those in Fig. 1, the composite polymer electrolyte prepared with Al₂O₃ activated acidic or Al₂O₃ activated neutral exhibits lower electrochemical stability window at 60 °C than one measured at 16 °C. As temperature increases, the strength of hydrogen bonding is reduced, thus the hydrogen bonding between ClO₄⁻ ion and Al₂O₃ cannot fully overcome the tendency of lithium salt anion decomposition.

3.2. Ionic conductivity of composite polymer electrolyte

The influence of the Al₂O₃ content on the ionic conductivity in the composite polymer electrolyte at 16 °C is shown in Fig. 4. In this experiment, an Al₂O₃

activated acidic was selected as an inorganic filler for preparing the composite polymer electrolyte, because electrochemical stability of composite polymer electrolyte prepared with Al₂O₃ activated acidic is superior to those of composite polymer electrolytes prepared with other fillers, as previously described. It is found that ionic conductivity passes a maximum value (1.0×10^{-7} S/cm) at 12 wt.% Al₂O₃. An increase of ionic conductivity with Al₂O₃ content is attributed to a reduction of crystallinity of composite polymer electrolyte. A reduction of crystallinity arises from random distribution of fine Al₂O₃ powder which may introduce the topological disorder to the polymer electrolyte. A polymer chain in the amorphous phase or the less ordered regions is more flexible, which results in an increase of segmental motion of the polymer. Over 12 wt.% Al₂O₃, the ionic conductivity decreases, because the inorganic fillers tend to impede ionic movement by acting as an insulator or an agglomerator, which will be proven by DSC and SEM. The DSC results of composite polymer electrolytes are summarized in Table 1. In this table, the enthalpy of melting (ΔH_m) is represented as that per unit weight of PEO, and crystallinity is estimated from the ratio of the experimentally determined ΔH_m to the

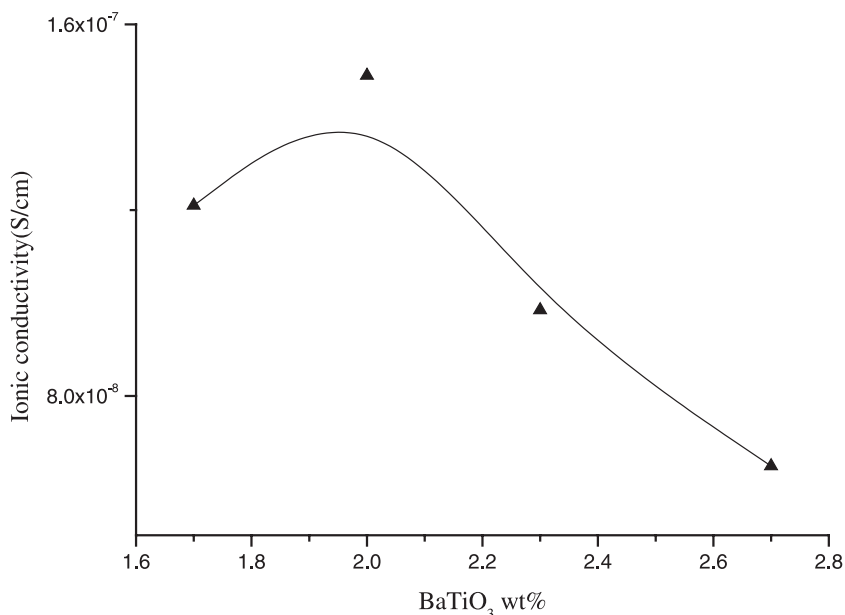


Fig. 6. The ionic conductivity variation of the (PEO)₈-LiClO₄-BaTiO₃ composite polymer electrolyte with BaTiO₃ filler content at 16 °C.

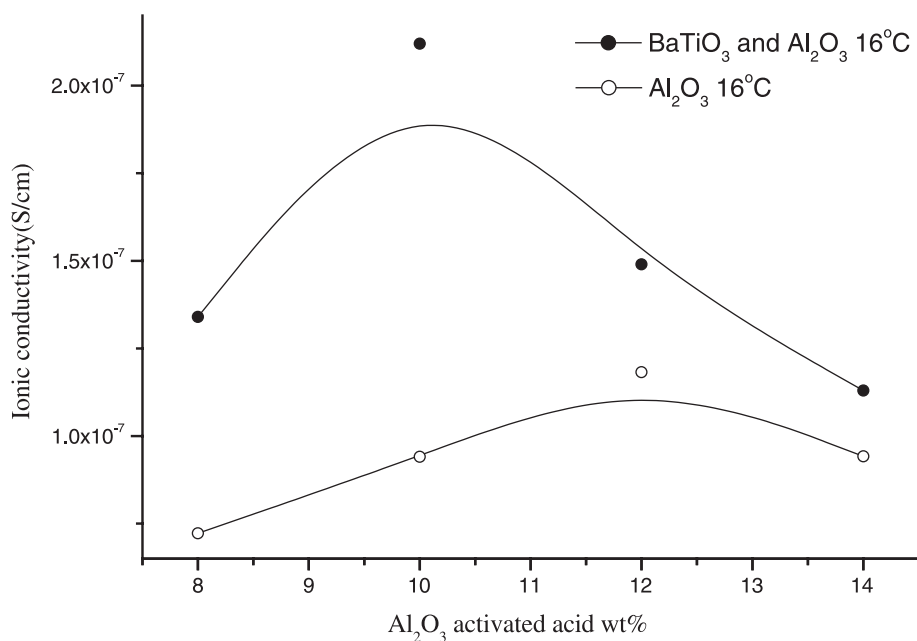


Fig. 7. Variation of ionic conductivity in the (PEO)₈-LiClO₄-Al₂O₃ activated acidic and (PEO)₈-LiClO₄-2 wt.% BaTiO₃-Al₂O₃ activated acidic system.

value of 203 J/g reported in the literature for the enthalpy of melting of 100% crystalline PEO [17]. It is found that the crystallinity is decreased with

increasing Al₂O₃ content up to 12 wt.%, but the crystallinity is increased again at 14 wt.% Al₂O₃. If too much Al₂O₃ is added, substantially homogeneous

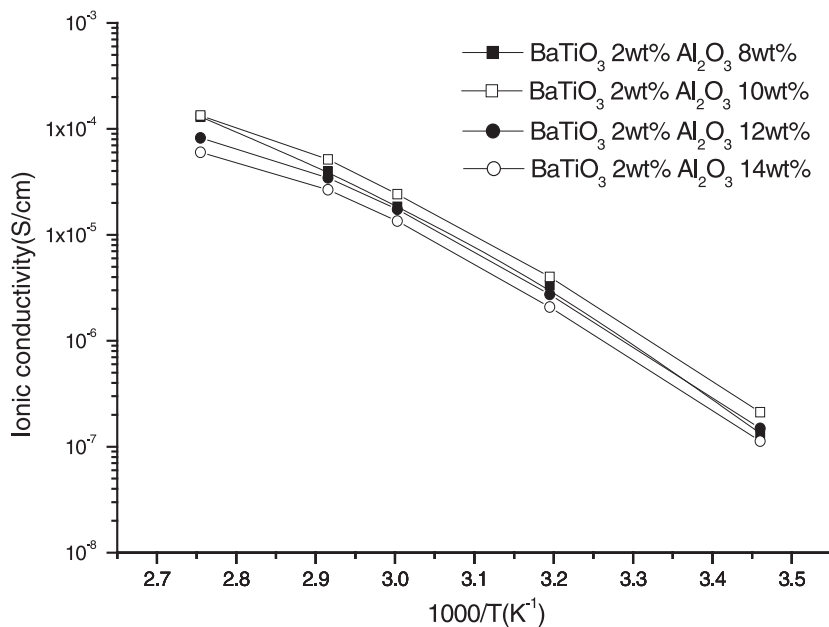


Fig. 8. Temperature dependence of ionic conductivity for the (PEO)₈-LiClO₄-2 wt.% BaTiO₃-Al₂O₃ activated acidic.

composite does not result, and therefore it cannot effectively hinder the crystallization of the polymer chain. Fig. 5 shows the SEM of the composite polymer electrolytes. The Al_2O_3 powders are observed to be uniformly distributed within complex when an Al_2O_3 composition is within 12 wt.%, but the Al_2O_3 agglomeration is observed in the complex containing 14 wt.% of Al_2O_3 . This result means that the Al_2O_3 content should be properly maintained to prevent phase discontinuities in the composite polymer electrolytes. That is to say, the composite polymer electrolyte having a high Al_2O_3 content may exhibit a tendency to separate into phase. From these results, it can be said that an addition of Al_2O_3 is necessary to reduce the crystallinity of the polymer electrolyte, but a proper Al_2O_3 content should be maintained to assure a highly distribution of the powder in the composite polymer electrolyte.

Fig. 6 represents the ionic conductivity as a function of ferroelectric BaTiO_3 content at 16 °C. The maximum conductivity is 1.5×10^{-7} S/cm at 2.0 wt.% BaTiO_3 content. An increase in ionic conductivity may be associated with the increase in the charge carrier concentration, as reported previously [13]. Ionic conductivity of $(\text{PEO})_8\text{-LiClO}_4\text{-2 wt.\% BaTiO}_3\text{-Al}_2\text{O}_3$ as a function of BaTiO_3 content is shown in Fig. 7. It is found that the conductivity values of the composite polymer electrolytes prepared with two fillers are higher than those of the composite polymer electrolytes prepared with one filler (Al_2O_3 or BaTiO_3). In the composite polymer electrolytes prepared with two fillers (Al_2O_3 and BaTiO_3), a role of ferroelectric BaTiO_3 is to enhance the charge carrier generation and one of Al_2O_3 is to reduce the crystallinity of the composite polymer electrolyte. Fig. 8 shows the temperature dependence of ionic conductivity for the $(\text{PEO})_8\text{-LiClO}_4\text{-2 wt.\% BaTiO}_3\text{-Al}_2\text{O}_3$ composite electrolyte. Over the temperature range studied, the $(\text{PEO})_8\text{-LiClO}_4\text{-2 wt.\% BaTiO}_3\text{-10 wt.\% Al}_2\text{O}_3$ composite polymer electrolyte has the highest conductivity. In this figure, an abrupt decrease in ionic conductivity is not observed in the temperature range considered. This result is due to the fact that the addition of fine ceramic powder enhances the degree of amorphocity of the polymer electrolytes, as explained in the above DSC results. Therefore, the $(\text{PEO})_8\text{-LiClO}_4\text{-2 wt.\% BaTiO}_3\text{-}$

Table 2

DSC result of the composite polymer electrolyte $(\text{PEO})_8\text{-LiClO}_4\text{-BaTiO}_3\text{-Al}_2\text{O}_3$ activated acid

BaTiO ₃ (2 wt.%) and Al ₂ O ₃ activated acid (wt.%)	T _g (°C)	T _m (°C)	ΔH _m (J/g)	Crystallinity (%)
8	-29.5	68.5	1.49	0.73
10	-27.8	69.7	0.21	0.10
12	-28.3	71.7	0.45	0.22
14	-28.2	77.6	0.60	0.29

Al_2O_3 composite polymer electrolyte plays like an amorphous polymer electrolyte (Table 2).

4. Conclusions

The addition of the inorganic filler (Al_2O_3 —activated acidic and neutral) enhances the electrochemical stability of the PEO-based polymer electrolyte. The enhancement is associated with the hydrogen bonding between surface group of Al_2O_3 and perchlorate anion. An improvement of the ionic conductivity for the composite polymer electrolyte prepared with two fillers (Al_2O_3 and BaTiO_3) is related to both the reduction of crystallinity by the Al_2O_3 and the increase of charge carrier concentration by the BaTiO_3 .

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