

Characterization of composite electrolytes based on a hyperbranched polymer

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Abstract

Composite polymer electrolytes composed of a hyperbranched poly[bis(triethylene glycol)benzoate] with terminal acetyl groups, $\text{LiN}(\text{CF}_3\text{SO}_2)_2$ as a lithium salt, and an inert ceramic filler such as $\alpha\text{-LiAlO}_2$ or $\gamma\text{-LiAlO}_2$ were prepared by solvent casting method. Addition of an appropriate amount of the fillers to fully amorphous pristine polymer electrolytes led to an increase in ionic conductivities and lithium ion transference numbers. All composite polymer electrolytes exhibited good compatibility with a lithium metal electrode, and also, addition of fillers improved their mechanical performance. The $\alpha\text{-LiAlO}_2$ filler was effective for improving the electrochemical compatibility with a lithium metal electrode, and the $\gamma\text{-LiAlO}_2$ filler was effective for enhancing the mechanical properties of the pristine polymer electrolytes. © 2000 Elsevier Science S.A. All rights reserved.

Keywords: Hyperbranched polymer; Ceramic fillers; Composite polymer electrolytes; Compatibility; Mechanical property; Electrochemical stability

1. Introduction

Application of polymer electrolytes to rechargeable lithium or lithium ion batteries nowadays has attracted much attention. Polymer electrolytes have been proposed for the realization of plastic-like, thin-layer type of batteries owing to their unique characteristics and promising performances [1,2]. At the beginning of this area, most efforts were made to investigate lithium ion conducting polymer electrolytes based on a linear poly(ethylene oxide) (PEO) because of its easy coordination with alkali metal ions. However, such problems as the unsatisfied morphological characteristics and insufficient mechanical property of linear PEO polymer electrolytes in high-temperature regions have been proposed for practical applications of the polymer electrolytes. To overcome these problems, composite polymer electrolytes with inert ceramic fillers, initially explored by Weston and Steele [3], followed by many researchers, have been demonstrated as one of the

effective candidates for fully solid lithium batteries, and recently it has been greatly developed [4–6]. Such composite polymer electrolytes showed improvements of interfacial stability with electrodes and mechanical properties and even an increase in lithium ionic conductivity.

It has been well established that, in solvent-free dry polymer electrolytes, the ionic conduction takes place predominantly in the amorphous region and the glass transition temperature of the polymer electrolytes might determine the ion mobility in the polymer to a great extent [7]. Recently, in addition to composite polymer electrolytes based on linear PEO, hyperbranched ion conductive polymeric materials have been prepared in order to find polymer electrolytes with novel physical and/or mechanical properties applicable for lithium batteries. One of interesting examples is a dendritic macromolecule with a large number of branching points, which results in a three-dimensional shape. Cloutet et al. [8,9] has reported the stepwise synthesis of comburst macromolecules containing a central polystyrene layer surrounded by a PEO layer. Moreover, Hawker et al. [10] and us [11] have prepared hyperbranched poly(ethylene glycol) derivatives containing diethylene and triethylene glycols and 3,5-dioxybenzoate branching units. All these hyperbranched polymers were demonstrated to be useful as polymer elec-

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trolytes because they have glass transition temperatures below room temperature and do not show melting points, that is, no detrimental effect due to crystallization. Up to now, investigations have been focused mainly to thermal and electrochemical characterizations in these materials [10–13], but not to their mechanical performances. For the purpose of practical applications of these hyperbranched polymer electrolytes for lithium batteries, it is also essential to improve their mechanical properties.

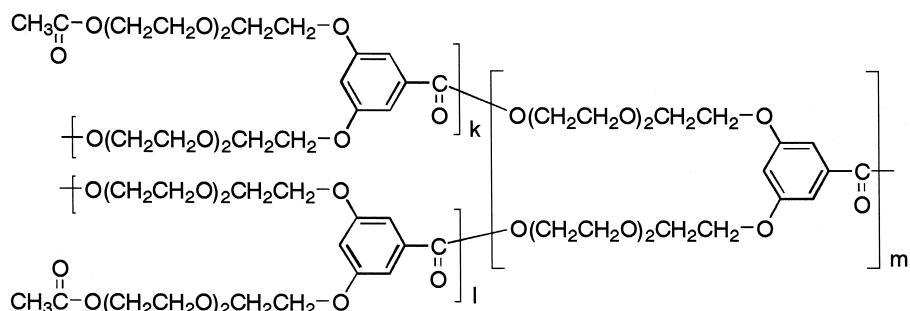
In this work, we investigated preparation of composite polymer electrolytes composed of hyperbranched poly[bis(triethylene glycol)benzoate] with terminal acetyl groups, $\text{LiN}(\text{CF}_3\text{SO}_2)_2$, and a lithium aluminate with alpha or gamma phase ($\alpha\text{-LiAlO}_2$ or $\gamma\text{-LiAlO}_2$) in various particle sizes, and effect of ceramic fillers on thermal

property, ion conduction, and electrochemical and mechanical performances in the composite polymer electrolytes.

2. Experimental

2.1. Materials

A hyperbranched polymer, poly[bis(triethylene glycol)benzoate] with terminal acetyl groups, was prepared according to the method reported previously [11] and its chemical structure is shown below, where a unit inside the bracket represents the repeat unit of the polymer that contains nine oxygen atoms.



Molecular weight of the hyperbranched polymer was determined by gel permeation chromatography to be 25000. $\alpha\text{-LiAlO}_2$ (10–20 nm in size) and $\gamma\text{-LiAlO}_2$ (0.1–0.2 μm in size), prepared by solid state reactions of lithium carbonate with alumina at 700–900°C for 5 h and 900–1100°C for 2 h, respectively, were used as ceramic fillers for composite polymer electrolytes in this work. Particle size of the fillers was determined by TEM measurements. Commercial lithium perchlorate (LiClO_4), lithium tetrafluoroborate (LiBF_4), and lithium trifluoromethanesulfonimide ($\text{LiN}(\text{CF}_3\text{SO}_2)_2$) were used without further purification except for drying 120°C and kept in a glove box.

2.2. Preparation of composite polymer electrolytes

Preparation of composite polymer electrolytes was carried out in an argon-filled glove box kept at a dew point of -95°C to avoid moisture contamination. Given amounts of hyperbranched polymer and lithium salt as LiClO_4 , LiBF_4 , or $\text{LiN}(\text{CF}_3\text{SO}_2)_2$ were dissolved in a purified acetonitrile and to the resulting solution was added an appropriate amount of a filler, and then further magnetically stirred until a homogeneous slurry was achieved. The

slurry was poured on a Teflon sheet and then the solvent was evaporated slowly at room temperature to obtain composite polymer electrolytes as films. All samples were finally dried under vacuum at 110°C overnight by using electric furnace equipped in a glove box, and then separated from the Teflon sheet and stored inside a glove box.

2.3. Measurements

Glass transition temperatures (T_g) of hyperbranched polymer and composite polymer electrolytes were determined by the differential scanning calorimetry (DSC) recorded on a Rigaku instrument operated under nitrogen. The 10–15-mg amount of samples was typically weighed, loaded in an aluminum pan, and then sealed. The sealed aluminum pan was heated to 150°C and quenched at -100°C , and then heated up again to 100°C at a heating rate of 10°C/min to record the DSC curves.

Conductivities of composite polymer electrolytes were measured with a two probe method after the samples were fixed inside a Teflon O-ring spacer with known thickness and sandwiched between two polished stainless steel (SS) discs acting as ion-blocking electrodes and set in a thermo-

stat oven chamber. A spring-loaded and gas-tight two-probe conductivity jig was employed for above purpose. A Teflon O-ring spacer was used to prevent short-circuiting and to maintain a fixed distance between electrodes during measurement at higher temperatures because the sample is soft and flexible under pressure. All AC impedance measurements were made by using Solartron 1260 frequency response analyzer over a frequency range of 1 Hz to 1 MHz and a temperature range of 25–115°C with amplitude of 10 mV. In order to satisfy interface contact, all samples were first kept at 80°C for at least 2 h and then cooled to room temperature for the measurements. At each temperature, the sample was kept inside an oven for 1 h before measurement to be allowed to equilibrate.

Electrochemical stability windows of the composite polymer electrolytes were evaluated by a linear sweep voltammetry at a scan rate of 10 mV/s by using a Li/composite polymer electrolyte/SS cell, where a lithium metal and an SS were used as a counter electrode and a working blocking electrode, respectively. A Solartron Schlumberger 1287 electrochemical interface was used to run the measurements.

Mechanical strength of pristine polymer electrolytes and composite polymer electrolytes were evaluated by thermal creep behavior of the impedance of the electrolytes at 80°C as a function of storage time. The samples for evaluation were sandwiched between ion-blocking SS electrodes and kept under pressure produced by the springs inside the jig.

3. Results and discussion

3.1. Bulk characteristics

Temperature dependence of the ionic conductivity for composite polymer electrolytes based on $\text{LiN}(\text{CF}_3\text{SO}_2)_2$ at a Li/O ratio of 1/9 was measured at $\alpha\text{-LiAlO}_2$ (10–20

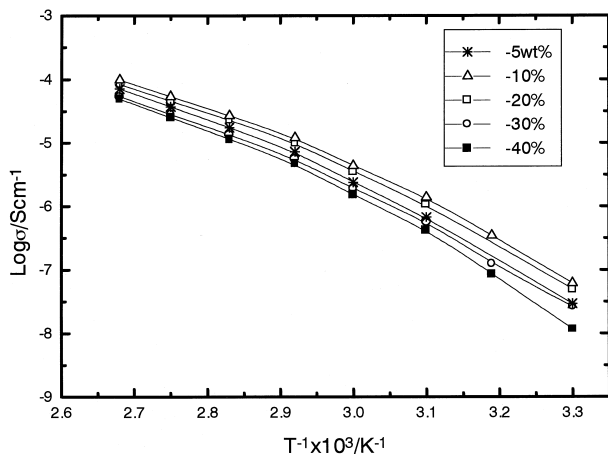


Fig. 1. Arrhenius plots for the composite polymer electrolytes at various $\alpha\text{-LiAlO}_2$ contents.

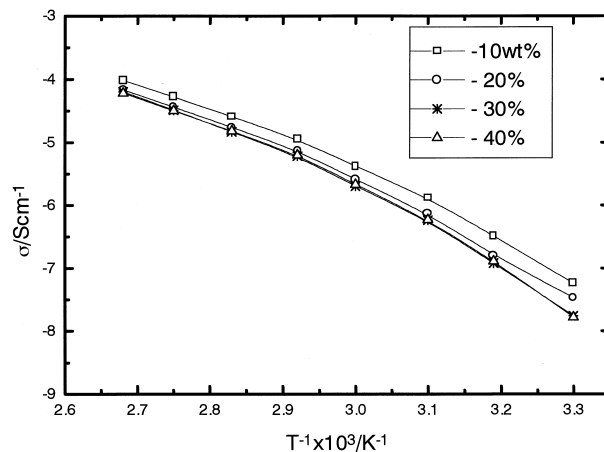


Fig. 2. Arrhenius plots for the composite polymer electrolytes at various $\gamma\text{-LiAlO}_2$ contents.

nm) contents of 5, 10, 20, 30, and 40 wt.% and at $\gamma\text{-LiAlO}_2$ (0.1–0.2 μm) contents of 10, 20, 30, and 40 wt.%, and the results are shown in Figs. 1 and 2, respectively. The ionic conductivities of all samples increase in a monotonic fashion with increasing temperature and obey the Vogel–Tammann–Fulcher relationship proposed for amorphous polymers [14–16]. This indicates that the ceramic fillers do not affect fully amorphous feature of the pristine polymer electrolytes except for only slight influence on T_g values as listed in Table 1.

The fully amorphous feature of the pristine polymer electrolyte and of the composite polymer electrolytes with the $\alpha\text{-LiAlO}_2$ or $\gamma\text{-LiAlO}_2$ fillers was also demonstrated by evaluating their electrical characteristics. After heating at 100°C and then quenched at 30°C, the ionic conductivities of the pristine polymer electrolyte and of the composite polymer electrolytes with 10 wt.% $\alpha\text{-LiAlO}_2$ content or 10 wt.% $\gamma\text{-LiAlO}_2$ content were monitored in a storage period for 1 week. No significant change in their conductivities was observed, indicating that no obvious crystallization occurs in all samples.

Effect of a filler content on the ionic conductivity at 80°C of the composite polymer electrolytes is shown in

Table 1

T_g values of pristine polymer electrolyte and composite polymer electrolytes with $\text{LiN}(\text{CF}_3\text{SO}_3)_2$ at various amounts of $\alpha\text{-LiAlO}_2$ or $\gamma\text{-LiAlO}_2$

Amount of Ceramic filler (wt.%)	T_g (°C)		
	Pristine polymer	Composite with $\alpha\text{-LiAlO}_2$	Composite with $\gamma\text{-LiAlO}_2$
0	–12.5	–	–
5	–	–15.0	–
10	–	–5.0	–8.0
20	–	–12.5	–8.0
30	–	–15.0	–8.5
40	–	–15.0	–8.0

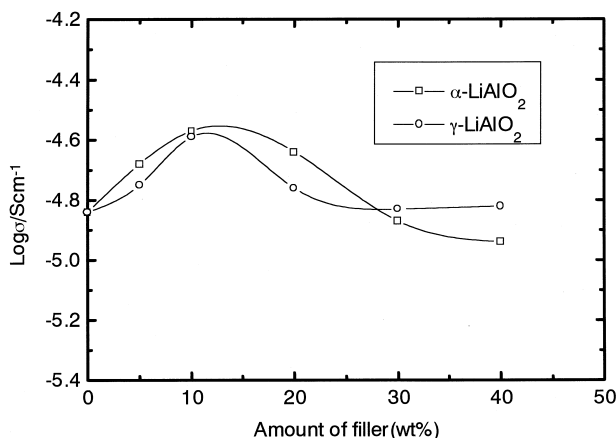


Fig. 3. Ionic conductivity of the composite polymer electrolytes as a function of the amount of α -LiAlO₂ and γ -LiAlO₂ fillers at 80°C.

Fig. 3. With an increase in filler contents for both composite polymer electrolyte systems, the ionic conductivities of both systems increase, reach a maximum value at a filler content of about 10 wt.%, and then decrease to that of the pristine polymer electrolyte. For the α -LiAlO₂ filler, the ionic conductivity at a content of 40 wt.% is lower than that of the pristine polymer electrolyte. However, for filler contents in the range of 5–20 wt.%, addition of the filler shows a distinct effect on an enhancement of the ionic conductivity, and also the α -LiAlO₂ filler seems to be more effective on the enhancement than the γ -LiAlO₂ one. Here, profile in Fig. 3 could be explained as follows: Electrical characteristics of the composite polymer electrolytes should be attributed to both kinds of phase of the ceramic fillers and surface properties. The α -LiAlO₂ filler is known to be a non-conductive phase for lithium ions, but it would have high surface activity because of a larger surface area due to its nanostructure. On the other hand, the γ -LiAlO₂ filler is known to be a conductive phase for lithium ions, but it has less surface activity compared to the α -LiAlO₂ one because of a smaller surface area due to its large particle size. Therefore, at lower filler contents, an interface between the polymer and the filler would contribute mainly to enhancement of total conductivity but, at higher filler contents, continuous non-conductive phase built up by the ceramic fillers would block transport of lithium ions.

Capuano et al. [6] reported a similar effect of the γ -LiAlO₂ filler on the conductivity of the (PEO)₈LiClO₄ composite. However, the temperature dependence of its ionic conductivity is very different from that of the composite polymer electrolytes based on hyperbranched polymer. Recently, Croce et al. [17] also reported the nanocomposite polymer electrolytes composed of a PEO-LiClO₄ electrolyte and a nanosized titanium oxide (TiO₂) or alumina (Al₂O₃) filler, where addition of both ceramic fillers increased the ionic conductivity of the composite polymer electrolytes to 10⁻⁵ S/cm, the value of which was about

two orders of magnitude higher than that of the pristine polymer electrolyte. It was found that the nanosized fillers would act as solid plasticizers for linear PEO based electrolytes and also kinetically inhibit crystallization of the ionic conductive amorphous phases. This effect of fillers was explained on the basis of high surface area of the dispersed fillers. Similar behavior is also reported in other references for composite polymer electrolytes based on linear PEO [18–20]. As the hyperbranched polymer in our work is fully amorphous, no crystallization effect would exist. So, influence of ceramic fillers on the ionic conductivity at ambient temperature for hyperbranched polymer systems is not so effective as crystalline polymer systems.

A lithium ion transference number (t_{Li^+}) in composite polymer electrolytes was evaluated by using cells with symmetrical non-blocking lithium metal electrodes according to the method reported by Bruce et al. [21,22] and calculated by the following equation:

$$t_{\text{Li}^+} = \frac{I_s(\Delta V - I_0 R_0)}{I_0(\Delta V - I_s R_s)}$$

where ΔV is a DC polarization applied to the cell, I_0 and I_s are initial and steady-state currents during the polarization, respectively, and R_0 and R_s are resistance of the cell, determined by AC impedance analysis, before and after the DC polarization process, respectively. The t_{Li^+} values of the pristine polymer electrolyte and of composite polymer electrolytes are summarized in Table 2, together with t_{Li^+} values of pristine polymer electrolytes with LiClO₄ and with LiBF₄ for comparison. Among the polymer electrolytes with three lithium salts, the polymer electrolyte with LiN(CF₃SO₂)₂ showed the highest transference number of 0.41. Moreover, for the composite polymer electrolytes based on LiN(CF₃SO₂)₂, t_{Li^+} values of 0.49 and of 0.50 were obtained for the α -LiAlO₂ filler and for the γ -LiAlO₂ one, respectively. This indicates that addition of both fillers to the polymer electrolytes based on LiN(CF₃SO₂)₂ is beneficial to transport of cations.

Electrochemical stability in a wide range is one of key criteria of polymer electrolytes for practical battery applications. In order to know the electrochemical stability of

Table 2

Ionic conductivity (σ), lithium ion transference number (t_{Li^+}), and breakdown voltage for pristine polymer electrolytes and composite polymer electrolytes with LiClO₄, LiBF₄, and LiN(CF₃SO₂)₂ at 80°C

Salts	Li/O	σ (S/cm)	t_{Li^+}	Breakdown voltage (V)
LiClO ₄	1/6	7.5×10^{-5}	0.21	4.7
LiBF ₄	1/6	3.5×10^{-5}	0.26	5.1
LiN(CF ₃ SO ₂) ₂	1/9	1.53×10^{-5}	0.41	4.7
LiN(CF ₃ SO ₂) ₂	1/9	6.6×10^{-5}	0.49	4.7
+ 10 wt.% α -LiAlO ₂				
LiN(CF ₃ SO ₂) ₂	1/9	6.4×10^{-5}	0.50	4.7
+ 10 wt.% α -LiAlO ₂				

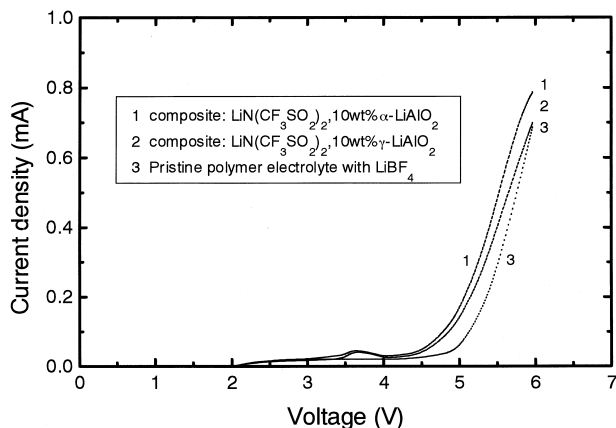


Fig. 4. Typical linear sweep voltammetry for the composite polymer electrolytes with the α -LiAlO₂ filler or with the γ -LiAlO₂ filler at 80°C. The scan rate is 10 mV/s.

the polymer electrolytes with LiClO₄, LiBF₄, and LiN(CF₃SO₂)₂ and their composite polymer electrolytes, linear sweep voltammetry measurements were carried out at 80°C at a scan rate of 10 mV/s by using an asymmetrical cell composed of SS as a working electrode and lithium metal as a counter electrode. Fig. 4 shows some typical current–voltage responses of the polymer electrolytes and the composite polymer electrolytes. Breakdown voltages as a measure of the electrochemical stability are summarized in Table 2. The polymer electrolyte with LiBF₄ exhibits the breakdown voltage higher than 5 V, indicating that it is the most electrochemically stable system among this work. The composite polymer electrolytes have also relatively high electrochemical stability as can be seen from the breakdown voltage of 4.7 V.

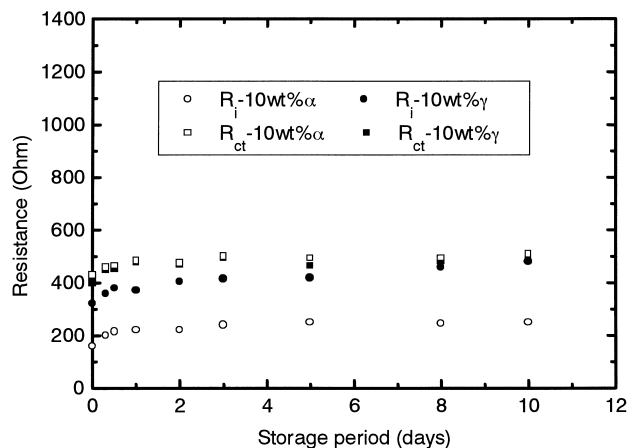


Fig. 6. Time dependence of passive layer resistance and charge transfer resistance of composite polymer electrolytes with various α -LiAlO₂ or γ -LiAlO₂ contents at 80°C.

3.2. Interface performance

Compatibility of polymer electrolytes with electrode materials is an important factor for applications of the polymer electrolytes to electrochemical devices. Impedance measurements by using a symmetrical Li metal/composite polymer electrolyte/Li metal cell kept under open-circuit conditions were carried out at 80°C in order to evaluate interfacial stability between the lithium metal and the polymer electrolytes. The impedance of the cell was monitored for 8 days and also a Teflon spacer was employed to keep a given thickness of the composite polymer electrolytes during the storage period. Fig. 5 shows a typical result obtained for the composite polymer electrolyte with 10 wt.% γ -LiAlO₂ content, where four different frequency regions were clearly observed. This impedance response is

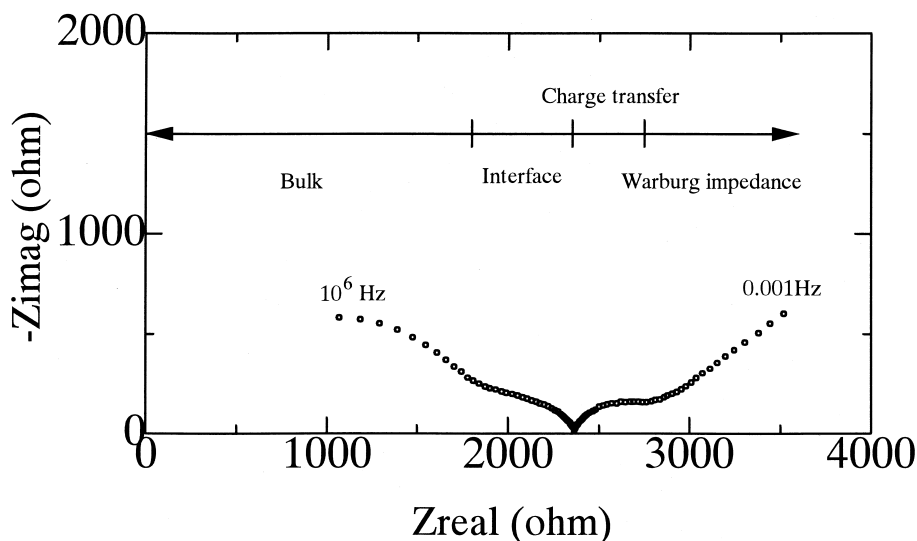


Fig. 5. Impedance response of the symmetrical lithium metal electrode cell composed of the composite polymer electrolyte with 10 wt.% γ -LiAlO₂ content stored at 80°C for 8 days.

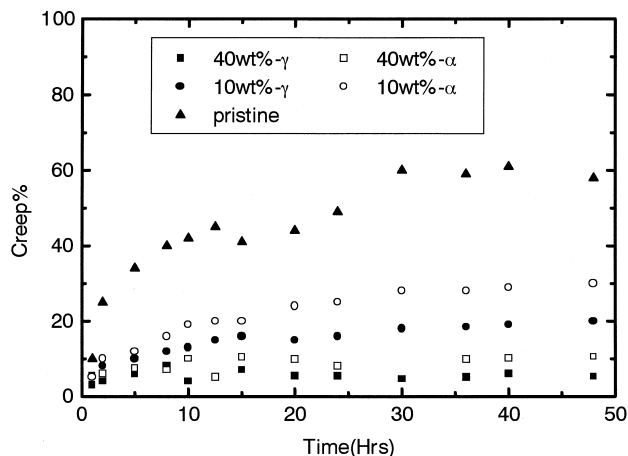


Fig. 7. Creep% vs. time of the pristine polymer electrolytes and the composite polymer electrolytes with the 10 and 40 wt.% α -LiAlO₂ contents and with the 10 and 40 wt.% γ -LiAlO₂ contents.

similar to that of composite polymer electrolytes based on linear crystalline PEO matrix [18,23]. The high-frequency region is assigned to the impedance of a continuous polymer phase (with the resistance of R_b), the followed semicircle is to the impedance of an interfacial passive layer between the composite polymer electrolyte and lithium metal (with resistance R_i), the semicircle at the followed lower frequency is to a charge transfer resistance (R_{ct}), and the linear part at the lowest frequency range is to the impedance relative to a diffusion process (Warburg impedance shown in Fig. 5), respectively.

Fig. 6 shows R_i and R_{ct} values at various storage times for the composite polymer electrolytes with 10 wt.% α -LiAlO₂ content or with 10 wt.% γ -LiAlO₂ content. The figure indicates that a stable interfacial passive layer between the composite polymer electrolyte and a lithium metal electrode is formed within a day and maintained during the followed storage period as can be seen from the almost constant value of R_i . Moreover, the passive layer formed on the lithium metal electrode exhibits a lower resistance in contact with the composite polymer electrolyte with the α -LiAlO₂ filler compared to that with the γ -LiAlO₂ filler, indicating that the former interfacial passive layer is more conductive. From this point, nanosized α -LiAlO₂ is considered to be a satisfactory ceramic filler for polymer electrolytes based on a hyperbranched polymer.

3.3. Thermal stability

It is well known that addition of inert ceramic fillers is an effective approach to improve mechanical performance of many kinds of polymer electrolytes [3,6,23]. Resistance of the polymer electrolytes is directly proportional to its thickness. Therefore, dimensional stability as the mechanical performance of the material can be estimated qualitatively by monitoring the resistance of the polymer elec-

trolytes. The percentage change in the thickness could be followed by the creep% defined as the following equation: $\text{creep}\% = (R' - R)/R \times 100\%$, where R and R' indicate an initial resistance and a resistance at any storage time, respectively. In Fig. 7, the thermal creep% change for the pristine polymer electrolyte and the composite polymer electrolytes are shown as a function of time. Addition of α -LiAlO₂ and γ -LiAlO₂ fillers depresses the creep% change to a lower extent, indicating that both fillers could be used as dimensional stabilizers. Moreover, action of the γ -LiAlO₂ filler is more effective than that of the α -LiAlO₂ one, especially at higher filler contents.

4. Conclusions

Both nanosized α -LiAlO₂ and γ -LiAlO₂ fillers improved mechanical properties of hyperbranched polymer electrolytes based on LiN(CF₃SO₂)₂. The γ -LiAlO₂ filler is more effective for an improvement of the mechanical strength compared to the α -LiAlO₂ one. However, the composite polymer electrolyte with the α -LiAlO₂ filler exhibited much better compatibility with a lithium metal electrode. Ceramic fillers could influence the conductivity of the fully amorphous pristine polymer electrolyte, and addition of 10 wt.% ceramic fillers gave the composite polymer electrolyte the highest ionic conductivity. Composite polymer electrolytes with the α -LiAlO₂ filler or with the γ -LiAlO₂ filler had favorable lithium ion transference number and electrochemical stability.

Acknowledgements

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