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Polystyrene-Al$_2$O$_3$ composite solid polymer electrolyte for lithium secondary battery

Yu-Jeong Lim[†], Yu-Ha An[†] and Nam-Ju Jo[*]

Abstract

In a common salt-in-polymer electrolyte, a polymer which has polar groups in the molecular chain is necessary because the polar groups dissolve lithium salt and coordinate cations. Based on the above point of view, polystyrene [PS] that has nonpolar groups is not suitable for the polymer matrix. However, in this PS-based composite polymer-in-salt system, the transport of cations is not by segmental motion but by ion-hopping through a lithium percolation path made of high content lithium salt. Moreover, Al$_2$O$_3$ can dissolve salt, instead of polar groups of polymer matrix, by the Lewis acid-base interactions between the surface group of Al$_2$O$_3$ and salt. Notably, the maximum enhancement of ionic conductivity is found in acidic Al$_2$O$_3$ compared with neutral and basic Al$_2$O$_3$ arising from the increase of free ion fraction by dissociation of salt. It was revealed that PS-Al$_2$O$_3$ composite solid polymer electrolyte containing 70 wt.% salt and 10 wt.% acidic Al$_2$O$_3$ showed the highest ionic conductivity of 9.78×10^{-5} Scm^{-1} at room temperature.

Keywords: polystyrene, Al$_2$O$_3$, solid polymer electrolyte, polymer-in-salt system, lithium secondary battery

Introduction

A lithium secondary battery using solid polymer electrolyte [SPE] is an attractive energy source for portable devices since the use of SPE makes the fabrication of safe batteries possible and permits the development of thin batteries with design flexibility. Most of the efforts to date have focused on poly(ethylene oxide) [PEO] as the host material for SPE [1-3]. However, it has a major drawback of having a low ionic conductivity (10^{-8} to 10^{-5} Scm^{-1}) at room temperature [4]. Thus, many researchers [5-7] have focused on the SPE consisting of the polymer with low glass transition temperature [T_g] and moderate concentrations of salt in order to overcome the low ionic conductivity of SPE, but high ambient conductivity has not yet been reached. Low ionic conductivity can be achieved from the fact that the ionic mobility strongly depends on the polymer segmental motion and that the cation transport number is low in the SPE at a high salt concentration. Therefore, new materials with unconventional conduction mechanisms are clearly needed [8].

In common SPEs, a polymer which has polar groups in the chain is necessary for electrolyte formation. The polar groups dissolve lithium salt and coordinate cations. The cations can move between coordinating sites in one chain or in neighboring chains, promoted by the segmental motion [9]. From this point of view, a polymer which has nonpolar groups is not suitable for the polymer matrix in common SPEs. However, in this new composite SPE consisting of polystyrene [PS] and having nonpolar groups, LiCF$_3$SO$_3$ and Al$_2$O$_3$ with polymer-in-salt system, the transport of cations is done by ion-hopping through an ion percolation path made of high content lithium salt instead of segmental motion. Moreover, Al$_2$O$_3$ can cause conductivity enhancement depending on the nature of the filler surface group [10]. In this work, the ionic conductivity of PS-Al$_2$O$_3$ composite SPE according to the salt content was checked, and the effect of Al$_2$O$_3$ type and content on ion conduction properties in PS-based composite SPE was investigated.

Experimental section
Materials

Polystyrene (Sigma-Aldrich Corporation, St. Louis, MO, USA) with a number average molecular weight (M_n) of 170,000 was used as received without undergoing

* Correspondence: namjujo@pusan.ac.kr
† Contributed equally
Department of Polymer Science and Engineering, Pusan National University, Jangjeon-dong, Geumjeong-gu, Busan, 609-735, South Korea

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further purification process. As salt, $LiCF_3SO_3$ (Sigma-Aldrich Corporation) was dried and stored in a desiccator under nitrogen. Three types of aluminum oxides [Al_2O_3] (Sigma-Aldrich Corporation) with acidic, neutral, and basic surface groups as fillers were also used. As an organic solvent, *N*-butyl acetate (Junsei Chemical Co., Ltd., Chuo-ku, Tokyo, Japan) was used in order to dissolve the materials.

Preparation of PS-based composite SPE films

An appropriate amount of PS was introduced into *N*-butyl acetate and stirred for 24 h; after that, a definitive amount of $LiCF_3SO_3$ was added to the solution and stirred again for 24 h. At the same time of the PS/$LiCF_3SO_3$ solution preparation, 5, 10, 15, and 20 wt.% Al_2O_3 were added to *N*-butyl acetate. Then, the solution was sonicated for 10 min and stirred for 24 h for dispersion. PS-based SPE was prepared by mixing the PS/$LiCF_3SO_3$ and Al_2O_3 solutions for 4 days. The solutions were directly cast on 3×3 cm^2 stainless steel plates after mixing and then allowed to dry in a vacuum oven for 5 days at 40°C.

Characterization

Ionic conductivity of the sample was measured by Gamry Instruments' (Warminster, PA, USA) Reference 600 impedance analyzer. Deconvolution of the composite bands of the Fourier transform infrared [FT-IR] spectra was accomplished by the best fits of constituent Gaussian peaks, and the fractions of salt forms were calculated by the peak fitting program of Origin 7.0 software (OriginLab Corporation, Northampton, MA, USA) to analyze the change of salt forms in SPEs. Scanning electron microscopy [SEM] was also used to observe the morphology of the specimen.

Results and discussion
Ionic conductivity
Ionic conductivities of PS-based composite SPEs with salt content

Figure 1 shows the ionic conductivities of PS-based SPEs with 0, 5, 10, 15, and 20 wt.% Al_2O_3 and various salt contents. In the common SPEs, the ionic conductivity increased with the salt content up to its peak and then the ionic conductivity decreased because the
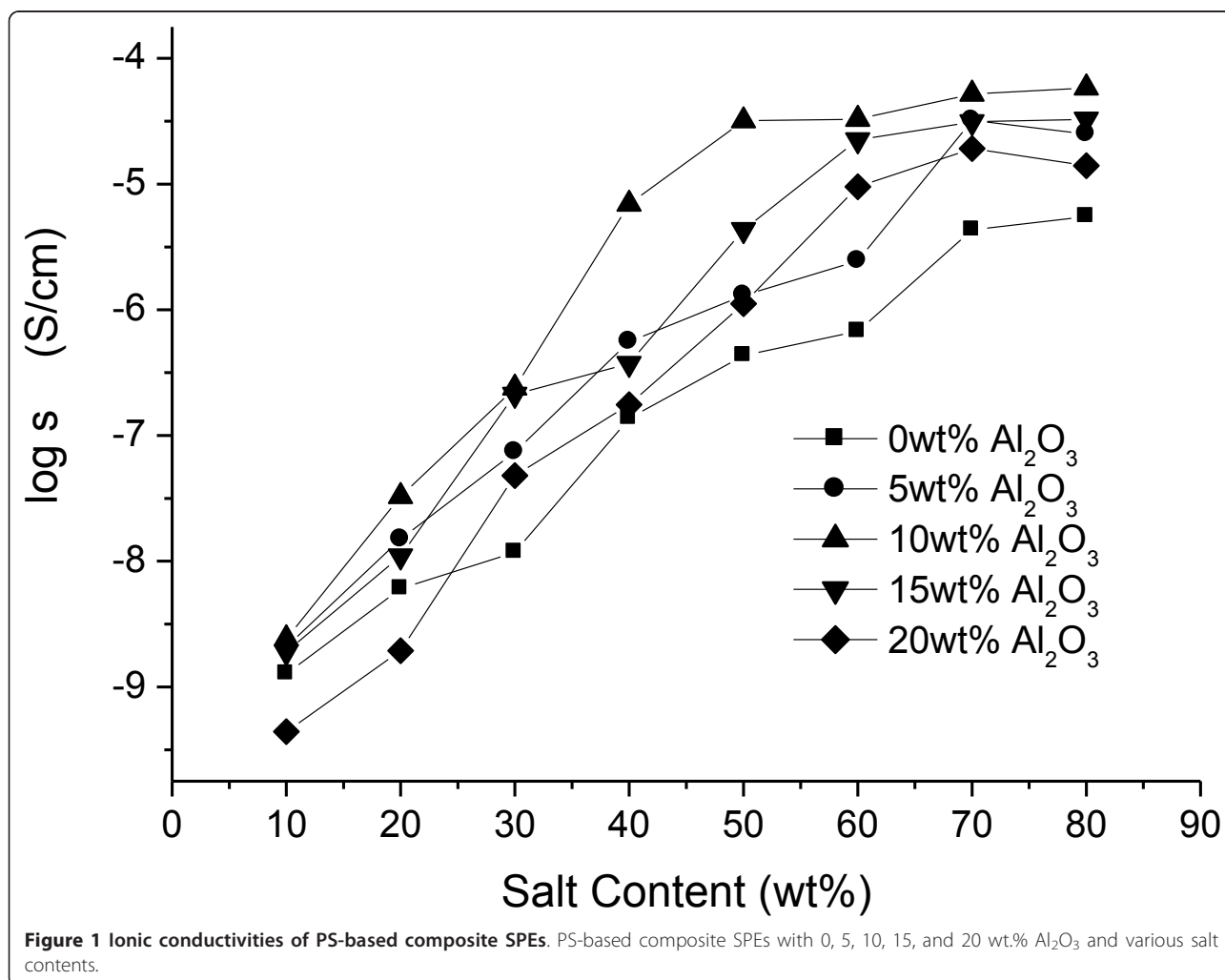

Figure 1 Ionic conductivities of PS-based composite SPEs. PS-based composite SPEs with 0, 5, 10, 15, and 20 wt.% Al_2O_3 and various salt contents.

polymer mobility decreased and T_g of the polymer increased as the salt content increased. However in PS-based composite SPEs, there is no decrease in the ionic conductivity because PS does not contribute to the dissociation of salts and transport of cations. The transport of cations is done by ion-hopping through the ion percolation path made of high content of salt instead of segmental motion, so the ionic conductivities increased with salt content.

Moreover, Al_2O_3 can dissolve the lithium salt instead of the polar groups in the polymer matrix using Lewis acid-base interactions between the surface group of Al_2O_3 and salt [10]. The sample consisting 70 wt.% salt and 10 wt.% Al_2O_3 shows the highest ionic conductivity of 5.83×10^{-5} Scm^{-1}.

Ionic conductivity of PS-based composite SPE according to Al_2O_3 type and content

Figure 2 shows the ionic conductivities of PS-based composite SPEs consisting 70 wt.% salt and different types of Al_2O_3. The ionic conductivity increased up to 10 wt.% Al_2O_3 and then decreased, irrespective of the Al_2O_3 type. As the content of Al_2O_3 increased over 10

wt.%, the aggregates of Al_2O_3 was observed in all types of Al_2O_3. This is related to the decrease in ionic conductivity at above 10 wt.% Al_2O_3. Among the samples, the maximum ionic conductivity was found for SPE with acidic Al_2O_3, and the ionic conductivity decreased in the order of SPEs with acidic, neutral, and basic Al_2O_3. This tendency may be related to the number of free ions by dissociation of salt. Salt can be dissociated by the interaction between salt anions and surface OH groups of Al_2O_3. Acidic Al_2O_3 has had the most OH groups which interact with salt, so the SPE having acidic Al_2O_3 can have the highest free-ion numbers. Neutral Al_2O_3 has had the second amount of surface OH groups, and basic Al_2O_3 has had the least surface OH groups. Thus, the ionic conductivity decreased in that order, and the highest ionic conductivity of 9.78×10^{-5} Scm^{-1} could be obtained at 10 wt.% acidic Al_2O_3.

FT-IR evidence of dissociated ions

In the polymer-in-salt system, ion clouds made of ion aggregates and ion pairs play an important role in ion conduction [11], so it is necessary to investigate the
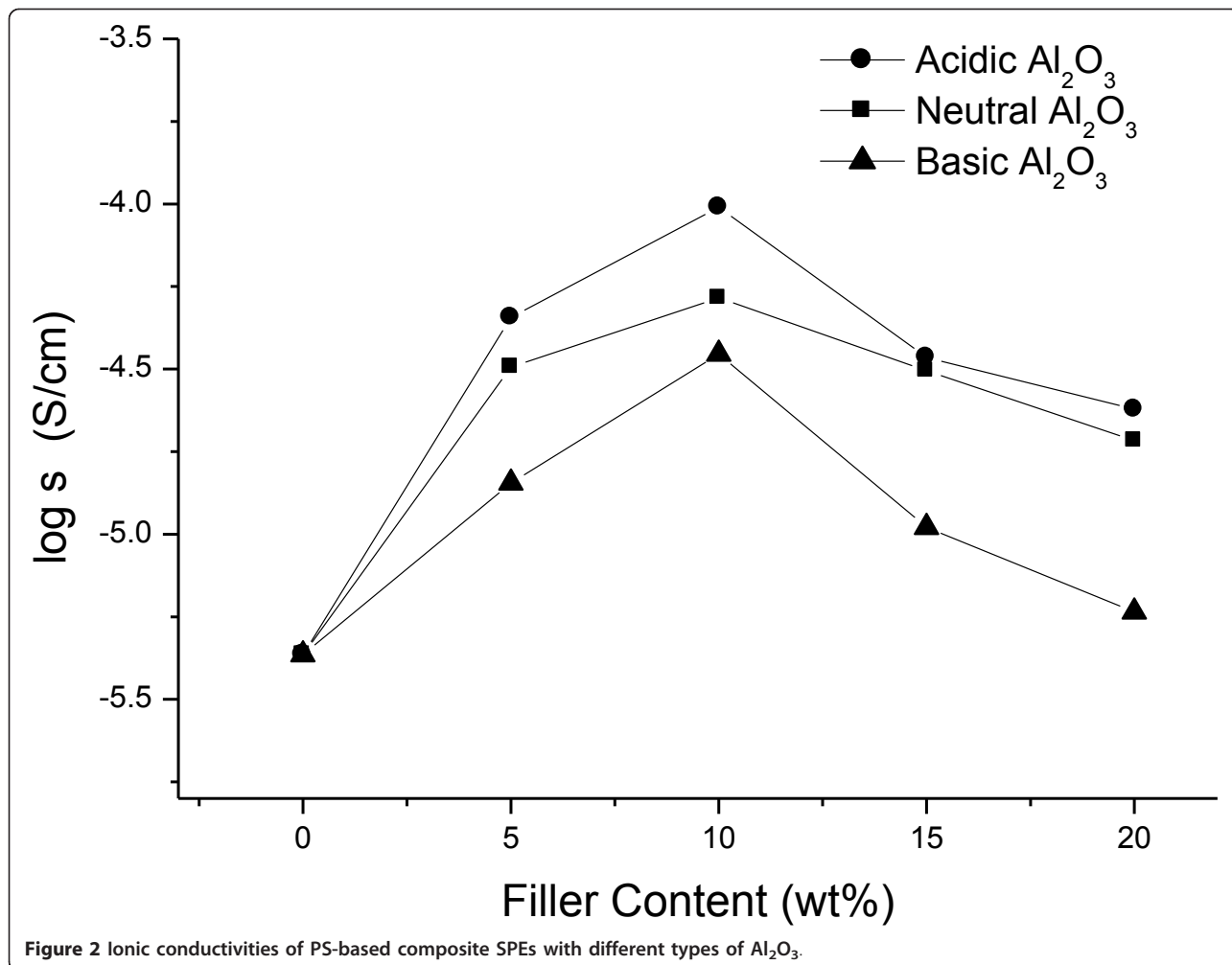

Figure 2 Ionic conductivities of PS-based composite SPEs with different types of Al_2O_3.

Table 1 Some band assignments for triflate species

Band	Wave number (cm^{-1})	Assignment
$v_s(SO_3)$	1,032	Free Tf$^-$ ions, solvent-separated pairs
	1,040	Ion pairs (LiTf), LiTf$_2^-$, LiTf$_3^{2-}$
	1,051	Li$_2$Tf$^+$ aggregate
	1,062	Li$_3$Tf^{2+} aggregate

change of salt form of the SPE films as salt concentrations increase. FT-IR spectra have confirmed the presence of ion pairs and aggregates in SPEs based upon poly(propylene oxide) [12-16] and PEO [17-24]. A clear distinction between free (dissociated) ions, contact ion pairs, and more aggregates may be observed in the vibrational spectra of the internal mode of anions, such as the triflate anion [Tf$^-$]. Ion association occurs at the SO$_3$ end of the anion; thus, the symmetric SO$_3$ stretching mode is highly sensitive to change in the coordination state of the anion. Band fitting of these regions has provided information pertaining to the types of aggregation and strengths of ionic interactions occurring in the SPEs.
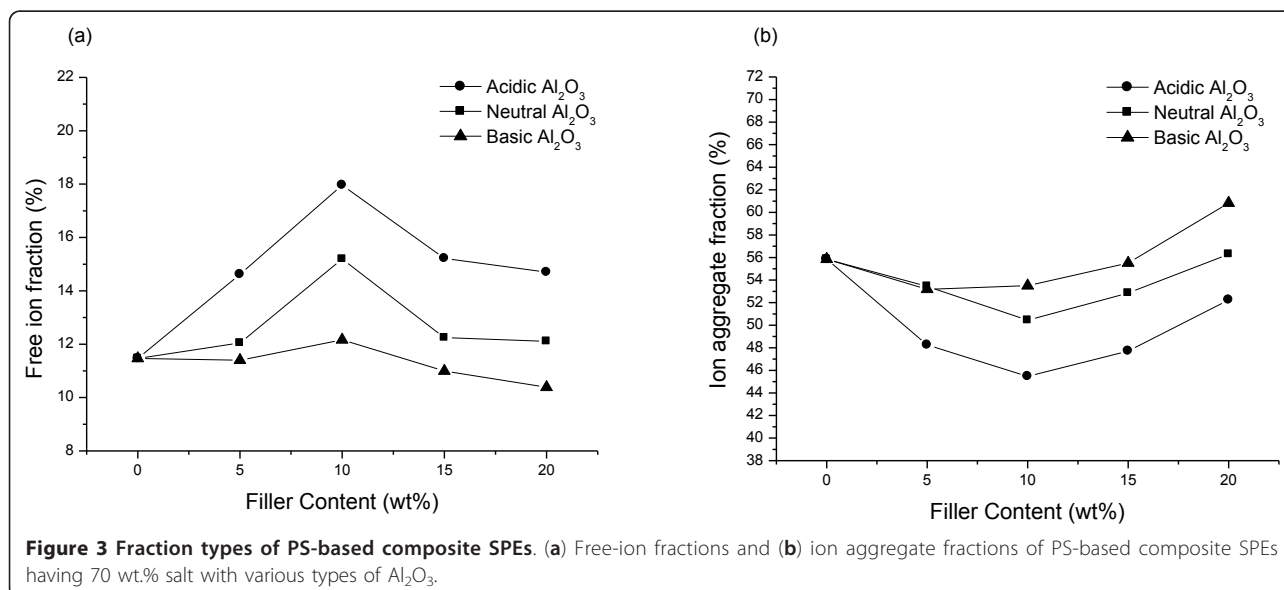
Above a certain salt concentration, the symmetric SO$_3$ stretching mode is found to consist of two or more peaks. The different anion environments may be attributed to ion association, in consideration of the nondegenerate A$_1$ symmetry of this mode. The symmetry of an anion is lowered by coordination to a cation. Band fitting of the SO$_3$ regions reveals the peak components which arise from various ion aggregates. Higher frequency components, corresponding to higher aggregates, may be observed with further increase in salt concentration [25]. Assignments for bands observed in

the symmetric SO$_3$ stretching regions are summarized in Table 1[18,26].

When Al$_2$O$_3$ is added, the anions have greater affinity toward the Al$_2$O$_3$ surface acid groups than the cations. Due to the polarizability of the Tf$^-$, a strong affinity can be expected between the Tf$^-$ and the Al$_2$O$_3$ surface acid groups. It results in the dissociation of the salt and makes the cations free [10,27]. The free-ion and ion aggregate fractions of PS-based composite SPEs having 70 wt.% salt with various types of Al$_2$O$_3$ are shown in Figure 3. As shown in Figure 3, for all cases, the free-ion fractions of SPE consisting 70 wt.% salt increased until the content of Al$_2$O$_3$ reached 10 wt.%. By adding more Al$_2$O$_3$, the free-ion fraction decreased. SPE with acidic Al$_2$O$_3$ having the most OH groups which interact with salt had the highest free-ion fraction. The free-ion fraction decreased in the order of SPEs with acidic, neutral, and basic Al$_2$O$_3$. This tendency was similar to that of the ionic conductivity. From this result, it could be known that the ionic conductivity was mainly influenced by the free-ion fraction. Also, the highest ionic conductivity could be obtained in the case of SPE with 10 wt.% acidic Al$_2$O$_3$ whose free-ion fraction was the highest and ion aggregate fraction was the lowest.

SEM images

Figure 4 shows the SEM images of PS-based composite SPEs with Al$_2$O$_3$ content. From the SEM images, we can see that the fillers are well dispersed, and there are no aggregates of Al$_2$O$_3$ until 10 wt.% Al$_2$O$_3$ is reached, but as more Al$_2$O$_3$ was added, the aggregates of fillers which might disturb the ion transport were observed. Thus, the ionic conductivity of PS-based composite

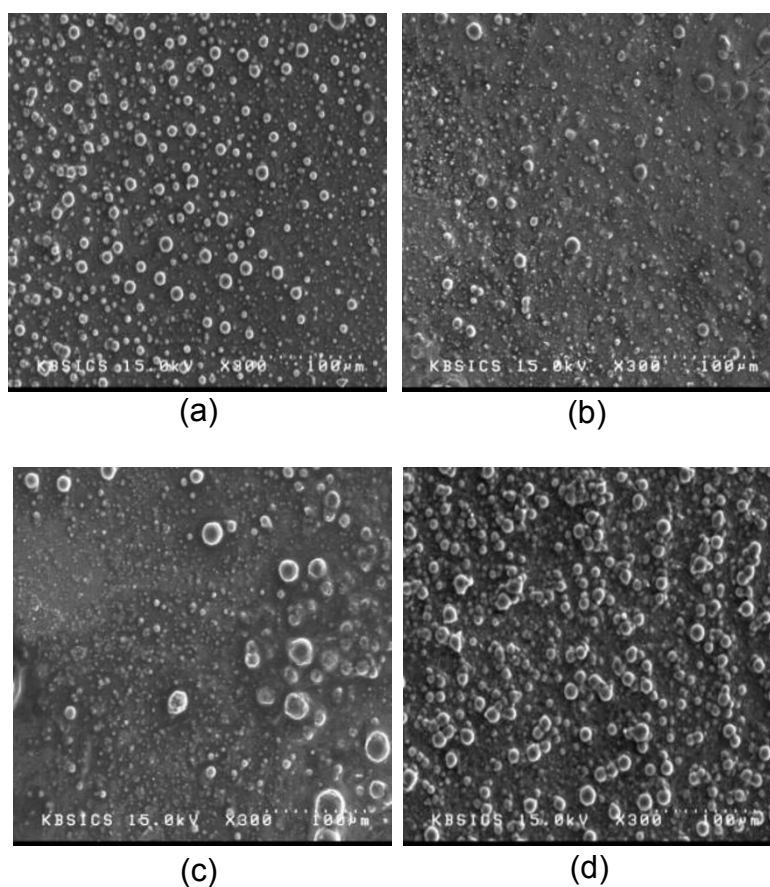**Figure 3 Fraction types of PS-based composite SPEs**. (**a**) Free-ion fractions and (**b**) ion aggregate fractions of PS-based composite SPEs having 70 wt.% salt with various types of Al$_2$O$_3$.

Figure 4 SEM images of PS-based composite SPEs. PS-based composite SPEs with (**a**) 5 wt.%, (**b**) 10 wt.%, (**c**) 15 wt.%, and (**d**) 20 wt.% Al_2O_3 contents at a magnification of ×300.

SPEs, as shown in Figure 2, increased up to 10 wt.% Al_2O_3, and then the ionic conductivity decreased.

Conclusions

Composite SPEs based on PS, $LiCF_3SO_3$, and Al_2O_3 were prepared, and the effect of the Al_2O_3 type and content on ion conduction properties of SPEs was investigated. As the salt content increased, the ionic conductivities increased continuously. In contrary of the common SPE, PS-based composite SPE has no decrease in ionic conductivity because PS does not contribute to the dissociation of salts and transport of cations. As the Al_2O_3 content increased, the ionic conductivity increased until the content of Al_2O_3 reached 10 wt.%. Then, the sample consisting 70 wt.% salt and 10 wt.% Al_2O_3 shows the highest ionic conductivity of 5.83×10^{-5} Scm^{-1}. The maximum ionic conductivity was found in SPE with acidic Al_2O_3. The ionic conductivity decreased in the order of SPEs with acidic, neutral, and basic Al_2O_3. This tendency may be related to the number of free ions by dissociation of salt. The SEM images show that the fillers are well dispersed, and there is no aggregate of fillers until 10 wt. % Al_2O_3 is reached. On the other hand, as more Al_2O_3 contents were added, the aggregates of fillers appeared. It seems that the aggregates of fillers disturb the ion transport, so the ionic conductivity increased up to 10 wt.% Al_2O_3, and then the ionic conductivity decreased. The highest ionic conductivity of 9.78×10^{-5} Scm^{-1} could be obtained at 10 wt.% acidic Al_2O_3.

Authors' contributions

YJL and YHA carried out the measurements and analysis of data. NJJ commented on various points and drafted the manuscript. All authors read and approved the final manuscript.

Competing interests

The authors declare that they have no competing interests.

References

1. Fenton DE, Parker JM, Wright PV: **Complexes of alkali metal ions with poly (ethylene oxide).** *Polymer* 1973, **14**:589.
2. Wright PV: **Electrical conductivity in ionic complexes of poly (ethylene oxide).** *Br Polym J* 1975, **7**:319-327.
3. Armand MB, Chabagno JM, Duclot MJ: *Fast Ion Transport in Solids* Amsterdam: Elsevier; 1979.
4. Kim S, Park SJ: **Interlayer spacing effect of alkylammonium-modified montmorillonite on conducting and mechanical behaviors of polymer composite electrolytes.** *J Colloid Interface Sci* 2009, **332**:145-150.
5. Lee JY, Lee YM, Bhattacharya B, Nho YC, Park JK: **Solid polymer electrolytes based on crosslinkable polyoctahedral silsesquioxanes (POSS) for room temperature lithium polymer batteries.** *J Solid State Electrochem* 2010, **14**:1445-1449.
6. Jia J, Lia B, Zhong WH: **Simultaneously enhancing ionic conductivity and mechanical properties of solid polymer electrolytes via a copolymer multi-functional filler.** *Electrochim Acta* 2010, **55**:9075-9082.
7. Jeong SK, Jo NJ: **The effect of silicate layers on electrochemical properties in nanocomposite solid polymer electrolytes.** *Key Eng Mater* 2007, **336-338**:526-529.
8. Wei X, Shriver DF: **Highly conductive polymer electrolytes containing rigid polymers.** *Chem Mater* 1998, **10**:2307-2308.
9. Gray FM: *Polymer Electrolytes: Electroactive Polymer Materials* Biggleswade: Turpin Distribution Services Ltd; 1997.
10. Jayathilaka PARD, Dissanauake MAKL, Albinsson I, Mellander BE: **Effect of nano-porous Al_2O_3 on thermal, dielectric and transport properties of the $(PEO)_9LiTFSI$ polymer electrolyte system.** *Electrochim Acta* 2002, **47**:3257-3268.
11. Jeong SK, Jo YK, Jo NJ: **Decoupled ion conduction mechanism of poly (vinyl alcohol) based Mg-conducting solid polymer electrolyte.** *Electrochim Acta* 2006, **52**:1549-1555.
12. Bernson A, Lindgren J: **Free ions and ion pairing/clustering in the system $LiCF_3SO_3$—PPOn.** *Solid State Ionics* 1993, **60**:37-41.
13. Schanta S, Torell LM: **Evidence of dissolved ions and ion pairs in dilute poly (propylene oxide)-salt solutions.** *Solid State Ionics* 1993, **60**:47-53.
14. Kakihani M, Schanta S, Torell LM: **Raman spectroscopic study of ion-ion interaction and its temperature dependence in a poly(propylene-oxide)-based $NaCF_3SO_3$-polymer electrolyte.** *J Chem Phys* 1990, **92**:6271-6277.
15. Lundin A, Jacobsson P: **Effect of high pressure on volume and ion-ion interaction in poly (propylene glycol) complexed with $LiCF_3SO_3$.** *Solid State Ionics* 1993, **60**:43-46.
16. Schantz S, Sandfhal J, Borjesson L, Torell LM, Stevens JR: **Ion pairing in polymer electrolytes; a comparative Raman study of $NaCF_3SO_3$ complexed in poly(propylene-glycol) and dissolved in acetonitrile.** *Solid State Ionics* 1988, **28-31**:1047-1053.
17. Wensjo A, Lindgren J, Thomas JO, Farrington GC: **The effect of temperature and concentration on the local environment in the system $M(CF_3SO_3)_2PEO_n$ for M = Ni, Zn and Pb.** *Solid State Ionics* 1992, **53-56**:1077-1082.
18. Bernson A, Lindgren J: **Free ions and ion pairing/clustering in the system $LiCF_3SO_3$–PPO_n.** *Solid State Ionics* 1993, **60**:37-41.
19. Yang L, Lin J, Wang Z, Zhou R, Liu Q: **Effects of plasticizers on properties of poly(ethylene oxide) complex electrolytes.** *Solid State Ionics* 1990, **40-41**:616-619.
20. Kakihani M, Schanta S, Torell LM: **Dissociated ions and ion-ion interactions in poly(ethylene oxide) based $NaCF_3SO_3$ complexes.** *Solid State Ionics* 1990, **40-41**:641-644.
21. Petersen G, Torell LM, Panero S, Scosati B, da Silva CJ, Smith M: **Ionic interactions in MCF_3SO_3-polyether complexes containing mono-, di- and trivalent cations.** *Solid State Ionics* 1993, **60**:55-60.
22. Papke BL, Ratner MA, Shriver DF: **Vibrational spectroscopic determination of structure and ion pairing in complexes of poly(ethylene oxide) with lithium salts.** *J Electrochem Soc* 1982, **129**:1434-1438.
23. Huang W, Frech R: **Dependence of ionic association on polymer chain length in poly(ethylene oxide)-lithium triflate complexes.** *Polymer* 1994, **35**:235-242.
24. Huang W, Frech R, Wheeler RA: **Molecular structures and normal vibrations of trifluoromethane sulfonate ($CF_3SO_3^-$) and its lithium ion pairs and aggregates.** *J Phys Chem* 1994, **98**:100-110.
25. Bishop AG, MacFarlane DR, McNaughton D, Forsyth M: **FT-IR investigation of ion association in plasticized solid polymer electrolytes.** *J Phys Chem* 1996, **100**:2237-2243.
26. Lindin A, Jacobsson P: **Effect of high pressure on volume and ion-ion interaction in poly (propylene glycol) complexed with $LiCF_3SO_3$.** *Solid State Ionics* 1993, **60**:43-46.
27. Kumar B, Scanlon LG: **Polymer-ceramic composite electrolytes: conductivity and thermal history effects.** *Solid State Ionics* 1999, **124**:239-254.