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Lithium Ion Conductivity of Polymer Electrolytes Based on Insoluble Lithium Tetrakis(pentafluorobenzenethiolato)borate and Poly(ethylene oxide)

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Lithium ion conductivity and the ion transport mechanism for heterogeneous polymer electrolytes composed of insoluble lithium tetrakis(pentafluorobenzenethiolato)borate (LiTPSB), which has weak interaction between the lithium ion and the counteranion, and high molecular weight poly(ethylene oxide) (PEO) have been investigated. In addition, the ionic conductivity of polymer electrolytes based on low molecular weight poly(ethylene glycol) dimethyl ether (PEGDME) or amorphous poly[tetra(ethylene glycol) methyl ether methacrylate] (PEGM) was also researched. LiTPSB is not soluble in any solvents and polymers, however its composites with poly(ether)s exhibited ionic conductivity. The lithium ion transport mechanism in the interfacial phase between LiTPSB and PEO was proposed. The apparent activation energy of ionic conductivity was smaller for LiTPSB/PEO (salt 50 wt %) than lithium trifluoromethanesulfonate (Litrif)/PEO. A high lithium ion transference number of 0.65–0.75 was also obtained for the insoluble LiTPSB/PEO system. A new peak of the melting point of PEO was observed in differential scanning calorimetry measurements of LiTPSB/PEO polymer electrolytes, and it suggested the formation of a new ion conducting phase in the interfacial region between LiTPSB and PEO.

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Lithium ion conducting dry polymer electrolytes have been attracting interest as safer alternatives to liquid electrolytes or gel polymer electrolytes in lithium secondary batteries for hybrid vehicles and electric vehicles.¹⁻³ High dissociative property, high electrochemical stability, and good thermal stability are necessary for lithium salts in polymer electrolytes. Several high dissociative lithium salts such as lithium orthoaluminate, lithium orthoborate, and lithium orthophosphate have been reported.⁴⁻¹⁰

We have reported lithium ion conducting ionic liquids which contained two methoxy [oligo (ethylene oxide)] and two electron withdrawing groups bonded to aluminate or borate complex center, which exhibited high ionic conductivity of 5×10^{-5} S cm⁻¹ at 30°C and high lithium ion transference numbers of 0.8,^{11,12} and polymer electrolytes containing fluoroalkane dicarboxylate substituted aluminate or borate backbone and two methoxy [oligo (ethylene oxide)] side chains, which exhibited high single lithium ionic conductivity of 10^{-5} S cm⁻¹ at 30° C.¹³ The relationship between ionic conductivity and chemical structure of electrolytes containing a complex structure was discussed by focusing on the negative partial charges in anions which were estimated by optimization calculations in MOPAC. Weak interaction between the lithium ion and the counter anion with dispersed negative charge was necessary for high ionic conductivity.

We recently reported the molecular design and synthesis of lithium tetrakis(pentafluorobenzenethiolato)borate (LiTPSB) which had weak interaction between the lithium ion and the counteranion. Lithium ion conductivity of LiTPSB/poly(vinylidene fluoride) (PVDF) or LiTPSB/poly(vinylidene fluoride-*co*-hexafluoropropylene) (PVDF-HFP) polymer electrolytes was higher than the LiTFSI/PVDF system.¹⁴

In this paper, we report the ionic conductivity and ion transport mechanism for heterogeneous polymer electrolytes composed of insoluble LiTPSB and high molecular weight poly(ethylene oxide) (PEO). In addition, the ionic conductivity of polymer electrolytes based on low molecular weight poly(ethylene glycol) dimethyl ether (PEGDME) or amorphous poly(ethylene glycol) methyl ether methacrylate (PEGM) was also investigated.

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Experimental

Materials.— Lithium borohydride (LiBH₄, 2.0 M solution in [tetrahydrofuran (THF), Aldrich], pentafluorothiophenol (Lancaster), and azobisisobutyronitrile (AIBN, Wako) were used as supplied. Lithium trifluoromethanesulfonate (Litrif, Tokyo Kasei Kogyou) was dried at 100°C for 24 h under vacuum. Poly(ethylene oxide) (PEO, Mw 5.0×10^6 , Aldrich) and poly(ethylene glycol) dimethyl ether (PEGDME, Mw 1000, $T_{\rm m} = 42$ °C, Aldrich) were dried at 50°C for 24 h under vacuum. Tetra(ethylene glycol) methyl ether methacrylate (Shin-Nakamura Chemical) was dried under reduced pressure after removing the polymerization inhibitor using activated alumina. THF was dried by refluxing over sodium before use. Unless otherwise stated, all materials were handled on a dry nitrogen line or in an argon glove box in order to rigorously exclude moisture.

LiTPSB was synthesized from LiBH₄ and pentafluorothiophenol by refluxing in THF. Purified LiTPSB was dried at 100°C for 24 h under vacuum after washing repeatedly with dry THF. The structure of LiTPSB was confirmed by Fourier transform infrared and elemental analysis. Detail synthesis process has been described in another report.¹⁴

Preparation of polymer electrolytes.— LiTPSB/PEO (LiTPSB 10, 20, 40, 50, 60, and 80 wt %) polymer electrolyte films were prepared by hot pressing at 90°C between poly(tetrafluorethylene) (PTFE) disks using a PTFE or a poly(ethylene) (PE) spacer to control film thickness (400 μ m) after mixing PEO with LiTPSB in an agate mortar. LiTPSB/PEGDME (LiTPSB 20, 40, 50, and 60 wt %) polymer electrolytes were prepared by mixing PEGDME with LiTPSB using magnetic stirring at 50°C. LiTPSB/PEGM (LiTPSB 30, 50, and 70 wt %) polymer electrolyte films were prepared by radical polymerization at 80°C after mixing tetra(ethylene glycol) methyl ether methacrylate with LiTPSB and AIBN.

Measurements.— Ionic conductivity was determined by ac impedance measurement in the frequency 1 MHz to 0.1 Hz (signal amplitude 10 mV) using a Solartron 1260 frequency response analyzer and 1287 electrochemical interface. Samples of thickness, controlled using a PTFE or a PE spacer, were sandwiched between stainless steel electrodes in an argon glove box.

Lithium ion transference number was determined for the sample

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Figure 1. Partial charges of TPSB anion and TPOB anion from the optimization calculations in MOPAC (PM5).

sandwiched between lithium metal electrodes using the ac impedance–dc polarization combined technique of $Evans^{15}$ modified by Abraham.¹⁶

The surface of LiTPSB/PEO polymer electrolyte films was observed by scanning electron microscopy (SEM) on a JEOL JSM-5600.

Thermal properties of the polymer electrolyte films were determined by differential scanning calorimetry (DSC) on a Perkin-Elmer Pyris 1 differential scanning calorimetry at a scan rate of 10° C min⁻¹ in the temperature range from -80 to 200°C.

Molecular structures were depicted using CAChe version 5.0 (Fujitsu). The structures and partial charges of the chemical samples were refined by performed a pre-optimization calculation in Mechanics using Augmented MM3, followed by performed an optimization calculation in MOPAC using PM5 parameters.

Results and Discussion

Characterizations .-- LiTPSB was designed for reduced interaction between the lithium ion and the counter anion in order to enhance the ionic conductivity of polymer electrolytes. Partial charges on atoms in the TPSB anion and the tetrakis(pentafluorophenolato) borate (TPOB) anion were estimated by optimization calculations in MOPAC using PM5 parameters, and these results are shown in Fig. 1. The boron atom has a negative formal charge, however a positive charge on the boron atom and negative charges on the oxygen atoms were shown for the TPOB anion. It was confirmed that the lithium ion interacted with negative oxygen atoms in the TPOB anion for the structure of LiTPOB by the results of optimized calculations. Negative charge on the boron atom, positive charges on sulfur atoms, and smaller negative charges on fluorine atoms were shown for the TPSB anion. It was confirmed that the lithium ion interacted with negative fluorine atoms in the TPSB anion for the optimized structure of LiTPSB. From these results, interaction between the lithium ion and the negative boron atom should be weak due to electrostatic repulsion from positive sulfur atoms around the anion center. Therefore, it was shown that the coordination sites of the lithium ion changed from oxygen atoms to fluorine atoms by replacing oxygen atoms with sulfur atoms of the anion, and it is expected that interaction between the lithium ion and the anion in LiTPSB is weak.

The lithium ion of LiTPSB complexes with THF in the ratio of 1:1 from the results of elemental analysis. However, LiTPSB was insoluble in polar and less polar solvents such as acetone, THF, acetonitrile, ethanol, diethyl ether, diglyme, γ -butyrolactone, dimethyl sulfoxide, dimethyl formamide, 1-methyl-2-pyrrolidinone, toluene, chloroform, hexane, 1,3-bis(trifluoromethyl) benzene, and water. This can be ascribed to the weaker interaction between the TPSB anion and solvents due to delocalization of the negative charge over the anion. LiTPSB was stable to hydrolysis because a specific thiol smell was not detected after storing in a humid atmosphere. The particle size of LiTPSB after grinding in an agate mortar was distributed from 100 nm to 2 μ m by size distribution



Figure 2. SEM image of the surface for LiTPSB/PEO (salt 50 wt %) electrolyte film.

measurement. The aggregates of LiTPSB particles were also observed and the size of the aggregates was distributed below 200 μm by SEM images. 14

LiTPSB/PEO (LiTPSB 10, 20, 40, 50, 60, and 80 wt %) polymer electrolyte films were prepared by hot pressing after mixing LiTPSB with PEO. White opaque films were obtained for all composition. Films containing less than 40 wt % of LiTPSB were mechanically strong, but films containing more than 40 wt % of LiTPSB were fragile. LiTPSB/PEGDME (LiTPSB 20, 40, 50, and 60 wt %) polymer electrolytes were prepared by mixing PEGDME with LiTPSB. White opaque hard waxes were obtained for all composition. LiTPSB/PEGM (LiTPSB 30, 50, and 70 wt %) polymer electrolytes were prepared by radical polymerization of tetra(ethylene glycol) methyl ether methacrylate with LiTPSB and AIBN. White opaque polymer electrolytes were obtained for all composition. Polymer electrolyte containing 30 wt % of LiTPSB was mechanically strong, but polymer electrolytes containing more than 30 wt % of LITPSB were fragile.

SEM image.— SEM image of the surface for LiTPSB/PEO (salt 50 wt %) film is shown in Fig. 2. There were rough areas of LiTPSB and smooth areas of PEO in the surface. LiTPSB particles dispersed in the bulk of the polymer electrolyte film.



Figure 3. DSC curves of (a) PEO, (b) LiTPSB/PEO salt 20 wt %, (c) salt 50 wt %, and (d) salt 80 wt % at a scan rate of 10° C min⁻¹.

Table I. VTF parameters and glass transition temperature (T_g) for LiTPSB/PEO polymer electrolytes (a dash indicates "not measured").

Salt content	VTF parameters (>70°C)		
(wt %)	$T_{\rm g}~(^{\circ}{\rm C})$	$A (K^{-1/2} S cm^{-1})$	<i>B</i> (K)
0	-51.6	-	-
20	-53.5	-	-
50	-53.8	0.025	1062
80	-48.8	-	-

Thermal properties.— LiTPSB was thermally stabile up to $350\,^{\circ}$ C in nitrogen flow by the thermogravimetric analysis (TGA) measurement.¹⁴

Thermal properties of LiTPSB/PEO (salt 20, 50, and 80 wt %) polymer electrolyte films were also investigated by DSC measurements at a scan rate of 10°C min⁻¹ in the temperature range from -80 to 200°C. DSC curves of PEO and LiTPSB/PEO polymer electrolytes are shown in Fig. 3, and glass transition temperature (T_g) is shown in Table I. Glass transition temperature and melting point $(T_{\rm m})$ were determined from the second heating cycle. Pure PEO, LiTPSB/PEO (salt 80 wt %) exhibited glass transition temperatures of -52 and -49°C, respectively. The change of the glass transition temperature for LiTPSB/PEO polymer electrolytes by increasing the amount of LiTPSB was very small as compared with the general Li salt/PEO system.¹⁷ This can be ascribed to the degree of the pseudocross-linking between the lithium ion and ethylene oxide chains of PEO. Pure PEO had a peak of the melting point at 73°C. Two peaks at 69 and 73°C were detected for LiTPSB/PEO (salt 50 wt %). The new peak at 69°C showed the formation of a new phase at the interface between LiTPSB and PEO. For LiTPSB/PEO (salt 80 wt %), the peak at 73°C disappeared and only a new peak at 69°C was observed.

Ionic conductivity.— The relationship between ionic conductivity and LiTPSB content for LiTPSB/PEO polymer electrolytes is shown in Fig. 4a. Although an insoluble LiTPSB pellet exhibited very low ionic conductivity below 10^{-9} S cm⁻¹ at 200°C, its composites with PEO showed good ionic conductivity at higher temperature than the melting point of PEO. Optimized ionic conductivity of 2×10^{-8} S cm⁻¹ at 30°C and 4×10^{-6} S cm⁻¹ at 80°C was obtained for LiTPSB/PEO (salt 50 wt %).

For general Li salt/PEO polymer electrolytes, the lithium ion is usually transported in amorphous phase by the segmental motion of the ethylene oxide chains. The ion transport mechanism for the heterogeneous polymer electrolytes containing insoluble LiTPSB is tentatively shown in Scheme 1. Since LiTPSB is insoluble in PEO, lithium ion transport is possible in the interfacial phase between LiTPSB and PEO.

The temperature dependence of ionic conductivity for LiTPSB/ PEO (salt 50 wt %) is shown in Fig. 4b as compared with Litrif/ PEO (EO:Li = 20:1) as a general Li salt/PEO system. It is interesting that heterogeneous LiTPSB/PEO polymer electrolytes show similar ionic conductivity to homogeneous Litrif/PEO polymer electrolytes below the melting point of PEO. However, the ionic conductivity of LiTPSB/PEO (salt 50 wt %) is lower than that of Litrif/ PEO (EO:Li = 20:1) above 70°C. This can be ascribed to low lithium ion carrier concentration in the interfacial phase because inside lithium ions in insoluble LiTPSB particles cannot move. Enhancement of the ionic conductivity based on melting of PEO and small temperature dependence of ionic conductivity above the melting point of PEO were observed for LiTPSB/PEO polymer electrolytes.

When ion motion depends on the relaxation phenomena of the host polymer for the amorphous polymer electrolytes, ionic conductivity is illustrated by Vogel-Tammann-Fulcher (VTF) equation¹⁸⁻²⁰



Figure 4. Ionic conductivity of LiTPSB/PEO electrolytes: (a) relationship between LiTPSB content and ionic conductivity at 80°C (\bigcirc), 70°C (\blacklozenge), 60°C (\blacksquare), 50°C (\blacktriangle), 40°C (\blacklozenge), and 30°C (\times); (b) temperature dependence of ionic conductivity for LiTPSB/PEO (salt 50 wt %) (\blacklozenge) and Litrif/PEO (EO:Li = 20:1) (\bigtriangleup).

$\sigma = AT^{-1/2} \exp[-B/(T - T_0)]$

A and B are constants which related to the concentration of charge carriers in the matrix and the activation energy for conduction, respectively. An initial value of T_0 was taken as $T_0 = T_g - 50$ °C. The Arrhenius plots of LiTPSB/PEO (salt 50 wt %) polymer electrolyte were well fitted to the VTF equation above the melting point of PEO, indicating that ion motion in heterogeneous polymer electrolytes containing insoluble LiTPSB also depended on the segmental motion of the ethylene oxide chains in the interfacial region. The VTF parameters of LiTPSB/PEO (salt 50 wt %) polymer electrolyte are shown in Table I.

It is expected for the enhancement of the ionic conductivity by using amorphous polymers. Therefore, polymer electrolytes based on low molecular weight PEGDME (Mw 1000) and LiTPSB were investigated. Optimized ionic conductivity of 1×10^{-6} S cm⁻¹ at 30°C and 1×10^{-5} S cm⁻¹ at 80°C was obtained for LiTPSB/PEGDME (salt 50 wt %). The temperature dependence of ionic conductivity for LiTPSB/PEGDME (salt 50 wt %) is shown in Fig. 5 as compared with Litrif/PEGDME (EO:Li = 20:1). Above 40°C, the ionic conductivity of LiTPSB/PEGDME by two orders of magnitude, and had a smaller temperature dependence. The large increase in the ionic conductivity from 30 to 40°C was due to melting of PEGDME.

Amorphous polymer electrolytes based on PEGM with oligo(ethyhylene oxide) side chains and LiTPSB were also investigated. Optimized ionic conductivity of 1×10^{-7} S cm⁻¹ at



Figure 5. Temperature dependence of ionic conductivity for LiTPSB/ PEGDME (salt 50 wt %) (\bullet) and Litrif/PEGDME (EO:Li = 20:1) (\triangle).

 30° C and 6×10^{-7} S cm⁻¹ at 80° C was obtained for LiTPSB/PEGM (salt 50 wt %). The temperature dependence of ionic conductivity of LiTPSB/PEGM (salt 50 wt %) is shown in Fig. 6 as compared with Litrif/PEGM (EO:Li = 20:1). LiTPSB/PEGM exhibited lower ionic conductivity than Litrif/PEGM by one order of magnitude at room temperature. However, LiTPSB/PEGM showed the same ionic conductivity as Litrif/PEGM at a low temperature. Therefore, the ionic conductivity of amorphous LiTPSB/PEGDME and LiTPSB/PEGM was higher than that of LiTPSB/PEO.

From the results of ionic conductivity for all host polymer systems containing insoluble LiTPSB, small activation energies of ionic conduction were observed above the melting point of host polymers. The apparent activation energy (E_a) was calculated with the Arrhenius equation

$\sigma = A_0 \exp(-E_a/RT)$

 A_0 and *R* are the pre-exponential factor and gas constant, respectively. The apparent activation energies of polymer electrolytes containing LiTPSB are shown in Table II as compared with those containing Litrif. It is difficult to compare the activation energies among each host polymer simply because the temperature range is different. Polymer electrolytes containing LiTPSB showed smaller activation energies than those containing Litrif. It is estimated that lithium ion transport is promoted by flexible interfacial PEO phase with low

Table II. Apparent activation energy (E_a) of ionic conduction calculated with the Arrhenius equation in PEO, PEGDME, and PEGM based electrolytes.

Sample	$E_{\rm a} ~({\rm kJ}~{\rm mol}^{-1})$
(a) PEO system	<i>T</i> :70–190°C
LiTPSB/PEO (salt 50 wt %)	26
Litrif/PEO (EO:Li = $20:1$)	41
(b) PEGDME system	<i>T</i> :40–190°C
LiTPSB/PEGDME (salt 50 wt %)	9
Litrif/PEGDME (EO:Li = $20:1$)	23
(c) PEGM system	<i>T</i> :30–80°C
LiTPSB/PEGM (salt 50 wt %)	31
Litrif/PEGM (EO:Li = 20:1)	48

glass transition temperature for polymer electrolytes containing LiTPSB.

Lithium ion transport in the interfacial region between LiTPSB and PEO for LiTPSB/PEO polymer electrolytes is illustrated in Scheme 2. The composite electrolyte system of LiTPSB with Litrif/ PEO was also investigated to discuss ionic conductivity in the interfacial phase between insoluble LiTPSB and ion conductive Litrif/PEO instead of salt-free PEO. The relationship between LiTPSB content (*x*) and ionic conductivity at 80°C of (*x*) (LiTPSB)-(100-*x*) (PEO) and (*x*) (LiTPSB)-(100-*x*) [Litrif/PEO (EO:Li = 20:1)] is shown in Fig. 7. Two maximum points of ionic conductivity were observed for 5 (LiTPSB)-95 (Litrif/PEO) and 50 (LiTPSB)-50 (Litrif/PEO) in the LiTPSB/Litrif/PEO system. This phenomenon can be explained by the filler effect of LiTPSB to Litrif/PEO phase for the first maximum point, and the optimized interfacial ion conduction between LiTPSB and Litrif/PEO for the second maximum point.

Lithium ion transference number.— Lithium ion transference numbers were determined using the ac impedance–dc polarization combined technique.¹⁶ Lithium single ion conduction is expected for polymer electrolytes containing insoluble LiTPSB, but lithium ion transference numbers of 0.73–0.75 at 50°C and 0.65–0.70 at 80°C were obtained for LiTPSB/PEO (salt 50 wt %). Insoluble LiTPSB anions were not fixed in the polymer electrolytes, however these anions were less mobile than usual anions in the general Li salt/PEO system ($t_{+} = 0.05-0.30$).^{21,22} Lithium ion transference numbers of LiTPSB/PEO (salt 50 wt %) decreased as the enhancement of temperature. This can be explained by the increased mobility of insoluble TPSB anion aggregates in flexible ethylene oxide chains of molten PEO at a high temperature.



Figure 6. Temperature dependence of ionic conductivity for LiTPSB/PEGM (salt 50 wt %) (\bullet) and Litrif/PEGM (EO:Li = 20:1) (\triangle).



Figure 7. Relationships between ionic conductivity and LiTPSB content (*x*) for (*x*) (LiTPSB)-(100-*x*) [Litrif/PEO (EO:Li = 20:1)] (\bullet) and (*x*) (LiTPSB)-(100-*x*) (PEO) (\triangle) at 80°C.

Conclusion

Lithium ion conductivity and the ion transport mechanism for heterogeneous polymer electrolytes composed of insoluble LiTPSB and high molecular weight PEO have been investigated. In addition, the ionic conductivity of polymer electrolytes based on low molecular weight PEGDME or amorphous PEGM was also researched. LiTPSB was not soluble in poly(ether)s, however its composite with poly(ether)s exhibited good ionic conductivity. The lithium ion transport mechanism in the interfacial region between LiTPSB and PEO was proposed. LiTPSB/PEO polymer electrolytes showed small apparent activation energy for ionic conduction and high lithium ion transference number.

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