

# Lithium ion conductivity of gel polymer electrolytes containing insoluble lithium tetrakis(pentafluorobenzenethiolato) borate

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Received 10 June 2005; received in revised form 21 June 2005; accepted 22 June 2005

Available online 11 August 2005

## Abstract

Lithium ion conducting gel polymer electrolytes composed of insoluble lithium tetrakis(pentafluorobenzenethiolato) borate (LiTPSB), poly(vinylidene fluoride-co-hexafluoropropylene) (PVDF-HFP) and ethylene carbonate-propylene carbonate mixed solvent (EC-PC) were prepared and their ionic conductivities and electrochemical stabilities were investigated. Ionic conductivity was largely dependent on the contents of EC-PC and LiTPSB. Gel polymer electrolyte containing optimized content of 50 (LiTPSB)–50 (PVDF-HFP/EC-PC (13:87 wt. %)) exhibited ionic conductivity of  $4 \times 10^{-4} \text{ S cm}^{-1}$  at 30 °C, lithium ion transference number of 0.33 and anodic oxidation potential of 4.2 V. © 2005 Elsevier B.V. All rights reserved.

**Keywords:** Gel polymer electrolyte; Electrochemical stability; Ionic conductivity; Lithium salt

## 1. Introduction

Solvent-free polymer electrolytes have been attracting attention as safer alternatives to liquid electrolytes for use in lithium secondary batteries and other electrochemical devices [1,2]. Polymer electrolytes based on poly(ether)s and dissociative lithium salts have been investigated actively focusing on methods to enhance ionic conductivity at room temperature. Acceleration of the segmental motion in poly(ether)s by using hyper-branched polymers [3,4], plasticizers [5] or inorganic fillers [6] has been reported. Since ionic conductivity of dry polymer electrolytes is not enough for lithium secondary batteries at room temperature, gel polymer electrolytes have been used in electrochemical devices currently.

We have recently reported design and synthesis of lithium tetrakis(pentafluorobenzenethiolato) borate (LiTPSB, Fig. 1) to have weak interaction between lithium ion and counter anion by reducing partial charges on the negative atoms in the anion using optimization calculations in MOPAC. Although LiTPSB is not soluble in any

solvents and polymers, its composites with poly(ether)s such as high molecular weight poly(ethylene oxide) (PEO) or low molecular weight poly(ethylene glycol) dimethyl ether (PEGDME), or poly(fluoroalkane)s such as poly(vinylidene fluoride) (PVDF) or poly(vinylidene fluoride-co-hexafluoropropylene) (PVDF-HFP) showed lithium ionic conductivity. And lithium ion transport mechanism in the interfacial phase between insoluble LiTPSB and host polymers was proposed [7,8].

In this paper, we wish to report ionic conductivity and electrochemical stability for heterogeneous gel polymer electrolytes composed of insoluble LiTPSB, PVDF-HFP and EC-PC. In addition, gel polymer electrolytes containing Litrif or LiTFSI were also investigated for comparison between gel polymer electrolytes containing insoluble LiTPSB and gel electrolytes containing soluble lithium salts.

## 2. Experimental

### 2.1. Materials

Lithium borohydride (LiBH<sub>4</sub>, 2.0M solution in THF, Aldrich), pentafluorothiophenol (Lancaster) and EC-PC (1:1

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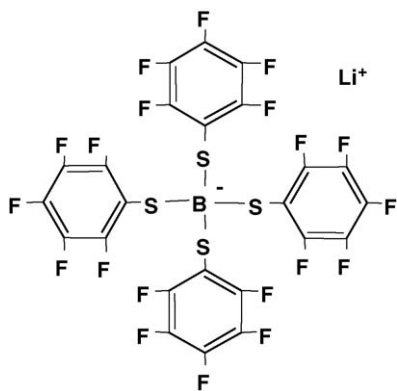


Fig. 1. Structure of LiTPSB.

volume, battery grade, Kishida Chemical) were used as supplied. Litrif (Tokyo Kasei Kogyou) and LiTFSI (Aldrich) were dried at 100 °C for 24 h under vacuum. PVDF-HFP ( $M_w$   $4.6 \times 10^5$ , Aldrich) was dried at 120 °C for 24 h under vacuum. Acetone and THF were dried rigorously before use. Unless otherwise stated, all materials were handled on a dry nitrogen line or in an argon glove box in order to exclude moisture rigorously.

LiTPSB was synthesized from  $\text{LiBH}_4$  and pentafluorophenol by refluxing in THF. LiTPSB was purified by washing with dry THF repeatedly, and dried at 100 °C for 24 h under vacuum. Detail process has been described in another report [8].

### 2.2. Preparation of gel polymer electrolytes

LiTPSB/PVDF-HFP/EC-PC gel polymer electrolytes were prepared by casting method. LiTPSB was dispersed to PVDF-HFP and EC-PC acetone solution by a magnetic stirring, and LiTPSB/PVDF-HFP/EC-PC acetone solution was removed to glass petri dish in an argon glove box. After acetone was removed under reduced pressure at room temperature, LiTPSB/PVDF-HFP/EC-PC gel polymer electrolytes were obtained. EC-PC was almost remained in gel polymer electrolytes by the yield of 95–100%.

### 2.3. 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. The thickness of gel polymer electrolytes, controlled using a PTFE or a PE spacer, were sandwiched between stainless steel electrodes in an argon glove box.

Lithium ion transference number of gel polymer electrolytes sandwiched between lithium metal electrodes was determined by the combined ac impedance–dc polarization technique [9] using a Solartron 1260 frequency response analyzer and a Hokuto Denko HZ-3000.

Electrochemical stability of gel polymer electrolytes was determined by cyclic voltammetry (CV) or linear sweep voltammetry (LSV) on stainless steel or aluminum working electrode ( $2.7 \times 10^{-1} \text{ cm}^2$ ), Li counter electrode at a scan rate of  $0.1 \text{ mV s}^{-1}$  using a Hokuto Denko HZ-3000.

Molecular structures were depicted using CAChe Version 5.0 (Fujitsu). The highest occupied molecular orbital (HOMO) energies of the chemical samples were generated by a MNDO wavefunction, at a geometry determined by performed a pre-optimization calculation in Mechanics using Augmented MM3, followed by an optimized geometry calculation in MOPAC using MNDO parameters.

## 3. Results and discussion

### 3.1. Characterization

LiTPSB was designed to have weak interaction between lithium ion and counter anion using optimization calculations in MOPAC. Weak interaction is estimated by the small partial negative charges on TPSB anion [7]. Therefore it is expected that LiTPSB is highly dissociative. However LiTPSB is insoluble in polar and less polar solvents such as acetone, THF, acetonitrile, ethanol, diethyl ether, diglyme,  $\gamma$ -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 weak interaction between TPSB anion and solvents due to delocalization of the negative charges over the anion.

LiTPSB/PVDF-HFP/EC-PC gel polymer electrolytes were prepared by casting method. White opaque gel polymer electrolytes were obtained for all compositions. Gel polymer electrolytes containing less than 70 wt.% ( $x=70$ ) of EC-PC were mechanically strong for  $(100-x)$  (LiTPSB/PVDF-HFP (40:60 wt.%))– $x$  (EC-PC) ( $x=30, 50, 70, 80, 90$ ) system. For  $x$  (LiTPSB)– $(100-x)$  (PVDF-HFP/EC-PC (13:87 wt.%)) ( $x=8, 30, 50, 70$ ) system, all gel polymer electrolytes were mechanically weak.

### 3.2. Ionic conductivity

Lithium ion transport in the interfacial phase between LiTPSB and PEO for LiTPSB/PEO dry polymer electrolytes was proposed due to insolubility of LiTPSB [7]. Therefore it is suggested that lithium ion is also transported in the interfacial conducting phase between LiTPSB and PVDF-HFP for LiTPSB/PVDF-HFP/EC-PC gel polymer electrolytes system.

Firstly LiTPSB/PVDF-HFP/EC-PC gel polymer electrolytes were investigated on EC-PC content. The content of LiTPSB to PVDF-HFP fixed in the ratio of 40–60 wt.%. Relationship between EC-PC content and ionic conductivity for  $(100-x)$  (LiTPSB/PVDF-HFP (40:60 wt.%))– $x$  (EC-PC) gel polymer electrolytes is shown in Fig. 2. Dry polymer electrolyte LiTPSB/PVDF-HFP (40:60 wt.%)

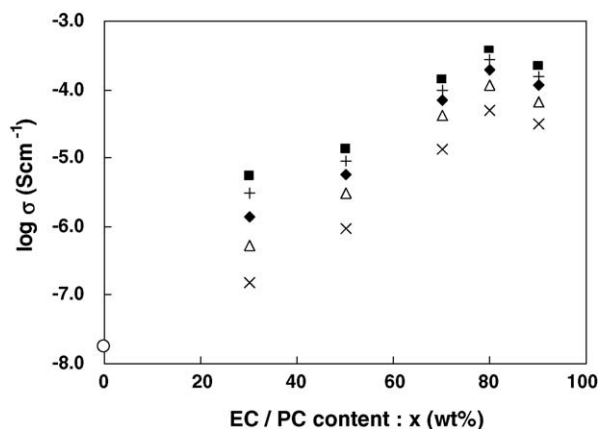


Fig. 2. Relationship between EC–PC content and ionic conductivity for (100 –  $x$ ) (LiTPSB/PVDF–HFP (40:60 wt.%))–( $x$ ) (EC–PC) system at 90 °C (○), 60 °C (■), 40 °C (+), 20 °C (◆), 0 °C (Δ), –20 °C (×).

( $x=0$ ) without EC–PC showed low ionic conductivity of  $2 \times 10^{-8} \text{ S cm}^{-1}$  at 90 °C [8]. Ionic conductivity largely increased by addition of EC–PC due to increased flexibility of the ion conducting interfacial phase. Optimized ionic conductivity of  $2 \times 10^{-4} \text{ S cm}^{-1}$  at 30 °C was obtained for 20 (LiTPSB/PVDF–HFP (40:60 wt.%))–80 (EC–PC). Ionic conductivity of 10 (LiTPSB/PVDF–HFP (40:60 wt.%))–90 (EC–PC) was lower than that of 20 (LiTPSB/PVDF–HFP (40:60 wt.%))–80 (EC–PC) because ion conducting interfacial phase reduced as decreasing LiTPSB.

LiTPSB/PVDF–HFP/EC–PC gel polymer electrolytes were also investigated on LiTPSB content. The content of PVDF–HFP to EC–PC fixed in the ratio of 13–87 wt.% similar to optimized 20 (LiTPSB/PVDF–HFP (40:60 wt.%))–80 (EC–PC). Relationship between LiTPSB content and ionic conductivity for ( $x$ ) (LiTPSB)–(100 –  $x$ ) (PVDF–HFP/EC–PC (13:87 wt.%)) gel polymer electrolytes is shown in Fig. 3. 8 (LiTPSB)–92 (PVDF–HFP/EC–PC (13:87 wt.%)) is the same sample to 20 (LiTPSB/PVDF–HFP (40:60 wt.%))–80 (EC–PC). Ionic conductivity was

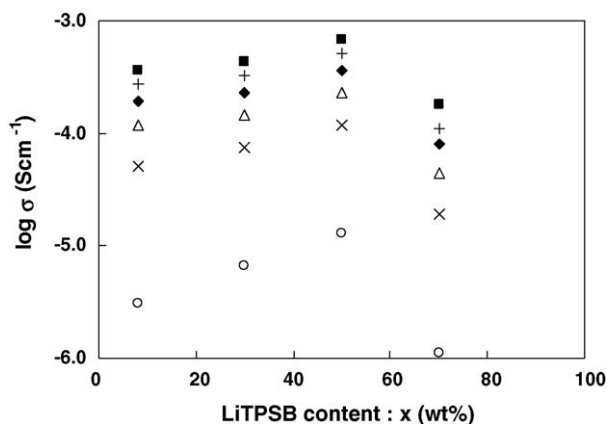


Fig. 3. Relationship between LiTPSB content and ionic conductivity for ( $x$ ) (LiTPSB)–(100 –  $x$ ) (PVDF–HFP/EC–PC (13:87 wt.%)) system at 60 °C (■), 40 °C (+), 20 °C (◆), 0 °C (Δ), –20 °C (×), –40 °C (○).

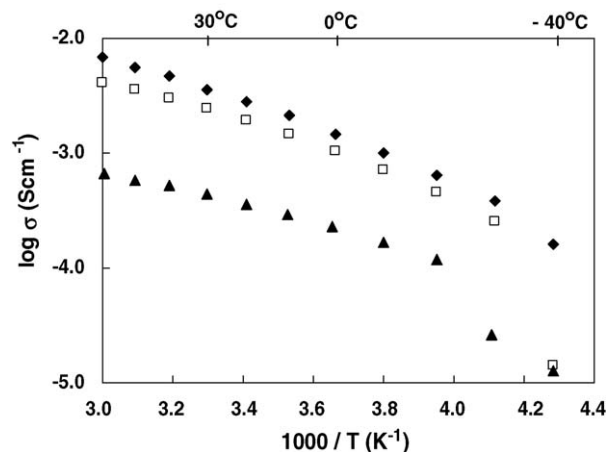


Fig. 4. Temperature dependence of ionic conductivity for 50 (LiTPSB)–50 (PVDF–HFP/EC–PC (13:87 wt.%)) (▲), 20 (PVDF–HFP)–80 (1 M LiTFSI/EC–PC) (◆) and 20 (PVDF–HFP)–80 (1 M Litrif/EC–PC) (□).

enhanced by addition of LiTPSB despite increased fragility of gel polymer electrolytes. Optimized ionic conductivity of  $4 \times 10^{-4} \text{ S cm}^{-1}$  at 30 °C was obtained for 50 (LiTPSB)–50 (PVDF–HFP/EC–PC (13:87 wt.%)). Although 8 wt.% of LiTPSB is too less to make effective contact between LiTPSB particles, continuous ion transport pathway can be formed by thick ion conduction layer on the particles.

Temperature dependence of ionic conductivity for 50 (LiTPSB)–50 (PVDF–HFP/EC–PC (13:87 wt.%)) gel polymer electrolyte is shown in Fig. 4 as compared with usual gel polymer electrolyte systems, 20 (PVDF–HFP)–80 (1 M LiTFSI/EC–PC) and 20 (PVDF–HFP)–80 (1 M Litrif/EC–PC). Ionic conductivity of 50 (LiTPSB)–50 (PVDF–HFP/EC–PC (13:87 wt.%)) was lower than that of the others by one order of magnitude. However, it is interesting that the gel polymer electrolyte containing the insoluble lithium salt can be a good ion conductor.

The apparent activation energy of ion conduction for LiTPSB/PVDF–HFP/EC–PC gel polymer electrolyte is compared with LiTPSB–PEO dry polymer electrolyte. Apparent activation energy ( $E_a$ ) was calculated with the Arrhenius equation:

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

$A_0$  and  $R$  are pre-exponential factor and gas constant, respectively. Activation energies for 50 (LiTPSB)–50 (PVDF–HFP/EC–PC (13:87 wt.%)) and 50 (LiTPSB)–50 (PEO) were 15 and 26  $\text{kJ mol}^{-1}$  [7], respectively. Lower activation energy in the gel system is advantageous for ion conduction at a low temperature.

### 3.3. Lithium ion transference number

Lithium ion transference numbers were determined using the technique combined ac impedance–dc polarization [9]. Dry polymer electrolyte LiTPSB/PEO exhibited high lithium ion transference number of 0.65–0.75 due to

low mobility of TPSB anions in insoluble LiTPSB [7]. Lithium ion transference numbers of 8 (LiTPSB)–92 (PVDF-HFP/EC-PC (13:87 wt.%)), 50 (LiTPSB)–50 (PVDF-HFP/EC-PC (13:87 wt.%)) and 20 (PVDF-HFP)–80 (1 M LiTFSI/EC-PC) gel polymer electrolytes were 0.40, 0.33 and 0.20 at 40 °C using a 10 mV dc potential, respectively. LiTPSB/PVDF-HFP/EC-PC gel polymer electrolytes exhibited lower lithium ion transference numbers of 0.33–0.40 than LiTPSB/PEO dry polymer electrolytes. This can be ascribed to the increased mobility of TPSB anions in flexible ion conducting phase. However lithium ion transference numbers of LiTPSB/PVDF-HFP/EC-PC gel polymer electrolytes were higher than those of LiTFSI/PVDF-HFP/EC-PC gel polymer electrolyte containing the soluble lithium salt.

### 3.4. Electrochemical stability

The electrochemical stability of 50 (LiTPSB)–50 (PVDF-HFP/EC-PC (13:87 wt.%)) gel polymer electrolyte was investigated by cyclic voltammetry or linear sweep voltammetry on stainless steel or aluminum working electrode ( $2.7 \times 10^{-1} \text{ cm}^2$ ), Li counter electrode at a scan rate of  $0.1 \text{ mV s}^{-1}$ . The cyclic voltammogram using stainless steel working electrode on the first cycle is shown in Fig. 5. LiTPSB/PVDF-HFP/EC-PC gel polymer electrolyte showed good lithium deposition and stripping process. The peak based on the reduction was not observed above 0 V, and the oxidation peak was observed above 4.3 V. The linear sweep voltammogram using aluminum working electrode is shown in Fig. 6. The oxidation peak was observed above 4.2 V similar to the result using stainless steel working electrode. It was confirmed that aluminum could be used as the current collector of the cathode.

HOMO energies of anions for LiTPSB and various lithium salts are shown in Table 1. LiTPSB exhibited not only low HOMO energy, but also relatively low anodic oxidation potential. These results agree to the correlation between HOMO energies and the anodic oxidation potentials of lithium salts [10–12].

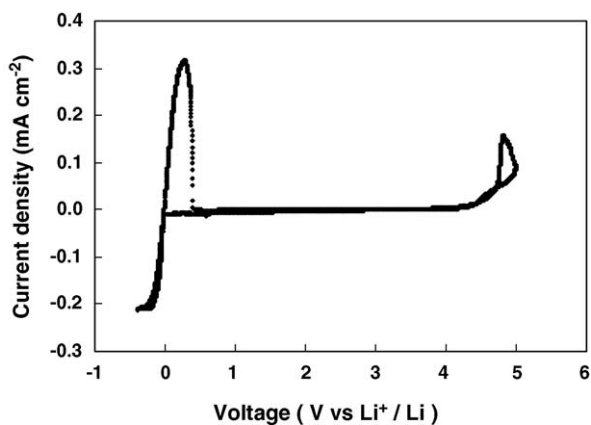


Fig. 5. Cyclic voltammogram of 50 (LiTPSB)–50 (PVDF-HFP/EC-PC (13:87 wt.%)) at  $0.1 \text{ mV s}^{-1}$  using stainless steel working electrode at 40 °C.

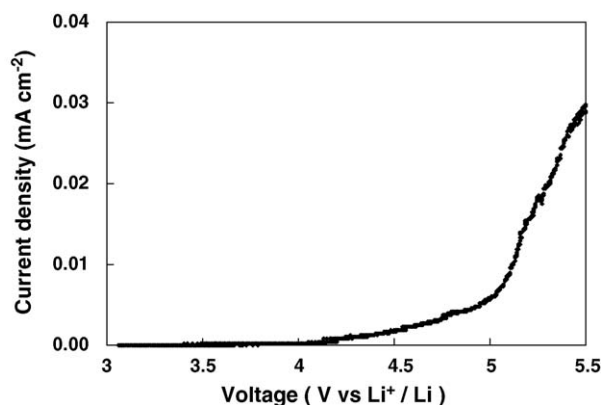


Fig. 6. Linear sweep voltammogram of 50 (LiTPSB)–50 (PVDF-HFP/EC-PC (13:87 wt.%)) at  $0.1 \text{ mV s}^{-1}$  using aluminum working electrode at 50 °C.

Table 1

HOMO energies of anions for LiTPSB and various lithium salts using the optimization calculations in MOPAC (MNDO)

Anion	HOMO energy (eV)
$\text{PF}_6^-$	–10.7
TFSI <sup>–</sup>	–9.6
trif <sup>–</sup>	–8.0
BOB <sup>–</sup>	–7.4
$[\text{B}(\text{OC}_6\text{F}_5)_4]^-$	–7.2
$[\text{B}(\text{SC}_6\text{F}_5)_4]^-$ (TPSB <sup>–</sup> )	–6.0

## 4. Conclusion

Lithium ion conducting gel polymer electrolytes composed of insoluble LiTPSB, PVDF-HFP and EC-PC were prepared by casting method. Ionic conductivity was largely dependent on the contents of EC-PC and LiTPSB. Optimized gel polymer electrolyte composed of 50 (LiTPSB)–50 (PVDF-HFP/EC-PC (13:87 wt.%)) showed ionic conductivity of  $4 \times 10^{-4} \text{ S cm}^{-1}$  at 30 °C, lithium ion transference number of 0.33 and anodic oxidation potential of 4.2 V using stainless steel or aluminum working electrode.

## Acknowledgement

This work was partially supported by Grant-in-aid for Scientific Research (B) (No. 16350099) from the Ministry of Education, Culture, Sports, Science and Technology of Japan.

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