

Influence of Lewis acidic borate ester groups on lithium ionic conduction in polymer electrolytes

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Polymer electrolytes having borate ester groups, which are part of the polymer matrix, have been prepared. The transference number of the lithium ions increases with increasing concentration of the borate ester groups, and therefore it is considered that the borate ester groups, having Lewis acidity, interact with Lewis basic anions. Furthermore, the transference numbers of lithium ions in the polymer electrolytes containing LiCF₃SO₃ or LiClO₄ were found to be higher than that in the electrolyte with LiN(CF₃SO₂)₂. *Ab initio* calculations were performed to estimate the interactions between the borate ester groups and the anions. The calculated results indicate that the borate ester group prefers to interact with a 'hard' basic anion, CF₃SO₃⁻ or ClO₄⁻. This is in good agreement with the obtained experimental results.

Introduction

Solid polymer electrolytes comprising polyether-alkali metal salt complexes have attracted much attention because of their potential for practical applications such as lithium secondary batteries, sensors and display devices.¹⁻⁴ The higher safety of solid polymer electrolytes is an advantage compared with conventional electrolytes using non-aqueous organic solvents, for example ethylene carbonate (EC), propylene carbonate (PC), dimethyl carbonate (DMC) and diethyl carbonate (DEC). However, the lower ionic conductivity of solid polymer electrolytes compared with that of the liquid electrolytes is considered to be the first disadvantage. For improvement of the ionic conductivity of solid polymer electrolytes, addition of the non-aqueous organic solvents⁵⁻⁸ or poly(ethylene glycol) (PEG) with a low molecular weight⁹⁻¹⁴ into the matrix polymer as a plasticizer has been proposed, which is expected to enhance the ionic mobility of the polymer electrolytes. However, addition of these organic solvents partially spoils the advantages of the solid polymer electrolytes, such as safety. The second disadvantage of the solid polymer electrolytes is a lower transference number of lithium ions, because the movement of the lithium ions is induced by segmental motion and the lithium ions are coordinated strongly with the oxygen atoms of the polyethers. In order to utilize the solid polymer electrolytes in practical electrochemical devices, it is necessary to enhance their ionic conductivity and the transference number of the lithium ions. These features can be achieved by enhancement of the dissociation of the supporting salts and by the decreasing mobility of the counter anions.

For electrolytes based on low molecular weight organic solvents, Lewis acidic compounds have been proposed as additives to enhance the dissociation of the supporting salts,¹⁵⁻¹⁹ which are expected to interact with Lewis basic anions. Addition of the Lewis acidic compounds is also effective to enhance the transference number of the lithium ions because the Lewis acidic compounds trap the counter anions. In these

reports, the boron compounds act as anion receptors because of the Lewis acidity of boron atoms. In addition, the incorporation of boroxine rings into polymer structures, which achieves a high transference number for lithium ions in polymer electrolytes, has been proposed.^{20,21} We have focused on PEG-borate ester (which acts as a Lewis acid) as a new type of plasticizer for polymer electrolytes and have reported the effects of PEG-borate ester on the ionic conductivity and thermal stability of the polymer electrolytes.^{22,23} Furthermore, we have also presented the preparation and characteristics, such as ionic conductivity, thermal stability and electrochemical stability, of solid polymer electrolytes having borate ester groups which are part of the matrix polymer.²⁴ However, the exact interactions between the Lewis acidity of the boron compounds and the Lewis basicity of anions have not yet been clarified.

In the present study, we have investigated the effect of the Lewis acidity of borate ester groups, which are fixed to the chains of the matrix polymer, on the ionic conductivity and transference number of lithium ions in the polymer electrolytes. We report the relationships between the concentration of the borate ester groups and ionic conductivity or transference number of lithium ions in the polymer electrolytes. Furthermore, the interactions between the Lewis acidity of the borate ester groups and Lewis basicity of anions based on Hard and Soft Acids and Bases (HSAB) theory have been investigated by *ab initio* calculations.

Experimental

The backbone polymer was prepared from poly(ethylene glycol) and boric acid anhydride as shown in Fig. 1.²⁴ The PEGs with various molecular weights (PEG150, PEG200, PEG400, PEG600, whose average molecular weights are 150, 200, 400, 600, respectively) were supplied from NOF Co. Ltd. LiN(CF₃SO₂)₂ (Fluka), LiCF₃SO₃ (Wako) and LiClO₄ (Wako)

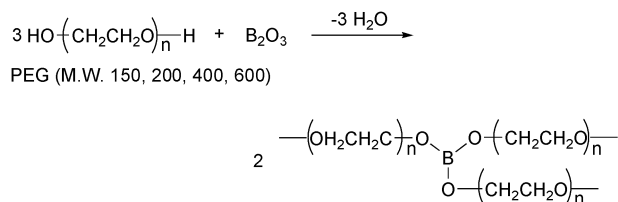


Fig. 1 Reaction scheme for preparation of the backbone polymer from poly(ethylene glycol) and boric acid anhydride.

as the supporting salts were used without further purification. Handling of all chemicals was carried out in an Ar-filled glove box (dew point: -76°C).

The polymer electrolyte films were prepared as reported in the previous paper.²⁴ The mixture of an appropriate amount of PEG, boric acid anhydride (B_2O_3), and a lithium salt, $\text{LiN}(\text{CF}_3\text{SO}_2)_2$, LiCF_3SO_3 or LiClO_4 , was taken together in a flask and stirred for 3 h. The concentration of the lithium salt in the polymer electrolyte was adjusted so that the molar ratio of lithium atoms to ether oxygen (EO) atoms is 1:24. The resulting homogeneous viscous solution was poured on to a Teflon plate and then stored for 24 h at 110°C under vacuum conditions in order to remove generated water. The extent of the reaction was determined by the amount of water generated. After completion of the reaction, self-standing solid polymer electrolyte films of *ca.* 1 mm thickness were obtained. The composition of polymer electrolyte, for example, one prepared from PEG200, boric acid anhydride and $\text{LiN}(\text{CF}_3\text{SO}_2)_2$, is represented as $\text{PEG200-B}_2\text{O}_3 + \text{LiN}(\text{CF}_3\text{SO}_2)_2$.

The ionic conductivity of the polymer electrolyte films was measured by the AC impedance technique using a computer controlled Hewlett-Packard 4192A LF impedance analyzer over the frequency range from 5 to 13 MHz. The polymer electrolyte films were cut into disks of 10 mm in diameter, sandwiched between stainless steel electrodes (SUS 304) and subjected to the impedance analyzer.

Thermal properties of the obtained polymer electrolyte samples were investigated by differential scanning calorimetry (DSC) using a DSC6200 calorimeter (Seiko Instruments). After the sample in an aluminium pan was cooled to -120°C at a scan rate of $10^\circ\text{C min}^{-1}$, measurements were carried out from -120 to 100°C at the same scan rate. An empty aluminium pan was used as reference.

The transference number for the lithium ions in the polymer electrolytes was evaluated by means of the combination of complex impedance and potentiostatic polarization measurements for the samples sandwiched between two lithium electrodes.

Ab initio Hartree-Fock (HF) self-consistent field molecular orbital calculations and density functional theory (DFT) calculations were performed using the Gaussian98 package.²⁵ Calculations for geometry optimizations were carried out at the HF level of theory using the standard 3-21G basis set. Subsequently, single point calculations for investigation of the energies of the optimized geometries were performed using DFT methods with the B3LYP^{26,27} form for exchange-correlation functionals and a 6-311G** basis set.

Results and discussion

Fig. 2 shows the DSC curves of the polymer electrolytes, $\text{PEG}_x\text{-B}_2\text{O}_3$ (x : 150, 200, 400, 600) + $\text{LiN}(\text{CF}_3\text{SO}_2)_2$ (Li:EO = 1:24). The glass transition point of the polymer electrolytes was observed in each curve. The glass transition temperature, T_g , was taken at the center of the heat capacity change encountered during the transition. As shown in Fig. 2, T_g values of the polymer electrolytes decreased with an increased molecular weight of the PEG; in other words, with decreasing the concentration of the borate ester groups which play a role

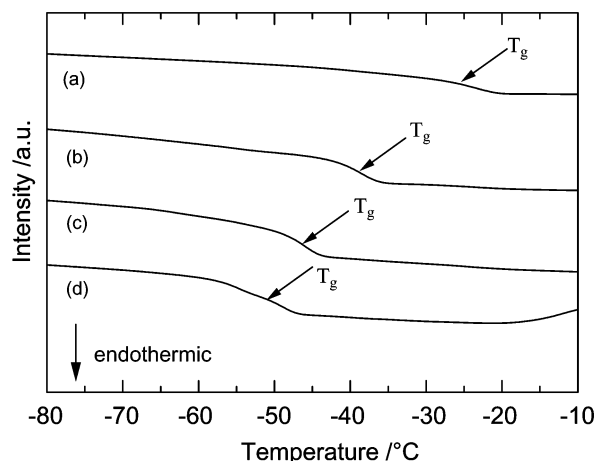


Fig. 2 DSC curves of $\text{PEG}_x\text{-B}_2\text{O}_3 + \text{LiN}(\text{CF}_3\text{SO}_2)_2$ (Li:EO = 1:24): (a) PEG150, (b) PEG200, (c) PEG400, (d) PEG600.

of crosslinking points in the polymer electrolytes. These results indicate that the mobility of the polymer chains increases with a decrease in the concentration of the crosslinking points, *i.e.* borate ester groups, in the polymer electrolytes because T_g is correlated with the segmental motion of polymer chains.

The temperature dependence for the ionic conductivity of the polymer electrolytes $\text{PEG}_x\text{-B}_2\text{O}_3$ (x = 150, 200, 400, 600) + $\text{LiN}(\text{CF}_3\text{SO}_2)_2$ (Li:EO = 1:24) is shown in Fig. 3. An increase in the ionic conductivity of the polymer electrolytes was observed with increasing the molecular weight of PEG. The highest ionic conductivity was found for the polymer electrolyte prepared from PEG600, whose values were $5.9 \times 10^{-5} \text{ S cm}^{-1}$ at 30°C and $3.0 \times 10^{-4} \text{ S cm}^{-1}$ at 60°C , respectively.

The temperature dependence exhibited a convex-profile in the Arrhenius-type plots as shown in Fig. 3. This phenomenon indicates that the ionic conduction mechanism of the polymer electrolyte samples does not obey the hopping model of carrier ions. This temperature dependence of the ionic conductivity is typically observed in polymer electrolytes and is expected to obey the free volume theory of polymers,²⁸⁻³¹ which is indicative of the temperature dependence for segmental motion of the polymer chains expressed by the William-Landel-Ferry (WLF) relationship.³² The WLF equation is represented as follows:

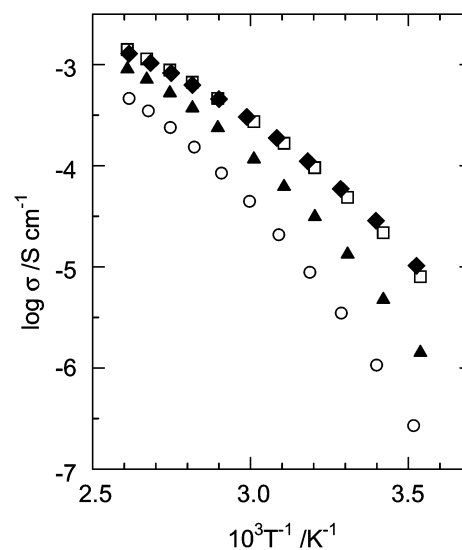


Fig. 3 Arrhenius plots of ionic conductivity for $\text{PEG}_x\text{-B}_2\text{O}_3 + \text{LiN}(\text{CF}_3\text{SO}_2)_2$ (Li:EO = 1:24): (○) PEG150, (▲) PEG200, (□) PEG400, (◆) PEG600.

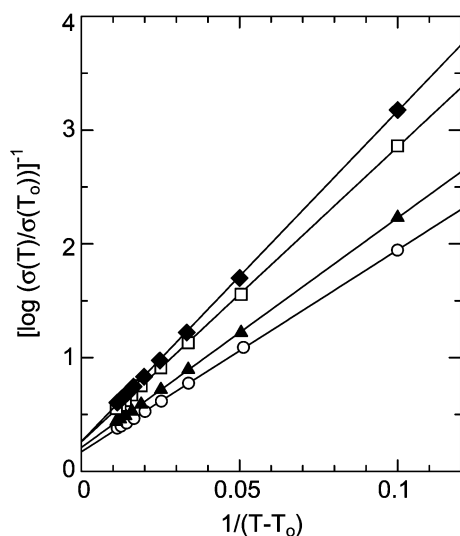


Fig. 4 WLF plots of ionic conductivity for PEG_x-B₂O₃ + LiN(CF₃SO₂)₂ (Li:EO = 1:24): (○) PEG150, (▲) PEG200, (□) PEG400, (◆) PEG600. $T_0 = 10$ °C.

$$\log \frac{\sigma(T)}{\sigma(T_g)} = \frac{C_1(T - T_g)}{C_2 + (T - T_g)} \quad (1)$$

where $\sigma(T)$ and $\sigma(T_g)$ are the conductivity values at temperatures T and T_g , respectively, and C_1 , C_2 are the WLF parameters for the temperature dependence of the ionic conductivity. However, the ionic conductivity at T_g , $\sigma(T_g)$, is difficult to measure in the present experiments because $\sigma(T_g)$ has too low a value to measure by the complex impedance measurement technique, and, therefore, 10 °C was selected as a reference temperature, T_0 . Eqn. (1) is rewritten as follows:

$$\log \frac{\sigma(T)}{\sigma(T_0)} = \frac{C'_1(T - T_0)}{C'_2 + (T - T_0)} \quad (2)$$

The parameters in eqn. (1) are calculated as follows:

$$C_1 = C'_1 C'_2 / [C'_2 - (T_0 - T_g)] \quad (3)$$

$$C_2 = C'_2 - (T_0 - T_g) \quad (4)$$

Fig. 4 shows WLF plots for the ionic conductivity of the polymer electrolytes PEG_x-B₂O₃ ($x = 150, 200, 400, 600$) + LiN(CF₃SO₂)₂ (Li:EO = 1:24). From the inverse of eqn. (2), the temperature dependence of the ionic conductivity is plotted as $[\log(\sigma(T)/\sigma(T_0))]^{-1}$ vs. $1/(T - T_0)$. It was observed as shown in Fig. 4 that $[\log(\sigma(T)/\sigma(T_0))]^{-1}$ varies linearly with $1/(T - T_0)$, which indicates that the temperature dependence of the ionic conductivity for the polymer electrolytes follows the WLF-type equation.

The WLF parameters C_1 , C_2 and $\sigma(T_g)$, were estimated from Fig. 4 and eqns. (2)–(4), and are summarized in Table 1. The estimated parameters were found to be close to the universal values of the WLF parameters, $C_1 = 17.4$ and $C_2 = 51.6$ K,³² which indicates that the temperature dependence of the ionic conductivity for the polymer electrolytes was dominated by that of the segmental motion of the polymer chains. Therefore, from the WLF plots and T_g values, the increase in ionic

Table 1 WLF parameters and $\sigma(T_g)$ of PEG_x-B₂O₃ + LiN(CF₃SO₂)₂ (Li:EO = 1:24)

Molecular weight of PEG	T_g /°C	C_1	C_2 /K	$\sigma(T_g)$ /S cm ⁻¹
PEG150	-28	10.6	59.1	1.00×10^{-11}
PEG200	-39	12.1	37.7	1.87×10^{-13}
PEG400	-48	14.7	22.1	1.58×10^{-16}
PEG600	-52	16.9	18.0	7.94×10^{-19}

conductivity with increasing the molecular weight of PEG, as shown in Fig. 2, is considered to be due to the increase in ionic mobility.

As shown in Table 1, $\sigma(T_g)$ increase with increasing concentration of the borate ester groups. Since the segmental motion of polymer chains is frozen at the glass-transition temperature, it is considered that mobility of the polymer chains at that temperature may be the same. Accordingly, the differences in the ionic conductivities of the polymer electrolytes at T_g are considered to arise due to the following three reasons: (1) the concentration of carrier ions at different T_g s is different; (2) the dissociation constant of the lithium salt is different because the polymer electrolytes from different PEGs have different T_g values; and (3) the mobility of carrier ions is different at different T_g s. The reason for the increase in $\sigma(T_g)$ is not clear in this case.

In order to investigate the effect of the borate ester groups on lithium salt, the transference number, t , of the lithium ions in the polymer electrolytes was estimated according to the equation presented by Abraham *et al.*¹³ as follows:

$$t_{Li^+} = \frac{I_{(\infty)} R_{b(\infty)} (\Delta V - I_{(0)} R_{e(0)})}{I_{(0)} R_{b(0)} (\Delta V - I_{(\infty)} R_{e(\infty)})} \quad (5)$$

where I is the current, ΔV is the applied potential, R_b is the bulk resistance, R_e is the interface resistance, and 0 and ∞ refer to the initial and steady-states, respectively. The estimated transference numbers of lithium ions in the polymer electrolytes PEG_x-B₂O₃ ($x = 150, 200, 400, 600$) + LiN(CF₃SO₂)₂ (Li:EO = 1:24) at 60 °C are summarized in Table 2. An increase in the transference number of lithium ions was found with increasing the concentration of the borate ester groups in the polymer electrolytes. Therefore, it is considered that the borate ester groups interact with the anions, and, accordingly, the movement of the anions is interrupted which enhances the transference number of the lithium ions in the polymer electrolytes.

In order to clarify the interactions between the borate ester groups and the anions more precisely, other lithium salts, LiCF₃SO₃ and LiClO₄ as well as LiN(CF₃SO₂)₂, were used as supporting electrolytes for the polymer electrolytes. Accordingly, for the investigation of the effects of the Lewis acidity of the borate ester groups in the polymer electrolytes on the anions, ionic conductivity and T_g of the polymer, electrolytes containing LiCF₃SO₃ or LiClO₄ were examined.

Fig. 5 shows the temperature dependence of the ionic conductivity of the polymer electrolytes, PEG_x-B₂O₃ ($x = 200, 600$) + LiN(CF₃SO₂)₂, LiCF₃SO₃ or LiClO₄ (Li:EO = 1:24). Arrhenius plots for the ionic conductivity of all samples were convex-profiles, and, accordingly, the temperature dependence of their ionic conductivities is expected to obey the WLF relationship.

WLF plots were carried out for polymer electrolytes containing LiN(CF₃SO₂)₂, LiCF₃SO₃ or LiClO₄ and were confirmed to be linear relationships comparable to those shown in Fig. 4. Obtained WLF parameters of the polymer electrolytes are summarized in Table 3. The temperature dependence for the ionic conductivity of the polymer electrolytes with LiN(CF₃SO₂)₂, LiCF₃SO₃ or LiClO₄ was found to be dominated by that of the ionic mobility correlated with the segmental motion of the polymer chains. The differences in T_g

Table 2 Transference number of PEG_x-B₂O₃ + LiN(CF₃SO₂)₂ (Li:EO = 1:24) at 60 °C

Molecular weight of PEG	t_{Li^+}
PEG150	0.64
PEG200	0.44
PEG400	0.17
PEG600	0.16

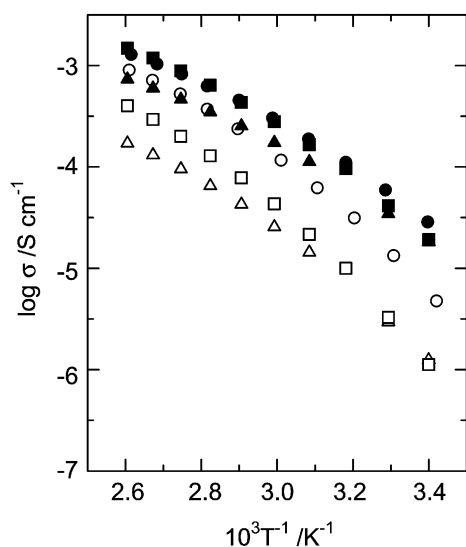


Fig. 5 Arrhenius plots of ionic conductivity for PEG $_x$ -B $_2$ O $_3$ + Li-salt (Li:EO = 1:24): (○) PEG200 + LiN(CF $_3$ SO $_2$) $_2$, (●) PEG600 + LiN(CF $_3$ SO $_2$) $_2$, (△) PEG200 + LiCF $_3$ SO $_3$, (▲) PEG600 + LiCF $_3$ SO $_3$, (□) PEG200 + LiClO $_4$, (■) PEG600 + LiClO $_4$.

of the polymer electrolytes with various lithium salts were small; on the other hand, however, large differences in $\sigma(T_g)$ values of the samples were found in Table 3. In this case, the difference in ionic conductivity at each T_g of the polymer electrolytes is considered to reflect the difference in the degree of lithium salt dissociation. Accordingly, it is expected that the degree of dissociation of LiCF $_3$ SO $_3$ or LiClO $_4$ in the polymer electrolytes is higher than that of LiN(CF $_3$ SO $_2$) $_2$. It is generally known that the degree of dissociation of LiN(CF $_3$ SO $_2$) $_2$ is higher than that of LiCF $_3$ SO $_3$ or LiClO $_4$ in a conventional matrix, PEO *etc.*, for polymer electrolytes.³³⁻³⁵ However, above results in the present polymer electrolytes indicate that the higher degree of dissociation of LiCF $_3$ SO $_3$ or LiClO $_4$ compared with that of LiN(CF $_3$ SO $_2$) $_2$ might be induced by the borate ester groups.

Transference numbers for the lithium ions in the polymer electrolytes PEG $_x$ -B $_2$ O $_3$ ($x = 200, 600$) + LiN(CF $_3$ SO $_2$) $_2$, LiCF $_3$ SO $_3$ or LiClO $_4$ (Li:EO = 1:24) are summarized in

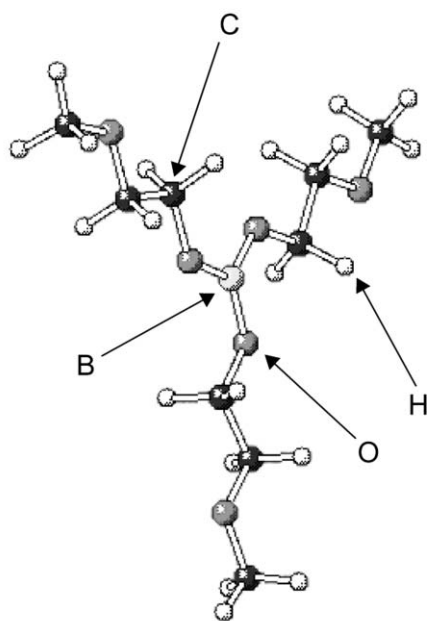


Fig. 6 Most stable geometry of the PEG-borate ester obtained with calculation (B3LYP/6-311G**//HF/3-21G*).

Table 3 WLF parameters and $\sigma(T_g)$ of PEG $_x$ -B $_2$ O $_3$ + Li-salt (Li:EO = 1:24)

Molecular weight of PEG	Supporting electrolyte	$T_g/^\circ\text{C}$	C_1	C_2/K	$\sigma(T_g)/\text{S cm}^{-1}$
PEG200	LiN(CF $_3$ SO $_2$) $_2$	-39	12.1	37.7	1.87×10^{-13}
PEG200	LiCF $_3$ SO $_3$	-38	9.9	66.0	2.51×10^{-11}
PEG200	LiClO $_4$	-34	12.1	53.0	1.26×10^{-11}
PEG600	LiN(CF $_3$ SO $_2$) $_2$	-52	16.9	18.0	7.94×10^{-19}
PEG600	LiCF $_3$ SO $_3$	-48	18.6	13.7	1.29×10^{-16}
PEG600	LiClO $_4$	-42	12.5	25.6	1.05×10^{-18}

Table 4 Transference number of PEG600-B $_2$ O $_3$ + Li-salt (Li:EO = 1:24) at 60 $^\circ\text{C}$

Supporting electrolyte	t_{Li^+}
LiN(CF $_3$ SO $_2$) $_2$	0.16
LiCF $_3$ SO $_3$	0.40
LiClO $_4$	0.45

Table 4. It was found that the transference number of the polymer electrolytes containing LiCF $_3$ SO $_3$ or LiClO $_4$ was higher than that of the electrolyte with LiN(CF $_3$ SO $_2$) $_2$. These results also indicate that CF $_3$ SO $_3^-$ and ClO $_4^-$ are attracted by the borate ester groups more effectively compared with N(CF $_3$ SO $_2$) $_2^-$.

In order to clarify the qualitative relationships between Lewis acidity of the borate ester groups and Lewis basicity of the anions, *ab initio* calculations were carried out. In the first place, the highest energy occupied molecular orbital (HOMO) and the lowest energy unoccupied molecular orbital (LUMO) of the backbone polymer in the polymer electrolytes were investigated. For simplification of the calculations, a PEG-borate ester whose EO chain length is $n = 1$ was chosen as a model for the matrix polymer. The most stable geometry of the PEG-borate ester obtained by the calculations for six starting geometries is shown in Fig. 6. Furthermore, mapping the HOMO and the LUMO for the most stable geometry of the PEG-borate ester was carried out, and the results obtained for the molecular orbitals are shown in Figs. 7 and 8, respectively. It was found in Fig. 7 that the HOMO exists around the oxygen atoms, and that the electron density around the oxygen atoms apart from the boron atom is higher than that around the

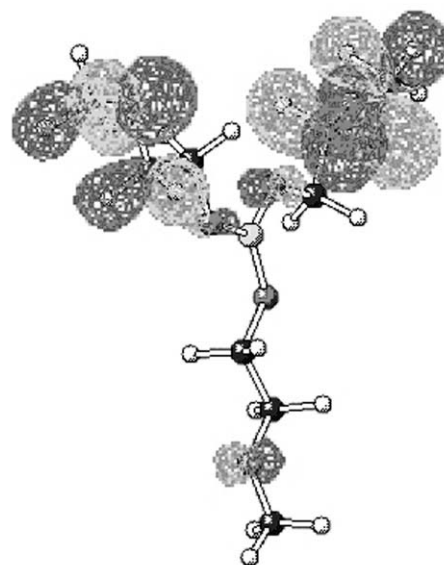


Fig. 7 Highest energy occupied molecular orbital (HOMO) of the PEG-borate ester.



Fig. 8 Lowest energy unoccupied molecular orbital (LUMO) of the PEG-borate ester.

oxygen atoms next to the boron atom. Therefore, it was considered that the lithium ion may interact more strongly with the oxygen atoms apart from the boron atom compared with the other oxygen atoms. On the other hand, Fig. 8 shows that the LUMO exists perpendicular to the BO_3 plane, which indicates a location for the interaction between the boron atom and a Lewis basic anion.

Furthermore, the interactions between the borate ester and the anions of the lithium salts $\text{LiN}(\text{CF}_3\text{SO}_2)_2$, LiCF_3SO_3 and LiClO_4 were investigated. For the investigation, the electronegativity, χ , and the hardness, η , of the anions were estimated by the following calculations. The total electron energies of each of the optimized anions whose charge valence is +1, 0 or -1 were calculated by using DFT, and subsequently ionization potentials, I , and electron affinities, A , are evaluated according to following equations:

$$I = E(\text{X}^{+1}) - E(\text{X}^0) \quad (6)$$

$$A = E(\text{X}^0) - E(\text{X}^{-1}) \quad (7)$$

where X means the anion molecule and E is the total electron energy of the anions. Subsequently, χ and η of the anions or molecules are defined as follows.^{36,37}

$$\chi = \frac{I + A}{2}, \quad \eta = \frac{I - A}{2} \quad (8)$$

The values obtained for χ and η of the anions are summarized in Table 5. According to the theory of Hard and Soft Acids and Bases (HSAB),^{38,39} 'hard' Lewis acids prefer to interact strongly with 'hard' Lewis bases, and, conversely, 'soft' Lewis acids prefer to interact strongly with 'soft' Lewis bases. In this case, PEG-borate esters are known as hard Lewis acids.⁴⁰ It was found in Table 5 that the order of both χ and η of the anions is $\text{CF}_3\text{SO}_3^- > \text{ClO}_4^- > \text{N}(\text{CF}_3\text{SO}_2)_2^-$. Therefore, it is considered that CF_3SO_3^- or ClO_4^- should interact more strongly with the PEG-borate ester compared with

Table 5 Ionization potential, I , electron affinity, A , electron negativity, χ , and hardness, η , of the anions

	I/eV	A/eV	χ	η
ClO_4^-	12.50	5.37	8.94	3.57
CF_3SO_3^-	13.37	5.24	9.31	4.07
$\text{N}(\text{CF}_3\text{SO}_2)_2^-$	10.82	5.51	8.17	2.66

$\text{N}(\text{CF}_3\text{SO}_2)_2^-$. These tendencies are in good agreement with the comparisons about $\sigma(T_g)$ (Table 3) and the transference number of the lithium ions (Table 4). Therefore, it is concluded that the boron atoms of the polymer backbone act as a 'hard' Lewis acid center and prefer to interact strongly with 'hard' Lewis bases such as CF_3SO_3^- and ClO_4^- in the polymer electrolytes, which enhances dissociation of the lithium salts and the transference number of the lithium ions.

Conclusion

We have studied the ionic conductivity, thermal properties and transference number of the lithium ions of the polymer electrolytes containing borate ester groups, which are fixed to chains of the matrix polymer. It was found that the ionic conductivity of the polymer electrolytes increases with decreasing concentration of the borate ester groups which play a role of crosslinking points. The increase in the ionic conductivity is considered to be due to the increase in the mobility of the carrier ions, which was implied by DSC studies. On the other hand, the transference number of the lithium ions increased with increasing concentration of the borate ester groups. Furthermore, the transference number in the polymer electrolyte containing LiCF_3SO_3 or LiClO_4 was found to be higher than that of the electrolyte with $\text{LiN}(\text{CF}_3\text{SO}_2)_2$. By comparing $\sigma(T_g)$ values of the polymer electrolytes with various lithium salts, LiCF_3SO_3 , LiClO_4 and $\text{LiN}(\text{CF}_3\text{SO}_2)_2$, it was expected that the degree of dissociation of LiCF_3SO_3 or LiClO_4 would be higher than that of $\text{LiN}(\text{CF}_3\text{SO}_2)_2$.

In order to clarify the qualitative relationships between the Lewis acidity of the borate ester groups and Lewis basicity of the anions, interactions between the borate ester group and the anions were investigated by *ab initio* calculations, by Hartree-Fock level and density functional theory. It was found that the boron atoms of the PEG borate ester act as a Lewis acid center and prefer to interact more strongly with 'hard' Lewis basic anions, CF_3SO_3^- and ClO_4^- , compared with $\text{N}(\text{CF}_3\text{SO}_2)_2^-$ in the polymer electrolytes. These tendencies are in good agreement with the obtained experimental results mentioned above. Therefore, it was confirmed by the *ab initio* calculations that the borate ester groups are effective in enhancements of the dissociation of lithium salts and the transference number of lithium ions in the polymer electrolytes with 'hard' Lewis basic anions.

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