Interaction between the Lewis Acid Group of a Borate Ester and Various Anion Species in a Polymer Electrolyte Containing Mg Salt

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To clarify the interaction between a Lewis acid and anionic species of the supporting salt incorporated in a polymer electrolyte, we designed a novel solid polymer electrolyte based on Mg salt complexes of poly-(ethylene glycol) (PEO) chains cross-linked by a borate ester group as a Lewis acid and examined the ionic conduction mechanism of the electrolyte. $Mg(ClO_4)_2$, $Mg(CF_3SO_3)_2$, and $Mg[(CF_3SO_2)_2N]_2$ were used as the Mg salt. To change the concentration of the Lewis acid in the polymer electrolyte, two different lengths of PEG chains, which were cross-linked by borate ester group, were used. By estimating the transport number of the Mg^{2+} cation ($t_{Mg^{2+}}$) of the electrolytes, it was found that the borate ester group interacts with anions with the consequence that $t_{Mg^{2+}}$ increases with increasing concentration of borate ester group. By measuring Raman spectra for the electrolyte containing $Mg(ClO_4)_2$ salt, it was also found that the concentration of the free ClO_4^- anion increased with the increasing concentration of the borate ester group in the polymer electrolyte, which implied that *the relative proportion of free Mg^{2+} carrier ion* also increased. The order of the $t_{Mg^{2+}}$ value was $Mg(ClO_4)_2 > Mg(CF_3SO_3)_2 \gg Mg[(CF_3SO_2)_2N]_2$. The change in the total energy due to the interaction between the PEG–borate ester and each anion species using ab initio calculation is in good agreement with the results of the $t_{Mg^{2+}}$ and Raman spectra. These results indicate that the borate ester group as a Lewis acid interacts with hard anions of ClO_4^- or $CF_3SO_3^-$ more strongly than the soft anion of $(CF_3SO_2)_2N^-$ to enhance the degree of dissociation of the salt and trap the anion in the polymer electrolyte.

1. Introduction

To create a new battery having much more safety compared with a lithium-ion battery and relatively high-energy density, magnesium is an attractive candidate for the anode material because of the divalence and the low potential of -2.3 V versus NHE.[1] The electrochemical equivalence is also high, 2.2 A h g^{-1}.[2] A number of studies on the electrode materials for the Mg-ion battery have been already performed and it has been known that several materials can insert the Mg^{2+} ion in themselves.[2-4] However, studies on a Mg^{2+}-conductive electrolyte, especially solid polymer electrolyte, seem to be fewer and more limited than those of the lithium ion. It is considered that the property of the divalent cation of magnesium causes serious problems for applying the poly(ethylene oxide) (PEO) polymer electrolyte to the Mg-ion battery; i.e., the reasons are (1) a strong electrostatic interaction between the Mg^{2+} cation and the counteranion, indicating that the Mg salt is difficult to dissociate in the polymer electrolyte, and (2) a strong electrostatic interaction between the Mg^{2+} cation and the ether oxygen

of the PEO chains in the matrix polymer, indicating that the mobility of the Mg^{2+} cation and the transport number might be low.

On the other hand, in our previous study, we have proposed a new type of solid polymer electrolyte conducting Li$^+$ cation by adding a PEG–borate ester having Lewis acidity as a plasticizer and showed that the PEG–borate ester is quite effective for getting high ionic conductivity, more than 10^{-4} S cm^{-1} at room temperature.[5,6] Moreover, we have investigated the influence of the Lewis acidity of the PEG–borate ester on the lithium ionic conductivity of the polymer electrolyte and suggested that the Lewis acidity of the PEG–borate ester enhances the degree of dissociation of the Li salt in the polymer electrolyte and traps the anion species to increase the transport number of the Li$^+$ cation.[7] Other research groups have also reported the effect of the Lewis acid and pointed out that the Lewis acid interacts with the anion of the Li salt to increase the ionic conductivity of the Li$^+$ cation in the polymer electrolytes.[8,9] Therefore, applying the concept of Lewis acidity to the Mg^{2+}-conducting polymer electrolyte is quite interesting and important for developing a novel Mg^{2+}-conducting polymer electrolyte having high Mg^{2+} ion conductivity and high Mg^{2+}

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R: $(CH_2CH_2O)_n$

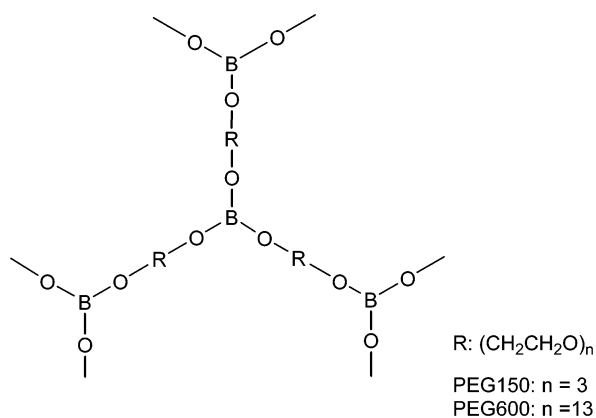PEG150: n = 3
PEG600: n =13

Figure 1. Structure of the polymer matrix.

transport number because the interaction between Lewis acid groups and counteranions may lead to a decrease with strong electrostatic interaction between the Mg^{2+} cation and the counteranion. Recently, we have reported a novel Mg^{2+}-conducting polymer electrolyte added the PEG−borate ester as a plasticizer and showed that the Lewis acidity of the PEG−borate ester influences on the ionic conductivity of the electrolyte.[10] Furthermore, we have developed another type of novel polymer electrolyte, in which the borate ester group as a Lewis acid is fixed in the matrix polymer of the PEO chains.[11] However, exact interaction between the Mg^{2+} cation and the anion, which gives the guiding principle to design Mg^{2+}-conductive solid polymer electrolyte having high Mg^{2+} conductivity and high transport number, is still unknown. Several researchers reported that the Mg^{2+} conductivity in polymer electrolytes depends on the kind of the counteranion species of the supporting salt;[12−15] however, in our knowledge, there is no report that clarify the interaction between the Lewis acid and the anion species of the salt quantitatively.

In the present study, by adding various kinds of Mg salts into the borate ester group fixed polymer electrolyte, we experimentally investigated the interaction between the borate ester group and the anions species more in detail by mainly using the ionic conductivity, the transport number of the Mg^{2+} cation, DSC measurement, and Raman spectroscopy. Furthermore, by ab initio calculation, we estimated the change in the total energy when the borate ester interacts with the anion species of the Mg salts on the basis of the hard and soft acids and bases (HSAB) theory.[16,17]

2. Experimental Section

The structure of the polymer matrix of the electrolyte was shown in Figure 1. To change the concentration of borate ester group in the polymer electrolyte, two different lengths of PEG chains, PEG150 and PEG600 (NOF Co. Ltd., the number of the PEG corresponds to the average molecular weight) were used. As a supporting salt, $Mg(ClO_4)_2$ (99%, Soekawa Chemical Co. Ltd.), $Mg(CF_3SO_3)_2$ (98%, Fluka), or an imide salt, Mg-$[(CF_3SO_2)_2N]_2$, was used without further purification. The imide salt was prepared by dissolving $MgCO_3$ in a slight excess of an aqueous solution of $HN(CF_3SO_2)_2$ (~97%, Fluka).[18−20] The $Mg[(CF_3SO_2)_2N]_2$ solution was filtered and precipitated at 100 °C. The obtained imide salt was finally dried in a vacuum at 140 °C for 24 h.

The polymer electrolyte films were prepared as reported in the previous paper.[7,21] At first, the appropriate amount of PEG150 or PEG600, Mg salt and B_2O_3 (99%, Soekawa Chemical Co. Ltd.) were mixed together in a flask and stirred

for 3 h. The molar ratio of magnesium atoms to ether oxygen atoms in the total ether chains of PEG was fixed to 1:64 or 1:32. The resulting homogeneous viscous solution was poured on a Teflon plate, and then by heating the solution at 110 °C for 24 h in a vacuum oven for the polymerization of the electrolyte, free-standing electrolyte films with about 1 mm thickness were obtained after cooling to room temperature. All these steps of the preparation were carried out in the Ar-filled glovebox (dew point: −76 °C). Hereafter the composition of polymer electrolyte, for example, the electrolyte prepared from PEG150, B_2O_3 and $Mg(ClO_4)_2$ whose ratio of Mg^{2+}/ether oxygen is 1/64, is represented as PEG150−B_2O_3 + $Mg(ClO_4)_2$ (Mg/EO = 1/64).

Ionic conductivity of the polymer electrolytes was measured by the ac impedance technique using Hioki3532 LCR Hitester impedance analyzer over the frequency range from 63 Hz to 4.5 MHz. The polymer electrolyte film was cut into disks of 10 mm in diameter, sandwiched between stainless steel electrodes (SUS 304), and subjected to the impedance analyzer. The measurement was performed under cooling condition by 10 °C, after heating the electrolyte samples until 110 °C for 2 h.

Thermal property of the obtained polymer electrolyte samples was investigated by differential scanning calorimetry (DSC) using DSC 6200 (Seiko Instruments). The measurement was carried out from −120 to +100 °C at the scan rate of 10 °C min^{-1}, after the sample in the aluminum pan was cooled to −120 °C at the same scan rate. The operation for the measurement was fixed as one cycle and repeated a few times. An empty aluminum pan was used as a reference.

The transport number of the Mg^{2+} cation was estimated by examining dc polarization for the electrolyte samples, which is proposed by Blonsky et al.[22] In this study, the sample was sandwiched between two Mg metal sheets as a nonblocking electrode and subjected to the dc polarization of 1 V at 60 °C.

The degree of the dissociation of the salt in the polymer electrolyte samples was investigated by laser Raman spectroscopy using NRS-2100 (JASCO Co. Ltd.). The excitation source was an Ar ion laser (514.5 nm, 50 mW). The spectral resolution was 2.0 cm^{-1}. The measurement was carried out at room temperature.

The more quantitative interaction between the borate ester group and the anions of the Mg salts was investigated by ab initio Hartree−Fock (HF) self-consistent field molecular orbital calculation and density function theory (DFT) calculation performed by the Gaussian 98 program.[23] As a model molecular structure of the borate ester group having PEGs, a PEG−borate ester, $B(OCH_2CH_2OCH_3)_3$, was used. The geometry of the PEG−borate ester was optimized by DFT method with B3LYP form for exchange-correlation function and 6-311+G** basis set after the optimization by HF method with 3-21G basis set. The anions, ClO_4^-, $CF_3SO_3^-$, and $(CF_3SO_2)_2N^-$, were similarly subjected to the ab initio calculation for the optimizations. From the results of the total electron energy of the molecule and the ions, the interaction between the PEG−borate ester and each anion was estimated by the equations based on HSAB theory[16,17] and discussed.

3. Results and Discussion

Figure 2 shows the temperature dependence of the ionic conductivity, represented in Arrhenius type, for the polymer electrolyte sample, PEGx−B_2O_3 (x = 150 or 600) + MgX$_2$ salt (X = ClO_4, CF_3SO_3, $(CF_3SO_2)_2$N) (Mg/EO = 1/64). The ionic conductivity of PEG600-used electrolytes was higher than the PEG150-used electrolytes in all case of containing each kind
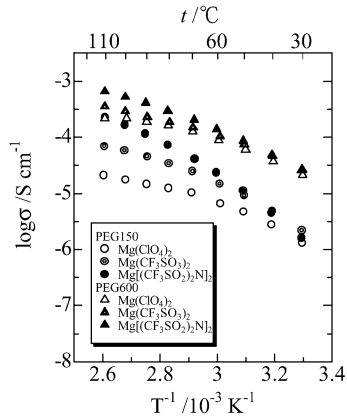
Figure 2. Arrhenius plots for ionic conductivity of PEGx−B$_2$O$_3$ + MgX$_2$ (Mg/EO = 1/64).

of Mg salt. As for the difference due to the kind of supporting salts, the electrolyte containing Mg[(CF$_3$SO$_2$)$_2$N]$_2$ salt showed the highest ionic conductivity in both case of the PEG150- and PEG600-used electrolytes. Recently, Morita et al.[14,15] reported an ionic conduction of Mg^{2+}-conducting polymer electrolyte composed of oligo(ethylene oxide)-grafted polymethacrylate matrix by adding a PEG−dimethyl ether plasticizer having low molecular weight (ca. 230−400). They also reported the ionic conductivities of the electrolyte containing these Mg salts, Mg-(ClO$_4$)$_2$, Mg(CF$_3$SO$_3$)$_2$, and Mg[(CF$_3$SO$_2$)$_2$N]$_2$, and the values are almost same as those of the PEG600-used electrolytes at the order of 10^{-4}–10^{-5} S cm^{-1} in the temperature range 60−30 °C. These results indicate that our prepared electrolyte exhibits one of the highest ionic conductivity containing Mg salt even without plasticizer having low molecular weight. All of the Arrhenius plots of the ionic conductivity exhibited convex profile. The convex profile of temperature dependence is typically observed in the case of ionic conduction in solid polymer electrolyte.[24−28] This result indicates that the ionic conduction mechanism of all of the samples is different from the hopping model of the carrier ions, which is applied to inorganic ionic conductors[29] or gel polymer electrolytes using low molecular solvents such as propylene carbonate (PC), ethylene carbonate (EC), and dimethyl carbonate (DMC).[30]

To clarify the ionic conduction mechanism in the present system, we examined the viscoelastic property including the glass transition temperature (T_g) of the polymer electrolyte samples by DSC. Figure 3 shows the DSC curves of the polymer electrolytes, corresponding with the results of the second cooling run. The compositions of the electrolytes are the same as those of the samples in Figure 2. As shown in Figure 3, only the T_g around −50 °C was observed for the electrolytes in the cooling run after the heating run. Because the ionic conductivity of the electrolytes was measured during the cooling condition after heating at 110 °C, the thermal situation in Figure 3 corresponds to that of Figure 2. In Figure 3, there is no peak corresponding crystalline phase formation and/or melting of crystalline phase. This result indicates that the polymer electrolyte is amorphous during the measurement of the ionic conductivity of the electrolyte.

Additionally, the glass transitions of the electrolytes containing each Mg salt were observed during the temperature range −44 to −32 °C for PEG150-used electrolyte and −57 to −53 °C for PEG600-used electrolyte. The T_g's of the polymer electrolytes are listed in Table 1. T_g is correlated with the frozen temperature of segmental motion of EO chains.[31−33] Accordingly, the mobility of the carrier ions is correlated with the T_g,
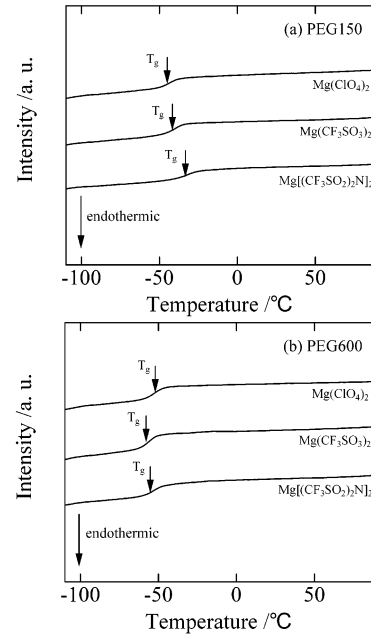

Figure 3. DSC curves of (a) PEG150−B$_2$O$_3$ + MgX$_2$ (Mg/EO = 1/64) and (b) PEG600−B$_2$O$_3$ + MgX$_2$ (Mg/EO = 1/64). second cooling run.

TABLE 1: Glass Transition Temperature (T_g) of PEGx−B$_2$O$_3$ + MgX$_2$ (Mg/EO = 1/64)

composition of electrolyte	T_g (°C)
PEG150−B$_2$O$_3$−Mg(ClO$_4$)$_2$	−44
PEG150−B$_2$O$_3$−Mg(CF$_3$SO$_3$)$_2$	−40
PEG150−B$_2$O$_3$−Mg[(CF$_3$SO$_2$)$_2$N]$_2$	−32
PEG600−B$_2$O$_3$−Mg(ClO$_4$)$_2$	−53
PEG600−B$_2$O$_3$−Mg(CF$_3$SO$_3$)$_2$	−57
PEG600−B$_2$O$_3$−Mg[(CF$_3$SO$_2$)$_2$N]$_2$	−53

for example, when the T_g of a polymer electrolyte is low, the mobility of the carrier ions in the polymer electrolyte is high. In the case of the present system, T_g's for PEG150-used electrolyte are higher than that for PEG600-used electrolyte. This result means that the T_g's of the electrolytes increased with increasing the amount of the cross-linked point by borate ester group, which indicates that the decrease in the mobility of the carrier ions is one of the reasons for decreasing the ionic conductivity of the polymer electrolyte containing each Mg salt, as shown in Figure 2.

The temperature dependence (Figure 2) usually observed by the ionic conduction mechanism is expressed by the William−Landel−Ferry (WLF) relationship[34] based on free volume theory.[35] It is generally thought that ion conduction in the solid polymer electrolyte occurs by the segmental motion of the polymer chains in amorphous region.[24−28]

According to the free volume theory, WLF equation is represented as follows:

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

where $\sigma(T)$ and $\sigma(T_g)$ are the conductivity at temperature T and T_g, respectively, and C_1 and C_2 are the WLF parameters of ionic conductivity. However, the ionic conductivity at T_g, $\sigma(T_g)$, is difficult to measure in the present experiments because $\sigma(T_g)$ is quite low to measure by the ac impedance measurement. Therefore, 30 °C was selected as a reference temperature, T_0, for this study. And then, eq 1 is rewritten as follows:
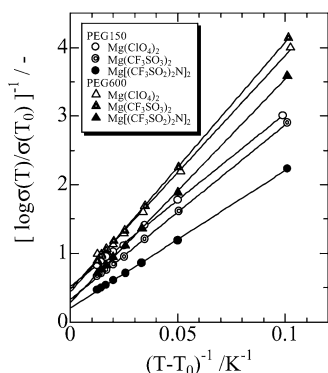
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Figure 4. WLF plots of ionic conductivity for PEGx−B$_2$O$_3$ + MgX$_2$ (Mg/EO = 1/64).

TABLE 2: WLF Parameters of PEGx−B$_2$O$_3$ + MgX$_2$ (Mg/EO = 1/64)

composition of electrolyte	C_1	C_2 (K)
PEG150−B$_2$O$_3$−Mg(ClO$_4$)$_2$	17	19
PEG150−B$_2$O$_3$−Mg(CF$_3$SO$_3$)$_2$	14	23
PEG150−B$_2$O$_3$−Mg[(CF$_3$SO$_2$)$_2$N]$_2$	19	14
PEG600−B$_2$O$_3$−Mg(ClO$_4$)$_2$	22	11
PEG600−B$_2$O$_3$−Mg(CF$_3$SO$_3$)$_2$	21	12
PEG600−B$_2$O$_3$−Mg[(CF$_3$SO$_2$)$_2$N]$_2$	23	11

$$\log \frac{\sigma(T)}{\sigma(T_0)} = \frac{C_1'(T - T_0)}{C_2' + (T - T_0)} \quad (2)$$

The WLF parameters in eq 1 are calculated from[27]

$$C_1 = C_1'C_2'/[C_2' - (T_0 - T_g)] \quad (3)$$

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

WLF parameters may be useful to discuss the ionic conduction mechanism of solid polymer electrolyte because the eq2 is rewritten as follows:

$$\left[\log \frac{\sigma(T)}{\sigma(T_0)}\right]^{-1} = \frac{C_2'}{C_1'(T - T_0)} + \frac{1}{C_1'} \quad (5)$$

It indicates that if $[\log \sigma(T)/\sigma(T_0)]^{-1}$ and $(T - T_0)$ are taken as the Y axis and X axis, respectively, the WLF plots of the ionic conductivity for the polymer electrolyte should become linear, in which C_2'/C_1' and $1/C_1'$ are the gradient and the y-intercept of the graph, respectively. As shown in Figure 4, the WLF plots for all of the electrolytes showed linear shape. It indicates that the temperature dependence of the ionic conductivity for the electrolytes follows the WLF type equation. The WLF parameters of the polymer electrolytes were calculated and are summarized in Table 2. As compared with the universal values of WLF parameters, $C_1 = 17.4$ and $C_2 = 51.6/K$,[34] the obtained parameters were found to be of same order to those. It implies that the temperature dependence of the ionic conductivity of the polymer electrolytes is dominated by the ionic transportation due to the segmental motion of the polymer chains in the electrolytes.

Next, the interaction between the borate ester group as a Lewis acid and the anion species of the salts will be discussed. If the borate ester group interacts with anion species, the anion will be weakly trapped. Therefore, the transport number of the Mg^{2+} cation ($t_{Mg^{2+}}$) should increase with the increasing concentration of the borate ester group in the electrolyte. At first, to investigate the strength of the interaction between the borate ester group and the anion species, the transport number of the

TABLE 3: Transport Number of the Mg^{2+} Cation ($t_{Mg^{2+}}$) of PEGx−B$_2$O$_3$ + Mg(ClO$_4$)$_2$ (Mg/EO = 1/64)

composition of electrolyte	$t_{Mg^{2+}}$
PEG150−B$_2$O$_3$−Mg(ClO$_4$)$_2$	0.51
PEG600−B$_2$O$_3$- Mg(ClO$_4$)$_2$	0.02

TABLE 4: Transport Number of the Mg^{2+} Cation ($t_{Mg^{2+}}$) of PEG150−B$_2$O$_3$ + MgX$_2$ (Mg/EO = 1/64)

composition of electrolyte	$t_{Mg^{2+}}$
PEG150−B$_2$O$_3$−Mg(ClO$_4$)$_2$	0.51
PEG150−B$_2$O$_3$−Mg(CF$_3$SO$_3$)$_2$	0.37
PEG150−B$_2$O$_3$−Mg[N(CF$_3$SO$_3$)$_2$]$_2$	0.20

Mg^{2+} cation ($t_{Mg^{2+}}$) was estimated. Additionally, by comparing the $t_{Mg^{2+}}$ for the electrolyte containing each Mg salt, the difference of the interaction strength due to the kind of the anion species should be found. $t_{Mg^{2+}}$ was estimated by subjecting to dc polarization for the samples and using the equation by Blonsky et al.[22] as follows:

$$t_+ = \frac{\sigma_+}{\sigma_+ + \sigma_-} = \frac{\sigma_+}{\sigma_{total}} = \frac{1/R_{total(\infty)}}{1/R_{total(0)}} = \frac{\Delta V/I_{(0)}}{\Delta V/I_{(\infty)}} = \frac{I_{(\infty)}}{I_{(0)}} \quad (6)$$

where t_+ is the transport number of the cationic species, σ_+ is the conductivity of the cationic species, σ_- is the conductivity of the anionic species, σ_{total} is the total conductivity of the electrolyte, $R_{total(\infty)}$ is the resistance at steady-state condition of the cell, $R_{total(0)}$ is the resistance at initial condition of the cell, ΔV is the applied constant potential between the electrodes (in our case ΔV is 1 V), and $I_{(0)}$ and $I_{(\infty)}$ are the current at the initial and steady states, respectively. The values of $t_{Mg^{2+}}$ for the PEG150- and PEG600-used electrolytes containing Mg(ClO$_4$)$_2$ salt are listed in Table 3. The value of $t_{Mg^{2+}}$ drastically increased with the increasing concentration of the borate ester group in the electrolyte, which indicates that the borate ester group as a Lewis acid interacts with and traps the ClO$_4^-$ anion of the Mg(ClO$_4$)$_2$ salt. Furthermore, the values of $t_{Mg^{2+}}$ for the PEG150-used electrolytes containing each Mg salt are summarized in Table 4. From the data in Table 4, it is found that the order of the $t_{Mg^{2+}}$ value was Mg(ClO$_4$)$_2$ > Mg(CF$_3$SO$_3$)$_2$ ≫ Mg[(CF$_3$SO$_2$)N]$_2$. It indicates that the borate ester group interacts with the ClO$_4^-$ and CF$_3$SO$_3^-$ anion more strongly than the (CF$_3$SO$_2$)$_2$N$^-$ anion.

As for the ionic conductivity of the electrolytes shown in Figure 2, the order of magnitude is Mg[(CF$_3$SO$_2$)N]$_2$ > Mg(CF$_3$SO$_3$)$_2$ > Mg(ClO$_4$)$_2$ in both cases of the PEG150- and the PEG600-used electrolyte. The value of the ionic conductivity from ac impedance exhibits the total ionic conductivity of the Mg^{2+} cation and the anion species. Therefore, in the case of the electrolyte containing Mg[(CF$_3$SO$_2$)N]$_2$, the ratio of the anion conductivity is higher than the other anion species and the total ionic conductivity may be higher.

Moreover, if the interaction between the borate ester group and anion species is strong, the negative charge of the anion decreases. As a result, the Coulombic interaction between the Mg^{2+} cation and the anion species should be weakened to promote the degree of dissociation of the Mg salt. This means that *the relative proportion of* the free anion in the electrolyte should increase. To investigate *the relative proportion of* the free anion in the polymer electrolyte, the Raman spectra of the electrolytes containing the Mg(ClO$_4$)$_2$ salt, whose anion was interacted more strongly by the borate ester group than the other anion species, were measured at same temperature, 25 °C. Figure 5 shows the Raman spectra of PEGx−B$_2$O$_3$ (x =150 or 600) + Mg(ClO$_4$)$_2$ (Mg/EO = 1/32 or 1/64) and the Mg(ClO$_4$)$_2$ salt,
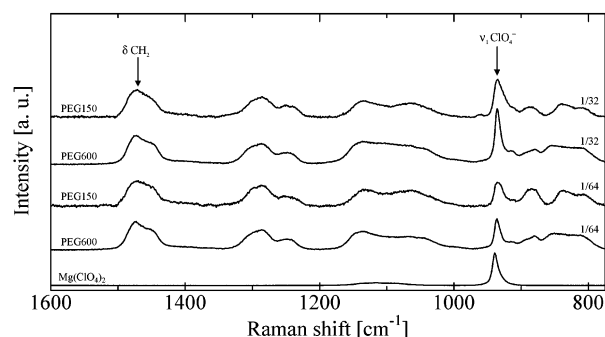
Figure 5. Raman spectra of PEGx−B$_2$O$_3$ (x = 150 or 600) + Mg(ClO$_4$)$_2$ (Mg/EO = 1/32 or 1/64) and Mg(ClO$_4$)$_2$ at 25 °C.

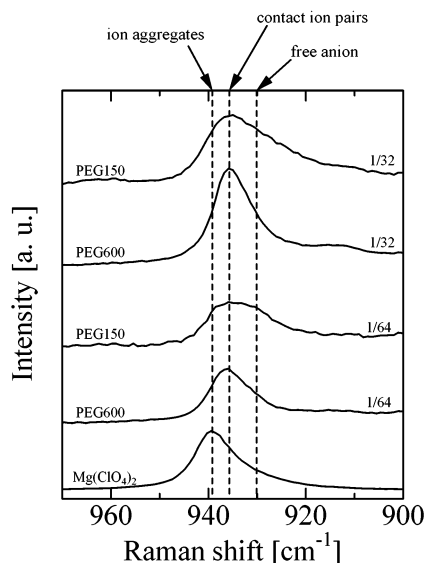**Figure 6.** Expanded data for the Raman spectra of PEGx−B$_2$O$_3$ (x = 150 or 600) + Mg(ClO$_4$)$_2$ (Mg/EO = 1/32 or 1/64) and Mg(ClO$_4$)$_2$ at 25 °C.

itself, respectively. The spectra are normalized by the integral area value of the deformation vibration peak for CH$_2$ (δ(CH$_2$)) of the polymer matrix around 1465 cm^{-1}, following the method by Rey et al.[36] From the result of Figure 5, the Raman spectrum for the ClO$_4^-$ anion (ν_1(ClO$_4^-$)) of the Mg(ClO$_4$)$_2$ salt in all of the polymer electrolytes appeared around 930 cm^{-1}. To discuss the peak for the ClO$_4^-$ anion in the electrolyte, the expanded data are shown in Figure 6. In general, it is known that the symmetric stretch band of the free ClO$_4^-$ anion (solvated ion and/or weakly trapped ion by borate ester) appears at 933 cm^{-1}, contact ion pairs at 948 cm^{-1}, and multiple ion aggregates at 955 cm^{-1} in the case of the LiClO$_4$ and NaClO$_4$ salts.[37,38] In the case of the Mg salt, 930 cm^{-1} for the free ClO$_4^-$ anion, 936 cm^{-1} for the contact ion pairs, and 939 cm^{-1} for the Mg-(ClO$_4$)$_2$, itself, were observed in the previous study.[10,11] From the result of Figure 6, it is found that *the relative proportion of* contact ion pairs and ion aggregates decrease and *the relative proportion of* free ClO$_4^-$ anion increase in the spectra of both PEG150-used electrolytes, which have higher concentrations of the Lewis acid by the borate ester group, as compared with those of the PEG600-used electrolytes. Therefore, it is considered that the borate ester group interacts with the ClO$_4^-$ anion in the electrolyte to promote the degree of dissociation of Mg(ClO$_4$)$_2$ salt and *the relative proportion of free Mg^{2+} carrier ion* also increases in the polymer electrolyte.

To investigate and clarify the interaction between the borate ester group and the anion species more quantitatively, ab initio
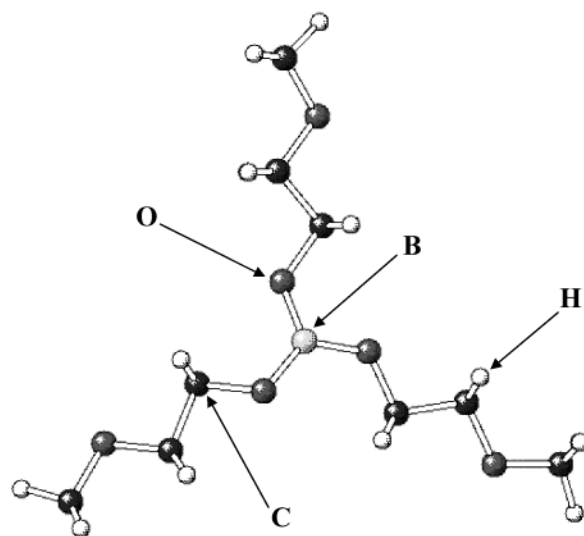

Figure 7. Optimized molecular structure of B(OCH$_2$CH$_2$OCH$_3$)$_3$. B3LYP/6-311+G**//HF/3-21G.
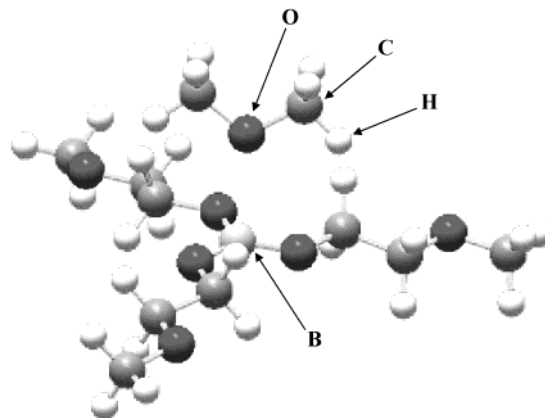

Figure 8. Optimized molecular structure of the complex of PEG−borate ester and dimethyl ether. B3LYP/6-311+G**//HF/3-21G.

calculation was performed for the PEG−borate ester shown in Figure 7 as a model molecule and each anion species. Figure 7 shows the most stable geometry of the PEG−borate ester, which was obtained by the optimization using the DFT method with B3LYP form for exchange-correlation function and 6-311+G** basis set after the optimization using the HF method with 3-21G basis set. However, in the case of the actual polymer electrolyte with the borate ester group, the functional group should interact with not only the anion species of the Mg salt but also the oxygen of the PEO chains of the matrix polymer as a Lewis base. Therefore, the oxygen of the PEO chains was substituted by a dimethyl ether (DME) and the molecular structure of the complex of the PEG−borate ester and the DME was optimized by the same method (Figure 8). As shown in Figure 8, the optimized molecular structure of the PEG−borate ester in the complex is almost the same structure shown in Figure 7. Moreover, the binding energy was −2.6 kJ mol^{-1} (−0.027 eV), which is quite a low value as the binding energy of complex formation. This means that the interaction between the borate ester group (Lewis acid group) and ether group (Lewis base group) is not strong. Therefore, in this study, the molecular structure of the PEG−borate ester shown in Figure 7 was selected as the most stable molecular structure and was used in the discussion below.

When the interaction between C and D occurs, the change in the total energy, ΔE, and the number of the transference electron

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TABLE 5: Absolute Electronegativity and Absolute Hardness for PEG−Borate Ester, Pentaglyme, and Anion Species

species	$E(X^{1-})$ (au)	$E(X^0)$ (au)	$E(X^{1+})$ (au)	χ (eV)	η (eV)
PEG−borate	−832.107366	−832.135869	−831.819816	3.91	4.69
pentaglyme	−924.402133	−924.464027	−924.156949	3.34	5.02
ClO_4^-	−760.745292	−760.932523	−760.735265	0.14	5.23
$CF_3SO_3^-$	−961.555515	−961.730421	−961.537879	0.24	5.00
$(CF_3SO_2)_2N^-$	−1827.496258	−1827.610421	−1827.40776	1.20	4.31

from D to C, ΔN, are represented as the following equations by Pearson et al.:[39,40]

$$\Delta E = -\frac{(\chi_C - \chi_D)^2}{4(\eta_C + \eta_D)} \quad (7)$$

$$\Delta N = \frac{(\chi_C - \chi_D)}{2(\eta_C + \eta_D)} \quad (8)$$

where χ and η refer to the *absolute electronegativity* and the *absolute hardness* for each species. The χ and η are calculated by the following equations:

$$\chi = \frac{(I + A)}{2} \quad (9)$$

$$\eta = \frac{(I - A)}{2} \quad (10)$$

where I and A refer the *ionization potential* and the *electron affinity* for each species. Furthermore, the I and A are calculated by the following equations:

$$I = E(X^{1+}) - E(X^0) \quad (11)$$

$$A = E(X^0) - E(X^{1-}) \quad (12)$$

where $E(X^0)$ refers the total energy of the object species and $E(X^{1-})$ and $E(X^{1+})$ refer those of the ion of the species having electron charge of −1 and +1, respectively. In this study, we chose the PEG−borate ester having no electron charge for the calculation of $E(X^0)$ of itself, and for the anion species, the species having electron charge of −1 was chosen. From each $E(X^0)$, $E(X^{1-})$, and $E(X^{1+})$, I, A, χ, and η were calculated and by using each χ and η, the interaction between the PEG−borate ester and the anion species was estimated. Here as a comparing object species having no borate ester group as a Lewis acid, pentaglyme, $(CH_3O(CH_2CH_2O)_5CH_3)$, was used because the number of oxygens as a Lewis base in the molecule is same as that in the PEG−borate ester. The total energies, $E(X^0)$, $E(X^{1-})$, and $E(X^{1+})$, and the estimated χ and η of the anion species are summarized in Table 5. According to the hard and soft acids and bases (HSAB) theory,[16,17] if the value of χ is higher, the species is a stronger Lewis acid and if the value of χ is lower, the species is a stronger Lewis base. Moreover, "hard" Lewis acids prefer to interact with "hard" Lewis bases, and "soft" Lewis acids prefer to interact with "soft" Lewis bases. As shown in Table 5, the value of χ for the PEG−borate ester is higher than that of the pentaglyme, which indicates that the PEG−borate ester is a stronger Lewis acid than pentaglyme. Furthermore, because the borate ester group is generally known to be as a hard Lewis acid,[41] the anion species having large η and small χ is considered to interact with the borate ester group more strongly. From the results in Table 5, the order of magnitude of η for the anion species is $ClO_4^- > CF_3SO_3^- \gg$

TABLE 6: Interaction between PEG−Borate Ester and Anion Species[a]

interaction	ΔE (eV)	ΔN
$ClO_4^- \rightarrow$ PEG−borate	−0.359	0.190
$CF_3SO_3^- \rightarrow$ PEG−borate	−0.348	0.190
$(CF_3SO_2)_2N^- \rightarrow$ PEG−borate	−0.204	0.150
$ClO_4^- \rightarrow$ pentaglyme	−0.250	0.156
$CF_3SO_3^- \rightarrow$ pentaglyme	−0.239	0.154
$(CF3SO_2)_2N^- \rightarrow$ pentaglyme	−0.122	0.114

[a] ΔE and ΔN correspond to the change in the total energy and the number of the transferred electron for each interaction, respectively. The arrows in the table show the transferring directions of electron.

$(CF_3SO_2)_2N^-$ and the order of χ is $ClO_4^- < CF_3SO_3^- \ll (CF_3SO_2)_2N^-$. Therefore, it is considered that hard strong anions of ClO_4^- and $CF_3SO_3^-$ should interact with the borate ester group more strongly than soft weak anion of $(CF_3SO_2)_2N^-$. Furthermore, the results of the actual energy change, ΔE, and the transference electron number, ΔN, by the interaction between the borate ester group and the anion species are summarized in Table 6. From the result of ΔE and ΔN values, it is found that the interaction of the PEG−borate ester with the ClO_4^- and $CF_3SO_3^-$ is stronger than $(CF_3SO_2)_2N^-$, which corresponds with the results of the $t_{Mg^{2+}}$ for the polymer electrolytes. Furthermore, the PEG−borate ester interacts with the anion species more strongly than the pentaglyme for all kinds of the anion species. It corresponds with the result of the Raman spectra for the electrolytes, which indicates that the borate ester group interacts with the anion species to promote the degree of dissociation of the Mg salts. From the above results, we concluded that the PEG−borate ester interacts with and traps the anion species of the Mg salts to promote the degree of dissociation of Mg salt in the polymer electrolyte and the borate ester group interacts with hard strong anions of ClO_4^- and $CF_3SO_3^-$ more strongly than soft weak anion of $(CF_3SO_2)_2N^-$.

4. Conclusions

To investigate the interaction between the Lewis acid and anion species of the salt, we produced a novel Mg^{2+}-conductive polymer electrolyte by adding various kinds of Mg salts into the borate ester group fixed polymer electrolyte. By estimating the $t_{Mg^{2+}}$ of the electrolytes, it is found that the strength order of the interaction between borate ester group and anion species was $ClO_4^- > CF_3SO_3^- \gg (CF_3SO_2)N^-$. The Raman spectra for the electrolytes containing $Mg(ClO_4)_2$ salt showed that the concentration of free ClO_4^- anion in the electrolyte increased with increasing the concentration of the Lewis acid, which indicates that *the relative proportion of free Mg^{2+} carrier ion* also increases. Furthermore, the quantitative value of the interaction between the borate ester group and the anion species estimated by ab initio calculation showed that the change in the total energy, ΔE, and the number of the transference electron, ΔN, corresponds with the results of the $t_{Mg^{2+}}$ and Raman spectra. According to the HSAB theory, in the case of applying the Lewis acid to the polymer electrolyte, using the salts having lower χ and η would be one of the key factor to obtain higher Mg^{2+}-conductive polymer electrolyte.

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