Lithium-Ion Batteries

A High Electrode-Reaction Rate for High-Power-Density Lithium-Ion Secondary Batteries by the Addition of a Lewis Acid[**]

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Lithium-ion secondary batteries using polymer electrolytes based on lithium-salt complexes of polyethers have attracted much attention because of their potential for practical applications, such as electric-, hybrid-, or fuel-cell vehicles.[1] Although enhancement of the charge-transfer reaction rate is important to fabricate high-power-density batteries, only a few investigations have been focused on the charge-transfer reaction at the electrode/polymer electrolyte interfaces.[2] Herein we describe a significant enhancement of the charge-transfer reaction rate by addition of Lewis acid to polymer electrolytes. This is, to our knowledge, the first report about the achievement of a high rate by the addition of additives to electrolytes.

Recently, we reported that poly(ethylene glycol) (PEG)-borate ester increases the ionic conductivity and transport number of lithium ions or magnesium ions of polymer electrolytes.[3] Since the borate ester groups, which act as Lewis acids, prefer to interact with anions, the increase in the conductivity and transport number is induced by enhancing the dissociation of the salts in polymer electrolytes.[3] These results indicate that the activity of lithium ions in the polymer electrolytes increases on addition of the PEG-borate ester. Therefore, the charge-transfer reaction rate should be enhanced by the addition of the Lewis acid, because the rate is proportional to the activity of lithium ions.[4]

Herein, we investigate the influence of the PEG-borate ester on the electrokinetics of the Li^+/Li couple in poly(ethylene glycol) dimethyl ether (PEGDME) based electrolytes. PEGDME solutions of $LiCF_3SO_3$ are used as a model of polymer electrolytes, and is similar to the amorphous conducting phase in high-molecular-weight poly(ethylene oxide). To evaluate the charge-transfer reaction rate at the electrode/electrolyte interfaces, the exchange current densities were studied by chronoamperometry with a microelectrode technique. Microelectrodes have several properties that facilitate the electrochemical analyses, such as minimization of the ohmic (IR) drop and charge current, and enhancement of the transport of electroactive ions to the electrode surface by spherical diffusion.[2,5]

Chronoamperometry was performed to obtain the exchange current densities. The measured coulombic efficiency of lithium deposition and dissolution was over 90 % in all cases, which means that no significant secondary reaction occurred at the interfaces. The exchange current densities obtained in the electrolytic solutions with various amounts of the PEG-borate ester are summarized in Figure 1. Significant increases in the exchange current densities of the electrolytes were found when the PEG-borate ester was added. Furthermore, the values of the exchange current densities show a maximum at each temperature with a PEG-borate ester content of 25 wt % to the standard solvent, PEGDME, which corresponds to a molar ratio of PEG-borate ester:the anion of almost 1:1. The maximum value at 333 K was 2.88 mA cm^{-2} which was 2.8 times larger than that without the PEG-borate ester.

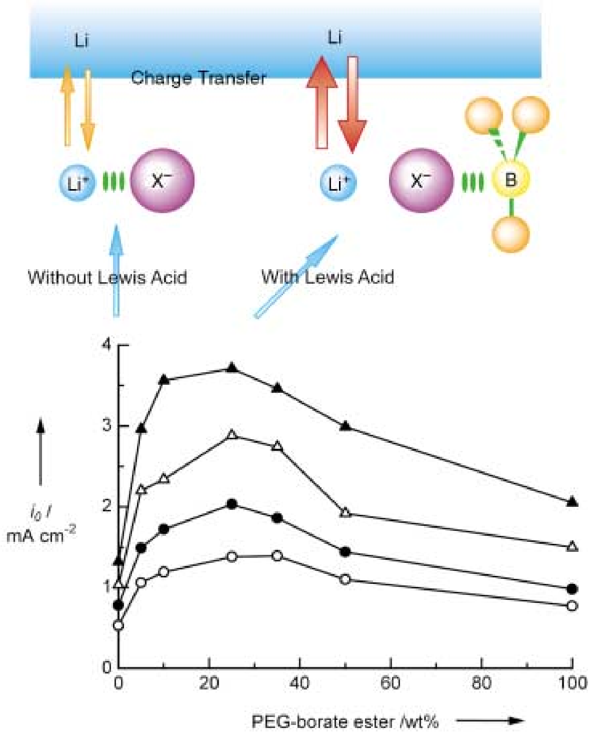

Figure 1. Bottom: The exchange current density i_0 versus the amounts of the PEG-borate ester in 0.5 M $LiCF_3SO_3$/PEGDME at various temperatures: ○ 313 K, ● 323 K, △ 333 K, ▲ 343 K. Top: The PEG-borate ester acting as a Lewis acid should increase the activity of the lithium ions by interacting with the counteranions (X^-) and thus bringing about the increases in the exchange current densities.

The exchange current density i_0 can be expressed as Equation (1),[2a,4] where A is the pre-exponential factor, a_{Li^+} is

$$i_0 = A\sqrt{a_{Li^+}}\exp(-\Delta G^*/RT) \qquad (1)$$

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the activity of lithium ions, ΔG^* is the Gibbs activation energy of the Li^+/Li couple reaction.

To investigate the factor for the increase in the exchange current density of the standard electrolyte with the PEG-borate ester, the activity of lithium ions and the Gibbs activation energy were studied. The activation energy was evaluated with the exchange current densities at various temperatures. The activation energy of the Li^+/Li couple reaction depends mainly on the solvation of the lithium ions. The activation energies were found to remain almost constant even with the addition of the PEG-borate ester (Table 1). Consequently, the main reason for the increase in the exchange current densities is the increase in the activity of lithium ions.

Table 1: Activation energies of the Li^+/Li couple reaction in 0.5 M $LiCF_3SO_3$/PEGDME with various amounts of PEG-borate ester.

PEG-borate ester [wt%]	ΔG^* [kJ mol^{-1}]
0 (only PEGDME)	28.9
5	30.7
10	30.3
25	29.7
35	29.4
50	29.2
100	29.9

The internal vibration modes of the counteranions make Raman spectroscopy very useful for the qualitative investigation of the activity of lithium ions in electrolytes.[6] From the Raman spectra of the polymer electrolytes, the ratio of the free ion, which corresponds to activity of lithium ions, was estimated (Figure 2). This result indicates that the ratio of free ions increased when the PEG-borate ester was added into the electrolytic solution but began to decrease once the amount of PEG-borate ester exceeded a certain threshold level. The ratio of the free ion was highest at the PEG-borate ester of 10–25 wt%, which agrees well with the observed changes in the exchange current density (Figure 1). Therefore, the Raman studies indicate an increase in the activity of lithium ions in the electrolytic solutions on the addition of the PEG-borate ester, which should bring the increases in the exchange current densities (see Figure 1).

To investigate solvation state of a lithium ion in the PEGDME and the PEG-borate ester in more detail, ab initio calculations were carried out (Figure 3). These show that a lithium ion coordinates with five oxygen atoms in the PEGDME (Figure 3a), while with the PEG-borate ester, the lithium ion coordinates to four oxygen atoms (Figure 3b). Additionally, the binding energies $E_{(\mathrm{bind})}$ between a lithium ion and the solvent molecule, PEGDME or the PEG-borate ester, were calculated with Equation (2), where $E_{(\mathrm{complex})}$ is the

$$\Delta E_{(\mathrm{bind})} = E_{(\mathrm{complex})} - \{E_{(\mathrm{solvent})} + E_{(\mathrm{lithium})}\} \qquad (2)$$

total electron energy for a lithium ion with the PEGDME or the PEG-borate ester. $E_{(\mathrm{solvent})}$ and $E_{(\mathrm{lithium})}$ are the total electron energy of the solvent molecule and the lithium ion, respectively.

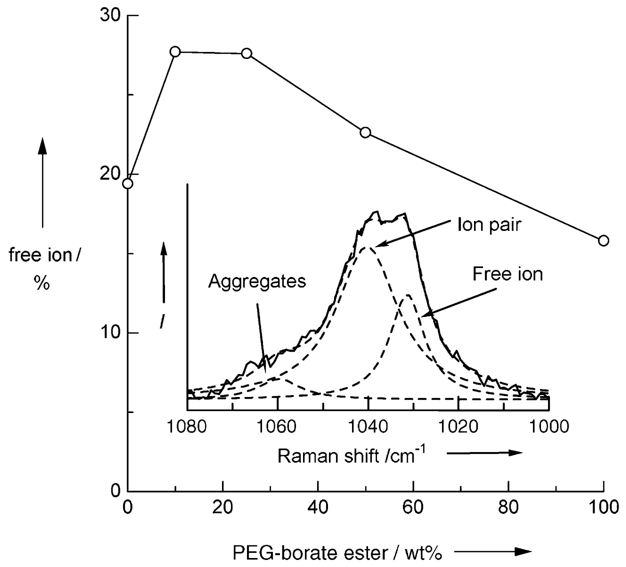

Figure 2. Fraction of free ions versus the amounts of the PEG-borate ester in 0.5 M $LiCF_3SO_3$/PEGDME at 313 K. The fraction is estimated from the Raman spectra (sample spectrum for 25 wt% of PEG-borate ester in 0.5 M $LiCF_3SO_3$/PEGDME is shown in the inset): The spectral band of the SO_3 symmetric stretching mode of $CF_3SO_3^-$ ($\nu_s(SO_3^-)$), which is observed around 1040 cm^{-1}, has been deconvoluted into three components: 1) the lower frequency component around 1034 cm^{-1} is attributed to "free ions"; 2) the component at about 1042 cm^{-1} is "ion pairs"; 3) the highest frequency component at around 1052 cm^{-1} is "multiple aggregated ions".[6] Therefore, the ratio of the free ion corresponds to the ratio of the area arising from free ions (dissociated ions) to that of all the components (aggregated and ion-paired as well as free ions).

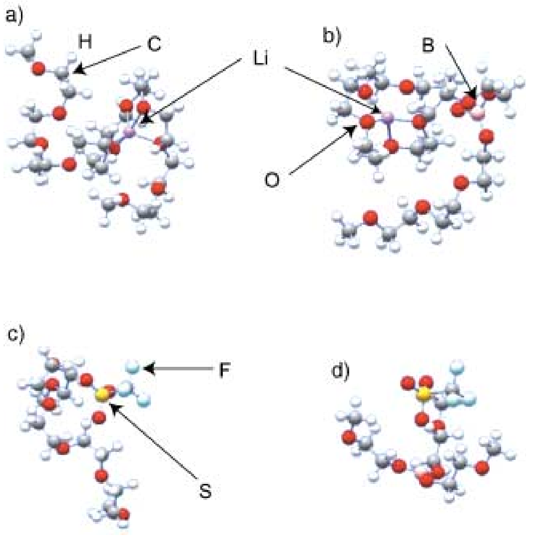

Figure 3. Stable geometries of the complexes from ab initio calculations: a) a lithium ion and the PEGDME, b) a lithium ion and the PEG-borate ester, c) $CF_3SO_3^-$ and the PEGDME, d) $CF_3SO_3^-$ and the PEG-borate ester.

$\Delta E_{(\mathrm{bind})}$ for a lithium ion with the PEGDME was found to be higher than that with the PEG-borate ester (Table 2). This

Table 2: Binding energies between lithium ion or the $CF_3SO_3^-$ ion and PEGDME or PEG-borate ester.

Interaction	ΔE [kJ mol^{-1}]	Coordination number[a]
Li^+–PEGDME	−464.5	5
Li^+–PEG-borate ester	−415.4	4
$CF_3SO_3^-$–PEGDME	−37.0	–
$CF_3SO_3^-$–PEG-borate ester	−44.6	–

[a] Coordination number: The number of ether oxygen atoms coordinating a lithium ion.

result suggests that a lithium ion coordinates preferably with the PEGDME than with the PEG-borate ester. The interactions between the $CF_3SO_3^-$ ion and the solvent molecule were also investigated by ab initio calculations. For simplification of the calculations, the PEG-borate ester whose ethylene oxide (EO) chain length is 1, $B\{(OC_2H_4)OCH_3\}_3$, was chosen as a model solvent molecule, and accordingly, the PEGDME with the corresponding EO chain length, $CH_3O(CH_2CH_2O)_5CH_3$, was also chosen. The stable geometries obtained for the $CF_3SO_3^-$ ion with the PEGDME or the PEG-borate ester are shown in Figure 3c and d. The binding energies between the $CF_3SO_3^-$ ion and the solvent molecule are also summarized in Table 2. Therefore, PEG-borate ester prefers to interact with the $CF_3SO_3^-$ ion as a Lewis acid, which leads to the enhancement of dissociation of a lithium salt. From these calculations for the solvation states of a lithium ion and a $CF_3SO_3^-$ ion in PEGDME or PEG-borate ester, lithium ions are preferably solvated with the PEGDME, where as the PEG-borate ester interacts preferably with the $CF_3SO_3^-$ ion. Therefore, when the PEG-borate ester is added into the electrolytes, the activity of lithium ions increases through the interaction between the PEG-borate ester and $CF_3SO_3^-$ ion, which is induced by the Lewis acidity of the PEG-borate ester. Furthermore, in the case of the excess amounts of the PEG-borate ester in the electrolyte, the solvation state of lithium ions is less preferable, and accordingly, the activity of lithium ions decreases. This consideration coincides with the activity of lithium ions obtained from the Raman spectroscopic studies (Figure 2).

In conclusion, the PEG-borate ester with its Lewis acidity was found to be effective in the exchange current density in PEGDME-based electrolytes. This increase is induced by the enhancement of the activity of lithium ions because of Lewis acidity of the PEG-borate ester. This novel method to achieve high charge-transfer reaction rate is promising for the development of high-power-density lithium-ion batteries for large-scale applications, such as electric-, hybrid- or fuel-cell vehicles.

Experimental Section

PEGDME ($M_w = 500$, $CH_3O(CH_2CH_2O)_{11}CH_3$) (NOF Co. ltd.) was used as a standard solvent for electrolytic solutions. $LiCF_3SO_3$ (99.995%, Aldrich) was used without further purification. The concentration of the solution was 0.5 mol dm^{-3}. All experiments were carried out in an Ar-filled glove box (dew point: −76 °C). The PEG-borate ester ($M_w = 500.4$, $B\{(OC_2H_4)_3OCH_3\}_3$) was prepared by a literature method.[2]

To prepare the nickel microdisc electrodes used as a working electrode a nickel wire with 50 μm diameter was sealed with a shrink-on tube made of Teflon and then cut to expose the cross-section of the wire surrounded by Teflon. The prepared microdisc electrode was polished with 0.3 μm diameter alumina powder before every experiment. As a reference/counter electrode, lithium foil was used. A Solartron SI 1287 electrochemical interface was used for electrochemical experiments. The steady-state currents of the deposition and stripping of lithium on the working electrodes at various over potentials versus the Li^+/Li couple were measured by chronoamperometry. From the steady-state currents (i) obtained at various overpotentials (η), the exchange current densities i_0 were estimated with the following Allen–Hickling equation [Eq. (3)] where F is the

$$\ln\left[\frac{i}{1-\exp(F\eta/RT)}\right] = \ln i_0 - \frac{\alpha F}{RT}\eta \qquad (3)$$

Faraday constant, R is the gas constant, T is an absolute temperature, and α is the transfer coefficient.[4]

Raman spectroscopic studies were performed with a JASCO NRS-2100. The excitation source was an Ar^+ laser operating at 514.5 nm and the laser power was 10 mW. The spectral resolution was 2 cm^{-1}. Ab initio calculations were carried out with the software Gaussian98.[7] Calculations for geometry optimizations were carried out at the HF level of the theory using standard 3-21G basis set. Subsequently single-point calculation for investigation of the energies of the optimized geometries was performed by using DFT methods with B3LYP[8] form for exchange-correlation functional and 6-311G** basis set.

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