

Determination of ionic self-diffusion coefficients of lithium electrolytes using the pulsed field gradient NMR

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Abstract

Pulsed field gradient NMR measurements were carried out to determine the self-diffusion coefficients of the Li ion (D_{Li}) and anion (D_F) by 7Li and ^{19}F species. The D_F of $LiCF_3SO_3$ in propylene carbonate (PC) solvent increased with the decrease of molar concentration and larger than D_{Li} in whole concentration region. The D_{Li} also increased with the concentration decrease and then saturated in the lower concentration region. The effective ionic radius of lithium estimated from the D_{Li} was about four times larger than that of naked Li ion. This indicates the solvation effect of PC on dissociated Li ions. In order to enhance the Li ion transport number of electrolytes, two types of acidic materials, trimethoxyborane ($(CH_3O)_3B$) and trimethyleneborate ($(CH_2)_3(BO_3C_3H_6)_2$) were added into PC solution of $LiCF_3SO_3$ changing the mixing ratio of the salt to the acid. The D_F decreased with the increase of $(CH_3O)_3B$ content in spite of the decrease of the solution viscosity. The addition of $(CH_2)_3(BO_3C_3H_6)_2$, on the other hand, induced decrease of both D_{Li} and D_F , mainly due to the increase of the solution viscosity. These results suggest that $(CH_3)_3BO_3$ is effective to increase the transport number due to the acidic trapping effect on anions. © 1999 Elsevier Science S.A. All rights reserved.

Keywords: Lithium electrolytes; Solvation effect; Pulsed-field gradient NMR

1. Introduction

A great demand of lithium secondary battery not only for the electric devices for communication but for electric vehicles and energy storage system has appeared in recent years from the point of environmental problem. The fact that many kinds of materials have the possibility to be applied to the cell components would also accelerate the investigation of this field.

The development of electrolytes has been directed to exchange the conventional electrolytes solution for solid type materials such as polymer electrolytes. It is expected that the polymer electrolytes are nonflammable, simplify the cell structure and cell fabrication process. Several trials to increase the ionic conductivity and the Li ion transport number in polymer electrolytes as well as in electrolyte solution have been proceeded. It is popular to put some

plasticizer into the polymer electrolytes to ensure strong charge dissociation [1]. Addition of inorganic salts in the polymer to co-polymerize the anion have also been tried [2]. This approach intends to restrict the migration of anions to increase the cation mobility and cation transport number.

Another possibility to increase the cation conductivity is to trap anions using acidic species [3]. This approach has been applied for the conductivity enhancement of solid electrolytes [4]. That is, the acidic species attract anions toward the surface due to the acid–base interaction to create the defect layer region (space charge region), which can be used for ionic migration inducing the enhanced interfacial conductivity. In the case of polymer electrolytes and electrolyte solutions, added acidic species attract dissociated anions of the salt and inhibit the migration of anions. Selection of appropriate acid would result in the effective increase of cation conductivity selectively.

In this study, the concentration dependence of the diffusion coefficients reflecting the degree of dissociation and

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the viscosity has been investigated first to elucidate the condition of cations and anions in electrolyte solutions. And then, we tried to add several acidic materials into the electrolyte solution for the purpose of inhibiting the anion mobility. In order to detect the mobility change of cation and anion independently, pulsed field gradient NMR technique has been applied to measure the self-diffusion coefficients [5,6].

2. Experimental

Lithium salt of LiCF_3SO_3 of Tomiyama chemical technology cooperation (more than 99% grade and water contained less than 200 ppm), without further purification and drying, were dissolved in propylene carbonate (PC), 1,2-dimethoxyethane (DME) and tetrahydrofuran (THF) in several molar concentrations (2 mM–2 M) in a high purity argon glove box at the dew point of -80°C .

Ionic conductivities of the $\text{LiCF}_3\text{SO}_3/\text{PC}$ solutions were measured by complex impedance technique using Model S-5720 Frequency Response Analyzer of NF Circuit Design Block Japan combined with potentiogalvanostat Model 2000S of Toho-giken in the frequency range of 1 Hz–10 kHz at 25°C .

The viscosity of the solutions was measured using the Ubbelohde viscometer. The relative values were estimated in comparison with the standard value of 2.513 cP of PC at 25°C .

Self-diffusion coefficient measurements were made at 194.3 MHz (^7Li) and 470.4 MHz (^{19}F) on a JEOL 500 MHz spectrometer. The stimulated echo pulse sequence was used [7].

The duration of the gradient pulse (δ) and the separation time between the two gradient pulses (Δ) were kept constant for each diffusion coefficient estimation in the range of a few ms for δ and 0.1–3 s for Δ depending on the sample. Gradient strength (G) has been changed to change the echo signal strength. After matching the two gradients and attaining equilibrium, spin echoes were acquired. Calibration of G was made using the ^1H in high purity D_2O .

3. Results and discussion

The self-diffusion coefficient change of ^7Li and ^{19}F with the change of molar concentration of salt in PC is shown in Fig. 1. Both D_{Li} and D_{F} increased with the decrease of molar concentration of the salt. The D_{Li} seems to reach the maximum in the concentration range less than 0.02 mol/l. This is due to the solvation effect of PC on the dissociated Li ions. In the higher concentration region than 1 M, D_{Li} and D_{F} were almost the same. This indicates the undissociated LiCF_3SO_3 is dominant species and the diffusion of LiCF_3SO_3 was detected both in ^7Li and ^{19}F probe

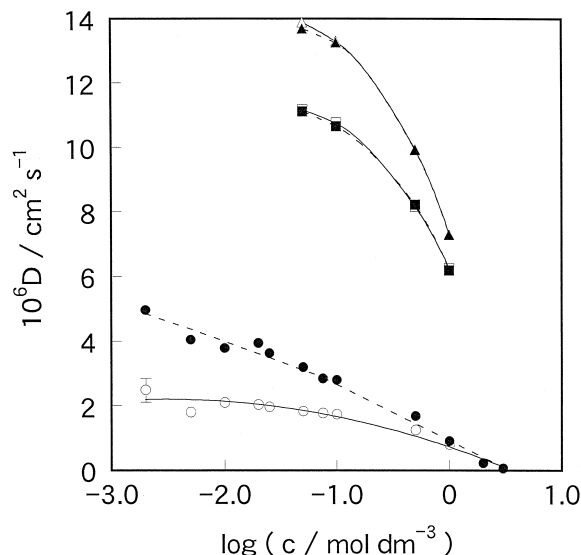


Fig. 1. Self-diffusion coefficients of lithium and fluoride species as a function of solution concentration of LiCF_3SO_3 in PC (○: ^7Li , ●: ^{19}F), DME (△: ^7Li , ▲: ^{19}F) and THF (□: ^7Li , ■: ^{19}F).

measurements in the high concentration solutions. This can be supported from the diffusion results of other type of solutions, dissolved in DME and THF in Fig. 1. These solvents have low dielectric constant ($\epsilon \sim 7.2$) compared with that of PC ($\epsilon \sim 65$), indicating the low dissociation degree of the salt. The D_{Li} and D_{F} of these solutions were the same in all measured concentration region. From these results, it is predictable that LiCF_3SO_3 species are dominant in the solution of low dissociation degree and the ions are dominant in the solution of high dissociation degree for the probe species of the diffusion measurements. Therefore, the composition of the detected species in the diffusion measurements depends on the dissociation degree of the salt.

Fig. 2 shows the molar conductivity change as a function of the solution concentration. In the case of PC solvent, the conductivity decreased with the increase of the concentration. This mainly attributes to the two factors, that is, the increase of macro viscosity and the decrease of dissociation degree with increasing the solution concentration. The viscosity change with the solution concentration could be seen in Fig. 3. Molar conductivities of DME and THF solutions were lower compared with that of PC solution especially in the low concentration region and almost independent of the concentration. This denotes that the dissociation degree of the salt is low in the measured concentration region. In the concentration of 0.1 M, for example, the conductivity of PC solution is more than 10 times as large as those of THF and DME solutions. This difference is mainly ascribed to the large dissociation degree of the salt in PC solution resulting in the high ion concentration in spite of the small self-diffusion coefficient reflecting the high viscosity of PC solution.

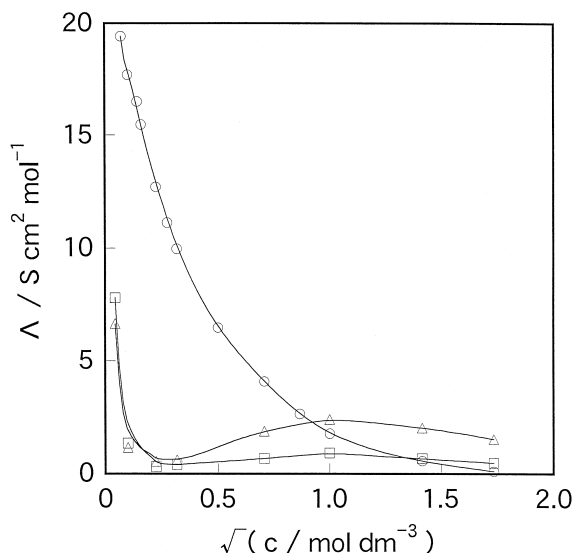


Fig. 2. Molar conductivity of LiCF_3SO_3 in PC (O), DME (Δ) and THF (\square) with the change of solution concentration.

In order to investigate the condition of dissociated ions in PC, ionic mobilities have been estimated from the conductivity and viscosity results. The diffusion coefficient D could be expressed by Einstein relation [8] as:

$$D = \mu_i kT / z_i e \quad (1)$$

where μ_i is the ionic mobility, k the Boltzmann constant, T the absolute temperature, z_i the charge of the ion. The Stokes' equation defines the mobility of fluid with radius r_i and the viscosity η ,

$$\mu = z_i e / 6 \pi \eta r_i. \quad (2)$$

Ionic radii of naked Li^+ (0.073 nm) and CF_3SO_3^- (0.27 nm) were used for r_i in the Eq. (2) [9]. The mobilities μ

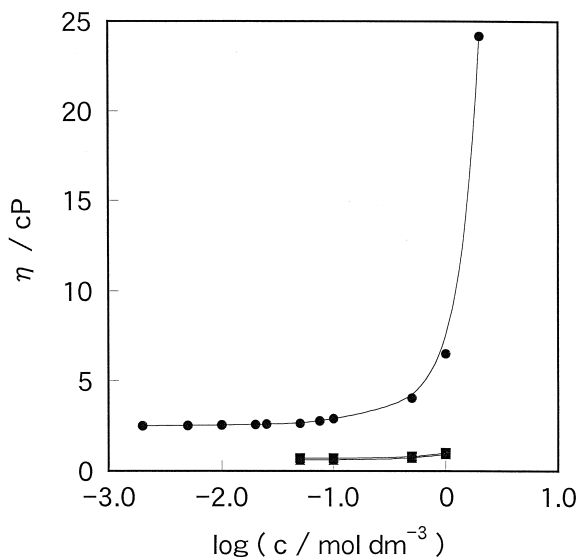


Fig. 3. Viscosity change of LiCF_3SO_3 in PC (●), DME (▲) and THF (■) with the change of solution concentration.

of lithium and anion species estimated from Eq. (1) using the results of the diffusion coefficient of NMR, and from Eq. (2) using the viscosity showed characteristic feature. That is, the gap between the lithium mobilities obtained from the two equations is large compared with the difference between the two mobilities of anion species. This indicates that the dissociated Li ions are larger in size than the naked ions due to the solvation by the solvent molecules of PC.

The effective ionic radius (r_{eff}) obtained from the combination of Eqs. (1) and (2) are plotted in Fig. 4. The r_{eff} of Li ion showed almost four times larger in size of the radius of naked Li ion and was almost independent of the solution concentration change. The r_{eff} of anion, on the other hand, increased with the increase in concentration. This characteristics could be realized as follows. In the low concentration region, the dissociation degree of the salt is high and most of the species exist as Li ions solvated by PC molecules. In the high concentration region, however, the dissociation degree is low and undissociated LiCF_3SO_3 species could be dominant in the solution. This would be confirmed by the result that the D_{Li} and D_{F} approach each other with the increase of the solution concentration. The radius of $\text{Li}(\text{PC})_4^+$, which is one of the predictable solvated ions [10], could be estimated as 0.37 nm. This is comparable with the radius of LiCF_3SO_3 of 0.35 nm. Therefore, the effective radius of lithium species does not change so much with the dissociation degree. It is probable that the estimated average value of 0.42 nm from Fig. 4, which is slightly larger than the average size of $\text{Li}(\text{PC})_4^+$ and LiCF_3SO_3 , suggests that other types of solvated ions (solvation with more than four PC molecules) are present in the solution. In contrast, the anion species, CF_3SO_3^- ,

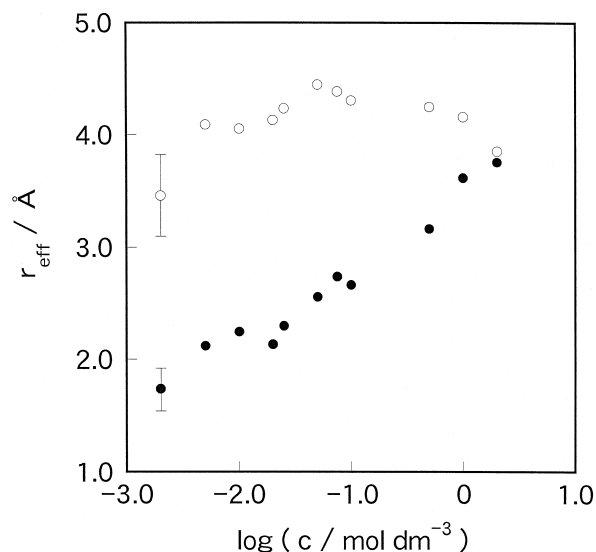


Fig. 4. Effective radius of lithium (O) and fluoride (●) species estimated from the self-diffusion coefficient and viscosity results (combination of Eqs. (1) and (2)) against the solution concentration.

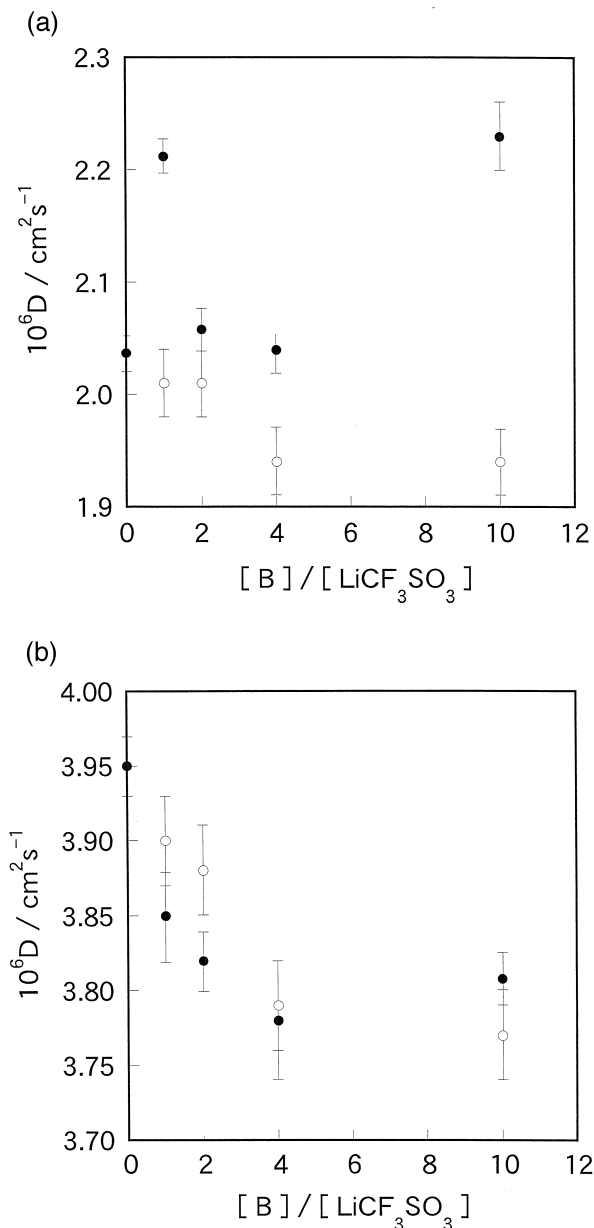


Fig. 5. Self-diffusion coefficients of (a) lithium and (b) fluoride species of $LiCF_3SO_3$ in PC (20 mM) added with $B(OCH_3)_3$ (●) and $(CH_2)_3(BO_3(CH_2)_3)_2$ (○) with the change of mixing molar ratio of boron to lithium.

which dominate in the low concentration region, are too large in size to be stabilized by solvation. They are substituted by the $LiCF_3SO_3$ molecules with the increase of the salt concentration. Therefore, the average size of the anion species will change from 0.27 nm to 0.35 nm depending on the dissociation degree.

As an effective approach to decrease the mobility of anions to enhance the Li ion transport number, acidic molecules were added into the solution. Acids have the characteristic of anion attraction. Then, the mobility of anions interacting with the acid would be reduced and the

transport number decreases. In order to confirm this idea, two types of acids, trimethoxyborate $B(CH_3O)_3$ as a monomeric acid (*acid 1*) and trimethyleneborate $(CH_2)_3O_2BO(CH_2)_3OBO_2(CH_2)_3$ as a dimeric acid (*acid 2*) were mixed into the PC solution of $LiCF_3SO_3$ changing the mixing molar ratio of boron to lithium. The diffusion coefficients of lithium and anion species of 20 mM solution against the boron to lithium molar ratio are shown in Fig. 5. The D_{Li} increased and the D_F decreased with the increase of mixing ratio of *acid 1*. The addition of *acid 2* resulted in the decrease both of D_{Li} and D_F . The conductivity and the viscosity of acid containing solutions are shown in Fig. 6. Addition of *acid 1* into the solution decreased the solution viscosity. On the other hand, addition of *acid 2* into the solution increased the solution viscosity. The fact that the D_F of the solution containing *acid 1* decreased contrary to the decrease of viscosity suggests that the *acid 1* molecules efficiently attract the anions to inhibit the anion migration. In the case of *acid 2* addition, the viscosity increased with increasing the acid content. Therefore, the reason of D_F decrease by the acid dispersion could not directly be attributed to the ineffective feature or to the increase of the solution viscosity. Because of the different viscosity change by adding the acids, the acidic point number effect in the D_{Li} and D_F using the monomeric and dimeric acids could not be confirmed.

In the case of 500 mM solutions, the D_F increased with the increase of mixing ratio of *acid 1* similarly to the increase of D_{Li} . And the D_{Li} and D_F decreased with the increase of *acid 2* content. These features would mainly reflect the viscosity change by the acid addition. Compared with the 20 mM solution, the viscosity change is steep with the change of mixing ratio of acid for 500 mM solution. Then the diffusion coefficients would be domi-

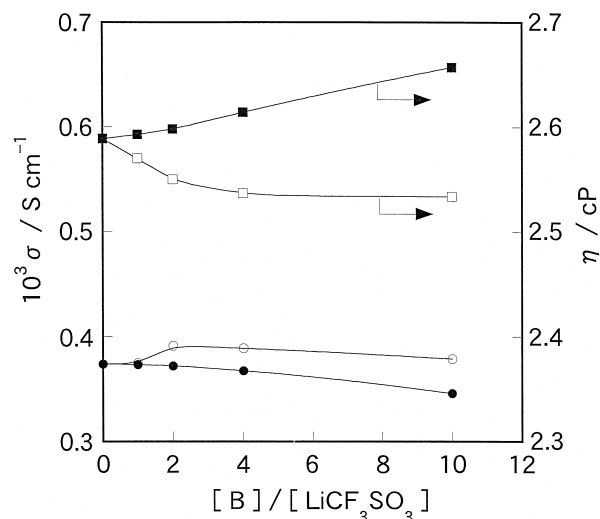


Fig. 6. Conductivity (○, ●) and viscosity (□, ■) change of $LiCF_3SO_3$ in PC (20 mM) added with $B(OCH_3)_3$ (open) and $(CH_2)_3(BO_3(CH_2)_3)_2$ (occupied).

nated by the change of viscosity in the high concentration solutions.

4. Conclusions

In this paper, the self-diffusion coefficients of lithium and fluoride species in the lithium electrolyte of LiCF_3SO_3 in PC were measured as a function of the molar concentration of the solutions. The effective ionic radius of the Li ions in the solution is larger than that of the naked Li ions and independent of the solution concentration. The anion size, on the other hand, was increased with the increase of the concentration. This feature suggests that the Li ions are solvated by the PC molecules after the salt dissociation although the anions are scarcely solvated by the solvent.

The addition of acidic molecule, $(\text{CH}_3\text{O})_3\text{B}$ showed the decrease of self-diffusion coefficient of anion species. As a

result, the transport number of Li ion estimated from the diffusion coefficients has increased. This suggests that the $(\text{CH}_3\text{O})_3\text{B}$ attracted anions to inhibit the anion mobility.

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