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Investigation of the solution condition of lithium electrolyte solutions with $LiCF_3SO_3$ salt

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Solution condition of the lithium electrolyte of $LiCF_3SO_3$ salt dissolved in propylene carbonate (PC), dimethoxyethane (DME) and tetrahydrofuran (THF) were investigated based on the measurements of the self-diffusion coefficients of lithium (D_{Li}) and anion (D_{F}) species using the pulsed-field gradient (PFG) NMR, viscosity and conductivity. D_{Li} and D_{F} decreased with the increase in the solution concentration for these electrolytes. This result reflects the change in the dissociation degree of the salt and the viscosity depending on the solution concentration. In the case of PC solution (the dielectric constant (ε) of PC: $\sim$65), measured D_{Li} and D_{F} were separated each other with the decrease in the concentration because the dissociation of the salt was promoted to increase the content of dissociated ions. With an increase in the concentration, the dissociation would be restricted and D_{Li} and D_{F} approximated each other, which means that the associated ion pairs are dominant in the solution. The effective ionic radius (r_{eff}) of cation species of PC solution estimated from the Stokes-Einstein relation using the diffusion coefficient and the viscosity results was four times greater than that of the naked lithium ion and independent of the dissociation degree. On the other hand, the r_{eff} of anion species changed depending on the dissociation degree. This suggests that the dissociated lithium ions are solvated by the PC solvent in the solution. DME and THF solutions did not show the solvation effect from the result of the change in r_{eff} with the concentration. This suggests that the dissociation degree of the dissolved salt was low due to the low ε of their solvents ($\varepsilon \sim 7.2$) and the ion pairs would dominant in the solutions independent of the solution concentration.

1. Introduction

One of the main objectives in the development of electrolyte solutions for lithium secondary batteries is to increase the lithium ion transport number. During the working process of a battery, the cations and anions migrate to the cathode and anode, respectively until a steady-state discharge current is reached. This results in the accumulation of lithium salt at the electrode interface indicating the interfacial polarization. Therefore, it is required for electrolytes that the anion migration is inhibited as much as possible and that the lithium ion conductivity is relatively enhanced from the aspect of practical application.

The conduction feature of the electrolyte solutions depend on the solution condition such as the concentration associated with the dissociation degree of the salt and solvation condition due to the interaction between the dissolved species and solvent. It is significant to make clear these properties in order to enlarge the conductivity and the lithium transport number. Pulsed-field gradient NMR technique [1, 2] has been applied to the investigation of the diffusion properties of the electrolyte solution. This technique directly gives the values of diffusion coefficients of cation and anion species individually by the detection of attenuation of the spin echo magnitude due to the translational motion applying the pulsed magnetic field gradient. Unfortunately, it is usually impossible for this procedure to distinguish the migration properties between the ions and ion pairs unless their surrounding conditions are different. Therefore, the estimated diffusion values of the conventional electrolyte solutions whose dissociation degrees are less than unity reflect the contributions from ions and ion pairs. However, this mixed result of diffusion gives us the chance to evaluate the salt condition in the solvent depending on the solution concentration with the help of other physical properties such as viscosity and conductivity. In this study, we discuss the condition of ionic species in the solutions which is associated with the conduction properties of the electrolyte solutions.

2. Experimental

The electrolyte solutions were prepared with the lithium salt of $LiCF_3SO_3$ of Tomiyama Chemical Technology Corporation (more than 99% grade and water is contained in less than 200 ppm) and the solvents such as in propylene carbonate (PC), 1-2 dimethoxyethane (DME) and tetrahydrofuran (THF) changing the molar concentrations (2 mM ∼ 2 M) in a glove box at the dew point of −80 °C.

The ionic conductivities of the electrolyte solutions were measured by a complex impedance technique using Model S-5720 Frequency Response Analyzer of NF Circuit Design Block Japan combined with potentiostat-galvanostat Model 2000S of Toho-giken Ltd., over the frequency range of 1 Hz ∼ 10 kHz at 25 °C.

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

Self-diffusion coefficient measurements were performed at 194.3 MHz (^{7}Li) and 470.4 MHz (^{19}F) on a JEOL 500 MHz spectrometer at 25 °C. The stimulated echo pulse sequence was used in the diffusion measurement [3–5]. The original spin echo is attenuated after applying the two gradient pulses according to the relation,

$$M = M_0 \exp\left[(-D(\gamma G\delta))^2\left(\Delta - \frac{1}{3}\delta\right)\right] \qquad (1)$$

where M_0 the original spin echo, D the diffusion coefficient, γ the gyromagnetic ratio, G the strength of the gradient pulse, δ the duration time of the gradient pulse, Δ the separation time between the leading edges of the two gradient pulses [6]. According to this relation, the spin echo decays exponentially as a function of the parameters of the gradient pulse and the diffusion coefficient could be estimated by fitting the Equation 1 to the decay curve. We put G as a variable parameter (the maximum value is ∼150 Gauss/cm), and δ and Δ values were kept constant for each process of the diffusion coefficient estimation in the range of 3 ms for δ and 100 to 300 ms for Δ depending on the sample. After matching the two gradient pulses and keeping the time more than five times of T_1 between each scan to attain the complete recovery of equilibrium condition, spin echoes were accumulated more than 20 times. The magnitude of G was calibrated using the diffusion value of ^{1}H in high-purity D_2O [7]. Temperature was also calibrated using the referenced diffusion value of ^{1}H in H_2O and ethanol [7].

3. Results and discussion

The D_{Li} and D_F of PC solution of $LiCF_3SO_3$ with the change in the molar concentration are shown in Fig. 1.

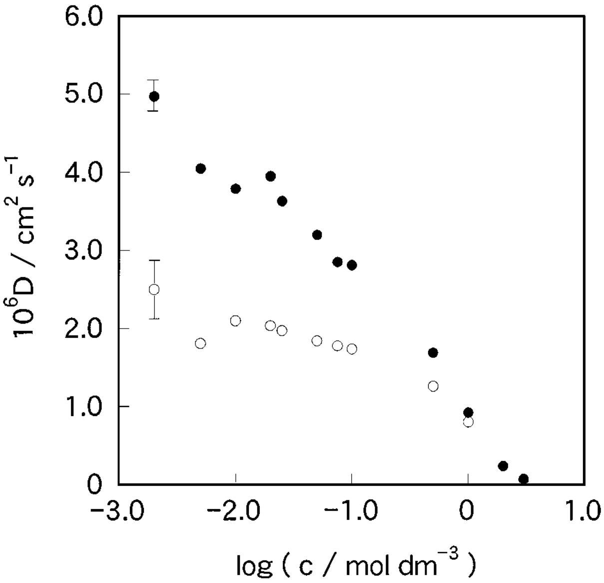


Figure 1 Self-diffusion coefficients of lithium (○) and fluoride (●) species against the molar concentration of $LiCF_3SO_3$ in propylene carbonate.

The experimental error of each data increased with the decrease in the solution concentration. The maximum errors are presented in the data points. The errors of other data were within the size of the symbols. Both D_{Li} and D_F increased with the decrease in the molar concentration of the salt. It seems that the change in D_{Li} was reduced with the decrease in the concentration and almost reached to the maximum in the range less than about 0.05 mol/l. The D_F, on the other hand, monotonously increased with the decrease in the concentration. In the concentration range greater than 1 mol/l, D_{Li} and D_F were the same. This changing feature is similar to several lithium electrolyte solutions [8], and reflects the variation in the dissociation degree of the salt with the solution concentration, and the solvation effect of PC on the dissociated ions. In the high-concentration region of the electrolyte solutions, undissociated ion pairs are dominant in the solution and the detected species for D_{Li} and D_F are the same, $LiCF_3SO_3$. Following the progress of dissociation with the decrease in the solution concentration, the dissociated Li^+ and $CF_3SO_3^-$ ions are dominant in the solution, and the estimated diffusion coefficients mainly reflect the ionic migration. In the case of DME and THF solvents, D_{Li} and D_F were completely the same in the measured concentration range of 0.05 to 1 M as shown in Fig. 2. This is because the dissociation degree of the salt is obviously low in DME and THF compared with that of in PC due to the low dielectric constant of DME and THF (DME, THF: ε ∼ 7.2, PC: ε ∼ 65). This means that the detected species of the DME and THF solutions in the PFG-NMR measurement are not ions but significant ion pairs of $LiCF_3SO_3$ for both D_{Li} and D_F. Therefore, the characteristic feature of diffusion change of PC solution that the D_{Li} and D_F altered independently with the concentration is due to the change in the content ratio between the dissociated ions and undissociated ion pairs in the solution depending on the dissociation degree.

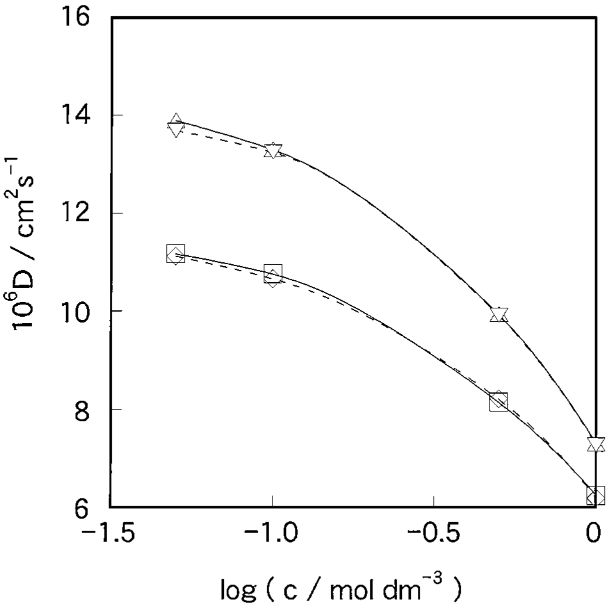


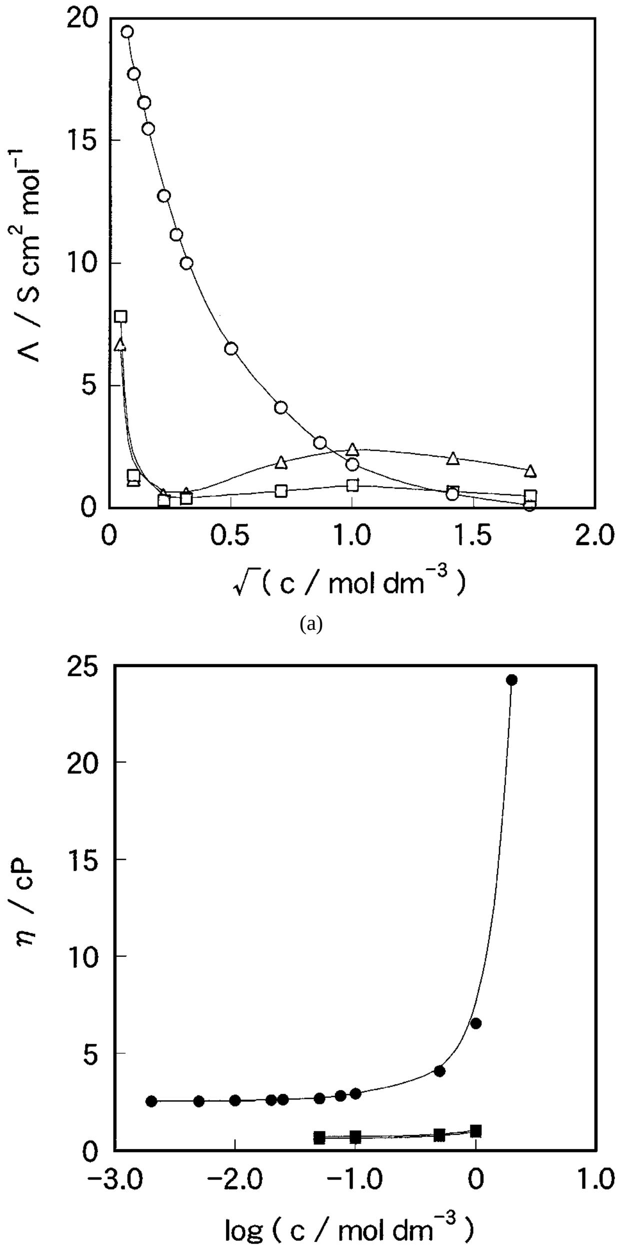
Figure 2 Self-diffusion coefficients of lithium (△:DME, □:THF) and fluoride (▽:DME, ◇:THF) species against the molar concentration of $LiCF_3SO_3$ in DME and THF. Lines are regressions.

Fig. 3 shows the molar conductivity change as a function of the salt concentration. In the case of the PC solvent, the conductivity decreased monotonously with the increase in the concentration. This tendency could be attributed to two factors, that is, the increase in the solution viscosity (Fig. 3b) and the decrease in the dissociation degree with the increase in the concentration. The solution viscosity increase with the concentration corresponds to the decrease in the ionic mobility due to the interaction between the carriers and solvent, whereas the reduction of the dissociation degree of the salt indicates the decrease in the ionic carrier concentration. As a result, the total conductivity, which reflects the contributions from both the mobility and the ionic carrier content, decreased monotonously with the increase in the concentration.

The conductivities of the DME and THF solutions in the concentration range higher than 0.05 mol/l were almost constant. This shows that the dissociation degree of the salt and then the ionic carrier content per mole were not affected by the solution concentration change in this range. This conductivity feature is consistent with the results of the diffusion coefficients in which the D_{Li} and D_F are the same, indicating the low dissociation degree. Obvious change in the conductivity of the solutions in the concentration lower than 0.05 mol/l may be due to the change in the dissociation degree of the salt.

In order to elucidate the solvated condition of the ionic species in the solution, we plotted the effective ionic radius (r_{eff}) in Fig. 4 estimated from the Einstein-Stokes relation, [9]

$$r_{eff} = \frac{kT}{(6\pi\eta D)} \tag{2}$$



(a)

(b)

Figure 3 Molar conductivity (a) and viscosity (b) of $LiCF_3SO_3$ in PC (○), DME (△) and THF (□) as a function of molar concentration of the solutions. Lines are regressions.

where k the Boltzmann constant, T the absolute temperature, η the solution viscosity and D the diffusion coefficient. This relation can be applied when some assumptions are satisfied. That is, the solvent is accepted as continuum for the solute molecules. And the size of ions is similar to that of the solvent molecules, and ions, in case of solvation, migrate with the solvent together without slipping at their interface. The r_{eff} of the lithium species of the PC solution exhibited a size about four times greater than the radius of naked lithium ion (0.076 nm) [10] and was almost independent of the concentration change of the solution. The r_{eff} of the anion of the PC solution, on the other hand, increased with the concentration increase. These characteristics could be realized as follows. In the low-concentration region, the dissociation degree of the salt is high and individual ions are the dominant species in the solution. The lithium ions would be easily solvated by PC molecules. In the high-concentration region, however, the dissociation degree is low and undissociated $LiCF_3SO_3$ species could be

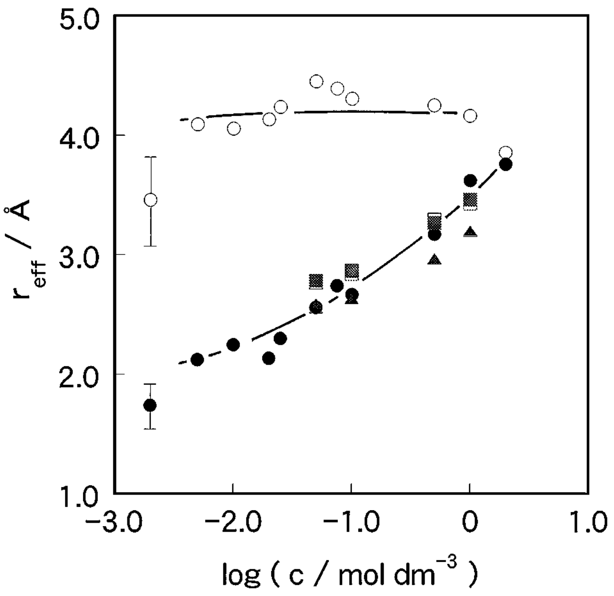


Figure 4 Effective ionic radius of lithium (○:PC, △:DME, □:THF) and fluoride (●:PC, ▲:DME, ■:THF) species against the molar concentration of the solutions. The values are estimated from the Stokes-Einstein equation using the results of self-diffusion coefficients and the viscosity. Lines are regressions.

dominant in the solution. The radius of solvated ion, $Li(PC)_4^+$, which is one of the predictable species in the PC solution [11], could be estimated as 0.37 nm. This is compatible with the radius of $LiCF_3SO_3$, 0.35 nm. Therefore, the effective radius of the lithium species, which is the average of solvated ions and ion pairs, does not change so much with the change in concentration and the dissociation degree. It is probable that the estimated value of 0.42 nm from Fig. 4 which is slightly greater than the ionic radii of $Li(PC)_4^+$ is due to the existence of other types of solvated ions (solvation with more than four PC molecules) in the solution. The average size of the anion species, on the other hand, changed from 0.27 nm (naked $CF_3SO_3^-$) to 0.35 nm ($LiCF_3SO_3$) depending on the concentration and the dissociation degree. This shows that there is no obvious solvation effect on the anion species contrary to the effect on cations.

In the case of THF and DME solutions, the r_{eff} of the lithium and fluoride species were the same and increased with the increase in the concentration in the measured region of 0.05 to 1 mol/l. In this concentration region, the dissociation degree of the salt is low as discussed in the results of the diffusion coefficient and conductivity. Therefore, the estimated r_{eff} of them would show the size of the undissociated $LiCF_3SO_3$. The concentration dependence of r_{eff} in spite of the low dissociation degree of the salt in these solvents is responsible for the gradual change in the diffusion coefficients in spite of the unchanged viscosity in the measured concentration range. This means that the intermolecular interaction between the dissolved species increases with the increase in the concentration. This effect influences on the diffusion coefficient independent of the macro viscosity, and result in the increase of the apparent molecular size with concentration.

The estimated r_{eff} values of anion species were smaller than that of naked anion (0.27 nm) in PC solution and that of ion pair (0.35 nm) in DME and THF solution in the lower concentration region. This is the deviation from the relation (2) as the assumptions suggested previously no longer hold good.

4. Conclusions

Self-diffusion coefficients of the cation (D_{Li}) and anion (D_F) species of $LiCF_3SO_3$ in PC, DME and THF solutions were measured using the pulsed-field gradient NMR technique. Solution concentration dependence of the D_{Li} and D_F reflected the dissociation degree of the salt and solvation effect in the solution. In the case of the PC solution, dissociattion was promoted with the decrease in the solution concentration, and the dissociated lithium ions were solvated by the PC solvent. In the case of DME and THF solutions, the dissociation degree is low independent of the solution concentration due to the low dielectric property of the solvents. As a result, the measured D_{Li} and D_F were the same because the detected species are the same ion pairs, $LiCF_3SO_3$. Solvation effect was confirmed from the estimated results of r_{eff} using the Einstein-Stokes equation. The r_{eff} of the cation species of the PC solution was independent of the solution concentration change. This contrasted with the r_{eff} of the anion species which was increased with the increase in the solution concentration. This indicates that the solvated lithium ions such as $Li(PC)_4^+$ with a radius of 0.37 nm are dominant in the low-concentration region and the undissociated ion pairs $LiCF_3SO_3$ with a radius of 0.35 nm are dominant in the high-concentration region of the solutions. It was found from this study that the diffusion coefficient measurements of each ionic species are effective for investigating not only the conduction properties but the solution condition that is significant in the development of the electrolyte materials.

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