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Relationship between Ionic Interaction and NMR Relaxation Behavior in $LiClO_4$-PC Solution Coexisting with Fumed Metal Oxide

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Dynamic properties related to ^1H NMR relaxation in SiO_2 fine powder/non-aqueous $LiClO_4$ solution was measured for using propylene carbonate (PC) and PC-1,2-dimethoxyethane (DME). The influence of solid phase and variation of effect of DME on ionic mobility is also discussed. For ^1H NMR spectra of PC-DME binary solution, adding of SiO_2 powder caused the broadening of NMR signal of ^1H in PC and DME molecules. In pure PC-DME system, since DME is preferentially affected by solids rather than PC, as the ratio of DME increased, values of solvent molecules detected by NMR decreased. In 1 mol/L $LiClO_4$/PC-DME system, as the ratio of DME in solution was higher, The interaction between the PC and the Li^+ ion is weakened by the decrease of the dissociation degree, and the mobility of the PC was restored.

Introduction

Lithium ion secondary batteries (LIBs) have high power, high energy density among rechargeable batteries, and are widely used from small electric devices such as mobile phones to electric vehicles. A separator made of an insulating material is present inside the LIBs to prevent a short circuit between the electrodes. The separator has a three-dimensional network structure, and an electrolyte is impregnated in the separator (1). As there are many solid-liquid interfaces, it is suggested that the interaction with the solid greatly influences the internal ionic conduction. Various studies on solid-liquid coexisting systems have been conducted so far, and it has been reported that the liquid phase among solid particles has different electrochemical properties (2, 3), thermal behavior (3-5), ionic interaction between dissolving species (3, 6), etc., from the original their properties of bulk solution. In addition, Bhattacharya et al. reported that Li^+ ionic conductivity increases significantly by adding oxide powder in non-aqueous electrolyte (7, 8). For the above reasons, an elucidation of liquid phase properties of solid-liquid interface in the non-aqueous electrolyte solution system is important for improving the performance of energy storage devices such as LIBs.

About the measurement technique, we focus NMR measurement. The chemical shift of NMR signal gives the information about structural changes and ionic processes in electrolyte solutions and it is sensitive. If molecule having high mobility due to not being restricted by ions or solids, signal is shape and its intensity is large because chemical exchange of nuclei is fast. On the other hand, if molecule having low mobility, signal is broadened and gradually eliminated for NMR measurement (9, 10). In addition, recent studies on molecular dynamics with NMR were carried out by spin-spin relaxation time, T_2 measurements. T_2 is defined as the process that the aligning nuclear spin after pulse irradiation returns to thermal equilibrium. These studies indicated the reciprocal relationship between T_2 and FWHM of each signal; $\nu_{1/2}$ as follows;

$$T_2 \propto {\nu_{1/2}}^{-1} \quad (1)$$

In the case of ^{1}H, that process is dipolar relaxation process, so T_2 is influenced by dipole having molecule. Thus, the stronger effect of other components on solvent molecules, the shorter T_2 is. NMR is useful to obtain the knowledge of the molecular mobility.

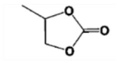
We have measured the relaxation behavior of NMR in a single solvent based non-aqueous electrolyte using fumed silica as a solid phase and found that solvent molecules are very strongly influenced by solids even in liquid phase 90 vol% (11). In addition, in real LIBs, low viscosity solvent such as 1,2-dimethoxyethane is added to a high dielectric constant solvent such as propylene carbonate to promote ionic dissociation to improve ionic conductivity (12). Therefore, in this study, we used non-aqueous binary electrolyte mixed with fumed silica as model system of LIBs, and investigated a selective interaction with solvent molecules, dependence on Li^+ ion concentration and DME mixture ratio, due to the influence of solid-liquid interface in NMR spectroscopy.

Experimental

Sample preparation

Fumed silica (200 ± 50 m^2g^{-1}, FS) was used as solid phase, and propylene carbonate (PC) and 1,2-dimethoxyethane (DME) mixed solvent or $LiClO_4$/PC-DME of predetermined concentration (0-1 mol/L) was used as liquid phase (DME=0-80 mol%). The properties of solvents are shown in Table. 1 (12).

Table. 1 The properties of organic solvents at 25 ˚C.

Solvent	Structure	η/ cP	ε	d / gcm^{-3}
PC		2.53	64.92	1.2
DME		0.46	7.2	0.86

Samples were prepared in Ar glovebox by mixing PC-DME or LiClO$_4$/PC-DME and fumed silica in NMR tube. A content of liquid phase were ranged from 94-100 vol% by gravimetry. Liquid content, ϕ, was determined as following equation;

$$\text{Liquid content } (\phi) = V_L / (V_L + V_S) \qquad (2)$$

where V_L and V_S are the volume of liquid phase and liquid phase, respectively. In this work, the V_L and V_S values were determined from following equation;

$$V_L = W_L / \rho_L \text{ , } V_S = W_S / \rho_S \qquad (3)$$

where W_L and ρ_L are the mass and the density of liquid phase, and W_S and ρ_S are those of solid phase, respectively.

^{1}H NMR measurement

The ^{1}H NMR spectra were obtained by a Varian INOVA 400 NMR spectrometer with 5mm SW probe (Varian, Inc.) To avoid mixing sample with deuterated solvent, the samples were put into inner of coaxial NMR sample tube (Wilmad-LabGlass, 516-CC-5) and D$_2$O was put into outer of that. The ^{1}H NMR chemical shifts were determined against external standards of deionized distilled water. The spin of the sample tubes was stopped during the measurement.

^{1}H qNMR measurement

^{1}H qNMR was performed with ^{1}H NMR spectra which was showed absolute intensity based on the principle of NMR (13). ^{1}H qNMR was defined as following equation;

$$\frac{N_x}{N_{ref}} = T \times 10^{\frac{Rg_{ref} - Rg_x}{20}} \times \frac{Ns_{ref}}{Ns_x} \times \frac{I_x}{I_{ref}} \qquad (4)$$

where N is the concentration of the chemical species that gives the NMR signal, Rg is the gain of the RF amplifier in the NMR spectrometer (i.e., receiver gain), Ns is the number of FID scans, and I is the integrated intensity of the NMR signal. The subscripts ref and x represent the external standard solution and the sample solution, respectively. T is a specific constant for the measuring system including the NMR sample tube and the entire NMR equipment, and it is almost one when a similar NMR sample tube and the same NMR equipment are used for measurements of an external standard solution and a sample solution. Because Rg and Ns can be optionally set, eq.4 shows an expression which expresses a proportion between integrated intensity of ^{1}H NMR spectra and concentration of nuclei. ^{1}H NMR measurement of deionized distilled water was performed with varying Rg and Ns in order to confirm quantitativity of eq.4.

Spin-spin relaxation time (T_2) measurement

The spin-spin relaxation time (T_2) of each sample was obtained by relaxation time measuring equipment (XiGo Nanotools, Inc., Acorn area). The sample was put into 5 mm diameter glass NMR tube. All experiments were performed at 25 ± 0.5 ˚C. We used the CPMG method showed in eq.5 (14).

$$M_{(\tau)} = M_{(0)} exp\left(\frac{-\tau}{T_2}\right) \tag{5}$$

where $M(\tau)$ is z-magnetization after pulse delay τ. In eq.5, T_2 value that averaged all intramolecular nuclear relaxation is obtained in this method.

Results and Discussion

^{1}H NMR and ^{1}H qNMR measurement

The result of ^{1}H NMR spectroscopy measurement of 1 mol/L PC-DME/FS (DME=45 mol%) samples indicated in Fig. 1. (The minute peak around 4.6 ppm was derived from ^{1}H of H_2O contained in D_2O in the outer tube.) Sharp peaks were observed in both PC and DME in the case only for liquid phase. In both PC and DME signals, broad signals were confirmed under the existence solid-phase. It was shown that the dynamic property of solvent molecules largely decreased in comparison with the case only for liquid phases. The liquid content dependences of ^{1}H NMR detection ratios of 1 mol/L PC-DME/FS (DME=45 mol%) were shown in Fig. 2. The ^{1}H NMR detection ratios are determined by the ratio of the overall signal intensity due to PC-DME for the sample without solid-phase and that for the sample with solid phase. Peak intensity is the sum of total of each proton of solvent molecules. The solid line represented the theoretical value of detected amount of PC and DME by ^{1}H NMR.

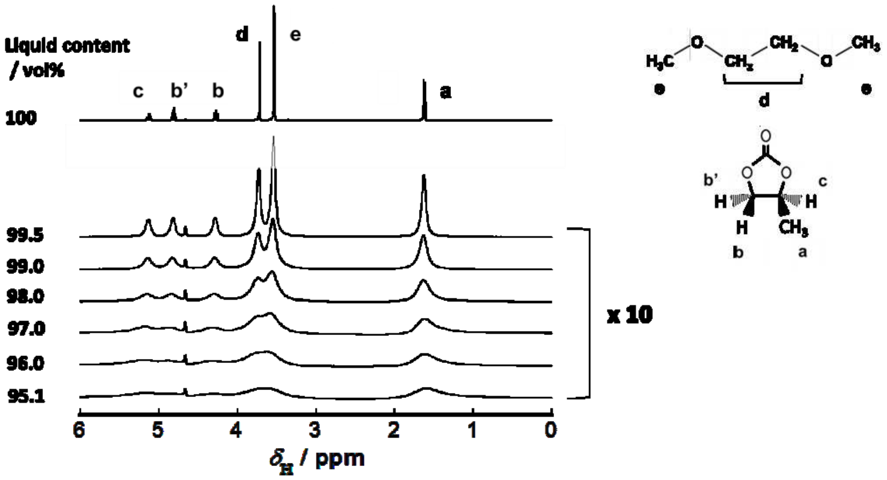


Fig. 1 Liquid content dependence of the ^{1}H NMR spectra for FS + 1 mol/L $LiClO_4$/PC-DME (DME=45 mol%) systems.

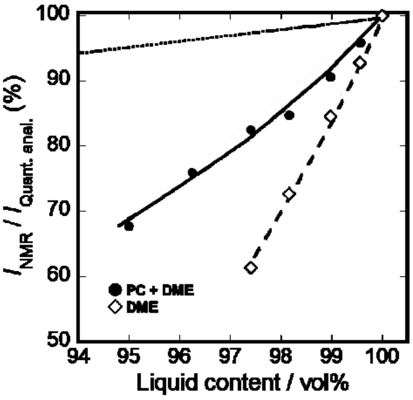


Fig. 2 Liquid content dependence of the ^{1}H NMR detection ratios for FS + 1 mol/L $LiClO_4$/PC-DME (DME=45 mol%) systems. The ^{1}H NMR detection ratios are determined by the ratio of the overall signal intensity for the sample without solid phase and that for the sample with solid phase.

The detected amount of PC and DME molecules decreased compared to solid line. It indicates that solvent molecules have low mobility due to being restricted by solids. The integrated intensity value of ^{1}H in DME is much smaller than the total integrated intensity value of PC and DME. It suggests that the mobility of DME molecules were restricted than that of PC molecules in PC-DME/FS system.

The liquid content and DME mixture ratio dependences of ^{1}H NMR detection ratios were shown in Fig. 3-4.

In pure PC-DME system, since DME is preferentially affected by solids rather than PC as described above, as the ratio of DME increased, values of solvent molecules detected by NMR decreased. On the other hand, in 1 mol/L $LiClO_4$/PC-DME system, as

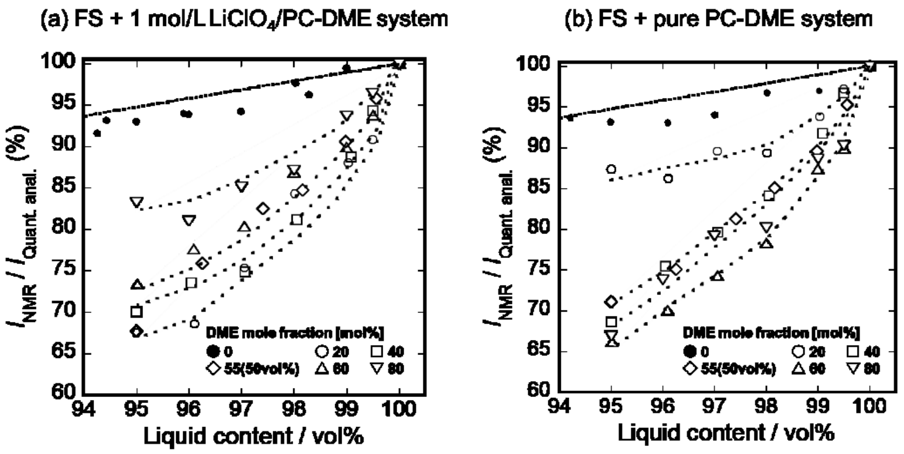


Fig. 3 Liquid content and DME mixture ratio dependence of the ^{1}H NMR detection ratios of PC and DME. The ^{1}H NMR detection ratios are determined by the ratio of the overall signal intensity due to PC and DME for the sample without solid phase and that for the sample with solid phase. (a) FS + 1 mol/L LiClO4/PC-DME solution systems. (b) FS + pure PC-DME solution systems.

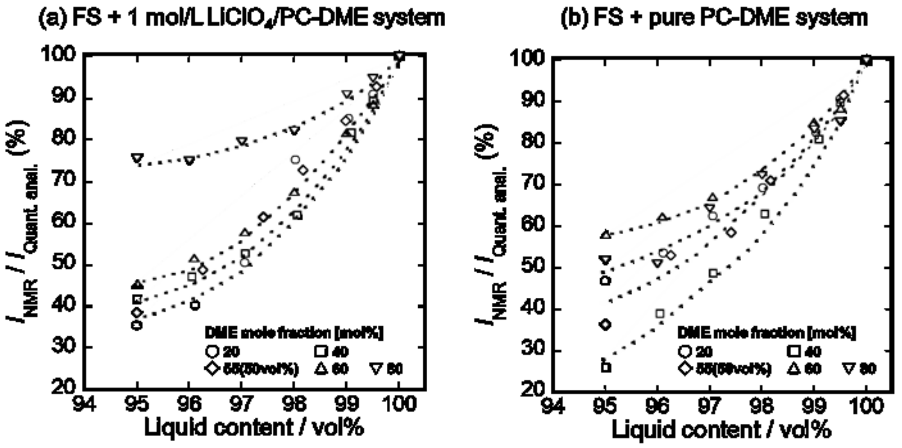


Fig. 4 Liquid content and DME mixture ratio dependence of the ^{1}H NMR detection ratios of only DME. The ^{1}H NMR detection ratios are determined by the ratio of the overall signal intensity due to DME for the sample without solid phase and that for the sample with solid phase. The measurement samples are as described in the caption of Fig. 3.

the ratio of DME in solution was higher, the detected value of solvent molecules increased. This change is related to the degree of ion dissociation. Matsuda et al. report that the degree of ion dissociation decreases and the ion-solvent interaction weakens as the ratio of DME increases in PC-DME mixed solvent system (15). PC-DME mixed solvent system, PC preferentially coordinates Li^+ ions. No NMR signal of the molecule bound strongly to ions can be obtained. The increase in NMR intensity suggests that the interaction between Li^+ ions and PC was weakened by the addition of DME and PC motility increased.

^{1}H Spin-spin relaxation time (T_2) measurement

The liquid content and PC-DME mixture ratio dependences of ^{1}H spin-spin relaxation time (T_2) of PC-DME were shown in Fig. 5. From Fig. 5, in PC-DME/FS system, T_2 decreased remarkably under only 0.5% existence solid-phase. The relaxation time relates the viscosity. The relaxation time by dipole-dipole interaction, i.e., $T_{1\mathrm{DD}}$ and

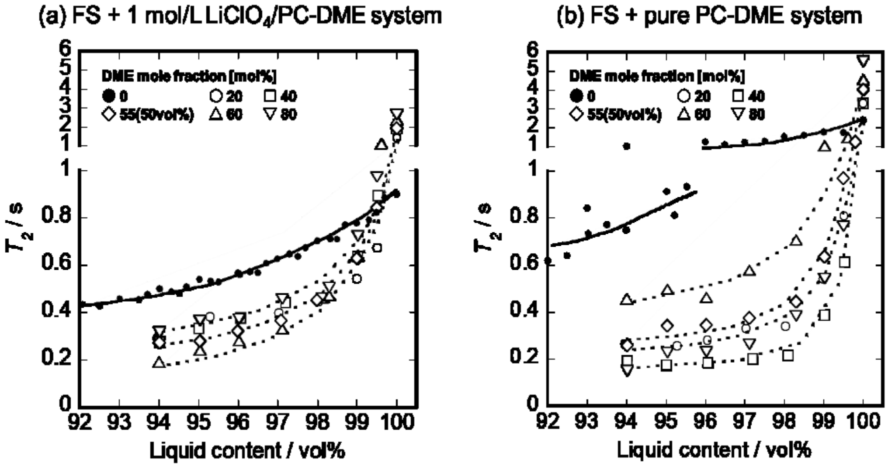


Fig. 5 Liquid content and DME mixture ratio dependence of the spin-spin relaxation time, T_2, of ^{1}H NMR due to PC and DME.

$T_{2\mathrm{DD}}$, is expressed by using correlation time as following equations (16);

$$\tau_c = \frac{4\pi a^3}{3k} \cdot \frac{\eta}{T} \qquad (6)$$

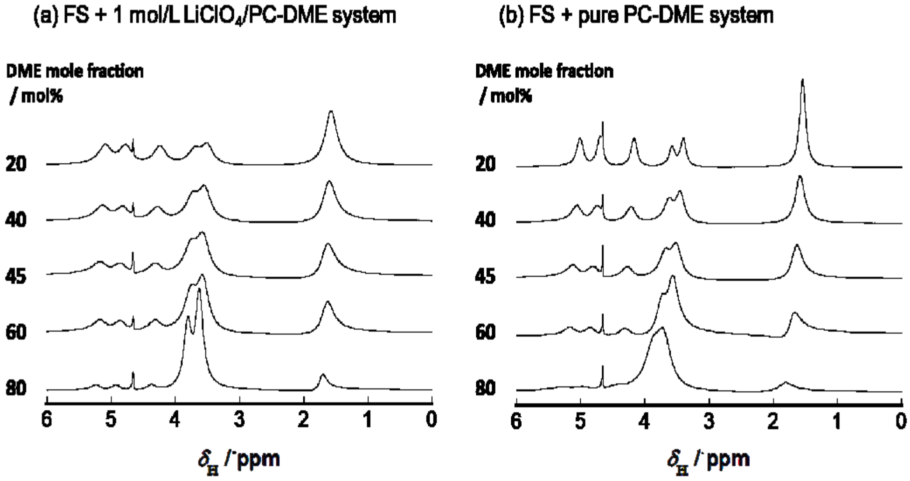


Fig. 6 DME mixture ratio dependence of the ^{1}H NMR spectra (ϕ =97 vol%).

$$\frac{1}{T_{1\mathrm{DD}}} = \frac{1}{T_{2\mathrm{DD}}} = 10a\frac{\gamma^4}{r^6}\tau_{\mathrm{c}} \qquad (7)$$

where η is the viscosity, T is the temperature, and a is the radius of the molecule of the sample liquid, respectively, and k is the Boltzmann constant. From eqs.6 and 7, as viscosity increases, the relaxation time shortens. Also, DME mixture ratio dependence of the ^{1}H NMR spectra was shown in Fig. 6. From eq. 1, the relaxation time is related to the shape of the spectrum. In the pure PC-DME system, DME tends to be bound to asolid, so the NMR signal of DME becomes one broad peak as the ratio of DME increases. On the other hand, in 1 mol/L $LiClO_4$/PC-DME system, the peak is also clear in 80 mol%. This result supports the increase in PC mobility due to the decrease of ion dissociation degree in the result of ^{1}H qNMR measurement.

Conclusions

NMR signal of ^{1}H in DME molecules was influenced by coexisting solid phase much more than that of PC molecules in PC-DME/FS system. In pure PC-DME system, since DME is preferentially affected by solids rather than PC, as the ratio of DME increased, values of solvent molecules detected by NMR decreased. In 1 mol/L $LiClO_4$/PC-DME system, as the ratio of DME in solution was higher, The interaction between the PC and the Li^+ ion is weakened by the decrease of the dissociation degree, and the mobility of the PC was restored. In the previous study of oxide powder + $LiClO_4$/PC-DME system, it has been reported that the Li^+ ionic conductivity is maximized at a certain DME mole fraction, and it decreases at higher contents (17). We concluded that the effect of adding DME is limited from these results.

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References

1. S. S. Zhang, *Journal of Power Sources*, **164**, 351-364, (2007).
2. S. Deki, S. Nakamura, A. Kajinami, Y. Kanaji, and M. Mizuhata, *J. Chem. Soc. Faraday Trans.*, **89**, 3805-3810, (1993).
3. M. Mizuhata, Y. Sumihiro, and S. Deki, *Phys. Chem. Chem. Phys.,* **6,** 1944-1951, (2004).
4. S. Deki, A. Kajinami, Y. Kanaji, M. Mizuhata, and K. Nagata, *J. Chem. Soc. Faraday Trans.*, **89**, 3811-3815, (1993).
5. M. R. Landry, *Thermochim. acta,* **433**, 27-50, (2005).
6. A. B. Béléké, M. Mizuhata, and S. Deki, *Vib. Spectrosc.*, **40**, 66-79, (2006).

7. A. J. Bhattacharyya, J. Maier, *Adv. Mater.*, **16**, 811-814, (2004).
8. A. J. Bhattacharyya, J. Maier, *Solid State Ionics*, **177**, 2565-2568, (2006).
9. P. Porion, A. M. Faugère, and A. Delville, *J. Phys. Chem. C,* **118**, 20429-20444, (2014).
10. B. Grünberg, T. Emmler, E. Gedat, I. Shenderovich, G. H. Findenegg, H.-H. Limbach, and G. Buntkowsky, *Chem. Eur. J.*, **10**, 5689-5696, (2004).
11. M. Takemoto, H. Maki, M. Mizuhata, *ECS Trans.*, **75(19)**, 1-9, (2017).
12. Xu. K, *Chem. Rev.,* **104***(***10)**, 4303-4418, (2004).
13. H. Maki, Y. Okumura, H. Ikuta, and M. Mizuhata, *J. Phys. Chem. C*, **118**, 11964-11974, (2014).
14. S. Meiboom, and D. Gill, *Rev. Sci. Instrum.*, **29**, 688-691 (1958).
15. Y. Matsuda, M. Morita, and K. Kosaka, *J. Electrochem. Soc.,***130**, 101-104, (1983).
16. J. W. Akitt, in *NMR and Chemistry: An Introduction to Modern NMR Spectroscopy*, Chap. 4.2, Chapman & Hall, London, 3rd edn, (1992).
17. H. Kimura, M. Mizuhata, S. Deki, unpublished.