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Ionic Diffusion Mechanism of Glucitol-Containing Lithium Polymer Electrolytes

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ABSTRACT: We investigated restricted diffusion of ionic species in glucitol-type lithium polymer electrolytes by observing echo-intensity changes of pulsed gradient spin echo NMR which reflect carrier diffusion behavior. Echo attenuation showed an anomalous feature attributable to deviation from random walk migration due to the restricted diffusion. The attenuation behavior depended on the diffusion time for measurement, Δ, in the range of 40 ms < Δ < 160 ms. This revealed that the size of the boundary structure which causes diffusion restriction was micrometer order. We speculated that a kind of micron size domain, which is an aggregation unit of entangled polymer chains, is responsible for the diffusion restriction. Simulations based on a rectangular model showed characteristic features of echo-changing behavior against two dominant factors: inherent diffusion coefficient, D, and domain size, a, which depend on variable parameters, observed temperature, T, and salt concentration, C, of the polymer electrolyte. Estimated D and a of the anion species by fitting the experimental data to a restricted diffusion model increased with increasing T and C. On the other hand, D and a of the cation species showed decreasing tendency with increased T and C. This difference would be attributed to their migration mechanisms: The cation is attracted by oxygen sites and takes the hopping process from site to site along the polymer chain in migration, whereas anion is weakly attracted by the polymer, leading to the migration free from the site-hopping process. Coulombic effect would provide stronger restricted situation on the cation compared with that due to the morphological domain structure, leading to the anomalous change in restriction parameters.

Introduction

Development of polymer electrolytes without a plasticizing solvent has been performed to complete secondary batteries with high safety and high energy density.[1] The fundamental conception of designing a polymer electrolyte is to take advantage of characteristic features of polymer chains. Polar groups aligned on polymer chains promote dissociation of the dissolved salt through Coulombic effect. Further, segmental motility of polymer chains activates the dissociated ion transport characterized by hopping on the polar sites. Lithium polymer electrolytes composed of poly(ethylene oxide) (PEO) are typical materials providing these features. That is, oxygen in ether groups attracts Li by Coulombic force to advance salt dissociation. The trapped cations hop from site to site, driven by the segmental chain motion. According to this established knowledge, many kinds of modification of PEO-type polymers have been performed to improve the conductivity.[2,3] However, it is also accepted that the lithium transport number, which represents the ratio of lithium cation conductivity over total conductivity, of PEO-type polymer electrolytes is too low to be used for devices compared with that of the electrolyte solution with the same salt. This is caused by the fact that the oxygen site in ether groups strongly attracts and traps Li^+ to restrict the cation migration in contrast to the free anions after dissociation. Therefore, it is necessary to develop a new type of polymer electrolyte with high Li mobility provided by high salt dissociation to produce a reliable battery system.[4]

Herein, we, for the first time, examined a glucitol-type polymer of Figure 1 comprising a glucitol unit and a methylene chain for a lithium polymer electrolyte by dissolving a lithium salt. The idea of this approach is that the glucitol unit is rich in oxygen sites, which are expected to promote salt dissociation. And the methylene chain would contribute to plasticizing the electrolyte, enhancing the ionic mobility. In practice, we found that the ionic conductivity of the glucitol-type lithium polymer electrolyte was about 2×10^{-4} S cm^{-1} at 25 °C, which was comparable to that of conventional PEO-type polymer electrolytes. Preliminary molecular orbital calculation of charge distribution on the glucitol polymer showed lower negativity of the oxygen sites compared with that of the ether oxygen in PEO-type polymer. These results suggest the possibility of high cation conductivity of glucitol polymer electrolytes reflecting the high total conductivity and weaker attractive force of polymer sites on the cation species.

Not only the molecular structure but also macroscopic morphology of the polymer dominates dynamic properties of polymer electrolytes.[5,6] Most polymer electrolytes have amorphous structure which provides random network pathways for carrier transport. However, the amorphous and random network is not necessarily

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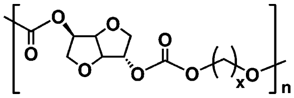

Figure 1. Glucitol monomer structure.

homogeneous. Entangled polymer chains would form an aggregation which is an unit of domain structure. As a result, carrier migration reflects the feature of the domain structure such as the domain size and the barrier height between the domains.

We previously confirmed the anomalous diffusive feature of PEO-type dry polymer electrolytes using pulsed gradient spin echo (PGSE) NMR.[6] In contrast to the conventional random walk behavior typically observed in electrolyte solutions and polymer gel electrolytes,[7,8] NMR echo signal change of ionic species of the polymer electrolyte showed a manner of restricted diffusion which appeared more clearly at the presence of morphological anisotropy induced by the applied stress. Further investigation of this phenomenon revealed that the restricted diffusive feature is fundamentally attributable to morphological inhomogeneity of the polymer electrolyte which has grown in the electrolyte preparation process.

Systematic investigation of restricted diffusion behavior associated with the structural feature of polymer electrolyte is significant for design of practical electrolyte materials controlling the dynamic performance. In this research, we would like to investigate the ion migration mechanism of new type glucitol polymer electrolytes associated with the polymer morphology through the interpretation of restricted diffusion behavior in PGSE-NMR measurements. In the process, we performed the simulation calculation on the basis of a boundary structure model in which carriers migrate affected by the boundary.[15] By the comparison of the observed echo attenuation and simulated results, we discuss the restricted diffusion mechanism of the individual ion reflecting the polymer morphology and Coulombic effect.

Experimental Section

Synthesis of a polycarbonate containing 1,4:3,6-dianhydro-D-glucitol was undertaken through polycondensation of 1,6-hexanediol and 1,4:3,6-dianhydro-2,5-bis-*O*-(4-nitrophenoxycarbonyl)-D-glucitol, which was prepared by reaction of 1,4:3,6-dianhydro-D-glucitol and 4-nitrophenyl chloroformate, in the presence of *N*,*N*-diisopropylethylamine and 4-(dimethylamino)pyridine in sulfolane at 60 °C, according to the literature.[9] The number-average molecular weight of the polycarbonate was estimated to be 41 000 by size exclusion chromatography (SEC) in chloroform at 40 °C using standard polystyrene. Polymer electrolytes were prepared by mixing an acetonitrile solution of the polymer and $LiN(CF_3SO_2)_2$, changing the ratio of [Li]/[monomer unit] = 0.2, 0.4, and 0.8, and casting the solution to evacuate the solvent to form dried membranes. Final thickness of the polymer electrolyte membranes was around 100 μm. Grass transition temperature of each electrolyte membranes was obtained by DSC measurement.

Diffusion behavior of the cation and anion species was observed using probe nuclei of ^{7}Li (117 MHz) and ^{19}F (283 MHz), respectively, by the PGSE-NMR technique.[10] Signal measurements were performed in a wide bore magnet (7.04 T) equipped with a JNM-ECP300W (JEOL Ltd.) spectrometer based on a stimulated echo sequence applying two gradient pulses of duration δ with an observation time Δ apart, as represented in Figure 2.[11] Half-sine-shaped gradient pulses were used in sequence because of getting a perfect matching of the two gradient pulses compared with that in square-shaped gradient pulses to enhance the data accuracy.[12] Typical values of parameters concerning the field gradient pulses were g = 10 T/m, δ = 0−5 ms, and Δ = 40, 80, and 160 ms. The range of diffusion time (40 ms ≤ Δ ≤ 160 ms) selected here covers the maximum range to obtain reliable data from the aspect of sample diffusivity and the equipment condition. To observe echo signal attenuation, δ was varied because time control is the most accurate way for changing parameter in this equipment. In the case of confirming the restricted diffusion behavior, echo attenuations with different Δ were compared. Carrier diffusivity of the membranes did not show anisotropy in a sheet in the comparison of the diffusion in parallel and perpendicular to the membrane plane. Then, several fragments of the film were put in an NMR sample tube randomly to produce a diffusion measurement sample. The spin−lattice relaxation times, T_1, of ^{7}Li and ^{19}F of this type of polymer electrolyte were 0.4 s (30 °C) and 0.6 s (30 °C), respectively.

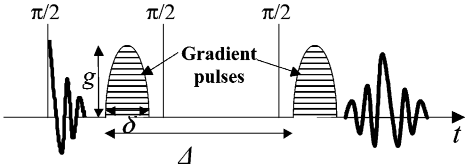

Figure 2. NMR pulse sequence used in the measurement of echo signal attenuation. δ is the duration time of the gradient pulse, g the strength of the gradient pulse, and Δ the diffusion time.

Theoretical Basis of Carrier Diffusion Observed in PGSE-NMR

(1) Echo Attenuation Features of Restricted Diffusion. We first summarize NMR spin echo signal behavior of diffusive species according to their environment. Echo intensity can be represented by a function of parameters in the pulse sequence applied in measurement. When the probed species migrate randomly following Brownian motion without any disturbance of chemical or physical barriers during a diffusion time, Δ, the observed spin echo signal intensity, M, is attenuated in a sequence as

$$M = M_0 \exp[-\gamma^2 D\delta^2 g^2(4\Delta - \delta)/\pi^2] \tag{1}$$

where M_0 is the initial echo intensity, γ is the gyromagnetic ratio of the probed nucleus, D is the diffusion coefficient of the species, δ is the pulse width of the field gradient, g is the strength of the field gradient, and Δ is the interval time of the two gradient pulses.[10−12] This relation reveals that the log plot of intensity against $\gamma^2\delta^2 g^2(4\Delta - \delta)\pi^{-2}$ yields a linear change, with a slope of D. Carrier diffusion in electrolyte solutions and most polymer gel electrolytes generally follows this variation because the carriers migrate randomly in the medium structure.

The echo attenuation deviates from eq 1 when the carrier meet with geometrical and/or chemical barriers during the diffusion time, Δ. The echo changing feature depends on the space between the barriers and the magnitude of the chemical interactive force.[13,14] The changing behavior could be evaluated on the basis of some models such as a rectangular box model defined by two parallel barriers between which carriers go back and forth[15] and a pore hopping model in which carriers pass through several interconnected pores of porous medium. In the former case, the echo attenuation of the motion colliding with the barriers repeatedly can be represented as

$$M(q,\Delta) = \frac{2[1-\cos(2\pi qa)]}{(2\pi qa)^2} + 4(2\pi qa)^2 \sum_{n=1}^{\infty} \exp\left(-\frac{n^2\pi^2 D\Delta}{a^2}\right) \frac{1-(-1)^n\cos(2\pi qa)}{(2\pi qa)^2-(n\pi)^2} \quad (2)$$

where $q = (2/\pi)(\gamma\delta g/2\pi)$ for the sine-shaped gradient pulse and a is the space between the barriers.[15] In this case, the log plot of the echo intensity as a function of $\gamma^2\delta^2g^2(4\Delta - \delta)\pi^{-2}$, by analogy with the plot of random walk migration for estimation of the D value, gives an oscillating or curved feature in attenuation.[6,15] The frequency of the oscillation depends on the magnitude of a, and the signal attenuation factor is correlated with D. Furthermore, the observed echo appearance depends on the diffusion time, Δ, in a sequence. At $\Delta \gg a^2/D$, the echo converges to the first term of eq 2, becoming independent of D, and at $\Delta \ll a^2/D$, the echo approaches to eq 1, which indicates the independence on a because of the scarce chance to collide with the barriers for most carriers.

The pore hopping model developed by Callaghan et al. represents an extended feature of the restricted situation in a porous structure.[15] Simulated echo attenuation showed an oscillating behavior in the intermediate diffusion time, similar to that of the rectangular box model. The obvious difference of this model assumption from the simple rectangular box model is that the porous space with boundaries is identified by two factors: the pore size and the mean spacing between the pores. Oscillating behavior of the echo intensity change is complicated due to contributions of the four morphological factors. On the very long time limit of diffusion, a random walk feature represented by an apparent diffusion coefficient, D_{app}, which indicates the average diffusivity of carriers passing through many pores, approximates the observed echo decay.

(2) Simulation of Echo Attenuation according to the Rectangular Box Model. As is shown in eq 2, echo attenuation behavior of the restricted diffusion in the space between the barriers is characterized by the diffusion coefficient of carrier, D, and the restricted space size, a, assuming the constant Δ. We then simulated the echo attenuation according to the rectangular box model with the variations of D and a in order to grasp the echo changing tendency first. This model has the advantage that it images most simple medium structure for restriction, and the correlation between the echo change and variables is easy to understand.[6] Figure 3 shows the echo intensity plot according to eq 2 with varying δ for several D and a values. The echo signal became more distinct in oscillating attenuation with increasing D although the oscillation frequency was independent of D, which is known from the same minimum position in the x-axis for all lines in Figure 3a. A straight solid line in the figure represents echo decay assuming random walk migration with D according to eq 1. The slope of the straight line is steeper than the attenuation undergoing diffusion restriction with the same D value. The oscillation frequency was affected by the domain size, a, as shown in Figure 3b. It increased with a becoming steeper in slope in the initial echo attenuation.

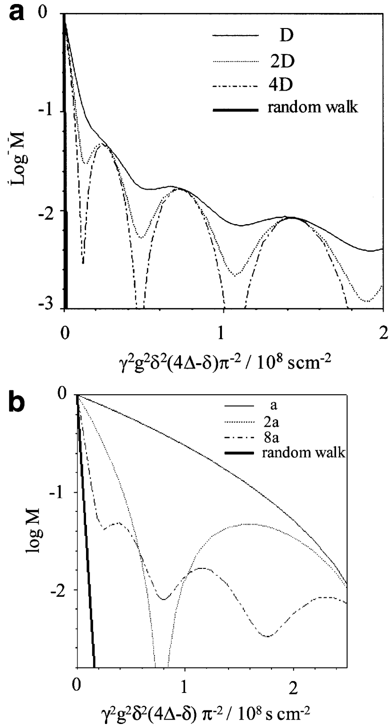

Figure 3. Simulation of spin echo intensity change based on the rectangular box model with changing (a) diffusion coefficient, D, and (b) restriction size, a. Used values for calculation are $a = 5.0$ μm, $D = 2 \times 10^{-6}$ cm^2 s^{-1} for (a) and $D = 2 \times 10^{-7}$ cm^2 s^{-1} for (b), $g = 1065$ G/cm, $\gamma = 10\,396$ rad/(s G), $\delta = 0-8$ ms, and $\Delta = 80$ ms.

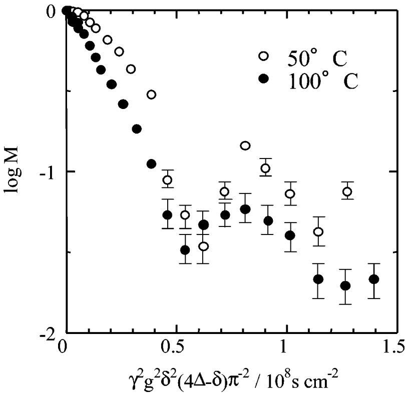

Figure 4. Spin-echo intensity change of ^{7}Li of a glucitol-type polymer electrolyte ([Li]/[monomer] = 0.2) at 50 and 100 °C. Experimental uncertainties in the echo amplitudes are represented by the error bars.

Results and Discussion

(1) Diffusion Behavior of Carriers in Glucitol-Type Polymer Electrolytes. Figure 4 shows typical changes in NMR spin-echo signal intensity of ^{7}Li observed at 50 and 100 °C for $\Delta = 80$ ms. We could find oscillating behavior in echo attenuation in the log M plot vs $\gamma^2g^2\delta^2(4\Delta - \delta)\pi^{-2}$. This behavior indicates that the carrier diffusion of this polymer electrolyte is different from the random walk migration generated in polymer gel electrolytes and electrolyte solutions. We then examined Δ dependence of the echo intensity change to roughly estimate the size, a, which is responsible for restricted diffusion behavior. As is discussed in the section of theoretical basis, echo attenuation of log M vs $\gamma^2g^2\delta^2(4\Delta - \delta)\pi^{-2}$ of the restricted diffusion process shows Δ dependence in the case of $\Delta \sim a^2/D$. At $\Delta \gg$

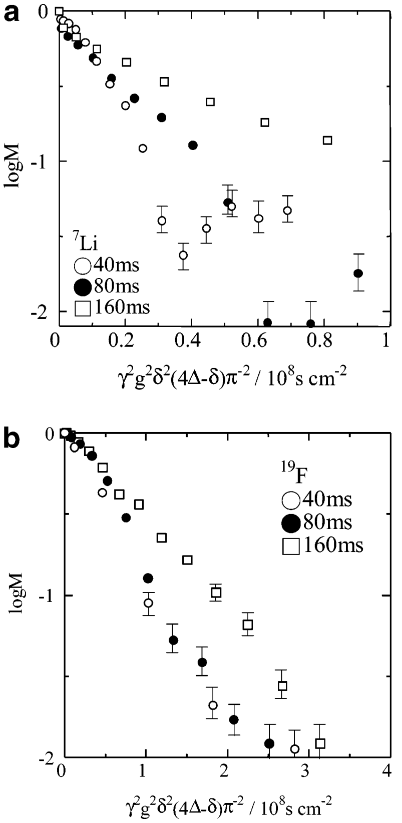

Figure 5. Spin-echo intensity changes of (a) ^{7}Li and (b) ^{19}F measured at diffusion times of 40, 80, and 160 ms at 30 °C. Experimental uncertainties in the echo amplitudes are represented by the error bars.

a^2/D, the plot becomes independent of Δ because the second term of eq 2 is neglected, and at $\Delta \ll a^2/D$ the plot becomes linear approximated by the random walk feature. Figure 5 represents the observed results of Δ dependence of echo intensity change for the cation and anion species. Echo attenuation showed individual curve depending on Δ. This suggests that the observed condition corresponds to the range of $\Delta \sim a^2/D$ for the glucitol-type polymer electrolyte. Considering the migration along the direction of the applied field gradient, the relation of a and Δ can be rewritten as follows:[16]

$$a = \sqrt{2D\Delta} \tag{3}$$

We can obtain 1.3 μm < a < 4 μm in the range of 40 ms < Δ < 160 ms, assuming the inherent diffusion coefficient, D within the range of 5×10^{-8}–5.0×10^{-7} cm^2 s^{-1} by analogy with the diffusion coefficient of homogeneous polymer gel electrolytes.[17,18] It is needed to consider here the meaning of a which is responsible for restricted diffusion behavior in the practical polymer electrolyte. The estimated micron-order size is orderly greater than the distance between the available sites for ion hopping or the length of a unit polymer chain. We speculate that the estimated size of micron order corresponds to that of a kind of domain structure that is an aggregation unit of entangled polymer molecules. The domain has grown in the solvent evaporation process during casting the precursor at the membrane preparation step. At the center of the domain, carriers could migrate randomly. However, at the boundary region of the domain, carrier migration is affected by the domain wall and the echo attenuation shows the restricted diffusion feature.

Table 1. Observed T_g of Glucitol-Type Polymer Electrolytes Estimated from DSC Measurement

[Li]/[monomer]	0.0	0.2	0.4	0.8
T_g/°C	30	28	25	22

(2) Observed Echo Attenuation with Temperature and Salt Concentration Variations. To confirm the cause of the restricted diffusion feature of the carrier species and investigate the diffusion mechanism in the glucitol-type polymer electrolyte, we varied two factors, measurement temperature (T) and dissolved lithium salt concentration (C), in the observation of NMR echo attenuation. These factors are correlated with plasticity of the polymer electrolyte and directly affect motility of both the carriers and medium polymer chains. It is acceptable that motility of carriers and medium polymer chains are enhanced with increasing T due to the thermal activation. Furthermore, increase in C also affects the plasticity of polymer electrolytes. This was confirmed by T_g observation of the electrolyte membranes represented in Table 1. With increasing the dissolved salt concentration, T_g decreased, indicating the increased plasticity. This result could be explained that the dissolved salt interferes polymerization of the glucitol monomers and averaged molecular weight of the polymer was kept small with dissolving the salt.[19] In practice, we also qualitatively observed that the polymer membrane softened up with the salt concentration increase. The salt concentration effect on the dry polymer electrolyte is fundamentally different from the tendency of polymer gel electrolytes or electrolyte solutions in which the viscosity increases with the salt concentration increase.[4,7] This change is based on the fact that increased salt results in raising the chance of collision and interaction among the dissolved species and solvent species, which leads to the viscosity increase. In the case of the dry polymer electrolyte, viscosity increment effect by the salt concentration increase would disappear due to the dominant polymerization inhibition effect of the salt.

It is useful to suppose the correlation between the variable parameters (T and C) and determining parameters of restricted diffusion (D and a) before discussing the experimental results. It is natural to think that D would increase with the increase in motility of the carriers and medium polymer chains as the result of plasticity increase. Therefore, D increase directly reflects T or C increase. For the change in a, which was assumed to be the domain size of an aggregation unit, polymer motility is a dominant factor. In thermally activated condition (increased T), the entangled polymer chains are relaxed. As a result, the domain boundary region would become ambiguous, indicating the expansion of the domain. It is also expected that reducing in polymerization degree accompanied by the enhanced C makes loose the polymer aggregation due to the reduced elasticity of the shorter polymer chains. Therefore, increases in T and C contribute to a increase in the domain model.

Figure 6 represents the observed NMR echo signals of cation and anion species probed by ^{7}Li and ^{19}F, respectively, at several temperatures. The plot shifted to the left with increased temperature for both species; that tendency concurs with increased D and a obtained from the simulated calculation in Figure 3. Therefore, we found that temperature change agrees with our prediction of enhanced D and enlarged a discussed

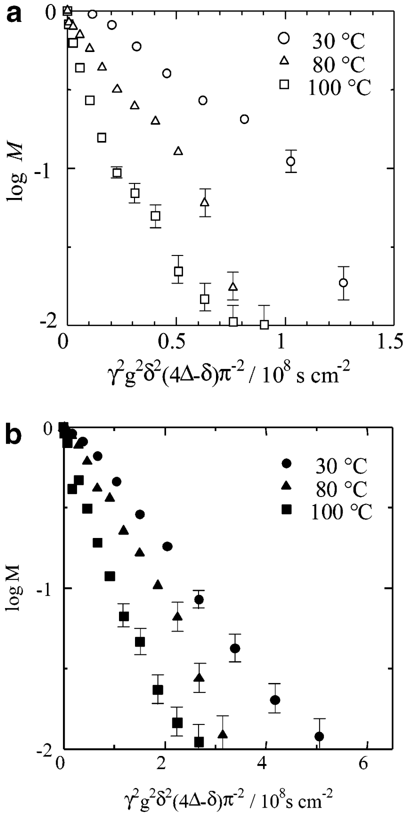

Figure 6. Spin-echo intensity changes of (a) ^{7}Li and (b) ^{19}F of glucitol-type polymer electrolyte ([Li]/[monomer] = 0.8) at 30, 80, and 100 °C. Experimental uncertainties in the echo amplitudes are represented by the error bars.

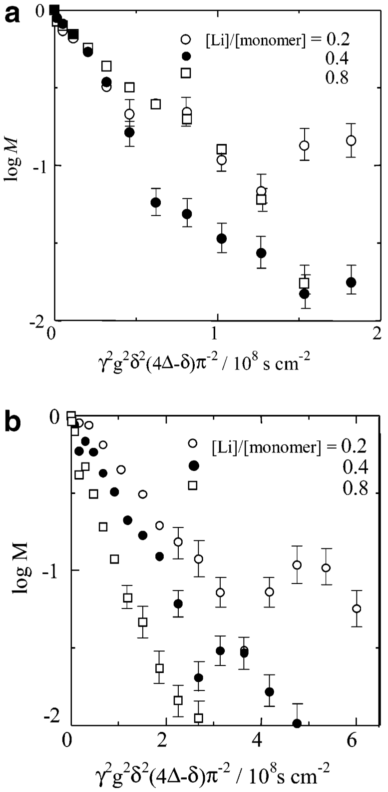

Figure 7. Spin-echo intensity change of (a) ^{7}Li and (b) ^{19}F of glucitol-type polymer electrolyte at 30 °C with different salt concentrations, [Li]/[monomer] = 0.2, 0.4, 0.8. Observed diffusion time, $\Delta = 80$ ms. Experimental uncertainties in the echo amplitudes are represented by the error bars.

above. It is also noted that the echo attenuation behavior is apparently different between the cation and anion species. That is, the nonlinear curved feature of the plot of log M vs $\Delta\delta^2$ was observed in the cation species in contrast to almost linear decay of the anion species. This would reflect the difference in restriction degree in diffusion between the cation and anion associated with the ion migration mechanism.

Figure 7 shows the comparison of echo intensity change of polymer electrolytes with different salt concentration. It is found that the changing feature was not so simple as that of temperature variation in Figure 6. This is because the salt concentration change affects not only polymer plasticity but also the carrier migration mechanism due to the change in site occupation fraction on the polymer chains. In addition, the domain morphology is inhomogeneous and depends on the salt concentration due to the salt localization and the domain size distribution which are generated in polymer preparation process. On the basis of the thorough understanding of the data complexity, we dared to fit the observed data to the restricted diffusion model of eq 2 in order to see the relative change of the parameters with a and evaluate the carrier migration mechanism from the changing behavior. Application of the rectangular model is not necessarily satisfactory to represent the real polymer electrolytes. However, it is useful and meaningful to apply the simplest model and evaluate the meaning of the estimated parameters correlated with the polymer structure which is responsible for the characteristic diffusion features.

Figure 8 gives the fitted result for each attenuation. Tentative estimation of D and a from the fitting is incorporated in the figure. It is found that the fitted results are no so good to reproduce the observed values especially in the attenuation of the anion species. It is possible that the deviation of the anion attenuation from the theory reflects the lower restricted condition in the anion diffusion attributed from the migration mechanism explained below. We then made much of fitting the initial decay curve and initial minimum point because the high-intensity regions are more reliable in data representing the morphological feature. As the result of the fitting, the changing tendencies of D and a were opposite between the cation and anion species. With increasing the salt concentration, both D and a of the anion species increased. This reveals that the increased salt concentration following the enhanced plasticity contributed to the enhancement of anion mobility and segmental motility of the polymer chains. On the other hand, D and a values of the cation species declined with the salt concentration opposite to the behavior of the anion species. This indicates that the fitted parameter variation of the cation does not reflect the plasticity change attributed to the salt concentration change.

We can say from these results that the restricted situation responsible for the ion migration mechanism is different between the cation and anion species. It is supposed that Li cation is preferentially attracted to oxygen of the glucitol polymer after the salt dissolution. The trapped Li cation migrates by hopping from site to site due to the attractive force of the sites.[20,21] An anion species, on the other hand, would be attracted by the positively charged species on the polymer (H^+), but the interaction is not so strong enough to trap the anion on the polymer chains.[4] This is because the larger anion size is not appropriate chemically and physically to be

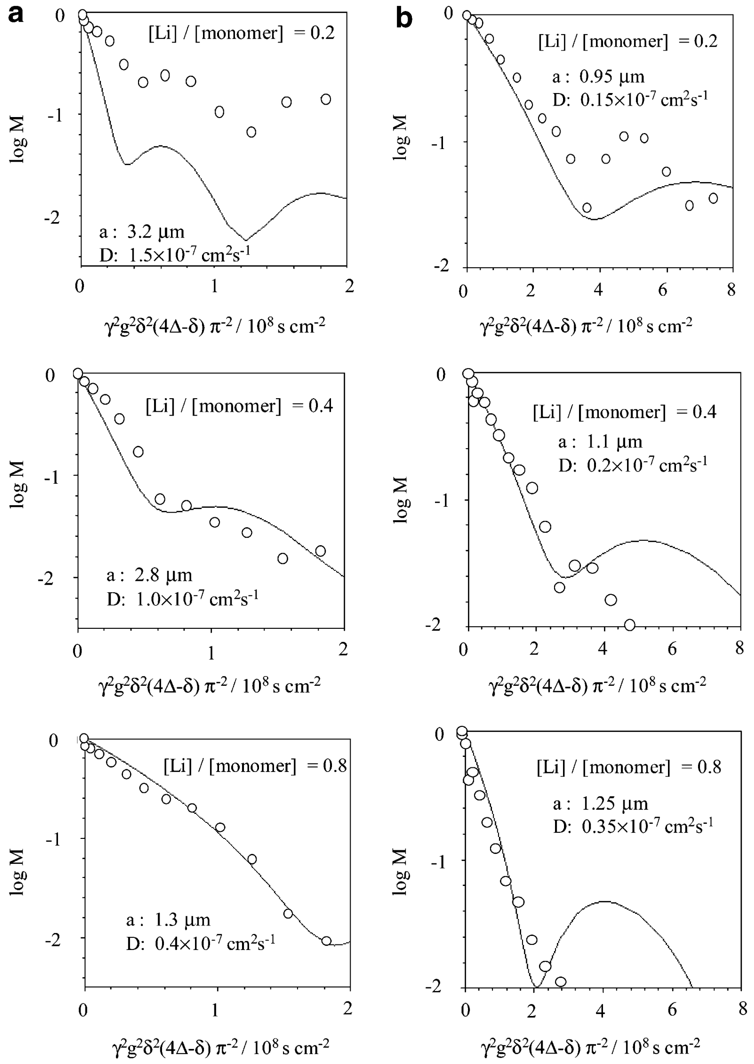

Figure 8. Fitting result according to the rectangular box model for spin-echo intensity change of (a) ^{7}Li and (b) ^{19}F of glucitol-type polymer electrolyte at 30 °C with different salt concentrations; [Li]/[monomer] = 0.2, 0.4, 0.8. Observed diffusion time, Δ = 80 ms.

trapped on the site due to the charge dispersion and steric hindrance. As a result, the cation migration in the polymer electrolyte is more restricted not only in micron-scale by the morphological effect of the polymer domain structure but also in nanoscale attributed to Coulombic interaction of the polymer sites. The different feature in the restricted condition between the cation and anion species has already observed in the PEO-type dry polymer electrolytes, in which the diffusion restriction was stricter in the cations compared with the anions from the echo oscillating behavior.[6]

In the glucitol-type polymer electrolyte, the cation would migrate by hopping on the sites which are located in the rigid glucitol group apart from the soft and mobile methylene chain. Therefore, enhanced segmental mobility ascribed to the increased plasticity would not contribute to cation mobility increase directly and rather disturb cation hopping. On the other hand, the anion migration could be linked with the activation of the chain segmental motion because the anions are located around the polymer equally. Anion diffusion is morphologically restricted by the polymer chains but is free from the site hopping motion. This is the reason why the anion attenuation did not agree with the ideal restricted diffusion theory and of the contrary feature of D with plasticity between the cation and anion species. Decreasing feature of a value of the cation with increased salt concentration and plasticity is anomalous from the aspect of motility activation. Although it is not easy to explain this phenomenon systematically, we speculate that increased number of cation reduces the available sites for hopping migration and results in increase in barrier height of the restricted region. This situation has been observed as decrease in a for the cation diffusion in the practical polymer electrolytes.

Conclusions

We elucidated anomalous diffusion behavior of new glucitol-type polymer electrolytes. Carrier diffusion showed a restricted situation of oscillating feature in NMR echo-signal attenuation. The size of the boundary region speculated from the diffusion time range, in which the echo depends on the diffusion time, was micrometer order. This fact indicates that the boundary region would be a kind of domain structure which is an aggregation of entangled polymer chains. Migration in the domain colliding with the boundary region showed the restricted diffusion behavior as the form of oscillating echo attenuation. Restricted diffusion behavior can be characterized by two parameters, inherent diffusion coefficient D and the size of the restricted space a in the model structure. These parameters depended on temperature and dissolved salt concentration. Temperature increase brought an increase in D and a because of thermal activation of carriers and polymer chains loosening the domain structure. Salt concentration increase also induced the changes of D and a variation. The parameters of the anion species increased with salt concentration according to the enhanced plasticity of the electrolyte. However, the variations of D and a of the cation were opposite to that of the anion. This anomalous feature reflects that the migration mechanism is different between the cation and anion species. Cations are strongly attracted by the oxygen sites by Coulombic effect and then take the hopping manner on the sites in migration. This situation would provide strict restricted condition in addition to the morphological restriction for the cation migration.

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