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Ionic Conduction Mechanism of PEO-Type Polymer Electrolytes Investigated by the Carrier Diffusion Phenomenon Using PGSE-NMR

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ABSTRACT: The diffusive behavior of the cation and anion species of the PEO-type polymer electrolyte has been investigated using pulsed gradient spin-echo NMR to elucidate the carrier conduction mechanism of the polymer electrolyte. Compared with the random diffusive behavior generally observed in electrolyte solutions, the carriers in the PEO-type polymer electrolyte showed a characteristic migration feature of a restricted condition especially after the application of stress on the membrane. This is attributed to carrier hopping along the polymer chains through Coulombic interaction between the carriers and the ethylene oxide sites on the chains. The restricted feature was in agreement with the simple boundary restriction model. The diffusion time dependence of the echo intensity change also supported the belief that the carrier migration in the polymer electrolyte followed the simple boundary model. Considering the actual situation of the polymer electrolyte, the polymer chains spread in all directions to create a random network structure, which consequently permits three-dimensional migration as random diffusion under the condition of long-time limit. The diffusion manner of the cation species along and across the stretched direction was different at 80 °C. This was due to the difference in the diffusion coefficient between the two directions from the fitted results according to the simple boundary model. This confirmed that the alignment of the sites in the polymer electrolyte by strain would be effective for creating a highly conductive pathway for lithium ion transport even if application of stress is disadvantageous for segmental mobility.

Introduction

Development of highly conductive polymer electrolytes for lithium has proceeded recently.[1] Replacement of the conventionally used electrolyte solution in lithium secondary batteries by a solid polymer electrolyte enhances the safety performance of the device due to the elimination of the organic solvent. This would accelerate widespread usage of the secondary battery for energy storage systems contributing to environmental conservation.

The main target of research on polymer electrolytes is to enhance the conduction properties to a level comparable to that of electrolyte solutions. Especially, the selective increase in the lithium ion conductivity or lithium ion transport number is required from the aspect of the charge transport process during battery operation.[2]

Designing of highly conductive polymer electrolytes should be performed systematically based on the ionic conduction mechanism. The conduction mechanism of polymer electrolytes has been discussed in several studies concerning the relaxation time of the polymer and analyses of the crystal structure.[3,4] In the case of typical polymer electrolytes of amorphous PEO-type material, it is accepted that lithium ions hop the oxygen sites of the ethylene oxide taking advantage of the characteristic segmental motion of the polymer chains. In contrast, the counteranions seem to be independent of the sites and migrate fairly freely in the polymer network. For a crystalline material of the PEO-type polymer electrolytes, it may be possible for the lithium ions to migrate through a cylindrical tunnel composed of pairs of PEO chains.[5] In this case, the anions stay out of the helical tunnel and are almost immobile. This model of the lithium transport tunnel is supported by the result in which the uniaxial stress on the crystalline PEO polymer showed anisotropy in conductivity enhanced along the stressed direction.[6]

On the basis of these results, we can speculate that the carrier migration in the polymer electrolyte is dominated by two factors: the site configuration as a static aspect and segmental mobility as a dynamic feature of the polymer chains. They would be associated with the conformation, the length, and cross-linking condition of the chains and the morphology of the chain network of the polymer electrolytes. Segmental mobility has been enhanced conventionally by adding a plasticizer such as an organic solvent or a low molecular weight polymer.[1] With increasing of the plastisizer fraction, the carriers would migrate linked with the solvent migration creating solvated ions. This type of polymer electrolyte can be categorized as a gel electrolyte.

In parallel to this approach, many trials of modification of the static structure have been performed. However, it would be difficult to obtain systematic results because the real conduction mechanism of the polymer electrolytes as a foundation of the structural designing has not been investigated through the dynamic properties of the carriers.

We have been measuring the mobility and the diffusion coefficient of the cation and anion species independently of the electrolyte materials from fluids to solids.[7−9] We found that the carriers in the polymer electrolyte

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without any solvent showed an anomalous feature of diffusion behavior depending on the stressed condition compared with the random diffusion observed in fluid materials. In this research, we tried to investigate the cause of the characteristic diffusive behavior of the carriers to establish the conduction mechanism of the PEO-type polymer electrolytes. To confirm the influence of the strain, which is associated with the site configuration, on the carrier transport, we prepared an amorphous sample having anisotropy by applying a uniaxial stress and compared the diffusive behavior with that of the isotropic sample. Finally, we would like to propose a direction for designing highly conductive polymer electrolytes based on the carrier migration mechanism.

Experimental Section

A PEO-type polymer of $-(CH_2CH_2O)_X$-$(CH_2CH(CH_2O(CH_2CH_2O)_2CH_3)O)_Y$-$(CH_2CH(CH_2OCH{=}CH_2)_2O)_Z$ [P(EO/EM-2/AGE)] (average molecular weight: 1.59×10^6) was prepared by anionic polymerization using the starting materials, ethylene oxide, 2-(2-methoxyethoxy)ethyl glycidyl ether, and allyl glycidyl ether. The molar ratio of the components was [EO]/[EM-2]/[AGE] = 80/20/1.7. The polymer and the $LiN(CF_3SO_2)_2$ were dissolved in acetonitrile in the fraction of [Li]/[O] = 0.06 to form a homogeneous solution and cast to prepare films of a thickness of about 40 μm after solvent evaporation. A melting point corresponding to the phase transition of this film was not observed in the thermal analyses under 100 °C, indicating that this polymer membrane has no crystallinity. Stressed samples were prepared from an initial film by (a) stretching and pressing with random force in a random direction (randomly stressed film) and by (b) stretching uniaxially to twice the length in a direction (uniaxially stressed film). The diffusion coefficients of the cation and anion species were measured using the probed nuclei of ^{7}Li (117 MHz) and ^{19}F (283 MHz), respectively, in both directions (along and across the stretched direction) by turning the sample position toward the direction of the field gradient. Spin-echo measurements were performed using a JNM-ECP300W wide-bore spectrometer (7.04 T) using a stimulated echo sequence with the application of the two gradient pulses for the diffusion measurement. The spin−lattice relaxation times, T_1, of ^{7}Li and ^{19}F in this polymer electrolyte were 0.18 s (25 °C), 0.22 s (80 °C) and 0.59 s (25 °C), 1.3 s (80 °C), respectively. Half-sine-shaped gradient pulses were used for the measurement of the diffusive behavior of the cation and anion species because they are useful for matching the two pulses in sequence compared with square-shaped pulses.[10,11] When the probed nuclei migrate during the duration time, Δ, according to the random walk model, the spin-echo intensity, M, is attenuated as

$$M \propto \exp[-\gamma^2 D \delta^2 g^2 (4\Delta - \delta)/\pi^2] \qquad (1)$$

Here γ is the gyromagnetic ratio, D the diffusion coefficient, δ the pulse width of the field gradient, g the strength of the field gradient, and Δ the interval time of the two gradient pulses. Typical values of the parameters for the field gradient pulses were g = 10 T/m, δ = 0−5 ms, and Δ = 30−160 ms.

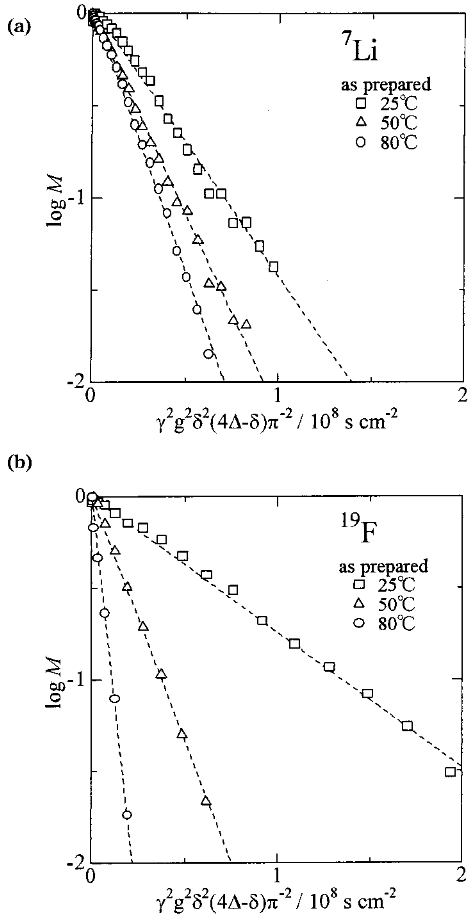

Figure 1. Spin-echo intensity change in (a) ^{7}Li for cation and (b) ^{19}F for anion species of the polymer membranes as-prepared.

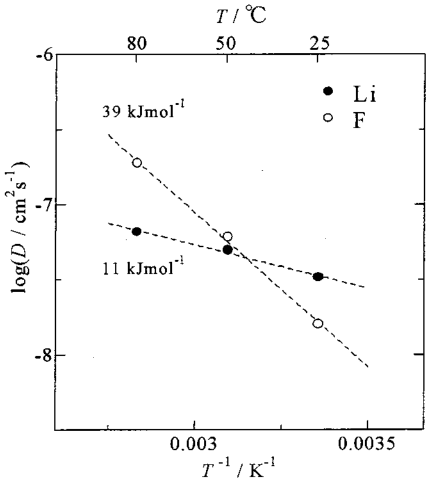

Figure 2. Temperature dependence of the diffusion coefficients of the cation and anion species. The estimated activation energies were 11 kJ/mol for the cation and 39 kJ/mol for the anion.

Results and Discussion

1. Effect of Random Stress on the Polymer Electrolyte Membranes.

Figure 1 shows the spin-echo intensity change at 25 °C in the cation and anion species of the polymer electrolyte membranes as-prepared as a function of the parameters of the gradient pulses following the relation of eq 1. Both species showed linear changes in the measured temperature range. This means that both carriers follow the Brownian motion based on random walk behavior in the membrane. The linearity was kept in the measured temperature range. Therefore, the slope of each plot corresponds to the magnitude of the apparent diffusion coefficient. The estimated values are summarized in Table 1. Figure 2 represents the temperature dependence of the diffusion coefficient for both species. The activation energies were 11 and 39 kJ/mol for the cation and anion species, respectively. This result reveals that the carrier migration mechanisms are apparently different between the cation and anion species. The interaction between the

Table 1. Diffusion Coefficient of the Cation and Anion Species of the Polymer Membranes As-Prepared and Uniaxially Stretched at 25 and 80 °C[a]

	$D(^7Li)/cm^2\ s^{-1}$				$D(^{19}F)/cm^2\ s^{-1}$			
			uniaxial				uniaxial	
temp/°C	as-prepared	random	||	⊥	as-prepared	random	||	⊥
25	3.3×10^{-8}	–	–	–	1.6×10^{-8}	–	–	–
80	6.6×10^{-8}	–	1.0×10^{-7}	–	1.9×10^{-7}	1.9×10^{-7}	1.9×10^{-7}	1.9×10^{-7}

[a] For the stretched sample, diffusion was measured along and across the stretched direction independently. The indications "||" and "⊥" represent the observed diffusion along and across the stretched direction, respectively. The indication "–" means that the spin-echo intensity change did not show the random diffusive behavior, and the apparent diffusion coefficient could not be estimated.

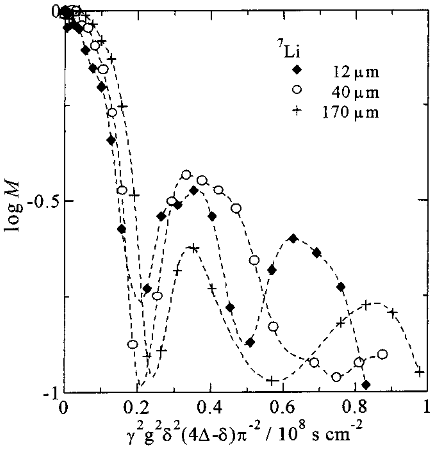

Figure 3. Spin-echo intensity change in the polymer membranes of several thickness stressed at random.

lithium ion and the oxygen site on the polymer is assumed to promote the lithium ion migration linked with the polymer segmental motion, lowering the activation energy of the lithium migration.

Compared with the random diffusive behavior of the initial polymer films, the film with applied random stress showed an anomalous change in the same plot of the echo intensity. Independent of the thickness of the film and the diffusion time Δ, the echo intensity was oscillated in the same plot as shown in Figure 3. This behavior is apparently attributed to the applied stress with random strength and in random directions on the amorphous polymer membranes.

This feature is analogous to the restricted diffusion behavior analyzed systematically in the literature.[12–14] When physical and/or chemical barriers are present on the pathway for carrier migration, the diffusion process cannot follow the random walk anymore and is restricted depending on the size of the bounded region and/or the strength of the interactive force. In this situation, it is known that the spin-echo signal intensity as a function of δ^2 shows a curved or, depending on the diffusion time for observation, an oscillating feature different from the linear change indicating random diffusion.

It is expected that the applied stress affected the morphology of the pathway for carrier migration and/or the interactive condition between the carrier and the polymer site. These effects would restrict the free migration due to the Brownian motion and would show anomalous behavior of the echo attenuation of the oscillating and curved features.

The appearance of the restricted diffusive behavior in the polymer electrolyte reflects that the carrier migration is closely associated with the configuration of the ethylene oxide sites. This also suggests that the migration feature can be controlled effectively by preparing an appropriate pathway taking advantage of physical and/or chemical effects. To observe the anisotropy of the carrier diffusion due to the site configuration change, we next prepared a uniaxially stressed polymer membrane and observed the diffusion behavior along and across the stressed direction.

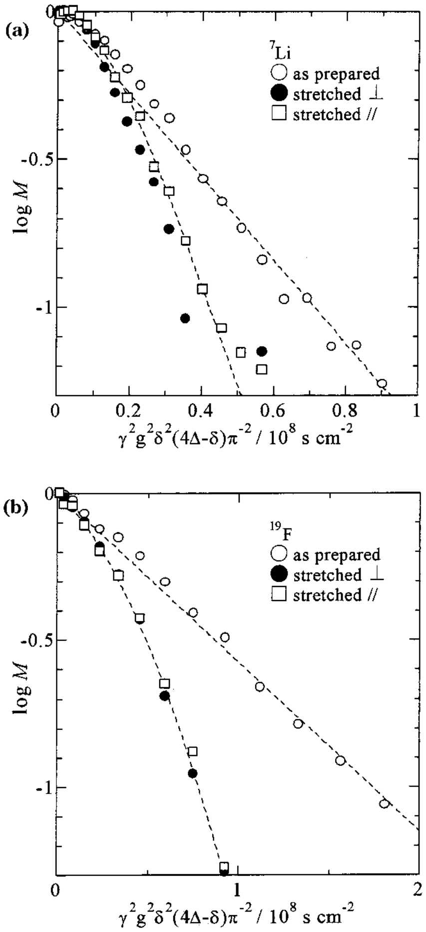

Figure 4. Spin-echo intensity change in (a) ^7Li and (b) ^{19}F of the polymer membranes stressed uniaxially: ⊥, diffusion perpendicular to the stretched direction; ||, diffusion along the stretched direction.

2. Diffusion Behavior of the Polymer Electrolytes with Applied Uniaxial Stress. Figure 4 shows the spin-echo signal attenuation during the diffusion of the cation and anion species of the uniaxially stretched film. The diffusion was observed along (||) and across (⊥) the stretched direction. Compared with the straight lines of the polymer film as-prepared, this film showed a different behavior of a curved tendency. Considering the oscillating behavior of the same plot of the randomly stressed film in Figure 3, it is reasonable to presume that this curved feature also reflects the restricted condition induced by the uniaxial stress. It was assumed that the diffusion depends on the direction of the stress. However, an obvious distinction in the diffusive behavior along and across the stretched direction of the film was not observed at 25 °C for the cation and anion species.

3. Carrier Migration Mechanism in the Polymer Electrolyte under the Restricted Condition. It was found that the carrier diffusion process of the polymer electrolyte, which apparently followed a random Brownian motion first, was restricted by the applied stress on the membrane. What is the real factor bounding the diffusion in the polymer electrolyte? What type of mechanism dominates the carrier transport in the polymer electrolyte? To elucidate these points, we first consult the proposed models of the restricted diffusion.

Observed spin-echo intensity during a diffusion process depends on the geometry and size of the migration space and the strength of the interactive force, if it exists, as well as the diffusion time Δ spent for it. In the space which spreads infinitely without any barriers, the carriers migrate randomly with the diffusion coefficient, D independent of Δ following the echo response of eq 1. In the case of diffusion in a spherical cavity of the diameter, a, or a rectangular box of the width, a, expressed by a simple boundary model here, the carriers migrate influenced by the wall of the cavity depending on Δ.[12,13] At $\Delta \ll a^2/D$, most of the carriers follow the Brownian motion in close proximity to the starting position except for the species near the wall of the cavity or box. The echo response then corresponds to eq 1. In the condition of $\Delta \gg a^2/D$, all species irrespective of the starting position may be found with equal probability anywhere in the cavity. In this case, the spin-echo intensity is independent of D and Δ and, in the case of a spherical barrier, follows the relation[8]

$$M \propto 9[(2\gamma\delta ga/\pi)\cos(2\gamma\delta ga/\pi) - \sin(2\gamma\delta ga/\pi)]^2/(2\gamma\delta ga/\pi)^6 \quad (2)$$

For the intermediate time scale, $\Delta \sim a^2/D$, the carriers migrate randomly with D reflecting the barrier effect. This situation can be represented simply for the restricting condition of a rectangular box as

$$M(q,\Delta) = \frac{2[1 - \cos(2\pi qa)]}{(2\pi qa)^2} + 4(2\pi qa)^2 \sum_{n=1}^{\infty} \exp\left(-\frac{n^2\pi^2 D\Delta}{a^2}\right) \frac{1 - (-1)^n \cos(2\pi qa)}{[(2\pi qa)^2 - (n\pi)^2]} \quad (3)$$

where $q = (2/\pi)(\gamma\delta g/2\pi)$ for the sine-shaped gradient pulse. The first term of eq 3 corresponds to the echo response at $\Delta \gg a^2/D$ for the diffusion in the rectangular box. As an extended model of the simple boundary restriction, a pore hopping model was proposed by Callaghan et al., which assumes the carrier migration in an array of interconnected pores.[12] That gives the spin-echo intensity response as

$$M(q,\Delta) = |S_0(q)|^2 F(q,\Delta)$$

$$S_0(q) = \int_j \rho_0(z' - z_j) \exp[i2\pi q(z' - z_j)]\, dz'$$

$$F(q,\Delta) = \exp\left(-\frac{4D_{\mathrm{eff}}\Delta}{b^2}\sin^2(\pi qb)\right) \quad (4)$$

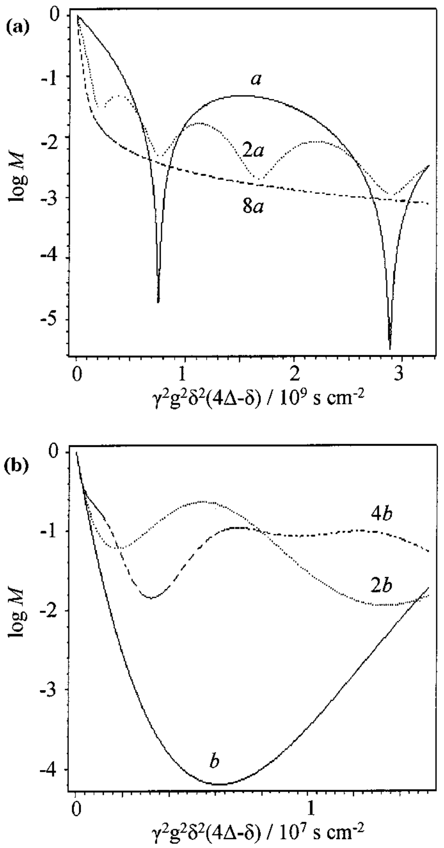

Figure 5. Typical behavior of spin-echo attenuation of the restricted diffusion process following (a) a single boundary model (rectangular box) with the parameters $a = 0.63\ \mu$m, $D = 3.3 \times 10^{-8}$ cm^2 s^{-1}, $\Delta = 80$ ms, $\delta = 0-3$ ms, $g = 1065$ G cm^{-1} and (b) a pore hopping model with the parameters $a = 0.40\ \mu$m, $b = 2.0\ \mu$m, $A = 0.4\ \mu$m, $B = 3.6\ \mu$m $D_{\mathrm{eff}} = 3.8 \times 10^{-6}$ cm^2 s^{-1}, $\Delta = 25$ ms, $\delta = 0-3$ ms, $g = 1065$ G cm^{-1} for different restricted sizes ((a) a, $2a$, $8a$, (b) b, $2b$, $4b$) following eq 3.

where b is the mean spacing between pores and D_{eff} is the description of the diffusion coefficient of the long-range permeation of the pore matrix undergoing Brownian motion. $S_0(q)$ is the structure factor of a single pore, and $F(q,\Delta)$ represents the motion between the pores. This representation suggests that the echo attenuation depends on both D_{eff} and Δ for the condition, $\Delta \geq b^2/2D_{\mathrm{eff}}$. Except for the completely random diffusion process of eq 1, the restricted diffusion under any conditions gives the curved features of the spin-echo intensity as a function of $\Delta\delta^2$ as in Figure 5.

Noting the starting part of decay in Figure 5, the observed diffusion behavior of the polymer electrolytes used in this research is more similar to the upward convex feature of a simple boundary model rather than the opposite feature of the pore hopping model of interconnected pores.

To determine the Δ dependence of the echo attenuation which reflects the correlation between the diffusion time and restricted size, we plotted the observed echo response as a function of δ for several Δ in Figure 6. With increasing Δ, the intensity change shifted to the left for both species. If the diffusion time was enough long to satisfy $\Delta \gg a^2/D$, the plot would be independent of Δ following eq 2. Therefore, this feature indicates that the diffusion time in the range corresponds to the intermediate time, $\Delta \sim a^2/D$, for the carrier diffusion of the polymer membrane. The lines in Figure 6 represent the fitted results using eq 3. It is acceptable

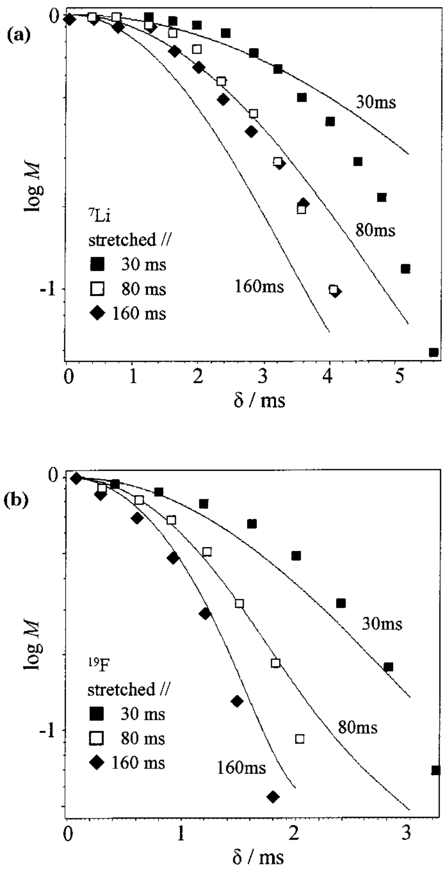

Figure 6. Δ dependence of the spin-echo attenuation as a function of δ. The lines are fitted results according to eq 3.

that the carriers in the polymer electrolyte would be restricted in migration characterized by the single boundary model from the fitted results.

The carriers of the polymer electrolytes migrate along the polymer chains by hopping on the sites connected with the segmental motion of the polymer chains. This feature of the migration on the fixed lanes is a factor of restriction. Further, the carrier mobility is closely associated with the polymer chain structure such as the configuration of the ethylene oxide sites and their distance and macroscopically the chain length which is responsible for the segmental mobility. Therefore, connecting and bending conditions of the polymer chains, which would be sensitive to the applied stress on the polymer, dominate the hopping direction of carriers. This would be another factor in the restriction of carrier transport. In practice, if the chain is entangled randomly, the carriers could not spread over but would go back and forth on the chains in space. On the basis of this consideration, it can be said that the carrier migration in the polymer membrane as-prepared has already been restricted independent of the application of strain.

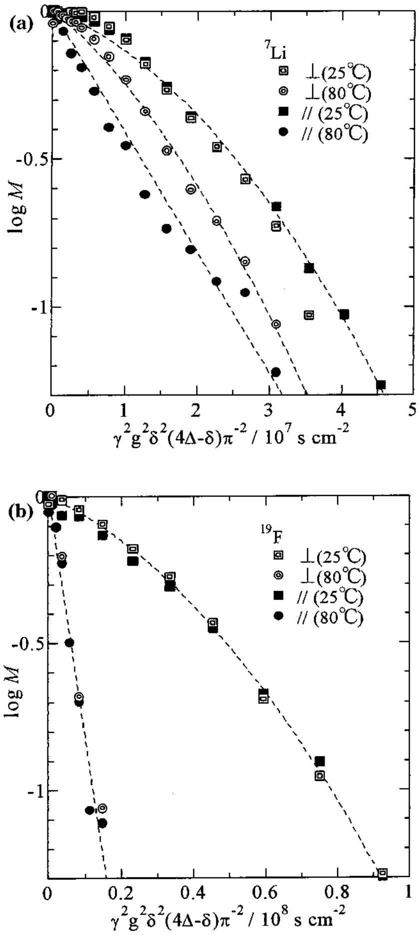

Figure 7. Spin-echo intensity change in (a) ^{7}Li and (b) ^{19}F at 25 and 80 °C.

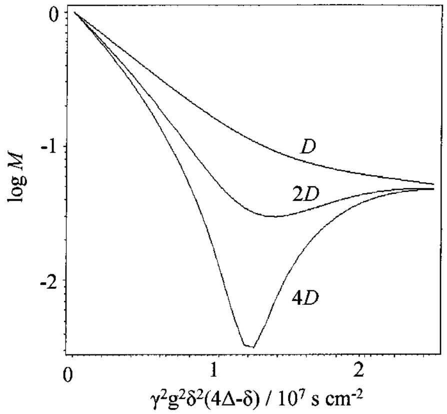

Figure 8. Spin-echo attenuation behavior simulated using eq 3 with the parameters $a = 5.1$ μm, $D = 4.0 \times 10^{-7}$ cm^2 s^{-1}, $\Delta = 80$ ms, $\delta = 0-3$ ms, $g = 1065$ G cm^{-1}.

Fitness of the restricted model represented by eq 3 to this polymer electrolyte was supported by the diffusion behavior under the thermally activated condition. Figure 7 represents the echo attenuation observed at 80 °C with the comparison of the results at 25 °C. With increasing temperature, the plot shifted to the left. Further, it is characteristic that the attenuation behavior of the cation along and across the stretched direction at 80 °C is different, although it is almost the same at 25 °C of the cation and for anion diffusion. Figure 8 represents the simulated result of eq 3 for a different diffusion coefficient, D. Actually, it is difficult to reproduce the results of Figure 7 using eq 3 by changing only D. This is because the real polymer electrolyte provides the three-dimensional restriction, although eq 3 assumes ideally one-dimensional restricted barriers. However, the changing tendency of the echo intensity with D of Figure 8 is in good agreement with the experimental results. It is expected from this result that the discrepancy between the diffusive behavior along and across the stretched direction for the cation at 80 °C is due to the anisotropic diffusion depending on the site configuration.

Considering the morphology of the polymer matrix, the chains are chemically cross-linked to spread the network in all directions. This situation seems to be rather similar to the hopping model of interconnected pores. In this case, in an adequately long time limit, every carrier moves randomly apart from the initial position, which is describable by an effective diffusion coefficient, D_{eff}. It is expected that, if the diffusion time could be varied long enough to satisfy the situation, echo attenuation corresponding to Figures 3 and 4 would show a linear change characterized by the slope, D_{eff}.

The diffusion manner of the anion species along and across the stretched direction was the same. The cation species, on the other hand, diffused with the different slope of the intensity decay between the two directions at 80 °C. This obviously reveals that the cation transport is closely correlated with the configuration of the ethylene oxide site. It should be mentioned that the apparent diffusion coefficient of the cation species along the stretched direction becomes faster than that of the as-prepared film (Table 1). Local alignment of the segment due to the uniaxial stress would support the lithium migration by creating a kind of transport tunnel suggested in the crystalline PEO electrolytes. In contrast, the anion diffusion is not associated with the polymer chains as closely. This indicates that the anions migrate in the polymer network in a fairly isotropic manner different from the hopping of the cations along the polymer chains through the Coulombic interaction between the cation and the anionic site on the polymer chains.

Applying a stress on the polymer membranes is opposite to the concept of enhancing the polymer chain segmental mobility because application of the stress results in reducing the plasticity of the polymer.[6] The enhancement of the diffusion coefficient of the cations along the stretched direction despite the disadvantage of the polymer dynamics proves the existence of a distinct migration mechanism independent of the segmental motion which has been accepted as the dominant factor for conduction in the amorphous polymer electrolytes. This is essentially in agreement with the result of the crystalline PEO-type polymer where the pairs of PEO chains fold to form cylindrical tunnels within which the lithium ions are located and hop on the ether oxygen sites.[5] Even in the amorphous phase, it is possible that the polymer chains are rearranged by the stress to create a chain configuration appropriate for smooth transport of the carriers. Effective combination of the segmental mobility and the static configuration to create a transport pathway would be significant for highly conductive polymer electrolytes.

Conclusions

The diffusion properties of PEO-type lithium polymer electrolytes were investigated using PGSE-NMR to elucidate the carrier migration mechanism. The amorphous polymer membranes as-prepared showed a random diffusion behavior for the cation and anion species. On applying a stress on the membranes, the spin-echo attenuation showed an anomalous change different from the random diffusion behavior. This change reflects the restricted diffusion feature added by the strain in the polymer chains. Consulting the typical restricted diffusion models, we could assume that the diffusion behavior observed in the polymer membrane with applied stress corresponds to the migration feature of a simple boundary model which represents the carrier migration in a closed space surrounded by a barrier. Under the condition of the intermediate diffusion time relative to the diffusion coefficient and the size of the closed space, $\Delta \sim a^2/D$, the echo attenuation behavior depends on the diffusion time. The observed condition for the polymer electrolyte in this research corresponded to this situation. The Δ dependence of the uniaxially stretched polymer membrane was in agreement with the changing tendency of the simple boundary restricted model. This is also supported by the diffusion behavior at elevated temperature. A temperature increase from 25 to 80 °C could be realized by the increase in the diffusion coefficient at the restricted migration process based on the analogy of the simulated results according to the simple boundary model. Diffusion coefficients of the cation species of the stretched membrane at 80 °C were enhanced along the stretched axis. It is possible that this enhancement proves new site configuration appropriate for the carrier migration different from that due to the segmental motion of the polymer chains. This is because the application of stress on the polymer reduces the plasticity and then depresses the segmental mobility of the polymer chains. Alignment of the polymer sites creates a pathway useful for carrier migration along the chain. Taking advantage of both the segmental motion of the chains and the pathway of the aligned sites could be significant for designing highly conductive polymer electrolytes.

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