Interactive Effect of the Polymer on Carrier Migration Nature in the Chemically Cross-Linked Polymer Gel Electrolyte Composed of Poly(ethylene glycol) Dimethacrylate

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The diffusion coefficient and conductivity of the chemically cross-linked polymer gel electrolyte composed of poly(ethylene glycol) dimethacrylate and LiBF$_4$-EC/EMC were measured in order to investigate the effect of the polymer on the nature of carrier migration in the gel. With an increase of the polymer fraction in the gel, the dissociation degree of the salt in the gel increased. This indicates that the polymer accelerated the dissociation of the salt in the progress of gelation. The dissociated cation and anion showed a different manner of change in the activation energy of diffusion with gelation. The cation, through Coulombic interaction, showed a decrease in activation energy, revealing a change in the migration mechanism to hopping on the oxygen sites linked with the segmental motion of the chains. The anion, on the other hand, showed an increase in the activation energy of diffusion. This means that the conduction mechanism essentially follows, as in solution, the mobility of the solvent correlated with enhanced viscosity due to gelation.

Introduction

Development of polymer gel electrolytes has been actively performed recently for the application to solid type lithium secondary batteries.[1] The polymer gel electrolyte could be conventionally divided into two groups depending on the bonding state of the polymer chains, a chemically cross-linked gel and a physically cross-linked gel. The gel composed of poly-(ethylene oxide) (PEO) is categorized in the former. Because of the homogeneously swollen structure, the chemically cross-linked gel is stable and reliable to keep much solution in a small amount of polymer without leakage of liquid. Furthermore, chemical linkage would lead to high heat resistance as compared with the gel of the physically cross-linked polymer network. Therefore, it is desirable to improve the lithium conductivity as well as the transport number of the PEO type polymer gel electrolyte for practical usage.

We have been investigating the conduction mechanism of the PVDF polymer gel electrolytes, which can be classified as a physically cross-linked gel, through the measurements of dynamic properties such as the diffusion coefficient and ionic conductivity. We found that the interaction between the salt (and/or ion) and the polymer in the gel dominates the mobility and concentration of the carrier in the PVDF type gel.[2–6] Control of the interactive effect is indispensable for designing gel electrolyte material, which provides high conductivity and safety performance.

The conduction properties of the PEO type polymer electrolyte without solvent have been studied previously in detail.[7–12] From the results, it was confirmed that the cations were solvated by coordination to the ether oxygen on the polymer chains. As a result, the motion of the cation is strongly correlated with the segmental motion of the polymer chain. In our study of the PEO

type polymer electrolytes using the pulsed gradient spin–echo NMR (PGSE-NMR) technique, the carrier migration mechanism has been proposed based on the diffusive behavior of the individual species.[13] The activation energy of the cation diffusion was 11 kJ mol^{-1}, which was lower than that of the anion, 39 kJ mol^{-1}, indicating that the diffusion processes are essentially different between the cation and the anion species in the polymer. Combined with the diffusive behavior of each species, we concluded that the cation is attracted by the polymer sites and hops on the sites linked with the segmental motion of the polymer chains.

On the basis of these results, it is reasonable to think that the interaction between the polymer and the salt influences carrier migration even in a gel composed of a PEO type polymer. In this research, we would like to know the effect of interaction in the gel on the carrier migration feature and investigate the difference in the conduction mechanism between the dry and the solution-containing PEO type polymer electrolytes. Through the measurement of the diffusion coefficients of the individual species, we will discuss and investigate these points.

Experimental Section

Nona(ethylene glycol) dimethacrylate (PEGDMA, CH$_2$=CCH$_3$-CO$_2$(CH$_2$CH$_2$O)$_9$COC(CH$_3$)=CH$_2$, purchased from Shin-Nakamura Chemical Industries, Co.) was used as a starting polymer material. A lithium electrolyte solution of 1.0 M LiBF$_4$ dissolved in the mixed solvents of ethylene carbonate (EC) and ethyl methyl carbonate (EMC) (1:1 in volume ratio) received from Tomiyama Chemical Co. was mixed with the polymer adding a polymerization initiator, 2,2′-azobis-isobutyronitrile (AIBN). The mixture was sealed in a glass tube to promote polymerization by heating at 80 °C for 1 h. The weight fraction of the solution in the gel was changed from 0 to 60%. The concentration ratio of lithium to oxygen site in the gel was estimated in Table 1.

The ionic conductivity of the gel electrolytes was measured by the complex impedance technique in the temperature range

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TABLE 1. Molar Ratio of the Lithium Salt to Oxygen Sites on the Polymer, [Li]/[O], in the PEGDMA-Based Polymer Gel Electrolytes

PEGDMA (wt %)	[Li]/[O]	PEGDMA (wt %)	[Li]/[O]
1	5.0	20	0.20
2.5	2.0	30	0.12
5	0.97	40	0.076
7.5	0.63	60	0.034
10	0.46		

of -10 to $+60$ °C. The frequency was changed from 10 to 100 kHz using a lock-in amplifier model 5210 (EG&G Instruments) connected with a Potentiostat/Galvanostat model 263A.

The diffusion coefficients of the electrolyte components in the gels were measured using the PGSE-NMR technique with the probed nuclei of ^{7}Li (116.8 MHz) for the cation species, ^{19}F (282.7 MHz) for the anion species, and ^{1}H (300.5 MHz) for the solvent species. The stimulated echo sequence was used for this measurement.[14] Two gradient pulses were applied in the sequence after the first and third $\pi/2$ pulses with a time interval Δ. In this PGSE-NMR experiment, the signal attenuation is described as

$$M \propto \exp[-\gamma^2 g^2 \delta^2 D(4\Delta - \delta)/\pi^2] \quad (1)$$
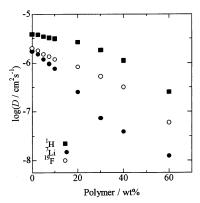
where γ is the gyromagnetic ratio of the observed nuclei, g is the strength of the field gradient pulse, δ is the width of the field gradient pulse, and D is the diffusion coefficient. The field gradient pulse used here is a half-sine-shaped pulse due to the advantage for matching the two pulses as compared with a square-shaped pulse.[15] Typical values of the parameters of the field gradient pulses were $g = 2.5-10.6$ Tm^{-1} for the pulse strength, $\delta = 0-5$ ms for the pulse width, and $\Delta = 80$ ms for the duration between the two gradient pulses. In the case of ^{7}Li and ^{19}F, only one signal having a single diffusion component was observed. This indicates that the gels were homogeneous for the migration of the cation and anion species within the time of NMR measurement, ~80 ms. In the case of ^{1}H, three signals assigned to the solvent species (EC, EMC) were observed. The diffusion coefficients of these were almost the same within experimental error.
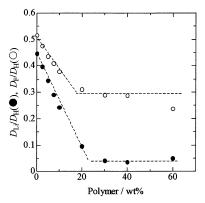
Results and Discussion

Diffusion Coefficients of the Polymer Gel Electrolytes. The diffusion coefficients of the cation, anion, and solvent species of the gels at 25 °C are shown in Figure 1 as a function of the polymer fraction in the gel. The changing slope of the log plot reflects the degree of polymer influence on the migration of each species.

The change in the diffusion value of the solvent species probed by ^{1}H is attributed to the viscosity change of the gel electrolyte. The viscosity change also influences the diffusion of the ionic species to the same degree.

The changing slopes of the cation and anion species were steeper than those of the solvent. To see this situation clearly, normalized diffusion values of the ionic species by the solvent diffusion coefficient, D_{Li}/D_H and D_F/D_H, were plotted in Figure 2. This indicates that the specific effect of the polymer on the charged species was due to other than the viscosity change with gelation in the polymer fraction range of $0-20$ wt %. In further detail, the change in the diffusion value of the cation species is steeper, revealing that the cation species was closely affected by the polymer sites in the progress of gelation.

Figure 1. Diffusion coefficients of the cation and anion species and the solvent species at 25 °C as a function of the polymer fraction in the gel.
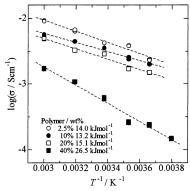

Figure 2. Normalized diffusion coefficients of the cation (●) and anion (○) species by the diffusion coefficient of the solvent species.

Observed diffusion coefficients in this research can be represented explicitly as

$$D_{Li(F)} = xD_{+(-)} + (1 - x)D_{pair} \quad (2)$$

where $D_{Li(F)}$ is the observed diffusion coefficient probed by ^{7}Li (^{19}F), $D_{+(-)}$ or D_{pair} is the inherent diffusion coefficient of the cation (anion) or ion pair, and x is the dissociation degree of the salt assuming that the dissociated ion and the associated ion pair exchange with each other quickly as compared with the measuring time of diffusion, 80 ms. As it is expected that the gelation affects both the dissociation condition (x) and the mobility of the species (D_+, D_-, D_{pair}), we have to consider their individual behaviors contributing to the change in the observed $D_{Li(F)}$. Furthermore, the effect of the polymer on the mobility could be divided into two terms: one is the physical barrier effect such as the percolation migration model and the other is the Coulombic interaction between the acidic or the basic sites on the polymer and the charged species. In the following sections, the dissociation degree of the salt and the mobility of the gels will be discussed through the estimation of the molar conductivity ratio from impedance and NMR measurements and the activation energy of the diffusion, respectively.

Polymer Effect on the Dissociation Degree of the Salt. Figure 3 shows the temperature dependence of ionic conductivity (σ) of the gel. In the progress of gelation from 2.5 to 40 wt % of polymer fraction change, the conductivity decreased about 2 orders of magnitude at 25 °C. Each gel showed a linear change in the Arrehenius type plot in the observed temperature range. Activation energy, estimated from the slope of each plot, increased with the increase in the polymer fraction in the gel represented in Figure 3.

Figure 3. Temperature dependence of ionic conductivity of the gels with several polymer fractions.

Using the conductivity result, we here propose an approach to evaluate the effect of polymer on the dissociation degree of the salt by gelation. The ionic conductivity, σ, is conventionally expressed as

$$\sigma = cxF(z_+ \mu_+ + z_- \mu_-) \tag{3}$$

where c is the salt concentration of the gel, x is the dissociation degree of the salt, F is the Faraday constant, $z_{+(-)}$ is the charge number of the cation (anion), and $\mu_{+(-)}$ is the ionic mobility of the cation (anion). Applying the Einstein relation, $D_{+(-)} = \mu_{+(-)}RT/zF$ and $z_{+(-)} = 1$ for lithium, the molar conductivity Λ_{imp} can be described as

$$\Lambda_{imp} = \frac{\sigma}{c} = \frac{F^2}{RT} x(D_+ + D_-) \tag{4}$$

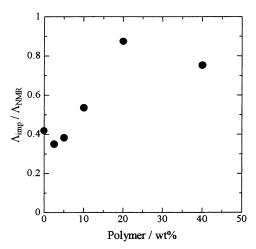where $D_{+(-)}$ implies the inherent diffusion coefficient of the ion. On the other hand, we could derive the molar conductivity Λ_{NMR} using the observed diffusion values by analogy with eq 4 as

$$\Lambda_{NMR} = \frac{F^2}{RT}(D_{Li} + D_F) =$$
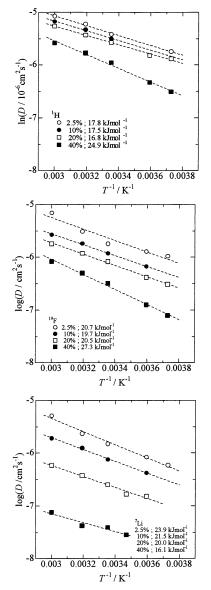
$$\frac{F^2}{RT}[x(D_+ + D_-) + 2(1 - x)D_{pair}] \tag{5}$$

The difference between eqs 4 and 5 is the term $(2F^2/RT)(1 - x)D_{pair}$, which is attributed to the associated ion pair species. The ratio of the molar conductivity, $\Lambda_{imp}/\Lambda_{NMR}$, can be represented as follows

$$\frac{\Lambda_{imp}}{\Lambda_{NMR}} = \frac{x(D_+ + D_-)}{x(D_+ + D_-) + 2(1 - x)D_{pair}} =$$

$$\frac{1}{1 + 2\left(\dfrac{1 - x}{x}\right)\dfrac{D_{pair}}{D_+ + D_-}} \tag{6}$$

It is expected that the evaluation of this value gives us information about x. Estimated results of the ratio using the experimental values are shown in Figure 4 as a function of the polymer fraction in the gel. With increasing of the polymer content up to 20 wt %, the molar conductivity ratio increased. This feature has to be explained by the change in the value of $2[(1 - x)/x][D_{pair}/(D_+ + D_-)]$ in eq 6. The term $D_{pair}/(D_+ + D_-)$ is expected to increase with the polymer fraction. This is because the effect of the polymer on the diffusion value is stronger for the charged species than for the neutral species of solvent as shown in Figure 1. As it would be accepted that the

Figure 4. Molar conductivity ratio estimated from impedance and NMR measurements, $\Lambda_{imp}/\Lambda_{NMR}$.

Figure 5. Temperature dependence of the diffusion coefficient of (a) solvent species probed by ^{1}H, (b) the anion species probed by ^{19}F, and (c) the cation species probed by [7]Li.

polymer effect on the ion pairs is comparable to the effect on the solvent species from the aspect of neutrality and their similar

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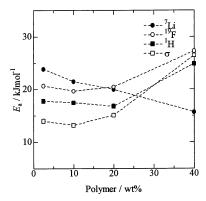*J. Phys. Chem. B, Vol. 106, No. 46, 2002* **12087**

Figure 6. Change in the activation energy for diffusion of each species as a function of polymer fraction in the gel.

size, the decreasing rate of D_+ and D_- is faster than that of D_{pair} with gelation. As a result, the term $D_{\text{pair}}/(D_+ + D_-)$ would increase with the polymer content in the gel. To reproduce the estimated result of Figure 4, the term $(1 - x)/x$ has to decrease to overcome the increased behavior of $D_{\text{pair}}/(D_+ + D_-)$ with the increase in the polymer in the gel. That is, the dissociation degree of the salt, x, increases with gelation.

The reason for the increase in the dissociation degree of the salt in the progress of gelation could be explained as follows. It is confirmed by molecular dynamics simulation and neutron scattering measurements that the coordination of five ether oxygens on the PEO chain to a lithium cation forms a stable coordination structure.[10,11] That corresponds to [Li]/[O] = 0.2 as in Table 1, which is achieved by the polymer addition of 20 wt % in the gel, showing the maximum value of $\Lambda_{\text{imp}}/\Lambda_{\text{NMR}}$. Therefore, the increase in the dissociation degree of the salt with the polymer fraction reflects that the progress in the effective coordination between the site and the lithium may be through Coulombic interaction.

Polymer Effect on the Migration Mechanism of Carriers. The carrier migration mechanism is characterized by the activation energy for migration of each carrier. The temperature dependence of the diffusion coefficient of each species is represented in Figure 5. Furthermore, the change in the activation energy with the polymer fraction in the gel is summarized in Figure 6. This plot shows the characteristic feature of migration of each species. The activation energy for diffusion of the cation species decreased to ∼25 kJ/mol with gelation in contrast with the increased changes in the activation energy of the anion, solvent species, and conductivity, which converged on ∼35 kJ/mol at 40 wt % of the polymer. This indicates that the carrier migration mechanism has become different for the cation and anion species in the progress of gelation.

As was confirmed in the previous section, gelation promoted dissociation in this type of gel. The dissociated ions next interact with the polymer through Coulombic force. The cation would be effectively trapped at the oxygen sites on the polymer chains. As a result, the cation tends to hop on the sites along the chains supported by the segmental motion of the chain rather than migrates randomly in the liquid. On the other hand, the

dissociated anions would be less interactive with the oxygen sites and could migrate fairly freely in the space of the entangled polymer chains, which is similar to the behavior of the solvent species. Therefore, the independent migration mechanism of the cation taking advantage of the polymer sites showed a reduced activation energy. The increased activation energy of the anion as well as the solvent species with gelation can be recognized as the increased barrier of the insulating polymer, which is macroscopically realized as the viscosity increases.

As shown in Figure 1, the diffusion value of the anion is larger than that of the cation, about 1 order of magnitude for the gel with 40 wt % polymer, indicating that the conductivity is contributed dominantly by anion transport in this range. This would be the reason that the value of activation energy of the anion species of the gel was in agreement with that of conductivity.

Conclusions

The effect of the polymer on the dissociation degree of the salt and the carrier migration mechanism of the polymer gel electrolyte composed of PEO and a lithium salt was investigated through conductivity and diffusion coefficient measurements. The polymer accelerated the dissociation of the salt in the progress of gelation. Furthermore, the dissociated cation and anion took a different migration pathway with gelation. That is, the cation, through Coulombic interaction, tended to hop on the oxygen sites and migrated linked with the segmental motion of the chains, leading to reduced activation energy for migration as compared with that in solution. The anion, on the other hand, is less interactive with the sites on the polymer. The conduction mechanism still followed the mobility of the solvent, showing increased activation energy in the progress of gelation due to the increased viscosity of the gel.

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