Designing of a Urea-Containing Polymer Gel Electrolyte Based on the Concept of Activation of the Interaction between the Carrier Ion and Polymer

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The development of new materials for energy conversion systems is a pressing need for dealing with the energy problem and environmental preservation of the earth. On the basis of these demands, a new type of polymer gel electrolyte for lithium secondary batteries was prepared in this research using the concept of restricting the anion mobility with the chemical interactive effect of a specific site of the polymer in the gel. The polymer having the urea group CBMEU was designed to use the electron donating and withdrawing effect of the urea group for attracting the cation and anion, respectively, for the demands of promoting the dissociation of the salt and reducing the anion mobility. To quantitatively confirm the interactive effect of the polymer site, a theoretical model was set up based on the observed dynamic values to estimate the dissociation degree of the salt and interactive force. Application of the model to the new polymer gel electrolyte (CBMEU gel) and the PEO-type gel for comparison showed that, during the progress of gelation, the interactive effect of the polymer on the ionic species promoted the dissociation of the salt and reduced the ionic mobility. The absolute value of the interactive force of the cation, γ_{cation}, was greater than that of the anion, γ_{anion}, for both gels. The ratio, $\gamma_{cation}/\gamma_{anion}$, of the PEO-type gel was three times larger than that of the new polymer gel electrolyte. This is attributed to the anion-attracting effect of the urea group of the CBMEU gel in contrast to only the cation-attracting behavior of the ether oxygen of the PEO-type gel. From this investigation, we proposed an idea to design the polymer gel electrolyte which provides a high dissociation degree and cation transport number based on the investigation of the dynamic properties.

Introduction

The priority for new material development for energy conversion systems is directed to safety and environmental preservation. The polymer gel electrolyte is one of the promising materials that goes along with this concept for practical application to fuel cells and secondary batteries.[1,2] The gel electrolyte could be categorized as a composite material composed of an electrolyte solution and a polymer. The form of a gel has several merits; the volatile solution can be reduced in the cell compared with the conventional electrolyte solution to avoid any liquid leakage and to make it easy for handling during the fabrication process.[3]

In parallel to the safety performance, high conductivity of the ionic species responsible for electric conduction is required as an essential feature for the electrolyte material. However, it is also a fact that the dynamic features of the electrolyte originate from its static nature such as the dissociation condition of the salt and the interaction among the salt (and/or ion), solvent species, and polymer in the gel. We have already found that the interaction between the polymer and salt (and/or ion)

dominates the dissociation degree of the salt, and the cation mobility is more restricted by the polymer attractive force in the PEO-based polymer gel electrolyte using the approach of the diffusion coefficient measurements.[4] The interactive effect of the PEO-type polymer on the dissolved salt has been also proved using the spectroscopic approaches such as IR, Raman, and NMR.[5−8] These results suggest the possibility that the ionic conductivity can be controlled in response to each requirement by taking advantage of the appropriate interactive effect of the polymer in the gel.

In this research, we prepared a new type of polymer gel electrolyte characterized by a polymer with the urea group (-HN−CO−NH-) based on the concept that the localized charge distribution on the polymer chains promotes the dissociation of the salt and changes the ionic mobility. By analogy of the ether oxygen of the PEO, which attracts the cationic species, it is expected that the urea group has the characteristic of the anion attraction after the formation of a salt with an acidic species.[9,10] It is interesting to compare the site effects on the salt dissociation and the ionic mobility between the urea-type gel and PEO-type gel.

To ascertain the site effects on the dynamic features of the gel, it is indispensable to directly evaluate the mobility of the individual ionic species, transport number, dissociation degree of the salt, and the magnitude of the interactive force of the polymer on the salt and/or ions. In a previous paper, we proposed a new approach for the estimation of the dissociation

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degree of the salt of the PVDF-type polymer gel electrolyte using the dynamic values, diffusion coefficient, and ionic mobility.[11] The key point of the approach is on the fact that the observed diffusion coefficient is contributed from both the ion and ion-pair, whereas the observed mobility is contributed from only the ion. The salt in the electrolyte (e.g., $LiPF_6$) under equilibrium conditions is generally represented by

$$LiPF_6 \rightleftharpoons Li^+ + PF_6^- \qquad (1)$$
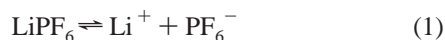
Under this situation, the observed diffusion coefficient (D_{obs}) and ionic mobility (μ_{obs}) of the species of the electrolyte material by the pulsed gradient spin−echo NMR can be denoted as

$$D_{obs(Li,F)} = xD_{(cation,anion)} + (1 - x)D_{pair}$$
$$D_{obs(H)} = D_{solvent} \qquad (2)$$
$$\mu_{obs(Li,F)} = x\mu_{(cation,anion)}$$

where x is the dissociation degree of the salt and the subscripts obs(Li,F) and obs(H) represent the observed dynamic values using the probed species of ^7Li or ^{19}F and ^1H, respectively.[12] The subscripts, (cation, anion), pair, and solvent, indicate the inherent values of the cation or anion, ion-pair, and solvent species, respectively. The inherent dynamic value of each species satisfies Einstein's relation under the ideal condition in which the species follows the Brownian motion in migration and is expressed for the ions as

$$D_{(cation,anion)} = \mu_{(cation,anion)} \frac{RT}{F} \qquad (3)$$

where F is the Faraday constant, and the charge of the species $z = 1$ is assumed. Each inherent value ($D_{(cation,anion)}$, $\mu_{(cation,anion)}$) is a function of the viscosity and temperature.[13] The viscosity is caused by the mixing of the species of different velocities and the interaction among the species. It is acceptable that the observed diffusion coefficient of the solvent species ($D_{obs(H)}$) reflects the effect of viscosity on the individual species (solvent, cation, anion) because the solvent species is independent of the dissociating condition of the salt and the Coulombic interaction in the gel. This means that $D_{obs(H)}$ can be recognized as an indicator of the viscosity of the gel. Using two samples of different viscosity, the dissociation degrees of their salt (x_1, x_2) were individually estimated following the derived equation composed of the observed values.[11] This research suggested that the dissociation degree of the salt decreased with the increase in the polymer content and, as a consequence, in the viscosity of the PVDF-type gel. It could be concluded that the polymer affects not only the carrier mobility but the dissociation condition of the salt in the polymer gel electrolyte.

It should be noted that there is the Coulombic interaction between the ion and polymer in addition to the viscosity effect in the polymer gel electrolyte designed in this study. We here extend the original model for estimation of the dissociation degree of the salt to express the situation that the ionic species selectively interact with the polymer and the neutral solvent species simply follow the viscosity effect. In the improved theoretical model, we can quantitatively estimate the interactive force as well as the dissociation degree of the salt. It is significant to compare the interactive force between the new polymer gel and the conventional PEO-type gel electrolytes to show the validity of the new idea of polymer designing.

To confirm the geometric feature of the gel under the interaction between the ion and polymer, ab initio molecular orbital calculations were carried out, estimating the charge distribution on the polymer unit and the interaction energies between the ion and polymer.

In this research, we would like to propose a process for designing the polymer gel electrolyte based on the observation of dynamic features of carrier ions.

Experimental Section

Nona(ethyleneglycol) dimethacrylate (PEGDMA, $CH_2{=}CCH_3$-$CO_2(CH_2CH_2O)_9COC(CH_3){=}CH_2$, purchased from Shin-Nakamura Chemical Industries, Co.) of an ethylene oxide type polymer and 1,2-cyclohexylene-bis[(methacryloyloxy)ethyl-ureido] (CBMEU, $C_6H_{10}(NHCONHC_2H_4OCOC(CH_3){=}CH_2)_2$, prepared by Itoh Oil Chemicals Co., Ltd.) of an urea group-containing polymer were used as the starting polymer materials. Hereafter, we use the abbreviation, PEO for PEGDMA to represent the ethylene oxide type polymer clearly. The lithium electrolyte solution of 1.4 M $LiPF_6$ dissolved in the mixed solvents of ethylene carbonate (EC) and ethyl methyl carbonate (EMC) (1:1 in volume ratio) was prepared using an original electrolyte solution (1.0 M $LiPF_6$-EC/EMC) and a lithium salt $LiPF_6$ both of which were purchased from Tomiyama Chemical Co. Then, the solution was mixed with the polymer by adding a polymerization initiator, 2,2′-azobisisobutyronitrile (AIBN, Nacalai Tesque, Inc.) for PEO and benzoyl peroxide (BPO, Wako Pure Chemicals Industries, Ltd.) for CBMEU, respectively. The mixture was sealed in a glass tube to promote polymerization by heating at 80 °C for 1 h.[4]

To confirm the stability of the gel electrolytes which consist of a lithium salt and urea group-containing polymer under charge transport process, charge/discharge performance was tested preparing coin-type cells with CBMEU gel. The charge/discharge efficiency after three cycles was 99.4%, which was comparable to that of the cell with an electrolyte solution without polymer (99.7%). Therefore, it is expected that CBMEU is stable to lithium salt enough to be applied to lithium secondary batteries.

The diffusion coefficients of the cation, anion, and solvent species in the polymer gel electrolyte were measured by the pulsed gradient spin−echo NMR (PGSE-NMR) technique with the probed nuclei of ^7Li (116.8 MHz) for the cation, ^{19}F (282.7 MHz) for the anion, and ^1H (300.5 MHz) for the solvent species using a JBM-ECP300W wide bore spectrometer.[14] In this study, the stimulated echo sequence was used for this application. The half-sine-shaped gradient pulse was applied twice in sequence after the first and third 90° pulses to detect the attenuation of the echo intensity according to the migration property of the probed species.[15,16] Typical values of the field gradient pulse parameters were $g = 2.5{-}10.6$ T/m for the pulse strength, $\delta = 0{-}5$ ms for the pulse width and $\Delta = 80$ ms for the interval between the two gradient pulses. As the echo intensity decay of ^7Li, ^{19}F, and ^1H showed a single component of random diffusion, the diffusion coefficient was estimated from the slope of log plot of intensity vs pulse width, δ. For ^1H spectra, several peaks assigned to EC and EMC appeared. The diffusion coefficients estimated from each peak were almost the same, indicating EC and EMC species are averaged in migration as a solvent. The potential in the range of $0{-}10$ V/cm was continuously applied from the start to the end of the spin−echo detection to selectively make the ionic species drift. The sample cell for the NMR measurement was composed of a 10-mm diameter cylindrical glass tube having two pairs of electrodes for potential application and the electric field detection.[17] A direct potential was applied in a direction parallel to the static

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magnetic field and the gradient field. The power supply was controlled to keep the detected potential constant, reversing the polarity every other measurement to inhibit the polarization and decomposition of the electrolyte material. Temperature-controlled air was allowed to flow around the small cell to maintain a constant temperature of 298 ± 0.1 K during the measurements.

Ab initio molecular orbital calculations were carried out using the Gaussian 94 program. Initial geometries of the polymer units were made using the molecular mechanics method of the Cerius2 (ver. 3.8) program. In the process, DREIDING 2.21 was used for the force field[18] and charge equilibration method was applied to calculate the charge of each atom of the molecule.[19] The geometries after the ionic species approach the polymer unit to interact were optimized by Ab initio molecular orbital calculations, using the Hartree−Fock method with the 3-21G basis set. The Mulliken charges and interaction energies were calculated for the optimized structures using the Hartree−Fock method with the 6-31G(d) basis set. The interaction energies between the carrier ion and the polymer in the gel were calculated based on the assumption, (interaction energy) = (the whole energy of the ion and polymer under the interactive state) − (the energy of the ion under the isolated state) − (the energy of the polymer under the isolated state).

Charge Distribution Condition of the Polymer Unit. The interactive effect between the ions and polymer can be speculated from the evaluation of the charge distribution condition on the polymer unit. Figure 1 shows the numerical results of the charge distribution before and after the approach of an ion to the polymer unit to form a stabilized structure. When a lithium ion approached the PEO unit, it became located near the ether oxygen as was expected. In the case of CBMEU, the lithium ion was effectively attracted by the carbonyl oxygen of the urea group, taking the optimized position between the two oxygen atoms. The distance between the lithium and the nearest negatively charged atom on the polymer was about 1.7− 1.8 Å independent of the kind of polymer. The anion, PF_6^-, was stabilized in the vicinity of the hydrogen of the urea group across which the lithium ion was attracted to the oxygen for the CBMEU gel. It is characteristic that the distance between the anion and the nearest species on the polymer was about 1.9 Å for CBMEU, which was obviously shorter than that between PF_6^- and PEO, 2.5 Å. These results suggest that the CBMEU polymer effectively attracts the anion species compared with the weak interaction of the PEO polymer for the anion, leading to the promotion of the dissociation of the salt and the reduction of the anion mobility.

Theoretical Derivation of the Dissociation Degree of the Salt under the Interactive Effect of the Polymer on the Salt and/or Ions. *(1) Dissociation Degree of the Salt Under the Salt/ Polymer Interaction.* The original idea first proposed for the estimation of the dissociation degree of the salt was based on the concept that all inherent dynamic values of the species such as $D_{(cation,anion)}$, $D_{solvent}$, and $\mu_{(cation,anion)}$ follow the viscosity change in a similar manner under no interactive effect on the species such as the PVDF-type polymer gel electrolyte.[11] Under this condition, the inherent dynamic values of two samples (1 and 2) having different viscosities had the correlation

$$\begin{bmatrix} D^2_{solvent} \\ D^2_{(cation,anion)} \\ D^2_{pair} \\ \mu^2_{(cation,anion)} \end{bmatrix} = \alpha \times \begin{bmatrix} D^1_{solvent} \\ D^1_{(cation,anion)} \\ D^1_{pair} \\ \mu^1_{(cation,anion)} \end{bmatrix} \quad (4)$$

where the superscripts 1 and 2 denote the sample 1 and sample 2, respectively, and α reflects the viscosity ratio, η_1/η_2, of the two samples when the Stokes' radius of the objective species is the same between the samples. This equation was based on the assumption that the Stokes−Einstein relation is held in this type of gel. This situation would be acceptable when the gel is a solution-rich sample in which the polymer plays a simple part to increase the solvent viscosity, which is inversely proportional to the carrier diffusion coefficient in the gel.[6,20] Combining eqs 2−4, the dissociation degree of the salt of each sample could be uniquely determined.[11]

On the other hand, for the situation when the polymer selectively interacts with the ions through the Coulombic force, the correlation of the two samples can be modified as

$$\begin{bmatrix} D^2_{solvent} \\ D^2_{pair} \end{bmatrix} = \alpha \times \begin{bmatrix} D^1_{solvent} \\ D^1_{pair} \end{bmatrix}$$

$$\begin{bmatrix} D^2_{(cation,anion)} \\ \mu^2_{(cation,anion)} \end{bmatrix} = \beta \times \begin{bmatrix} D^1_{(cation,anion)} \\ \mu^1_{(cation,anion)} \end{bmatrix} \quad (5)$$

Parameter β indicates the ratio of the force (ξ_1/ξ_2), which acts on the charged species during the diffusion, including the viscosity effect (η) and Coulombic interaction (f). It is reasonable to think β is different between the cation and the anion even in the same gel; therefore, it could be better to rewrite $\beta_{(cation,anion)}$.

When we use the subscript or superscript, "0", for the original electrolyte solution and "i" ($i = 1,2,3...$) for a gel sample having each polymer fraction, the observed dynamic values could be represented as follows.

$$\begin{bmatrix} D^0_{obs} \\ D^i_{obs} \\ \mu^i_{obs} \end{bmatrix} = \begin{bmatrix} x_0 & 1 - x_0 & 0 \\ x_i\beta^i & (1 - x_i)\alpha^i & 0 \\ 0 & 0 & x_i\beta^i \end{bmatrix} \times \begin{bmatrix} D^0_{cation} \\ D^0_{pair} \\ \mu^0_{cation} \end{bmatrix} \quad (6)$$

$$\alpha^i = D^i_{solvent}/D^0_{solvent}$$

When $\alpha = \alpha^2/\alpha^1$ and $\beta = \beta^2_{(cation,anion)}/\beta^1_{(cation,anion)}$ are taken for two gel samples, the dissociation degree of the salt of each gel could be represented as

$$x_1 = \frac{\mu^1_{obs(Li,F)}(\beta/\alpha)(A^1_{(Li,F)}\alpha - A^2_{(Li,F)})}{A^1_{(Li,F)}\mu^2_{obs(Li,F)} - A^2_{(Li,F)}\mu^1_{obs(Li,F)}(\beta/\alpha)}$$

$$x_2 = \frac{\mu^2_{obs(Li,F)}(A^1_{(Li,F)} - A^2_{(Li,F)}/\alpha)}{A^1_{(Li,F)}\mu^2_{obs(Li,F)} - A^2_{(Li,F)}\mu^1_{obs(Li,F)}(\beta/\alpha)} \quad (7)$$

$$A^i_{(Li,F)} = D^i_{obs(Li,F)} - \mu^i_{obs(Li,F)}(RT/F), \; i = 1,2$$

(2) Dissociation Degree of the Salt under the Interaction Proportional to the Polymer Fraction in the Gel. To estimate the absolute value of the dissociation degree of the salt, the parameter β has to be confirmed. In practice, β could not be derived from the observed dynamic values in contrast to α, which can be denoted as the ratio of $D_{obs(H)}$ between the two samples because the solvent species is neutral in charge and simply follows the viscosity during migration. We now propose an assumption to represent the interactive effect that the parameter β is contributed from the effects of the viscosity and
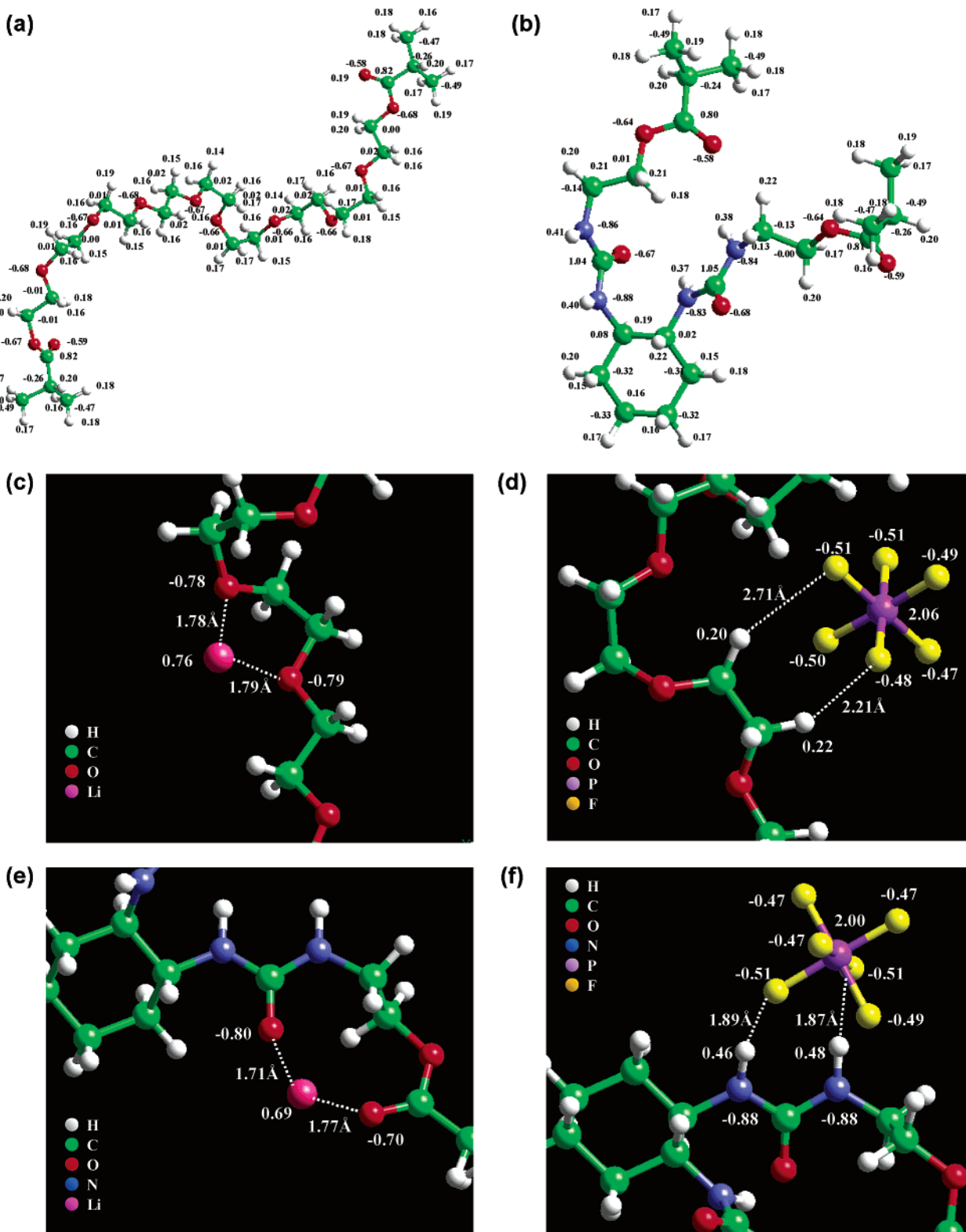
Figure 1. Calculated results of the charge distribution before and after the approach of an ion to the polymer unit to form a stabilized structure with the estimated distance between the ion and the nearest atom of the polymer. (a) PEO, (b) CBMEU, (c) PEO and Li$^+$, (d) PEGDMA and PF$_6^-$, (e) CBMEU and Li$^+$, and (f) CBMEU and PF$_6^-$. The ends of the chain of polymer units (panels a and b) are of the polymerized condition.

Coulombic interaction (γ), which is proportional to the polymer content, it is written for *i*-sample of the gel as

$$\beta^i_{(cation,anion)} = \alpha^i + p^i \gamma_{(cation,anion)} \tag{8}$$

where p^i is the polymer fraction in the gel. To determine γ and the absolute value of each species, D_{ion}, we need to measure

the dynamic values of at least three samples ($i = 1,2,3$) with different viscosities.

Therefore, applying eq 8 and the observed values (D_{obs}, μ_{obs}) of a species of three samples to eq 6, the individual parameter (x_i, $\gamma_{(cation,anion)}$, $D^i_{(cation,anion)}$, D^i_{pair}) ($i = 1,2,3$) could be determined.

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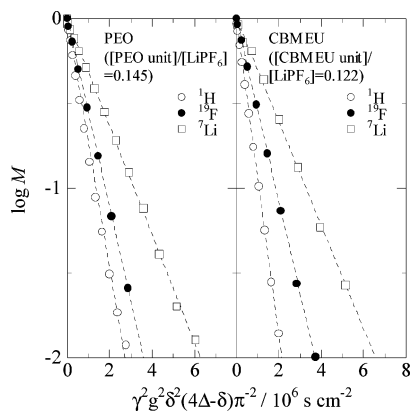*J. Phys. Chem. B, Vol. 107, No. 34, 2003* **8809**

Figure 2. NMR spin−echo signal decay of diffusion coefficient measurement for PEO − 1.4 M LiPF$_6$ − EC/EMC (1:1) and CBMEU − 1.4 M LiPF$_6$ − EC/EMC (1:1).
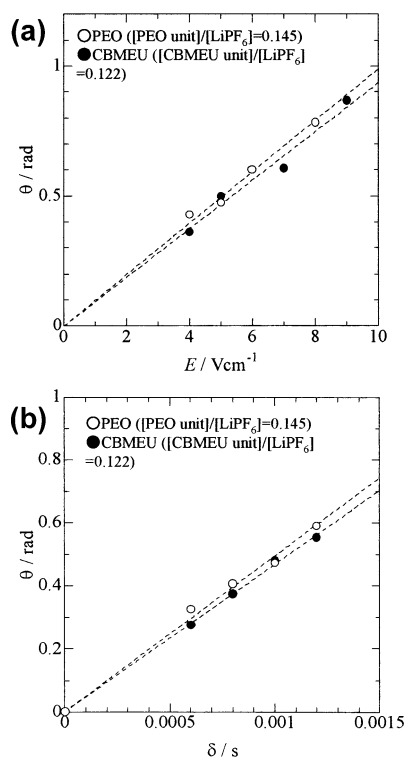

Figure 3. (a) Applied potential dependence and (b) gradient pulse width dependence of the phase shift of the NMR spin−echo signals of the anion species probed by ^{19}F of CBMEU − 1.4 M LiPF$_6$ − EC/EMC (1:1) (●) and PEO − 1.4 M LiPF$_6$ − EC/EMC (1:1) (○).

Results and Discussion

The spin−echo intensity of the mobile species is attenuated under the gradient pulses for the diffusion measurement according to the relation of[12]

$$M = M_0 \exp(-q^2 D_{\text{obs(Li,F,H)}}\Delta)$$
$$q = 2\gamma\delta g\pi^{-1} \qquad (9)$$

Figure 2a shows the log-plot of the intensity by changing one of the parameters, δ. The linear change in each species reveals that the carrier follows the random walk motion in the gel electrolyte. $D_{\text{obs(Li,F,H)}}$ was estimated from the slope of each decay. Figure 3a,b shows the E dependence and δ dependence of the phase component of the spin−echo intensity of the fluoride species, respectively, by application of the electric field during the diffusion measurement. Their slope corresponds to

the observed ionic mobility according to the relation,

$$M_\nu = M_0 \exp(iq\nu\Delta - q^2 D_{\text{obs(Li,F)}}\Delta)$$
$$M_\nu/M = \cos(\theta) \qquad (10)$$
$$\theta = q\nu_{\text{obs(Li,F)}}\Delta = q\mu_{\text{obs(Li,F)}}E\Delta$$
$$q = 2\gamma\delta g\pi^{-1}$$

The estimated values of $\mu_{\text{obs(F)}}$ from each plot were in agreement with each other, indicating that the obtained value reflects the mobility without any influence of additional drifting due to thermal convection. Table 1 summarizes the observed diffusion coefficients and observed ionic mobilities of the PEO and CBMEU polymer gel electrolytes.

Figure 4 represents the changing behavior of the dissociation degree of the salt, x, applying the observed dynamic values of two gel samples as a function of β/α according to eq 7. The value of x at $\beta/\alpha = 1$ corresponds to the dissociation degree of the salt without any Coulombic interaction between the ion and polymer. The decrease in the value of the abscissa reveals the enhancement of the interactive effect. The increasing tendency of the value of x with the increase in the interactive effect of Figure 4 means that the attractive force, if it is, promotes the dissociation of the salt in this polymer gel electrolyte. The two curves crossed at $x_1 = x_2 = 1$. As the change in x greater than unity was negligible due to the nature of the degree of dissociation, this result reveals that x_1 is always greater than x_2 independent of the absolute values of the observed diffusion coefficient and observed mobility. This feature is attributed to the original model in which the observed diffusion coefficient can be represented by the average of the diffusion of the dissociated ion and the associated ion-pair with the weight of the dissociation degree of the salt denoted in eq 2. It seems reasonable that the large interactive effect changes the order of the absolute value of x_1 and x_2. In practice, if we consider another term which is attributed to D_{pair} such as the form of $D_{\text{pair}} \times D_{\text{ion}}$ in eq 2, the intersection would be less than unity and x_1 and x_2 could be reversed in the meaningful range of the dissociation degree.

Table 2 represents the estimated values of the dissociation degree of the salt, the inherent dynamic value of each species, the lithium transport number, and the interactive force, $\gamma_{\text{(cation,anion)}}$, using the observed values of three gel samples according to eq 6 based on the assumption of eq 8. In the table, x_0, D_{cation}^0, D_{anion}^0 of the solution without polymer were estimated by extracting the values of three gel samples. Therefore, the reliability of the values of the solution are low compared with those of the gel samples. The dissociation degree of the salt and lithium transport number decreased with the increase in the polymer fraction in the gel. It can be presumed from Figure 4 that the decreasing tendency of the dissociation degree of the salt with gelation would be steeper than this result if there is no interactive effect of the polymer on the charged species.

Figure 5 is the plot of the inherent diffusion coefficient of the cation and anion. With an increase in the polymer fraction in the gel, each value monotonically decreased. In the case of the PEO gel, the decrease in D_{cation} was steeper than that of D_{anion}. On the other hand, the changes in the slopes of D_{cation} and D_{anion} of the CBMEU gel were almost the same. This suggests that the cation species selectively attracted by the polymer are restricted in diffusion in the PEO gel. On the other hand, the steep change in D_{anion} of the CBMEU gel compared

TABLE 1: Experimentally Observed Dynamic Values (D_{Li}, D_F, D_H, μ_F) of the Gels

PEO

polymer/wt %	[PEO unit]/[LiPF$_6$]	$D^i_{obs(Li)}/10^{-6}\,cm^2\,s^{-1}$	$D^i_{obs(F)}/10^{-6}\,cm^2\,s^{-1}$	$D^i_{obs(H)}/10^{-6}\,cm^2\,s^{-1}$	$\mu^i_{obs(F)}/10^{-5}\,cm^2\,s^{-1}\,V^{-1}$
0.0	0.000	1.13	1.72	2.35	
6.5	0.125	0.699	1.23	1.99	4.29
7.5	0.145	0.642	1.19	1.94	3.44
9.73	0.193	0.550	1.12	1.85	2.63

CBMEU

polymer/wt %	[CBMEU unit]/[LiPF$_6$]	$D^i_{obs(Li)}/10^{-6}\,cm^2\,s^{-1}$	$D^i_{obs(F)}/10^{-6}\,cm^2\,s^{-1}$	$D^i_{obs(H)}/10^{-6}\,cm^2\,s^{-1}$	$\mu^i_{obs(F)}/10^{-5}\,cm^2\,s^{-1}\,V^{-1}$
0.0	0.000	1.13	1.72	2.35	
3.0	0.072	0.905	1.39	2.19	5.11
5.0	0.122	0.644	1.27	2.10	4.10
7.5	0.188	0.438	1.03	1.93	3.05

TABLE 2: Estimated Dynamic Values (x, D_{anion}, D_{pair}, γ_{anion}, γ_{cation}, D_{cation}, t_{cation}) of the Gels

PEO

polymer/wt %	[PEO unit]/[LiPF$_6$]	x_i	$D^i_{anion}/10^{-6}\,cm^2\,s^{-1}$	$D^i_{pair}/10^{-6}\,cm^2\,s^{-1}$	γ_{anion}	γ_{cation}	$D^i_{cation}/10^{-6}\,cm^2\,s^{-1}$	t^i_{cation}
0.0	0.000	1.38	1.45	1.65			1.21	0.45
6.5	0.125	0.90	1.23	1.23			0.638	0.34
7.5	0.145	0.74	1.20	1.19	-0.31	-3.03	0.451	0.27
9.73	0.193	0.61	1.14	1.11			0.166	0.13

CBMEU

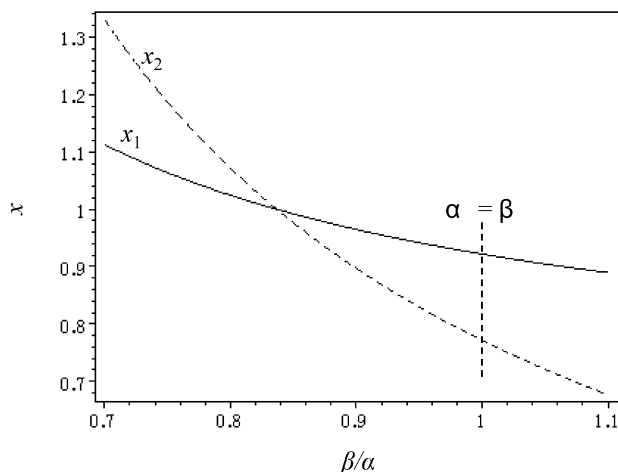| polymer/wt %	[CBMEU unit]/[LiPF$_6$]	x_i	$D^i_{anion}/10^{-6}\,cm^2\,s^{-1}$	$D^i_{pair}/10^{-6}\,cm^2\,s^{-1}$	γ_{anion}	γ_{cation}	$D^i_{cation}/10^{-6}\,cm^2\,s^{-1}$	t^i_{cation}
0.0	0.000	0.88	1.65	2.27			0.975	0.37
3.0	0.072	0.96	1.36	2.11			0.859	0.39
5.0	0.122	0.89	1.18	2.02	-1.45	-2.38	0.479	0.29
7.5	0.188	0.87	0.903	1.86			0.221	0.20

Figure 4. Dissociation degree of salts, x_1 and x_2, estimated from eq 7. The observed values used for this estimation are $D^1_{obs(Li)} = 9.05 \times 10^{-7}\,cm^2\,s^{-1}$, $D^1_{obs(F)} = 1.39 \times 10^{-6}\,cm^2\,s^{-1}$, $D^1_{obs(H)} = 2.15 \times 10^{-7}\,cm^2\,s^{-1}$, $\mu^1_{obs(F)} = 5.11 \times 10^{-5}\,cm^2\,s^{-1}\,V^{-1}$, $D^2_{obs(Li)} = 6.44 \times 10^{-7}\,cm^2\,s^{-1}$, $D^2_{obs(F)} = 1.27 \times 10^{-6}\,cm^2\,s^{-1}$, $D^2_{obs(H)} = 2.10 \times 10^{-7}\,cm^2\,s^{-1}$, $\mu^2_{obs(F)} = 4.10 \times 10^{-5}\,cm^2\,s^{-1}\,V^{-1}$.

with the behavior of D_{anion} of the PEO gel indicates that the anion is effectively attracted and reduced in mobility.

The changing features of the inherent diffusion values of the cation and anion are reflected to the cation transport number as shown in Figure 6. With the increase in the polymer fraction in the gel, t_{Li} was decreased due to the faster decrease in D_{cation} than in D_{anion}.

Figure 7 shows the change in the dissociation degree of the salt, x, with the polymer content in the gel. During the polymer fraction change from 0 to 10 mol %, the dissociation degree of the salt of CBMEU did not change very much in contrast to the abruptly changing feature of x of PEO. The dissociation
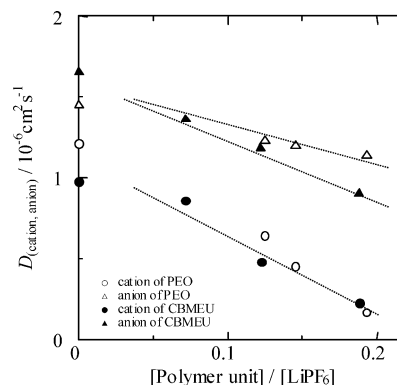

Figure 5. Inherent diffusion coefficients of the cation and anions estimated from the proposed model as a function of the polymer fraction in the gels. CBMEU − 1.4 M LiPF$_6$ − EC/EMC (1:1) (●, ▲) and PEO − 1.4 M LiPF$_6$ − EC/EMC (1:1) (○, △).

degree of the salt is directly associated with the carrier concentration in the electrolyte. It can be said that the polymer interactive effect on the promotion of the salt dissociation is more effective in the CBMEU polymer. This may be because both the cation and anion are simultaneously attracted to the urea group in the CBMEU gel in contrast to only the cation attraction of the ether oxygen in the PEO gel.

A comparison of the γ value between the cation and anion or between the CBMEU and PEO gels is effective for directly evaluating the interactive effect. The value of $|\gamma_{cation}|$ was almost the same between CBMEU and PEO. On the other hand, $|\gamma_{anion}|$ of CBMEU was ~5 times larger than that of PEO. This would be due to the electron-withdrawing effect of the urea group of the CBMEU gel. In each gel, the absolute value of γ_{cation} was larger than γ_{anion}. These results reflect the changing behavior of the inherent diffusion values in which D_{cation} was more restricted in migration than D_{anion} with the increase in polymer fraction in the gel.
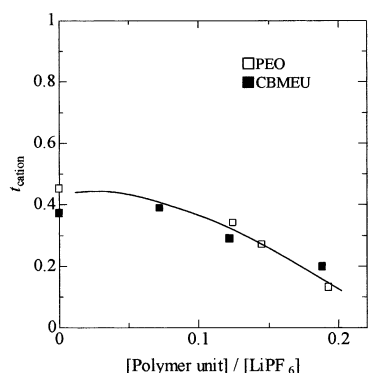
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Figure 6. Transference number of the cation estimated from the proposed model as a function of the polymer fraction in the gels.
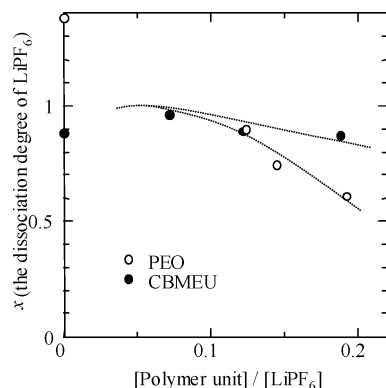

Figure 7. Degree of dissociation of LiPF$_6$ estimated from the proposed model as a function of the polymer fraction in the gels.

TABLE 3: Calculated Results of the Potential Energy of Interaction between the Carrier Ions and the Solvent Species or the Polymer in the Gel

	solvents		polymers	
ions	EC	EMC	PEO	CBMEU
Li$^+$	−57.8	−52.7	−86.6	−113.7
PF$_6^-$	−18.8	−7.0	−14.2	−27.2

Table 3 represents the ab initio calculated results of the potential energy of interaction between the carrier ion and the solvent species or the polymer in the gel. The interaction energy of the cation with the solvent was greater than that of the anion. This results in the solvation condition of the cation. This feature is similar to the interactive effect of the ion with the polymer. The cation interaction energy with the polymer is 4−6 times stronger than that of the anion for both the PEO and CBMEU gels. This is attributed to the charge distribution condition that the ether oxygen and urea oxygen showed negatively charged features. On the other hand, the weak interaction of the anion with the polymer was different between the two polymers. The CBMEU is twice as attractive to the anion compared with the value of PEO. This can be realized that due to the presence of the nitrogen atoms the protons of the urea linkage are more electropositive (0.48) than those of PEO (0.22) and therefore attract the anion more strongly. This is also confirmed from the distance between the anion and polymer at the equilibrium condition.

The relative value of the interaction energy between the cation and anion or between the CBMEU and PEO were in agreement with that of γ which is estimated from the dynamic values listed in Table 2. In practice, the interaction between the ions and polymer competes with the interaction between the ions and solvents as is shown in Table 3. However, for the purpose of comparison of the attractive effect on the ions between different types of gels having the same electrolyte solution, it is effective to evaluate γ. Both gels suggest that the electron-donating sites on the polymer effectively attract the cation of the carriers by more than four times compared with the effect of the electron-withdrawing site to attract the anion of the carriers. These results confirmed that the estimation of the interactive force from the dynamic values is an optimal approach to investigate the interaction factor which is responsible for carrier migration mechanism of the polymer gel electrolytes.

Conclusions

A new polymer gel electrolyte (CBMEU) providing the urea group which acts as the attractive sites for cations and anions was prepared and the dynamic properties for the individual ionic species were investigated. To evaluate the static features such as the dissociation degree of the salt and interactive force of the polymer, a theoretical model based on the dynamic properties was constructed and applied to this gel electrolyte. It was found that both the cations and anions were attracted by the polymer resulting in the mobility decrease with the polymer content in the gel. Especially, the anion of the CBMEU gel was strongly attracted to the polymer in contrast to the anion of the PEO-type gel which weakly interacted with the polymer. The situation that both ions were attracted by the polymer would be responsible for maintaining the high dissociation degree of the salt even with the increase in the polymer fraction in the gel. In practice, the dissociation degree of the salt of the PEO-type gel monotonically decreased with the polymer content following the viscosity increase.

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