

## Design of Lithium Polymer Gel Electrolyte Using Ion-polymer Interaction

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A new polymer gel electrolyte for lithium secondary batteries was developed on the concept of restricting the anion mobility with the chemical interactive effect of a specific site of the polymer. The polymer having the urea group (CBMEU) was designed in order to use the electron donating and withdrawing effect of the urea group for attracting the cation and anion, respectively. In order to quantitatively confirm the interactive effect of the polymer site in the gel, a theoretical model was constructed based on the observed dynamic values. The absolute value of the interactive force of the anion,  $\gamma_{\text{anion}}$ , was five times greater than that of PEO-type gel. This resulted in the promotion of the dissociation of the salt and reducing the anion mobility of the CBMEU polymer gel electrolyte.

Key Words: polymer gel electrolytes, urea group, diffusion coefficient, ionic mobility, interactive force

### 1. INTRODUCTION

Lithium secondary batteries have been used in many electric devices due to their high power and high energy density. To extend the application field of the batteries, development of new electrolyte materials is an important and urgent matter.

Design of electrolyte materials would direct to 1) high lithium conductivity and 2) high safety which indicates the reduction of non-aqueous solvent and self-supporting performance. One of the candidates for these demands is the polymer gel electrolyte [1,2,3].

A role of polymer in the gel electrolyte is that the polar groups on the polymer chains attract ions to promote the dissociation of the lithium salt due to the Coulombic interaction. This situation has been already confirmed in the PEO-type polymer gel electrolyte in which the ether oxygen attracts Li. The dissociated ions could be supported in migration by the segmental motion of the polymer chains in addition to the fluidity of the solvent effect of the gel.

The objective of this research is to investigate the interactive state between the ion and polymer which dominates the dissociation condition of the salt and, after dissociation, ionic mobility of the cation and anion species. Based on the quantitative estimation, we would like to establish a designing concept of polymer gel electrolytes providing high lithium ion conductivity and lithium transport number.

To reach the goal, we prepared a new type polymer having urea groups in it[4]. This is based on the idea of attracting the anion species to promote the salt dissociation with reducing the anion mobility [5,6]. And we estimated the ion-polymer interactive force, dissociation degree of the salt, cation transport number as well as inherent dynamic values such as diffusion

coefficient and ionic mobility of individual species from the studies of NMR spectroscopy and derivation of a new theoretical model.

### 2. EXPERIMENTAL

Nona(ethyleneglycol)dimethacrylate (PEGDMA,  $\text{CH}_2=\text{C}(\text{CH}_3)\text{CO}_2(\text{CH}_2\text{CH}_2\text{O})_9\text{COC}(\text{CH}_3)=\text{CH}_2$ , purchased from Shin-Nakamura Chemical Industries, Co.) of an ethylene oxide type polymer and 1,2-cyclohexylene-bis[(methacryloyloxy)ethylureido] (CBMEU,  $\text{C}_6\text{H}_{10}(\text{NHCONHC}_2\text{H}_4\text{OCOC}(\text{CH}_3)=\text{CH}_2)_2$ , prepared by Itoh Oil Chemicals Co., Ltd.) of an urea group-containing polymer were used as the starting polymer materials. The lithium electrolyte solution of 1.4M  $\text{LiPF}_6$  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  $\text{LiPF}_6$ -EC/EMC) and a lithium salt  $\text{LiPF}_6$  both of which were purchased from Tomiyama Chemical Co. The solution was mixed with the polymer by adding a polymerization initiator, 2,2'-azobisisobutyronitrile (AIBN, Nacalai Tesque, Inc.) for PEGDMA 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 hour [7].

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  $^7\text{Li}$  (116.8 MHz) for the cation,  $^{19}\text{F}$  (282.7 MHz) for the anion and  $^1\text{H}$  (300.5 MHz) for the solvent species using a JBM-ECP300W wide bore spectrometer [8]. 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  $90^\circ$  pulses to detect the attenuation of the echo intensity according to the migration property of the probed species [9,10]. The diffusion time,  $\Delta$  which corresponds to the interval of two gradient pulses was typically 80 ms. As the echo intensity decay of  $^7\text{Li}$ ,  $^{19}\text{F}$  and  $^1\text{H}$  showed a single component of random diffusion, the diffusion coefficient was estimated from the slope of log plot of intensity vs. pulse width,  $\delta$ . The potential in the range of 0 – 10 V/cm was continuously applied from the start to the end of the spin-echo detection in order 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 [11]. A direct potential was applied in a direction parallel to the static magnetic field and the gradient field. The power supply was controlled in order to keep the detected potential constant, reversing the polarity every other measurement in order 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 K  $\pm$  0.1 K during the measurements. The measurement scheme is represented in figure 1.

Ab-initio molecular orbital calculations were carried out using the Gaussian 94 program. The geometries after the ionic species approach the polymer unit in order 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.

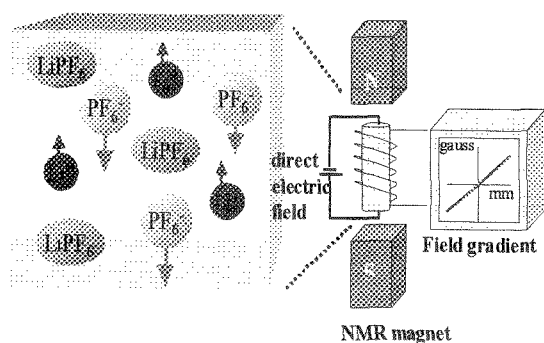


Figure 1 Measurement scheme of diffusion coefficient and ionic mobility using NMR spectroscopy. Diffusion coefficient measurement detects the probed species following the random walk migration. Ionic conductivity measurement detects the probed ions which respond to the direct electric field.

### 3. RESULTS AND DISCUSSION

#### 3.1 Molecular structure of polymer after ion approach

Figure 2 represents the optimized molecular structures of (a) CBMEU polymer and (b) PEGDMA polymer after an anion ( $\text{PF}_6^-$ ) approach. It is characteristic that the distance between the polymer and anion species is fairly shorter in CBMEU polymer compared with that in PEG polymer. This is in contrast to the fact that the distance between the cation and polymer was almost the same between the two polymers. It is acceptable that the urea group is effective to attract the anion species.

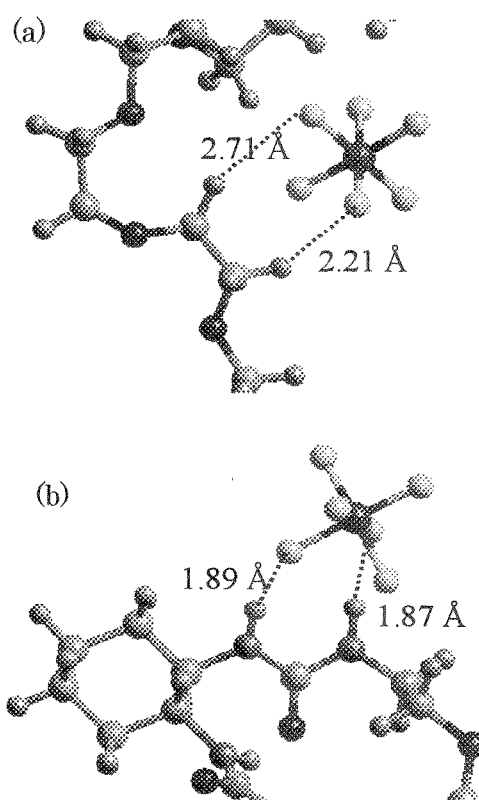


Figure 2 Optimized molecular structure of (a) PEGDMA and (b) CBMEU polymers after anion approach. The averaged distance between the anion and polymer was 2.46 Å for PEGDMA and 1.88 Å for CBMEU.

#### 3.2 Theoretical model for estimation of static state of polymer gel electrolyte

To evaluate the interactive effect quantitatively, we constructed a theoretical model to estimate the static values based on the dynamic values. Observed values can be expressed as follows [12,13].

$$\begin{aligned}
 D_{obs(Li,F)} &= xD_{(cation,anion)} + (1-x)D_{pair} \\
 D_{obs(H)} &= D_{solvent} \\
 \mu_{obs(Li,F)} &= x\mu_{(cation,anion)} \\
 D_{(cation,anion)} &= \mu_{(cation,anion)} \frac{RT}{F}
 \end{aligned} \quad (1)$$

It is noted that the contributions from ion and ion-pair to the observed values are different between the observed diffusion coefficient and ionic mobility. In the case of no interaction between the ion and polymer, the inherent dynamic values of two different samples which are different in polymer fraction in the gel is represented as

$$\begin{bmatrix} D_{solvent}^2 \\ D_{(cation,anion)}^2 \\ D_{pair}^2 \\ \mu_{(cation,anion)}^2 \end{bmatrix} = \alpha \times \begin{bmatrix} D_{solvent}^1 \\ D_{(cation,anion)}^1 \\ D_{pair}^1 \\ \mu_{(cation,anion)}^1 \end{bmatrix} \quad (2)$$

where  $\alpha$  is the viscosity ratio which is directly obtained from the observed diffusion coefficient of solvent species. This relation stands because the mobilities of all species, irrespective of their charged condition, depend on the gel viscosity in the same way.

On the other hand, when the chemical interaction is present between the ion and polymer in the gel, the relation has to be extended as follows [4].

$$\begin{bmatrix} D_{solvent}^2 \\ D_{pair}^2 \end{bmatrix} = \alpha \times \begin{bmatrix} D_{solvent}^1 \\ D_{pair}^1 \end{bmatrix} \quad (3)$$

$$\begin{bmatrix} D_{(cation,anion)}^2 \\ \mu_{(cation,anion)}^2 \end{bmatrix} = \beta \times \begin{bmatrix} D_{(cation,anion)}^1 \\ \mu_{(cation,anion)}^1 \end{bmatrix}$$

This is because Coulombic interaction acts only on the ionic species. We then assumed that the extended factor,  $\beta$  is a summation of viscosity effect and interactive effect as

$$\beta_{(cation,anion)}^i = \alpha^i + p^i \gamma_{(cation,anion)} \quad (4)$$

where  $\gamma$  is the interactive force per unit polymer,  $p$  is the polymer fraction in the gel. As a result, introducing eq. (4) into eq. (1) and solving the simultaneous equations for at least three different samples ( $i = 1,2,3$ ) after substituting the observed values (diffusion coefficient and ionic mobility), the inherent dynamic values, interactive force and dissociation degree of the salt can be estimated individually.

Table 1 shows the list of the values of observation and estimation. It is characteristic that the anion interactive force of the urea-containing gel is more than four times greater than that of PEG-gel. It is acceptable that the first intention to use the urea-group to attract the anion has been succeeded from this result.

The attractive force for cation is still stronger than that for anion. However, compared with the dominant effect on the cation in the PEG-gel, the anion interactive effect has been enhanced relative to the effect on the cation in the urea-containing gel.

Dissociation degree of the salt and cation transport number are plotted in figure 3. The dissociation degree of the salt in CBMEU gel was kept in high values even in the high polymer fraction in the gel compared with the change of PEGDMA gel. It is general that the dissociation degree of the salt decreases with increasing the gel viscosity. Therefore, the high value in CBMEU-gel is due to the effective interaction between the polymer site and ionic species.

The cation transport numbers which were estimated from the inherent mobilities were almost the same between the two gels at the comparison of [poly. unit]/[Li]. If we assume the changing behavior against [polymer site]/[Li], CBMEU gel would be more effective in increasing the cation transport number.

Table 1 Observed and estimated values of diffusion coefficient (D), ionic mobility ( $\mu$ ), dissociation degree of the salt ( $x$ ), interactive force ( $\gamma$ ) and transport number ( $t$ ).

PEGDMA								
[PEG unit]/[LiPF <sub>6</sub> ]	$D_{obs(F)}/10^{-6}cm^2s^{-1}$	$\mu_{obs(F)}/10^{-3}cm^2s^{-1}V$	$D_{cation}/10^{-6}cm^2s^{-1}$	$D_{anion}/10^{-6}cm^2s^{-1}$	$x$	$\gamma_{cation}$	$\gamma_{anion}$	$t_{cation}$
0.000	1.72	-	1.21	1.45	1.38	-3.03	-0.31	0.45
0.125	1.23	4.29	0.638	1.23	0.90			0.34
0.145	1.19	3.44	0.451	1.20	0.74			0.27
0.193	1.12	2.63	0.166	1.14	0.61			0.13
CBMEU								
[CBMEU unit]/[LiPF <sub>6</sub> ]	$D_{obs(F)}/10^{-6}cm^2s^{-1}$	$\mu_{obs(F)}/10^{-3}cm^2s^{-1}V$	$D_{cation}/10^{-6}cm^2s^{-1}$	$D_{anion}/10^{-6}cm^2s^{-1}$	$x$	$\gamma_{cation}$	$\gamma_{anion}$	$t_{cation}$
0.000	1.72	-	0.975	1.65	0.88	-2.38	-1.45	0.37
0.072	1.39	5.11	0.859	1.36	0.96			0.39
0.122	1.27	4.10	0.479	1.18	0.89			0.29
0.188	1.03	3.05	0.221	0.903	0.87			0.20

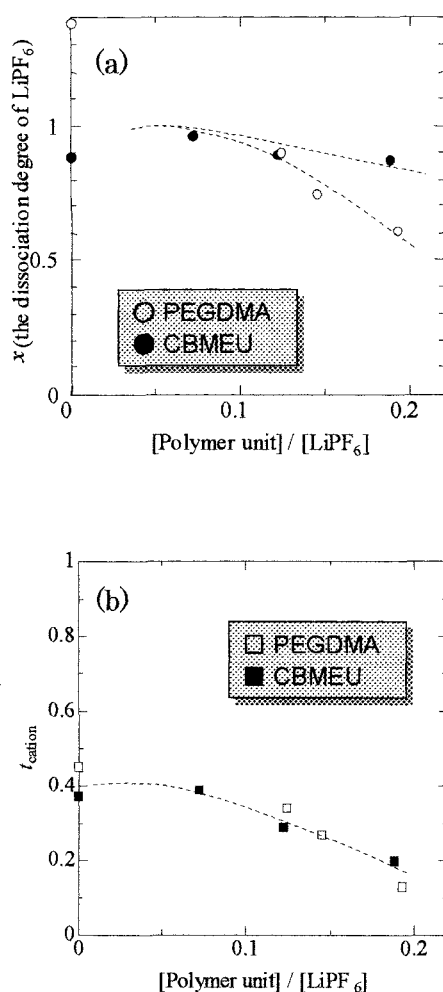


Figure 3 (a) Dissociation degree of the salt and (b) cation transport number of PEGDMA and CBMEU gels as a function of concentration ratio of polymer to lithium salt.

#### 4. CONCLUSION

A polymer gel electrolyte composed of urea-containing polymer, CBMEU showed a effective attractive feature of anion species. The attractive force was estimated to be  $\gamma_{\text{anion}}$  of CBMEU ( $-1.45$ )  $>$   $\gamma_{\text{anion}}$  of PEGDMA ( $-0.31$ ).

A theoretical model for evaluation of static values using the observed dynamic values was an effective approach to investigate the microscopic state of polymer gel electrolytes. This research of combination of measurement and theoretical analyses provides an available process for designing of conductive materials according to the individual demand.

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