

# Ionic Conduction Properties of PVDF–HFP Type Gel Polymer Electrolytes with Lithium Imide Salts

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Conduction properties of gel polymer electrolytes composed of lithium imide salts,  $\text{LiN}(\text{CF}_3\text{SO}_2)_2$ ,  $\text{LiN}(\text{C}_2\text{F}_5\text{SO}_2)_2$ , and PVDF–HFP copolymer were investigated using the pulsed-field gradient NMR and complex impedance techniques. The diffusion coefficients of the gel decreased with an increase in the polymer fraction in the gel. Carrier concentration exhibited 3 orders of magnitude variation in the fraction change in polymer from 80% to 20%. These results suggest that the polymer interacts with the electrolyte to affect the carrier concentration and mobility of the gel electrolytes. The interactive effect of polymer would be detected in the measurements of spin–lattice relaxation time ( $T_1$ ). The deviation of the symmetric curve of the temperature dependence of  $T_1$  could be divided into two components, one was consistent with the component of solution and independent of the polymer fraction and the other depended on the polymer fraction in the gel.

## Introduction

Polymer gel electrolytes have been developed recently for application to lithium secondary batteries. The preparation was originally based on the concept of taking advantage of two individual components, electrolyte solution and polymer.<sup>1</sup> As a result, it acquires some advantages. One is high conductivity which is almost comparable to that of the conventional electrolyte solutions in case of high solution fraction. The safety performance may be improved as the solvent is kept in the polymer network structure. This prevents the solution from being ignited easily by the chemical reaction. Furthermore, the total cell system would be simplified with the gel electrolyte because we do not need to prepare a sealed package to prevent the solution leakage. This promotes efficiency of fabrication. Therefore, the large-scale batteries would be achieved with the polymer gel electrolytes for use in electric vehicles and electric power storage systems.

Despite these promising features, the fundamental conduction properties of the gel electrolytes are not well known. It is generally accepted that the gel is a composite or hybrid material composed of the electrolyte solution and polymer. In the conventional sense, the conductivity is mainly dominated by the solution. However, it is reasonable to consider that there are some kinds of interactions between the heterogeneous species, such as ionic species and polymer or solvent species and polymer, especially in the case of the polymer which has polar groups at the chains such as PVDF.<sup>2–4</sup> The ion–polymer interaction in the PMMA-type gel electrolytes was definitely indicated by Qureshi et al.<sup>5</sup> The interactions would depend on the kinds of salt, solvent, polymer, and mixing ratio between the polymer and solution. These interactive effects would dominantly contribute to the conductivity of the gel.

The objective of our research is to investigate the effect of the polymer on the conduction properties of gel polymer electrolytes in order to elucidate the factors that dominate the conductivity and the conduction mechanisms. For the investiga-

tion, electrochemical impedance technique for ionic conductivity and spectroscopic nuclear magnetic resonance for self-diffusion coefficients were applied to the PVDF-type gel materials.

## Experimental Section

The gel samples were prepared using the casting technique with the starting materials  $\text{LiN}(\text{CF}_3\text{SO}_2)_2$  (TFSI) and  $\text{LiN}(\text{C}_2\text{F}_5\text{SO}_2)_2$  (BETI) as lithium salts, the mixture of ethylene carbonate and diethyl carbonate (2:3 in volume fraction) as a solvent, and PVDF–HFP (Kynar 2751) copolymer from Elf-atochem company as a polymer substrate. Changing the mixing ratio of polymer to solution, several gel samples were prepared to compare the conduction properties between them.

Ionic conductivity was measured by the complex impedance technique over the frequency range of 0.1 Hz to 1 MHz and the temperature range of  $-35\text{ }^\circ\text{C}$  to  $70\text{ }^\circ\text{C}$  using the HP2192a analyzer and Solartron SI1250 frequency analyzer combined with SI1287.

The diffusion coefficients of cation and anion species were measured by the application of the field gradient technique using the probed nuclei of  $^7\text{Li}$  (116.8 MHz) for cation and  $^{19}\text{F}$  (282.7 MHz) for anion.<sup>6</sup> In the pulse sequence used for measurements, two field gradient pulses were applied.<sup>7</sup> When the probed nuclei translate during the interval  $\Delta$ , the spin–echo is attenuated according to the relation

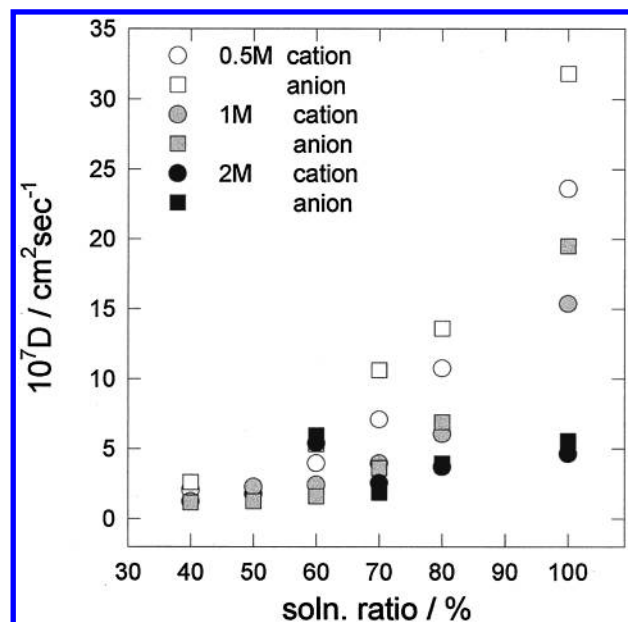
$$M = \exp[-\gamma^2 D \delta^2 g^2 \Delta] \quad (1)$$

where the  $\gamma$  is the gyromagnetic ratio,  $D$  the diffusion coefficient,  $\delta$  the pulse width of the field gradient,  $g$  the strength of the field gradient, and  $\Delta$  the duration time of the two pulses.<sup>8</sup> We then estimated the diffusion coefficient values by fitting the attenuated spin–echo strength to eq 1.

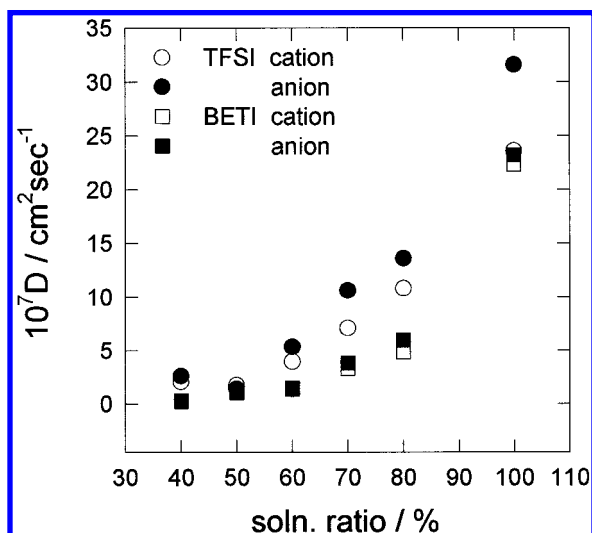
## Results and Discussion

Figure 1 shows the diffusion coefficients of gel electrolytes with  $\text{LiN}(\text{CF}_3\text{SO}_2)_2$ . Two parameters were varied in this result. One is the concentration of the solution mixed with the polymer

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**Figure 1.** Self-diffusion coefficients of cation (○) and anion (□) species of gel polymer electrolyte with  $\text{LiN}(\text{CF}_3\text{SO}_2)_2$ . White marks: 0.5 M solution. Gray marks: 1 M solution. Black marks: 2 M solution mixed with the PVDF–HFP polymer.

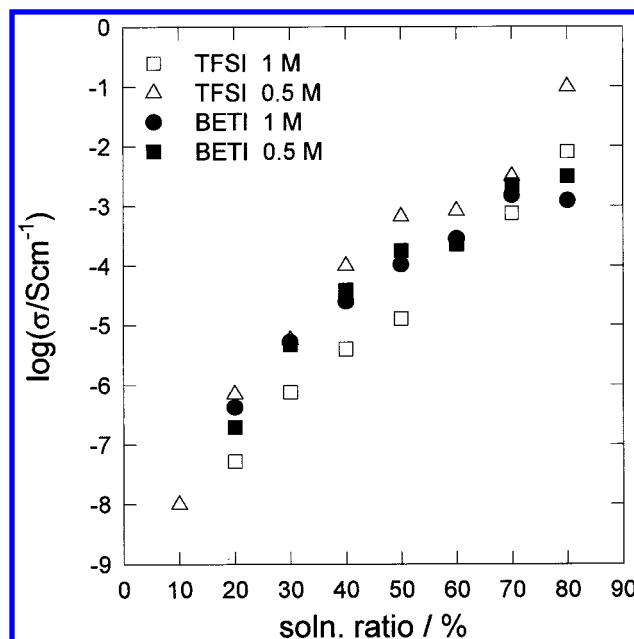


**Figure 2.** Self-diffusion coefficients of cation (open) and anion (filled) species of gel polymer electrolytes with  $\text{LiN}(\text{CF}_3\text{SO}_2)_2$  [TFSI] (○) and  $\text{LiN}(\text{C}_2\text{F}_5\text{SO}_2)_2$  [BETI] (□).

and the other is the mixing ratio of polymer to solution in the gel. The lower the concentration of the solution in the gel, the higher was the diffusion value. This reflects the solution viscosity and the dissociation degree of the salt, depending on the solution concentration.<sup>9</sup>

For the change in the mixing ratio of polymer to solution, two characteristic features were found. One is that the diffusion coefficients decreased with an increase in the polymer fraction in the gel. This means that the polymer in the gel affects the mobility of the carriers. The other feature is that the diffusion values of cation and anion species approached each other with an increase in the polymer fraction in the gel. This suggests that the dissociation degree of the salt decreased with the polymer content despite the constant concentration of the solution in each variation of  $x$ -axis direction.

Figure 2 shows the comparison of the diffusion coefficients of the gel electrolytes with the lithium salts,  $\text{LiN}(\text{CF}_3\text{SO}_2)_2$  (TFSI) and  $\text{LiN}(\text{C}_2\text{F}_5\text{SO}_2)_2$  (BETI). In the case of BETI salts,



**Figure 3.** Ionic conductivity of gel polymer electrolytes including TFSI 1 M solution (□), TFSI 0.5 M solution (△), BETI 1 M solution (●), and BETI 0.5 M solution (■).

the cation and anion values were always the same, even in the solution without polymer, in contrast to the results of TFSI salt in which the anion diffusion value was higher than the cation value. This does not indicate the lower dissociation degree of the salt because the BETI has larger anions with higher polarity compared with that of TFSI, which promotes the dissociation. We would rather conclude that this feature shows the lower diffusion value of anion of BETI gel compared with that of TFSI gel due to the larger anion size.

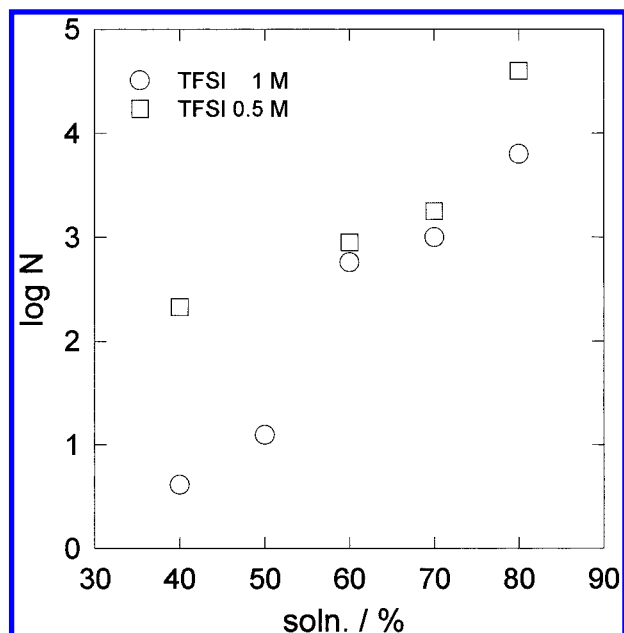
The cation diffusion values of both salts were almost the same in case of solution. However, the value of BETI steeply decreased with an increase in the polymer fraction, which was different from the changing behavior of TFSI gel. If the dissociation degree of the salt did not change by gelation, both cation values would decrease in the same manner. This result reflects that the dissociation degree of the salt has changed with the progress in gelation, and the effect of the polymer on the dissociation degree depended on the kind of the salt.

We can briefly summarize the results so far obtained as follows. The dissociation degree of the salt changed with the polymer. That is, the carrier concentration is affected by the polymer. Also the mobility, which is another factor of the conductivity, changed with the polymer. According to this view, we have an inevitable question. What is the nature of the polymer effect on the mobility of the carriers? To determine this, we elucidated the change in the carrier content and mobility of each gel further.

For the quantitative estimation of carrier content change, ionic conductivity was measured as shown in Figure 3. The conductivity of the gel electrolytes with the lithium imide salts showed an orderly change. This behavior is completely different from that of the conventional percolation model composed of a conductor and an insulator.

Using the conductivity results and the values of the diffusion coefficients by PFG–NMR, we estimated the relative content of the carrier concentration  $N$  as shown in Figure 4 according to the Nernst–Einstein equation

$$N = kT\sigma/De^2 \quad (2)$$

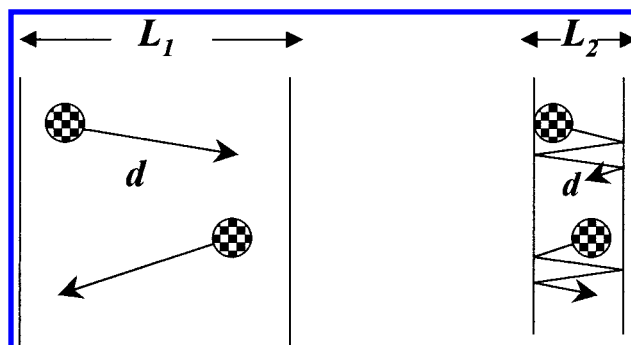


**Figure 4.** Relative content of carrier concentration ( $N$ ) as a function of solution fraction in the gel electrolytes including TFSI 1 M solution (○) and TFSI 0.5 M solution (□).

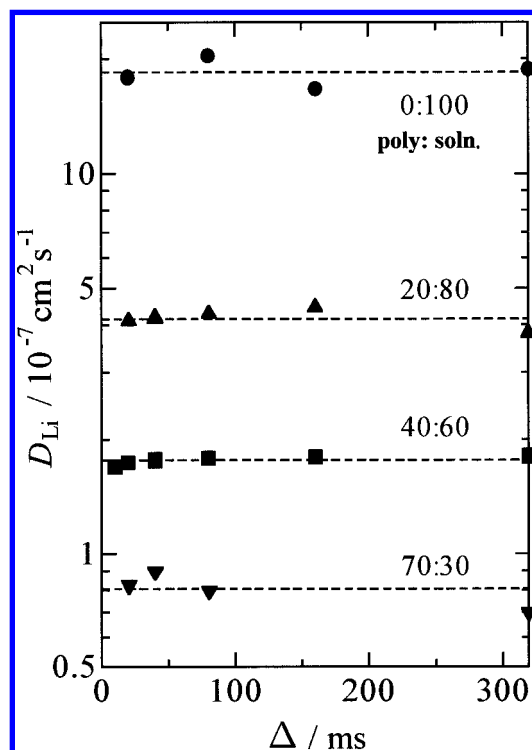
where  $k$  is the Boltzmann constant,  $T$  the absolute temperature,  $\sigma$  the conductivity, and  $e$  the elementary electric charge.<sup>10</sup> The gel electrolyte with  $\text{LiN}(\text{CF}_3\text{SO}_2)_2$  exhibited a 3 order of magnitude variation in the carrier concentration with the polymer fraction change from 20 to 60% in the gel. This variation is apparently greater than the difference in the net solution content in the gel (almost six factors of magnitude) among the gel samples in the fraction range. Therefore, we found that the polymer in the gel electrolyte seriously affected the dissociation degree of the salt.

We finally discuss the effect of the polymer on the mobility of the carriers in the gel. We propose to divide the effect into two categories.<sup>6</sup> One is a physical blocking effect of the polymer. The polymer would act as insulating materials and interfere physically with the carrier migration.<sup>11</sup> In this case, the conduction mechanism of the gel would essentially follow the mechanism of the solution. The other effect would be characterized by the chemical interactive effect. In this case, the conduction property would be modified correlated with the motion of the polymer different from the original feature of the solution.

Concerning the physical effect of polymer, it could be detected as a restricted diffusion. Figure 5 illustrates the situation that the carrier migrates within the barriers. If the size of the migration region is smaller than the total migration distance, as in the case of Figure 5b, the apparent diffusion coefficient is reduced compared with the value of the free diffusion process. This is because the shift of the position from the start to the end is just detected at the measurement.<sup>12</sup> And the migration distance corresponds to the diffusion time used at the measurements. Figure 6 represents the diffusion time dependence of the diffusion coefficients of the gel samples with different composition.<sup>6</sup> The cation diffusion coefficients of any type of gels were independent of the diffusion time in the range from 20 to 320 ms, changed at the measurements. This result means that the carriers do not take the blocking effect of polymer barriers in this migration range. The migration distance estimated from the diffusion time for the gel with the mixing ratio of 20:80, for example, was in the range from 2  $\mu\text{m}$  to 10  $\mu\text{m}$ . In practice, the size of 2  $\mu\text{m}$  is comparable to the cavity size which



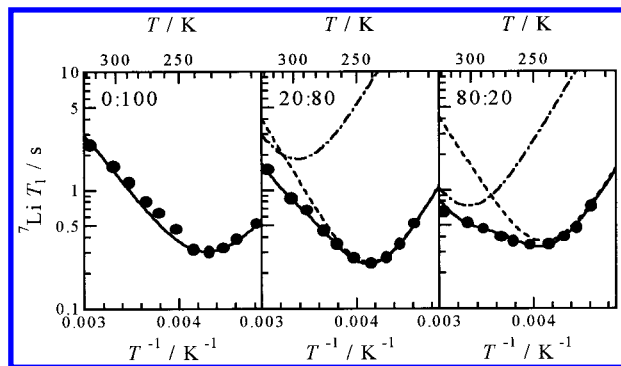
**Figure 5.** Model of carrier migration in the gel.  $L$ , cavity size of polymer;  $d$ , total migration distance for one measurement. (a) No restricted condition ( $L_1 \gg d$ ) and (b) restricted condition by the polymer barriers ( $L_2 < d$ ).



**Figure 6.** Diffusion time ( $\Delta$ ) dependence of self-diffusion coefficients of cation species for the gel electrolytes of polymer to solution, 0:100, 20:80, 40:60, and 70:30.

was estimated from the SEM photograph. However, the result of Figure 6 does not give the evidence of the existence of those cavities. Therefore, we can exclude the structural model that the electrolyte solution is kept in the conduction paths which are formed by the linked cavities of the polymer. We would rather conclude that the carriers in the solution migrate randomly among the polymer chains. And the effect of the polymer on the carriers would be detected not in the micron range but more in the microscopic range.

To investigate the effect of the polymer on the mobility in the more microscopic range, the spin-lattice relaxation time,  $T_1$ , was measured for the gel electrolytes (Figure 7).<sup>13</sup> The temperature dependence of  $T_1$  of the solution without polymer showed a symmetrical behavior.<sup>6</sup> This indicates one component of the relaxation process. With an increase in the polymer fraction in the gel, the plot appeared to be asymmetric in form. We supposed as one of the possibilities that this feature is due to the appearance of new relaxation process by gelation. We then divided the measured temperature dependence of  $T_1$  of each gel sample into two relaxation components using the least-



**Figure 7.** Temperature dependence of spin–lattice relaxation time ( $T_1$ ) of gel electrolytes of polymer to solution, 0:100, 20:80, and 80:20.

squares method. The component of the low-temperature region was almost consistent with the relaxation process of the solution and independent of the polymer fraction. On the other hand, the component of high-temperature region changed with the polymer content. It was ascribed to the polymer.<sup>14</sup> We can say that the polymer affects the mobility of carriers through the relaxation process of high-temperature component.

The other reason of the deviation of the temperature dependence plot of  $T_1$  from the symmetry curve of the solution would be responsible for the distribution of the state related with the amorphisity condition in the gel and with the interaction between the polymer and the electrolyte.

We cannot determine whether the polymer effect on the mobility is chemical or physical from these results. However, considering the effect of the polymer on the dissociation degree of the salt, the chemical interactive effect of the polymer would also contribute to the mobility of the carriers in this type of gel electrolytes.

## Conclusions

We measured the diffusion coefficients of cation and anion species of lithium gel electrolytes composed of lithium imide salts,  $\text{LiN}(\text{CF}_3\text{SO}_2)_2$  or  $\text{LiN}(\text{C}_2\text{F}_5\text{SO}_2)_2$ , the solvent, EC/DEC, and copolymer of PVDF–HFP. With an increase in the polymer fraction in the gel, the diffusion values decreased and both values

approached each other. This means that the polymer affects the mobility and carrier content through the influence on the dissociation degree of the salt. The quantitative estimation of carrier content change using the diffusion coefficient and conductivity results exhibited a 3 order of magnitude variation of carrier content among the gels with the composition from 60:40 to 20:80. The diffusion coefficient was independent of the diffusion time in the range from 20 to 320 ms. This means that, for example, the carriers do not detect the blocking effect of polymer in the migration range from 2 to 10  $\mu\text{m}$  for the gel of 20:80 (polym:soln). The spin–lattice relaxation time of the gel samples showed two components. One was consistent with the relaxation process of the solution without polymer and independent of the polymer fraction in the gel. The other component which appeared in the higher temperature region, depended on the polymer content. We found that the polymer affects the mobility of the carriers through the latter relaxation process.

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