

## Carrier Migration Mechanism of Physically Cross-Linked Polymer Gel Electrolytes Based on PVDF Membranes

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The conduction properties of PVDF polymer gel electrolytes prepared by the phase inversion method were investigated through the diffusion coefficient and conductivity in order to confirm the conduction mechanism. The gel conductivity is associated with the total solution uptake which depends on the gelation process. The solution introduced in the polymer is stored in the pores and then penetrates into the polymer chains for swelling the polymer network. In the case of a highly porous polymer membrane, this process proceeds by repeating the steps to form a homogeneous gel finally. However, the gelation process of a low porosity membrane would be stopped if the swollen polymer collapses the pores because the solution cannot continue to be supplied into the pores from outside even if the polymer chain network has not reached swelling saturation. The microscopic migration feature of the carriers in the gel electrolyte is reflected in the diffusion coefficient of the cation and anion species. The apparent transport number estimated from the observed diffusion coefficients changed steeply for a gel of 70 vol % porosity. This reflects the change in the migration mechanism of the carriers. The mobility of the carriers contributing to the polymer swelling in the vicinity of the polymer would be affected by the polymer chains through Coulombic interaction in addition to a physical barrier effect. The PVDF polymer was found to be effective in enhancing the lithium transport number due to selective interaction with the anion.

### Introduction

Gel polymer electrolytes have been actively developed for application as highly conductive electrolyte materials for lithium secondary batteries and fuel cells for energy storage systems.<sup>1</sup> It is possible for the gel electrolytes to provide high conductivity comparable to electrolyte solutions and self-supporting ability leading to improvement in safety and cost reduction. However, these two aspects essentially conflict with each other in coexistence because the conductivity of the gel is generally dominated by the fluidity of the substrate. The higher the solution fraction, the higher is the conductivity of the gel. Providing both features in a gel has not been achieved yet.

The original idea of the phase inversion technique for the preparation of gel electrolytes was to form highly porous polymer membranes first and store as much solution in the pores as possible.<sup>2</sup> It was presumed that the conductivity of the gel simply depended on the solution held in the pores of the membrane. That is, the carrier content would be determined by the amount of the solution incorporated in the pores, and the mobility of the ions would follow the property of the solution. However, the solution trapped in the pores causes swelling of the polymer chains with time to form a swollen polymer network. It is expected that the migration feature of the carriers in the swollen region would be different from that in the mass of solution trapped in the cavities.<sup>3</sup> However, the contribution of the swollen region to the total conductivity has not been analyzed systematically.

Investigation of the conduction mechanism corresponds to the understanding of how the carriers migrate in what sort of structure affected by what kind of interactions in the gel electrolytes. This is necessary for designing the materials in response to the intended use. The mechanism is correlated with the morphological factors, such as the network structure of the swollen polymer and the distribution condition of the pores to trap the solution, which are concerned with the field of carrier migration. Further, from the microscopic point of view, the interaction between the carriers (and/or the salt) and polymer dominates the carrier mobility and concentration.

We have already proposed that the gelation process is strongly correlated with the conduction mechanism through measurement of the dynamic properties of the gel electrolyte materials.<sup>4,5</sup> After the membrane is immersed in the solution bath, the solution enters the pores first to occupy them. The trapped solution in the pores next penetrates into the network of the polymer chains to swell them. On repeating these processes, solution injection and penetration several times, the gel reaches an equilibrium state in which the flow of the solution apparently stops. The first process of gelation would depend on the porosity and pore size of the membrane, and the polymer swelling process following next would be correlated with the distribution condition of the pores and the interfacial structure between the polymer and the pore space through which the solution enters. The situation at each step is responsible for the carrier migration property of the gel electrolyte.

What sort of morphology and chemical structure of the polymer are appropriate for carrier migration for high conductivity of gel electrolytes? What are the dominant factors in mobility and carrier content? To answer these questions, we examined in this research the correlation between the migration

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features of the carriers and the physical properties of the initial membranes such as porosity and pore size which are associated with the content of solution uptake after gelation. The characteristics of this research are to measure the diffusion coefficient of the cation and anion species individually.<sup>3,4</sup> This makes it possible to evaluate the migration property of each ion and systematize the migration mechanism. Finally, we intend to propose a concept for preparing the gel polymer electrolytes applicable to practical charge-transfer systems.

## Experimental Section

The porous polymer membranes were prepared by the phase separation method using several kinds of solvents.<sup>6</sup> The PVDF homo-polymer (Elf Atochem) was used as a starting material. High porosity membranes of the PVDF homo-polymer (samples D1, D2) were prepared starting from the solution with the solvents, triethyl phosphate (TEP) and *N*-methyl-2-pyrrolidone (NMP). The solution was first cast at room temperature onto a glass plate to form films of around 300  $\mu\text{m}$  thickness, which after 30 s were immersed in a water bath at 10  $^{\circ}\text{C}$  to precipitate the polymer. The membranes were leached for 48 hs under running water and then immersed in deionized water for the same period prior to being dried in air. The dried membranes showed a thickness that varied from 100 to 200  $\mu\text{m}$ , depending on the composition of the cast solution. Low porosity membranes (samples B1, B2) were prepared starting from the blending of the PVDF polymer with dibutylphthalate (DBP) at 200  $^{\circ}\text{C}$  for 30 min using a Brabender internal mixer. Films having a thickness of about 100  $\mu\text{m}$  were prepared by compression molding at 200  $^{\circ}\text{C}$  and were then quenched in a water bath within a few seconds. Plasticizer extraction was finally carried out in a large excess of a nonsolvent for PVDF, and the resulting membranes were dried by exposure to air. Nonporous membrane (sample A) was prepared by the casting method using the highly boiling solvent of NMP. We also used purchased PVDF membranes (Durepore, Millipore Co.) (samples C1, C2, C3) of 70 vol % porosity and different pore sizes of 0.1  $\mu\text{m}$  and 5  $\mu\text{m}$ . These films were immersed in a 1 M electrolyte solution composed of  $\text{LiN}(\text{CF}_3\text{SO}_2)_2$  (Li-TFSI) and a mixture of ethylencarbonate and diethyl carbonate (EC/DEC, 2/3 volume ratio) for 3 days following the conventional phase inversion technique to prepare the gels. The weight change after immersing the films into the solution was measured to estimate the solution uptake at the equilibrium state of the gel.

Scanning electron microscopy (SEM) measurements were carried out under vacuum ( $10^{-1}$  Pa) after sputtering gold on both sides of the sample films to confirm the pore size, pore distribution, and gelation condition.

Ionic conductivity was measured by the complex impedance technique over the frequency range from 0.1 Hz to 1 MHz and the temperature range from  $-35$   $^{\circ}\text{C}$  to 70  $^{\circ}\text{C}$  using an HP 4192A analyzer and a Solartron SI1250 frequency analyzer combined with an SI 1287.

The diffusion coefficients of the cation and anion species were measured by the application of field gradient pulses to NMR (pulsed gradient spin-echo (PGSE)-NMR) using the probed nuclei,  $^7\text{Li}$  (116.8 MHz) and  $^{19}\text{F}$  (282.7 MHz) on a JNM-ECP 300W wide bore spectrometer. In the pulse sequence used for the measurements, two field gradient pulses were applied. When the probed nuclei migrate during the interval between the half-sine-shaped gradient pulses, the spin-echo intensity,  $M$ , is attenuated according to the relation

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

where  $\gamma$  is the gyromagnetic ratio,  $D$  is the diffusion coefficient,  $\delta$  is the pulse width of the field gradient,  $g$  is the strength of the field gradient, and  $\Delta$  is the duration time of the two gradient pulses.<sup>7</sup> We then estimated the diffusion coefficient values by fitting the attenuated spin-echo signal with  $\delta$  to eq 1.

## Results and Discussion

**Theoretical Derivation of the Relationship between the Real and Apparent Transport Numbers.** The lithium transport number is one of the significant factors defining the carrier migration properties of a lithium electrolyte material. However, the real values could not be estimated exactly and were sometimes substituted with approximated ones obtained by electrochemical measurements. The diffusion coefficient, one of the dynamic properties of ionic conductors, obtained from NMR spectroscopy would be applied to estimate the transport number because it is responsible for the transport behavior of the individual species. If we assume that the observed values reflect the migration of only the ionic species, we can simply estimate the transport number using them and evaluate the efficiency of transport of the objective ion.

However, the observed diffusion coefficient of a probed species of electrolyte materials does not always reflect the diffusion of the ion.<sup>8</sup> When the dissociation degree of the salt in the solution is not unity as in the case of a highly concentrated solution, the observed diffusion coefficient obtained from the measurement probed by  $^7\text{Li}$  and  $^{19}\text{F}$  represents the averaged value of diffusivity of the dissociated ion and the associated ion-pair weighted by the probability of existence,

$$\begin{aligned} D_{\text{obs}}^{\text{cation}} &= xD_{\text{Li}} + (1-x)D_{\text{pair}} \\ D_{\text{obs}}^{\text{anion}} &= xD_{\text{F}} + (1-x)D_{\text{pair}} \end{aligned} \quad (2)$$

where  $D_{\text{Li}}$ ,  $D_{\text{F}}$ , and  $D_{\text{pair}}$  are the inherent diffusion coefficients of the cation, anion, and ion-pair, respectively, and  $x$  is the probability of existence of the ion corresponding to the dissociation degree of the salt statistically.<sup>8</sup> The apparent lithium transport number estimated from the observed diffusion coefficient can be derived as

$$t_{\text{app}} = \frac{D_{\text{obs}}^{\text{cation}}}{D_{\text{obs}}^{\text{cation}} + D_{\text{obs}}^{\text{anion}}} = \frac{x D_{\text{Li}} + (1-x) D_{\text{pair}}}{x(D_{\text{Li}} + D_{\text{F}}) + 2(1-x) D_{\text{pair}}} \quad (3)$$

The real transport number of lithium is the function of only the inherent diffusion values represented as

$$t_{\text{real}} = \frac{D_{\text{Li}}}{D_{\text{Li}} + D_{\text{F}}} = \frac{x D_{\text{Li}}}{x(D_{\text{Li}} + D_{\text{F}})} \quad (4)$$

The difference between the real and apparent transport numbers can be written as

$$\begin{aligned} t_{\text{real}} - t_{\text{app}} &= \frac{c(2b-a)}{a(a+2c)} \\ a &= x(D_{\text{Li}} + D_{\text{F}}) \\ b &= x D_{\text{Li}} \\ c &= (1-x) D_{\text{pair}} \end{aligned} \quad (5)$$

This means that the sign of  $(2b-a)$  determines the relative magnitude between  $t_{\text{real}}$  and  $t_{\text{app}}$  because  $a$ ,  $b$ , and  $c$  are positive. In the case of  $(2b-a) \geq 0$ , that is,  $D_{\text{Li}} \geq D_{\text{F}}$ ,

$$t_{\text{real}} \geq t_{\text{app}} \quad (6)$$

Then, in the case of  $D_{\text{F}} \geq D_{\text{Li}}$ ,

$$t_{\text{app}} \geq t_{\text{real}} \quad (7)$$

The relation between  $D_{\text{Li}}$  and  $D_{\text{F}}$  directly reflects the relation between  $D_{\text{obs}}^{\text{cation}}$  and  $D_{\text{obs}}^{\text{anion}}$  according to eq 2. As a result, we can summarize the relationship between the apparent and real transport numbers as follows:

$$\begin{aligned} t_{\text{real}} &\geq t_{\text{app}} && \text{at } D_{\text{obs}}^{\text{cation}} \geq D_{\text{obs}}^{\text{anion}} \quad (\equiv t_{\text{app}} \geq 0.5) \\ t_{\text{real}} &\leq t_{\text{app}} && \text{at } D_{\text{obs}}^{\text{cation}} \leq D_{\text{obs}}^{\text{anion}} \quad (\equiv t_{\text{app}} \leq 0.5) \end{aligned} \quad (8)$$

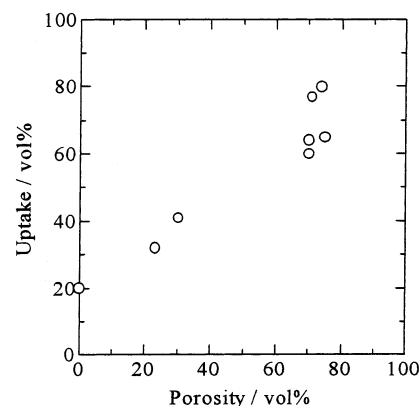
The real transport number is larger than the apparent transport number if the apparent value is larger than 0.5, and the real transport number is smaller than the apparent transport number if the apparent value is smaller than 0.5.

**Dynamic Properties Associated with the Gelation Condition.** Figure 1 shows the change in the solution uptake by gelation as a function of the porosity of the membrane. Absolute values are listed in Table 1. With an increase in porosity of the membrane, the content of the solution uptake was enhanced. Even a dense membrane without pores (sample A) showed a solution uptake of about 20 vol %. In this case, different from the porous membrane, the solution became immersed in the polymer only from the membrane surface. The increasing behavior of the solution uptake showed a change in slope at 70 vol % porosity. This reveals that the amount of the solution uptake is not simply proportional to the total volume of the cavities but is correlated with the consequent swollen process of the polymer chains especially for the highly porous membrane.

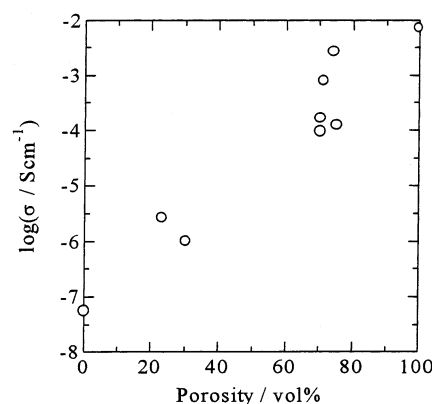
During the second step of the gelation process, the solution penetration from the pores into the polymer network, the pore space would be reduced by the swollen polymer. In the case of a membrane with low porosity, the swollen polymer collapses the pores even with a small amount of inserted solution. As a result, the gelation process no longer proceeds due to a lack of space for incorporation of the solution even if it is possible for the polymer network to absorb the solution for swelling. On the other hand, for the membranes with high porosity, the two steps of gelation, the solution-holding and polymer-swelling processes, can be repeated until the space for solution incorporation is squashed by swelling and/or the polymer network reaches a saturated condition of swelling. Finally, a homogeneous gel composed of fully swollen polymer and the residual solution in the pores would be achieved at the equilibrium state. Therefore, the anomalous change in the solution uptake at the porosity of ~70 vol % would be mainly attributed to the enhancement of the swelling efficiency of the network polymer correlated with the porosity and the distribution of the pores retaining the residual solution in the pores.

Comparing gels with almost the same porosity but different pore size, (samples D1 and D2, or samples C1 and C2, C3 in Table 1), the solution uptake is almost the same within experimental error. This result reveals that the final solution uptake is independent of the pore size which may be correlated with the solution incorporation speed in the first step of gelation.

Figure 2 shows the change in conductivity with the porosity of the polymer membrane in parallel to the list of values in Table 1. With an increase in the porosity, the conductivity also increased. Corresponding to the change in the solution uptake with porosity, the conductivity abruptly increased above 70



**Figure 1.** Solution uptake of the polymer membrane as a function of the porosity.



**Figure 2.** Ionic conductivity of the gel electrolyte as a function of the porosity of the polymer membrane.

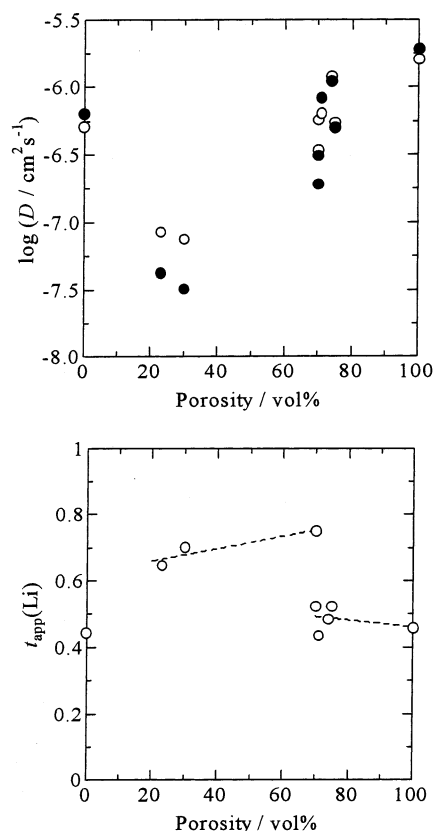
% of porosity. It is accepted that the conductivity is roughly proportional to the amount of the solution uptake. However, the dispersion of conductivity by a magnitude of over 30 at 70 vol % porosity reveals that not only the total amount of the solution but the network formation condition of the swollen polymer dominates the conduction property of the gel electrolyte.

Diffusion coefficient assumes the mobility of individual nuclear species. Figure 3a shows the diffusion coefficient of the cation and anion species probed by  $^7\text{Li}$  and  $^{19}\text{F}$ , respectively, as a function of the porosity of the polymer membrane. We found that the observed diffusion coefficients of the cation and anion species were nearly the same for the gels of the polymer with more than 70 vol % porosity. In the range below 70 vol % porosity, the diffusion value of the cation species was greater than that of the anion species. As a result, the apparent transport number of lithium estimated from these values was larger than 0.5 in this range as shown in Figure 3b. According to the results of the theoretical derivation in the previous section, these results suggest that the real transport number is larger than the apparent value of  $\geq 0.5$  at a porosity  $\leq 70$  vol % and is smaller than the apparent value of  $\leq 0.5$  at a porosity  $\geq 70$  vol %. It is amazing that the apparent transport number and then the real transport number changed abruptly at 70 vol % porosity, indicating the possibility that the carrier migration mechanism of the gel has changed at that point.

As was previously said, the carrier migration mechanism is associated with the interactive effect of the polymer on the salt dissociation and carrier mobility. As shown in Table 1, the gels of samples C1, C2, C3, and D2 showed two components of diffusion. This means that the gels are composed of two phases,

**TABLE 1: Morphological and Dynamic Properties of Polymer Membranes and Gel Electrolytes after Immersing the Membranes in 1 M Li-TFSI-EC/DEC**

sample	pore size $\mu\text{m}$	porosity vol %	uptake vol %	$\sigma$ $\text{S cm}^{-1}$	$D(^7\text{Li})$ $10^{-7} \text{ cm}^2 \text{ s}^{-1}$	$D(^{19}\text{F})$ $10^{-7} \text{ cm}^2 \text{ s}^{-1}$	$t_{\text{app}}(\text{Li})$
solution	—	—	—	$6.9 \times 10^{-3}$	19.0	23.1	0.45
A	0	0	20	$5.6 \times 10^{-8}$	5.1	6.4	0.44
B1	---	23	32	$2.7 \times 10^{-6}$	0.9	0.4	0.65
B2	0.3	30	41	$1.0 \times 10^{-6}$	0.8	0.3	0.70
C1	5	70	60	$9.8 \times 10^{-5}$	5.7 (0.73)	1.9 (0.77)	0.75
					0.8 (0.27)	0.3 (0.23)	
C2	0.1	70	64	$1.7 \times 10^{-4}$	3.4	3.1 (0.94)	0.52
						0.2 (0.06)	
C3	0.1	75	65	$1.3 \times 10^{-4}$	5.5	5.0 (0.95)	0.52
						0.3 (0.05)	
D1	1	71	77	$8.2 \times 10^{-4}$	6.4	8.3	0.44
D2	30	74	80	$2.7 \times 10^{-3}$	11 (0.75)	11 (0.82)	0.48
					2.9 (0.25)	3.1 (0.18)	

**Figure 3.** (a) Diffusion coefficient of the cation (○) and anion (●) species and (b) apparent lithium transport number of the gel electrolyte as a function of the porosity of the polymer membrane.

the swollen polymer region by the penetrated solution and the residual solution trapped in the cavities of the polymer membrane. The values in the parentheses represent the fraction of existence of each component estimated from the NMR echo intensity ratio. Most of the salt and ions in the solution trapped in the cavities in the gel would be noninteractive with the polymer due to their location far from the polymer chains. The dissociation condition of the salt and the carrier mobility are then dominated by the property of the original solution. That is, the dissociation degree of the salt of the solution depends on the dielectric constant of the solvent, and the carrier mobility is determined by the solution viscosity. Therefore, the apparent transport number of the gel having much of the residual trapped solution in addition to the saturated swollen polymer would be similar to that of an independent solution. In the case of the solution which dominantly penetrated into the polymer to swell the polymer chains, the salt and the dissociated ions would be

influenced by the polymer because the species are in the vicinity of the polymer chains and can be affected. Especially the Coulombic effect of the polymer sites would promote salt dissociation and act differently on the cation and anion species. The experimental results in Figure 3 show that the diffusivity of the anion of the solution-poor gels was apparently lower than that of the cation, which may indicate that the polymer would attract anions selectively to restrict the migration.

It is concluded that the interactions between the polymer and the associated ion-pairs and/or dissociated ions dominate the conductive feature of the ions. If the interaction accelerates the dissociation through the solvation process by the polymer, carrier concentration would be enhanced. When the charged ions interact with the polymer through Coulombic force, the ionic mobility is affected selectively apart from the physical shielding (blocking) effect of the insulating polymer. The chemical interaction of the ionic carriers with the polymer would provide a new migration mechanism different from the random migration in the solution, such as hopping among the sites, which is typical in solid electrolytes. It was found that the interactive effect of the PVDF polymer enhanced the lithium transport number of the gels prepared from the low-porosity polymers. On the contrary, the gels having substantial solution uptake dominated by the 'trapped solution', which is independent of the polymer effect concerning the transport behavior, would secure the high diffusivity of each ion due to the fluidity of the solution.

It should be noted that the gel having a highly diffusive component does not always show high conductivity. That can be recognized from a comparison of the dynamic results between D1 and D2 in Table 1. This is because the NMR measurement projects the mobility of the diffusive phases regardless of the amount of the responsible species, so long as it is more than the detection limit. On the other hand, conductivity reveals comprehensive information on the carrier content and its mobility of all conductive and insulating phases constituting the sample. It should also be mentioned that the diffusion values of sample A is anomalously larger than that expected from the porosity as shown in Figure 3a. Nonporous condition at the surface and the inside of sample A membrane was confirmed by the observation of the SEM photograph. The conductivity of it reflects the lowest porosity as is shown in Figure 2. We expect from these results that fairly large values of diffusion coefficient comes from the trapped solution localized at the surface of the membrane which could not penetrate into the inside of the polymer network due to the tight surface structure.

From the material design point of view of the polymer gel electrolyte of a cell, preparation of highly diffusive paths appropriate for reversible carrier migration during the charge/discharge process would be required. Further in detail, the



conductive performance should be distinguished depending on the part of the electrolyte, bulk and interface. For the bulk of the electrolyte, a high lithium transport number is required for stable and reversible charge transfer during the charge–discharge process. At the interfacial region with the electrodes, heterogeneous connection responsible for the smooth lithium transfer across it has to be guaranteed. For this part, a solution-rich electrolyte is appropriate to cover the interface with the electrode to promote the smooth migration of lithium even sacrificing the efficiency of lithium transport. A combination of different types of electrolyte to satisfy each demand as an inclinational-function material would provide an electrolyte applicable to battery cells satisfying the two ideal factors, high conductivity and safety.

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