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Investigation of the Conduction Mechanisms of Lithium Gel Polymer Electrolytes Based on Electrical Conductivity and Diffusion Coefficient Using NMR

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ABSTRACT: Conduction mechanisms of the polymer gel electrolytes of lithium were investigated from the electrical conductivity and diffusion coefficient by pulsed gradient spin echo NMR. The gel electrolytes prepared by the phase inversion method showed characteristic features in conductivity depending on the kind of the nonsolvent used during the polymer preparation process. This is first due to the solution content retained in the polymer. The diffusion coefficients of some gels were composed of two components which are attributed to the two phases: the trapped solution in the cavities in the polymer framework structure and the swollen polymer chains. The swollen polymer is closely correlated with the high conductivity of this type of gel electrolyte through the interactive effect between the electrolyte and the polymer chains.

Introduction

The development of polymer gel electrolytes of lithium is one of the effective approaches to preparing the reliable lithium secondary batteries which satisfy the demands for application to large-scale systems.[1] The cycle performance and reliability of the cells and/or batteries essentially depend on the conductive properties of the electrolytes as well as the interfacial reactions between the electrolyte and the electrode. However, investigation of the ionic conduction mechanisms of polymer gel electrolytes has just now started.[2,3] In the field of polymer gel electrolytes, understanding of the interactive effect of the polymer chains on the electrolyte is significant because the effect directly influences the dissociation of the salt and the ionic mobility.

The polymer gel electrolytes can usually be prepared by two procedures. One is casting in which the polymer substrate and the electrolyte solution are dissolved simultaneously, and the mixing solvent is finally removed to form a gel.[4] Another is the phase inversion method, which first prepares the porous polymer membranes using a nonsolvent and then introduces the electrolyte into the polymer to form a gel by immersing the film into the electrolyte solution.[5,6] The phase inversion technique for the polymer gel preparation is suitable for cell fabrication because the cautious treatment of the electrolyte solution, which usually avoids water, can be used in the final process of cell assembling.

During the gelation process of the polymer membranes prepared by the phase inversion method, the solution can be trapped in the cavities of the porous polymer. Furthermore, the solution will penetrate into each polymer chain to form a swollen gel. We have already found that this occurs in a stepwise manner, in which the solution first enters dominantly into the cavities and next penetrates into the polymer chains to form a homogeneous gel in the equilibrium state.[7] The conductivity of the gel electrolyte first depends on the solution content, which is proportional to the carrier concentration, held in the polymer substrate. The properties of the electrolyte solution contributing to the swelling of the polymer chains would be influenced by the size, morphology, and the chemical (acid/base) property of the polymer chains. These factors could be controlled by changing the kind and/or the content of the added nonsolvent in the case of the phase inversion method. Interactions between the polymer chains and the electrolyte in the swollen polymer also affect the mobility and carrier content.

Elucidation of the conduction mechanisms, that is, the quantitative determination of the factors affecting the conduction properties, is difficult based only on electrochemical measurements. As we have been proposing, the NMR technique is one of the attractive approaches to investigate the dynamic behavior of each ionic species.[3,7,8] Many attractive researches have been done to investigate the conduction properties especially on the gel and polymer electrolytes.[9−12] In this study, we measured the diffusion coefficients of the cation and anion species of the gel electrolytes and discussed the factors responsible for the conductivity of the gels prepared by the phase inversion method using several kind of nonsolvents.

Experimental Section

Gel polymer electrolytes were prepared by the phase inversion technique. The PVDF−HFP polymer (Elf Atochem) was dissolved in a mixture of a volatile solvent (acetone) and nonsolvent x (x = methanol, pentane, toluene, hexane, cyclohexanol, and butanol) with the proportion of the nonsolvent low enough to allow dissociation and high enough to allow phase separation during evaporation. The weight ratio of PVDF−HFP to the nonsolvent was 2 to 1. These nonsolvents were selected on the basis of the idea that the chemical structure and the size of the nonsolvent species would influence the pore size of the polymer during the solvent evaporation process. The prepared solution was cast as a film on a glass substrate, and the solvents were allowed to evaporate. The prepared films were kept under vacuum for 12 h at 100 °C to remove the traces of nonsolvents. All of the experiments

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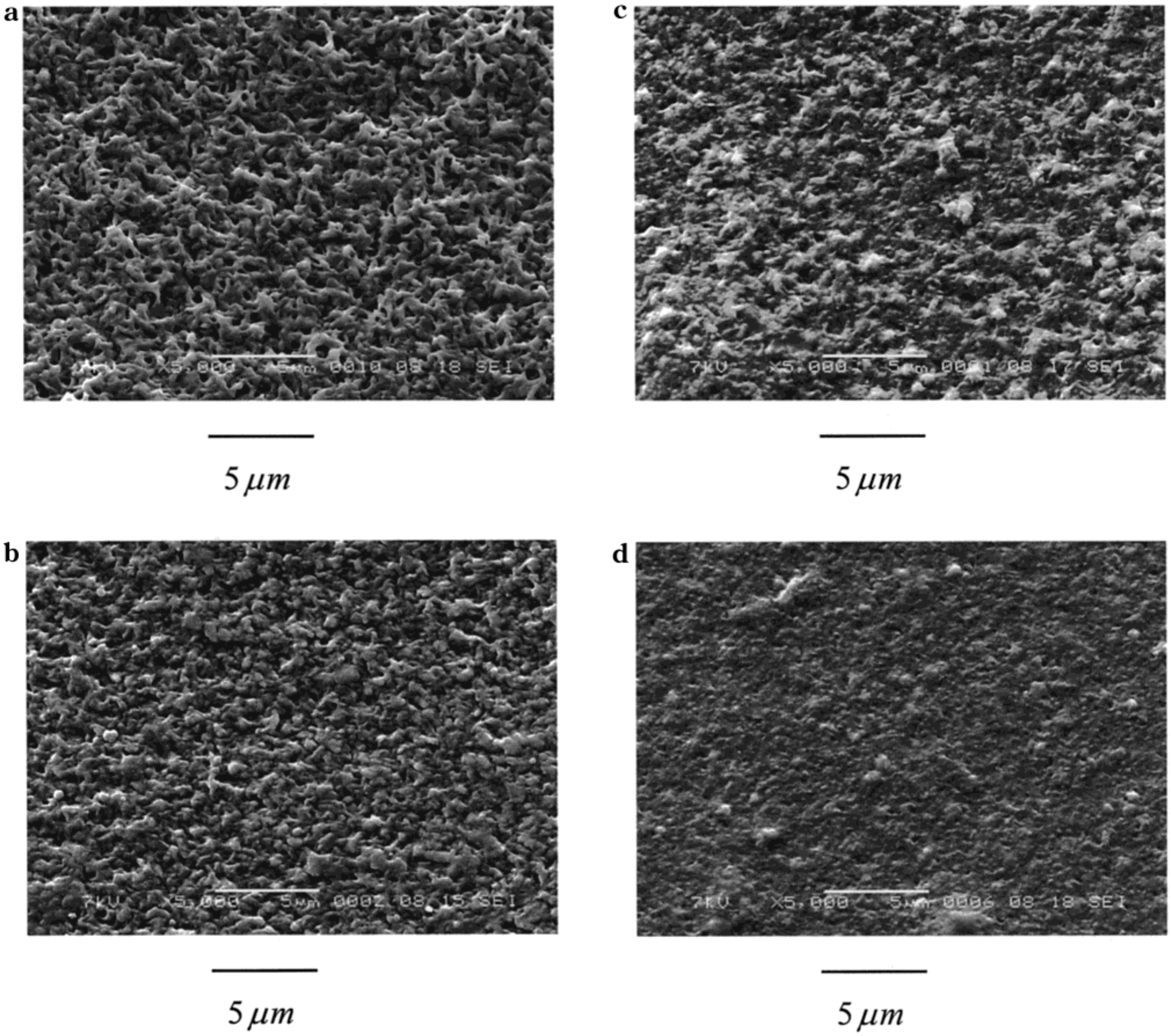

Figure 1. SEM photographs of polymer membranes prepared with (a) cyclohexanol, (b) toluene, (c) pentane, and (d) hexane.

Table 1. Weight Ratio of the Solution to the Polymer Substrate of Gel Electrolytes after Immersing the Polymer Membranes Prepared with Different Nonsolvents in a 1 M Solution of $LiN(CF_3SO_2)_2$ in EC/DEC

	butanol	methanol	cyclohexanol	toluene	pentane	hexane
solution fraction (wt %)	41	38	54	55	44	47
polymer fraction (wt %)	59	62	46	45	56	53

were performed in a dry room with a dew point of ~80 °C. The films were immersed in a 1 M solution of $LiN(CF_3SO_2)_2$ in EC/DEC for 1 week.

The morphology of the prepared polymer membranes was observed using scanning electron microscopy.

Conductivity of the gel electrolytes was measured by the complex impedance technique in the temperature range of −35 to 70 °C and the frequency range of 0.1 Hz to 1 MHz using an HP4192A analyzer and a Solartron SI1250 frequency response analyzer with an SI 1287 interface.

The diffusion coefficients of the ionic species were measured using the pulsed gradient spin echo NMR (PGSE-NMR) technique with the probed nuclei of ^{7}Li (116.8 MHz) for the cation and ^{19}F (282.7 MHz) for the anion. For this study, the stimulated echo sequence was used for this application.[13] The gradient pulse was applied twice in sequence after the first and third 90° pulses. Typical values of the parameters of the field gradient pulse were $g = 0.2-1.2$ T/m for the pulse strength, $\delta = 0-6$ ms for the pulse width, and $\Delta = 80$ and 600 ms for the duration between the two gradient pulses.

Results and Discussion

The morphology of the polymer membranes observed by the SEM in Figure 1 showed characteristic features depending on each polymer. The polymers prepared with cyclohexanol and toluene had porous structures. On the other hand, the polymers prepared with pentane and hexane showed the form of higher density without cavities. These results are due to the difference in the solvent evaporation process during the formation of the polymer membranes.

Table 1 shows the weight ratio of the solution to the polymer substrate after gelation. It seems reasonable that the polymer membranes which were observed to have high porosity from the SEM photographs held most of the solution by taking advantage of the cavities.

Figure 2 represents the temperature dependence of the conductivity of the gel electrolytes. The conductivity was normalized by the solution content in the gel in

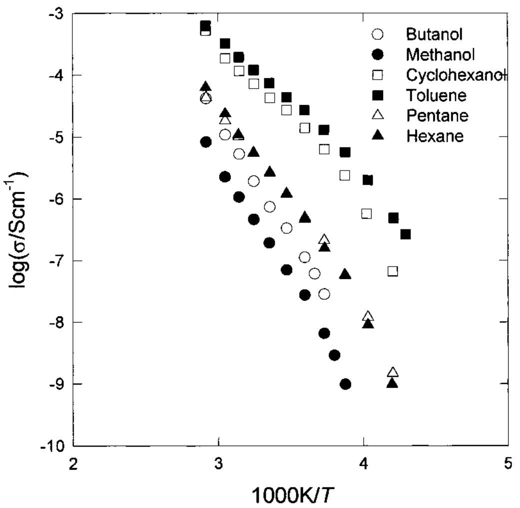

Figure 2. Temperature dependence of the normalized conductivity of gel electrolytes.

order to maintain the apparent carrier content constant to compare the morphological effect of the polymer framework on the conductivity. The gel prepared with toluene or cyclohexanol showed the highest conductivity, which is about 3 orders of magnitude larger than that of the gel prepared with methanol at 25 °C. This reveals that the porous polymer structure is effective for the formation of the conduction paths for carrier migration. Here, we can propose two possibilities to recognize the result. One is that the high conductivity is dominantly attributed to the solution trapped in the cavities in the polymer framework. The porous structure retains a large amount of cavities in which the electrolyte solution can be held. Another idea is that the high conductivity is mainly due to the swollen polymer chains. It is easy for each polymer chain which constructs the porous network structure to contact the solution uniformly. The penetration of the solution will then result in a homogeneously swollen gel forming the network conduction paths of the swollen polymer chains. To confirm this hypothesis concerning the dominant conduction mechanism, the diffusion coefficient of each ionic species was measured.

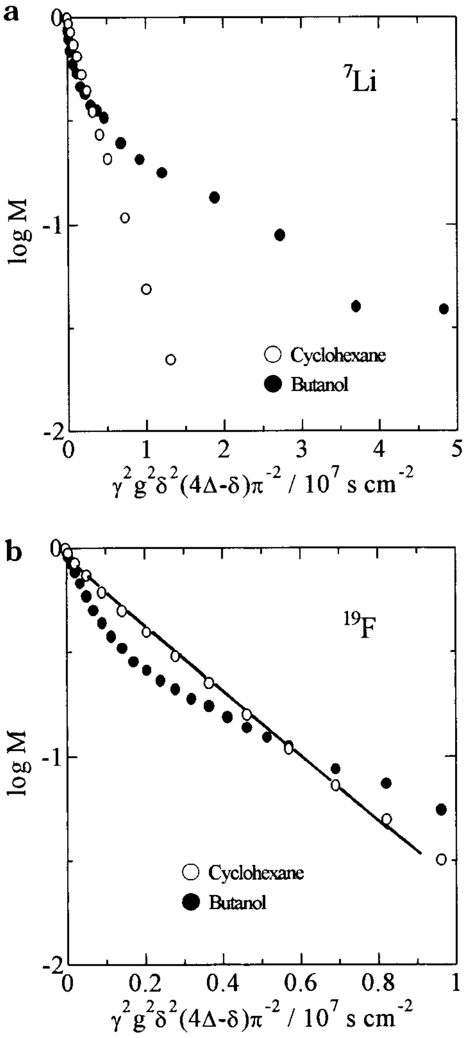

Figure 3. NMR spin echo signal decays of (a) ^{7}Li and (b) ^{19}F of the gels with the membranes prepared with cyclohexane and butanol.

Table 2. Diffusion Coefficients of Gel Electrolytes[a]

	$D(^7\text{Li})$/cm^2 s^{-1}		$D(^{19}\text{F})$/cm^2 s^{-1}	
	fast	slow	fast	slow
butanol	1.07×10^{-6} (0.50)	6.91×10^{-8} (0.50)	1.55×10^{-6} (0.66)	1.82×10^{-7} (0.34)
methanol	2.07×10^{-6} (0.74)	2.82×10^{-8} (0.26)	1.38×10^{-6} (1.00)	
cyclohexanol		3.11×10^{-7} (1.00)		4.07×10^{-7} (1.00)
toluene		3.08×10^{-7} (1.00)		4.58×10^{-7} (1.00)
pentane	1.23×10^{-6} (0.17)	3.25×10^{-8} (0.83)	1.58×10^{-6} (0.71)	4.64×10^{-8} (0.29)
hexane	2.12×10^{-6} (0.18)	8.06×10^{-8} (0.82)	1.91×10^{-6} (0.83)	7.39×10^{-8} (0.17)

[a] The values in parentheses are the fraction of the diffusion component when two components appeared.

Figure 3 shows the typical echo signal decays for the diffusion coefficient estimation. Numerical results of the diffusion coefficient estimated by the least-squares fitting are summarized in Table 2. The gels with the membranes prepared by cyclohexane and toluene showed single decay, in contrast to the gels using other solvents representing the two components of the diffusion process. The values in the parentheses represent the fraction of the carrier content responsible for each diffusion component in the gel estimated from the fitted prefactors of the signal decay. In the case of the gels which have two components in the diffusion process, we can find several characteristic features. First is the fast diffusion value which was the order of 10^{-6} cm^2 s^{-1} and which agrees with the value of the conventional electrolyte solution. Therefore, it is natural to assume that the fast component comes from the ion migration in the solution in the cavities. If we can assume this, it can be accepted that the slow component of the diffusion is due to the carrier migration in the swollen polymer from the analogy of the gels discussed previously.[7] Two components of the diffusion were independent of the diffusion times, 80 and 600 ms. This indicates that the slow component is not restricted due to the morphological barriers, which was observed in another type of gel,[7] within the measured diffusion distance. Second is that the fraction ratio between the fast and slow components depended on the kind of gel. The gels using butanol and methanol had a large fraction of the fast component in the cation, in contrast to the gels using pentane and hexane which showed a large fraction of the slow component. This reflects the difference in the fraction of the phases consisting of the trapped solution in the cavities and the swollen polymer. Further, the ratio of the fast to the slow components was reversed between the cation and anion for the gels prepared with pentane and hexane. This anomalous feature suggests that the interactions between the dissociated ions and the polymer chains are present differently for each ion. The results of the gels show that the lithium ion is mobile in the swollen polymer rather than in the trapped solution, although the anions are immobile in the swollen polymer. This reveals that the anions are more significantly affected by the surrounding polymer chains which may be due to the coulomb interaction.

In the previous paper, we attributed the fast component of the diffusion ($\sim 10^{-7}$ cm^2 s^{-1}) to the carrier migration in the swollen polymer and the slow component ($10^{-8}-10^{-9}$ cm^2 s^{-1}) to the migration in the trapped solution in the cavities.[7] In the case of the previous gel, the cavity size was controlled to ~ 1 μm, and entangled fine polymer chains were observed from the SEM photographs. After gelation, the fine polymer chains were swollen, crushing the cavities, and then prepared the closed spaces of the cavities. As a result, the carrier migration in the cavities was restricted by the polymer barriers.[14] The morphology of the gels prepared in this research would be different from this situation. The polymer membranes in this case did not show the systematic structure of the entangled fine polymer chains as shown in the previous type of polymer. Therefore, swelling of the polymer by gelation does not influence the cavity size as seriously as to form closed spaces of the pores. In this case, the solution in the cavities can move through the continuous space formed by the connected cavities. This is the reason that the fast diffusion component comparable to the value of the solution was detected in this study. On the other hand, the carrier migration in the swollen polymer is affected by the polymer through chemical and/or physical interactions.[3,15] The effects reduced the diffusion coefficient of the carriers sometimes in orderly fashion depending on the strength of the interaction. Therefore, the slow diffusion component of this study would correspond to the carrier migration in the swollen polymer.

The gels of the membranes prepared with the solvents cyclohexane and toluene showed a single diffusion process. This means that the homogeneously swollen polymer was formed and dominant in the gel. It seems to be difficult to think that the exchange of the carrier species between the two migration regions became fast to be averaged in these gels, keeping the same morphological situation as those having two diffusion components. The single diffusion component process would suggest that most of the immersed solution contribute to the swelling of the polymer to prepare the homogeneous gel, and the residual trapped solution, if it is, is a small amount and highly dispersed to be not enough to form the conduction paths of the solution in the gel.

By comparison of the diffusion coefficients and conductivity, we can state that the larger the fraction of the diffusion in the swollen polymer, the higher was the electrical conductivity. The single component of the diffusion, which is attributed to an almost homogeneous swollen gel, showed the highest conductivity. These results reveal that the homogeneous distribution of the conduction paths through the network of the swollen polymer chains is dominant for high conductivity, rather than the conduction paths of the solution in the gel electrolyte.

Conclusions

Polymer gel electrolytes prepared by the phase inversion method showed different features in the conductivity depending on the kind of nonsolvent used in the polymer preparation process. The conductivity was associated with the porous structure of the polymer framework structure. Diffusion coefficient measurements of these gels for investigation of the microscopic properties of the carrier migration revealed two components in the diffusion in some gels. On the basis of the value of the diffusion coefficient and the morphological properties, the fast component of the diffusion could be assigned to the carrier migration in the trapped solution in the cavities in the polymer and the slow component would be attributed to the swollen polymer. The electrolyte in the swollen polymer was strongly affected by the polymer chains influencing the ionic mobility. The gels having a single component of the diffusion showed the highest conductivity. Therefore, the conduction paths are dominated by the network of the swollen polymer chains.

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