

# Ionic conduction mechanisms of lithium gel polymer electrolytes investigated by the conductivity and diffusion coefficient<sup>☆</sup>

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## Abstract

Conduction properties of the polymer gel electrolytes of lithium were investigated based on the electrical conductivity and diffusion coefficient using the pulsed gradient spin echo NMR technique. The gel electrolytes prepared by the phase inversion method showed characteristic features in diffusive behavior depending on the kind of immiscible solvent used during the preparation process of the porous polymer membranes. The diffusion coefficients of several kinds of gel were composed of two components that were attributed to the different phases, the trapped solution in the cavities in the membrane and the swollen polymer chains due to the immersed solution. The swollen polymer dominates the high conductivity of this type of gel electrolytes due to the homogenous network appropriate for carrier migration through the chains.

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**Keywords:** Gel polymer electrolyte; Conduction mechanism; Diffusion coefficient; Conductivity; Pulsed gradient spin echo NMR

## 1. Introduction

PVDF-type polymer gel electrolytes have been actively investigated for application to lithium solid polymer batteries [1]. It is recognized that the PVDF polymer constitutes a two-phase separated gel composed of the swollen polymer chains and the solution retained in the cavities of the porous polymer [2]. Therefore, it is expected that both phases contribute to the carrier migration. We have been investigating the conduction mechanism of this type of gel electrolyte. We have found significant points concerning the gelat-

ion as follows. The gelation is carried out stepwise; the solution first enters into the pores and then penetrates into the polymer to swell the polymer chains. The swelling condition of the gel depends dominantly on the porosity and the pore size of the polymer membrane. After the gelation, the interaction between the carriers and the polymer chains in the swollen polymer affects the components of conductivity such as the carrier concentration through the dissociation condition and mobility.

Based on these results, we can speculate on several factors of the gel which dominate the conduction properties of the carriers. For the polymer substrate, the porosity, pore size, amorphicity, chain structure, and the degree of polymerization would be important. From the aspect of the electrolyte solution, the dissociation degree of the salt, the concentration, viscos-

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ity and the dielectric constant would be involved in the carrier migration properties.

The objective of this research is to investigate the morphological effect of the polymer substrate on the conduction property of the PVDF-type lithium gel electrolytes. Depending on the porosity and pore size of the polymer substrate, the occupation fraction of the swollen polymer phase and the solution phase would change. As a result, the interactive effect between the carriers and the polymer is also affected. Through this investigation, we would like to obtain ideas for controlling and designing a gel electrolyte material that has the required level of conductivity.

## 2. Experimental

Gel polymer electrolytes were prepared by the phase inversion technique [3,4]. The PVDF-HFP copolymer (Elf Atochem) was dissolved in a mixture of a volatile solvent (acetone) and an immiscible non-solvent  $x$  ( $x$ =methanol, pentane, toluene, hexane, cyclohexanol, or butanol) with the proportion of the non-solvent low enough to allow dissociation and high enough to allow phase separation during evaporation. The weight ratio of the PVDF-HFP to the non-solvent was 2 to 1. These non-solvents were chosen based on the idea that the chemical structure and the size of the non-solvent species would influence the pore size of the polymer during the solvent evaporation process. The prepared solution was cast on a glass substrate to evaporate the solvents to form a film. The prepared films were kept under vacuum for 12 h at 100 °C to remove the traces of the non-solvents. All of the experiments were performed in a dry room with a dew point of 80 °C. The films were immersed in a 1-molar solution of  $\text{LiN}(\text{CF}_3\text{SO}_2)_2$  in EC/DEC (2/3 in volume) for 1 week.

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

The electrical 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 HP 4192A 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 technique with the probed nuclei of  $^7\text{Li}$  (116.8 MHz) for the cation and  $^{19}\text{F}$  (282.7 MHz) for the anion species. For this study, the stimulated echo sequence was used for this application [5]. The gradient pulse was applied twice in sequence after the first and third  $90^\circ$  pulses. Typical values of the parameters of the field gradient pulse were  $g=0.2\text{--}1.2$  T/m for the pulse strength,  $\delta=0\text{--}6$  ms for the pulse width and  $\Delta=80$  and 600 ms for the interval between the two gradient pulses.

## 3. Results and discussion

Fig. 1 shows the SEM photographs of typical polymer membranes. These are two typical polymer samples prepared using cyclohexanol and pentane. The membrane prepared with cyclohexanol showed a porous structure having a pore size of 1  $\mu\text{m}$ . On the other hand, the membranes prepared with pentane showed a tight structure with low porosity. We could find that the porous condition depends on the immiscible solvent used.

Table 1 shows the weight ratio of the electrolyte solution to the polymer substrate after gel formation. The polymers prepared with cyclohexanol and toluene had the largest amount of the solution uptake. This result agreed with the SEM photographs in which the polymer from these solvents showed a highly porous structure.

We measured the diffusion coefficient of the cation and anion species to observe the dynamic properties of the individual carrier. Fig. 2 represents a typical plot of the NMR signal intensity of the lithium species. The gels of the polymer membranes prepared using butanol, methanol, pentane and hexane showed a change in slope of the plot of the filled marks. This means that there are two different mechanisms for carrier migration in these gel polymer electrolytes.

The diffusion coefficients of each gel estimated from the slope of the intensity change are summarized in Table 1. Only the gels prepared from cyclohexanol and toluene showed a single component of the diffusion process of both the cation and anion species. In the case of two-component gels, the diffusion values are different from each other in an orderly manner.

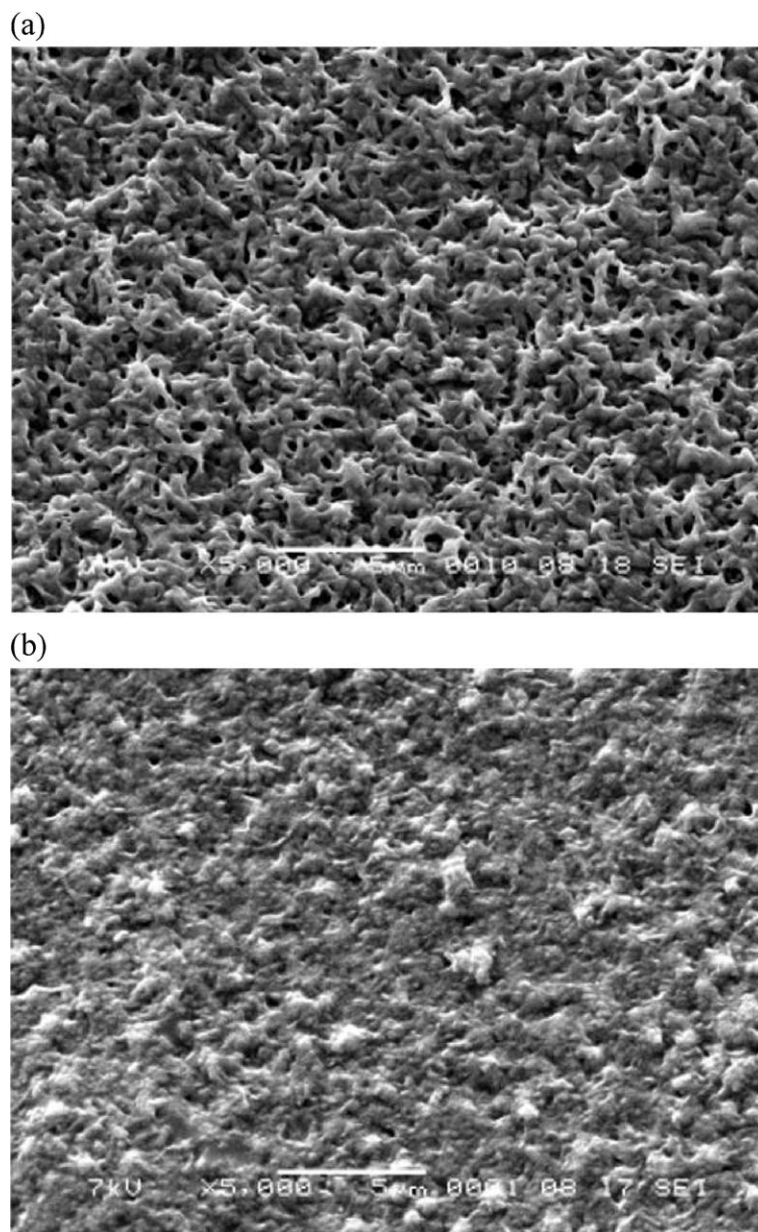


Fig. 1. SEM photographs of the gel electrolytes composed of the PVDF-HFP polymer membranes which were prepared using (a) cyclohexanol and (b) pentane.

The fast one corresponds to the diffusion of the carriers in the conventional solution. The slow diffusion component agreed with the value of the gel prepared by the casting technique having the same

solution fraction. Therefore, we assigned the location of each component as follows. The fast diffusion process is attributed to the solution trapped in the cavities in the porous polymer membranes. This is the

Table 1

Solution fraction and the diffusion coefficients of the gel electrolytes prepared with different immiscible solvents

	Solution fraction (wt.%)	$D(^7\text{Li})$ ( $\text{cm}^2 \text{s}^{-1}$ )		$D(^{19}\text{F})$ ( $\text{cm}^2 \text{s}^{-1}$ )	
		Fast	Slow	Fast	Slow
Butanol	41	$1.07 \times 10^{-6}$ (0.50)	$6.91 \times 10^{-8}$ (0.50)	$1.55 \times 10^{-6}$ (0.66)	$1.82 \times 10^{-7}$ (0.34)
Methanol	38	$2.07 \times 10^{-6}$ (0.74)	$2.82 \times 10^{-8}$ (0.26)	$1.38 \times 10^{-6}$ (1.00)	
Cyclohexanol	54		$3.11 \times 10^{-7}$ (1.00)		$4.07 \times 10^{-7}$ (1.00)
Toluene	55		$3.08 \times 10^{-7}$ (1.00)		$4.58 \times 10^{-7}$ (1.00)
Pentane	44	$1.23 \times 10^{-6}$ (0.17)	$3.25 \times 10^{-8}$ (0.83)	$1.58 \times 10^{-6}$ (0.71)	$4.64 \times 10^{-8}$ (0.29)
Hexane	47	$2.12 \times 10^{-6}$ (0.18)	$8.06 \times 10^{-8}$ (0.82)	$1.91 \times 10^{-6}$ (0.83)	$7.39 \times 10^{-8}$ (0.17)

residual solution which could not disperse into the polymer for swelling. The slow diffusion component would be due to the carrier migration inside the swollen polymer chains. The orderly difference between them in spite of the same carriers in the solution indicates that the carriers inside the swollen region interact with the neighboring sites of the polymer, reducing the carrier mobility compared with that of the solvated ions in the solution [4,6].

Fig. 3 shows the temperature dependence of the conductivity of these gel samples. The order of the conductivity, toluene>cyclohexanol>pentane>hexa-

ne>butanol>methanol, agreed with the order of the solution uptake in the gel. The gels having the highest conductivity also showed a single component of the diffusion process. Even if there was a highly diffusive phase caused by the trapped solution, it did not contribute to the total conductivity. This is because the trapped solution would be in the closed cavities that could not contribute to the direct current of the charged species [7]. Preparation of a homogeneous network of the swollen polymer chains would be effective for the long-range carrier migration for high conductivity of this type of gel electrolyte.

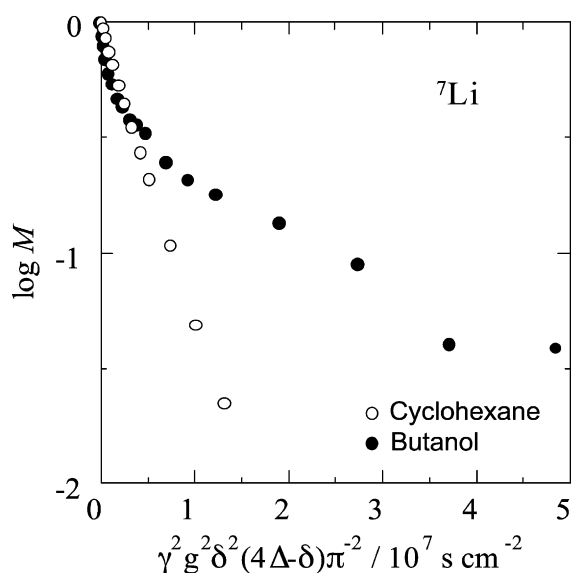


Fig. 2.  $^7\text{Li}$  NMR signal intensity change of the gels prepared with cyclohexanol (○) and butanol (●).

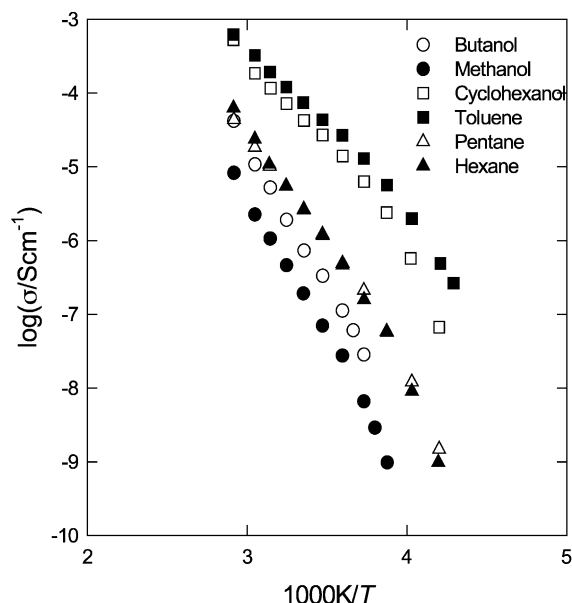


Fig. 3. Temperature dependence of the conductivity of the gel electrolytes.

#### 4. Conclusions

PVDF-type polymer gel electrolytes have two conductive phases; one is the swollen polymer chains and the other is the solution retained in the cavities. The swollen polymer network is the dominant phase for the total conductivity of the gel electrolytes. Highly conductive gel electrolytes were prepared with a porous polymer membrane which showed a single component of the diffusion process. This would be due to smooth movement of the solution into the polymer from the first-trapped cavities, resulting in homogeneous three-dimensional network chains appropriate for carrier migration.

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