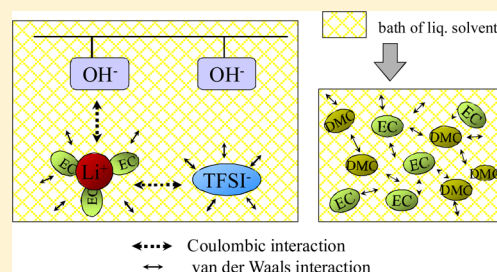


Evaluation of Interactive Effects on the Ionic Conduction Properties of Polymer Gel Electrolytes

Yuria Saito,^{*,†} Miki Okano,[†] Keigo Kubota,[†] Tetsuo Sakai,[†] Junji Fujioka,[‡] and Tomohiro Kawakami[‡][†]National Institute of Advanced Industrial Science and Technology, 1-8-31, Midorigaoka, Ikeda, Osaka, 563-8577 Japan[‡]Kuraray Company Ltd., 2045-1 Sakazu, Kurashiki, Okayama, 710-0801 Japan

ABSTRACT: Ionic mobility of electrolyte materials is essentially determined by the nanoscale interactions, the ion–ion interactions and ion–solvent interactions. We quantitatively evaluated the interactive situation of the lithium polymer gel electrolytes through the measurements of ionic conductivity and diffusion coefficients of the mobile species of the lithium polymer electrolytes. The interactive force between the cation and anion in the gel depended on the mixing ratio of the binary solvent, ethylene carbonate plus dimethyl carbonate (EC/DMC). The gel with the solvent (3:7 EC:DMC) showed minimal cation–anion interaction, which is the cause of the highest ionic mobility compared with those of the other gels with different solvents. This suggests that the cation–anion interaction does not simply depend on the dielectric constant of the solvent but is associated with the solvation condition of the lithium. In the case of the gel with the 3:7 EC/DMC solvent, most of the EC species strongly coordinate to a lithium ion, forming the stable solvated lithium, $\text{Li}(\text{EC})_3^+$, and there are no residual EC species for exchange with them. As a result, the solvating EC species would be a barrier that restricts the anion attack to the lithium leading to the smallest cation–anion interaction. On the other hand, interaction between the cation and polar sites, hydroxyl and oxygen groups of ether of the polyvinyl butyral (PVB) and polyethylene oxide (PEO) polymer, respectively, in the gels was another dominant factor responsible for cation mobility. It increased with increasing polar site concentration per lithium. In case of the PVB gels, cation–anion interaction increased with an increasing polymer fraction of the gel contrary to the independent feature of PEO gels with the change of the polymer fraction. This indicates that the cation–anion interaction is associated with the polymer structure of the gel characterized by the kind and configuration of polar groups, molecular weight, and network morphology of the polymer.



INTRODUCTION

In the field of lithium secondary batteries, development of reliable solid electrolyte materials free from liquid leakage and flammability is strongly desired for the replacement of liquid electrolyte solutions. The polymer gel electrolyte, which includes the mobile ionic species in the gel, is a promising material due to its high conductivity and self-supporting structure.^{1,2}

It is generally accepted that the ionic conductivity of the electrolyte material decreases with increasing viscosity of the medium. However, the ionic mobility of the gel electrolyte is fairly high, contrary to the expectation from the large viscosity of the gel. This is because the ions in the gel migrate through the nanoscale pathways of the solution in the network of the entangled polymer chains. Tightly cross-linked polymer chains could keep the liquid solvent inside the network to form a self-supporting gel structure compatible with the solid form. The solidlike form of the electrolyte needs no serious sealing of the battery to prevent liquid leakage. Therefore, it is acceptable that the polymer gel is an ideal form of the electrolyte material for lithium secondary batteries from the aspects of high conductivity and safety performance.

Lithium polymer gel electrolytes are composed of three elements: a lithium salt, a liquid organic solvent, and a polymer.

The lithium salt is the source of the lithium ions which assume the charge transport. The liquid solvent dissolves and dissociates the lithium salt for ionization and is the primary medium for ion transport. The polymer holds the solution in the network structure and, in some cases, affects the salt dissociation and ionic mobility when Lewis basic or acidic polar groups, which could interact with the ionic species, are present on the polymer chains. The conventional idea for preparation of polymer gel electrolytes was to mix a highly conductive electrolyte solution, such as $\text{LiPF}_6/\text{EC}/\text{DEC}$, with a highly compatible polymer as polyethylene oxide (PEO) or with a porous polymer membrane, such as polyvinylidene fluoride (PVDF).^{3–6} The polymer of those gels is expected simply to be the container of the electrolyte solution. We supposed that it is effective to make active use of the polymer as a second medium for promotion of the salt dissociation and ionic mobility.

It is acceptable that the conduction property and the structural stability of the gel electrolytes are essentially assigned to the interactions among the presenting species, ions, associated salt and solvent molecules, and polar sites on the

Received: May 1, 2012

Revised: July 24, 2012

Published: July 25, 2012



polymer chains. Dissociation of the lithium salt starts with the solvation of the polar solvent species on the lithium. The dissociation degree of the salt depends on the strength and number of the solvation bonding for a lithium. On the other hand, mobility of an ionic species of the gel, according to Einstein's relation, is associated with the microviscosity that originated from the interactions with the surrounding ions, molecular species, and polar sites. These interactions are broadly classified as the Coulombic effect and van der Waals effect depending on the charged condition of the interactive species. The stronger the attractive force on the ion concerned, the lower the ionic mobility becomes. Furthermore, stability of the gel morphology is governed by the balance of all interactions in the gel.

What course should we take to design the ideal polymer gel electrolytes? In order to promote the salt dissociation to increase the carrier concentration, it is common to use the liquid solvent with a high dielectric constant and donor number. The polar solvent species could strongly coordinate to a lithium, forming solvated lithium ions and promoting the salt dissociation. However, enlargement of the lithium ion by solvation is disadvantageous from the aspect of ionic mobility according to the Stokes–Einstein equation.⁷ In addition, the strongly solvated lithium ion needs a large activation energy for desolvation, which is a rate-determining process of charge transport at the solid electrolyte interphase (SEI) between the electrolyte and electrode in the cell. Here, we suppose that the polymer could assume the salt dissociation in place of the liquid solvent. That is, the attractive effect of the polar groups of the polymer on the ions could promote the salt dissociation and control the ionic mobility. If, for example, the Lewis acidic groups are arranged on the polymer chains, anions are selectively attracted and the anion mobility could be reduced, which is profitable for increasing the lithium transport number as well as promotion of the salt dissociation. Therefore, it is acceptable that the polymer in the gel should be used more actively as a functional solvent for ionic-conductivity enhancement.

The objective of this research was to explore the fundamental factors responsible for ion-conduction properties for designing new lithium polymer gel electrolytes systematically in accordance with the logical indexes. For that purpose, we first evaluated the inherent ionic mobilities, dissociation degree of the salt, and ion transport number of the gel electrolytes correlated with the functional group structure of the polymer. These values reflect the structure and size of the mobile ions and the viscosity that the ions feel as resistance in migration.⁶ We then proposed and applied the new approach of evaluating the microviscosity on each ionic species attributed to the interaction between the ion and surrounding species and polar sites.

In this research, we mainly used polyvinyl butyral (PVB)-type polymers for gel electrolytes in expectation of application to new gel electrolytes. PVB is synthesized by acetalization of the hydroxyl (OH) groups of polyvinyl alcohol (PVA) with *n*-butyl aldehyde and, consequently, has OH groups, butyral (BA) groups, and acetyl (OAc) groups on the chains. Via control of the degree of acetalization, the relative content of the OH and BA groups can be changed systematically. The OH group is a strong Lewis base and attracts lithium, affecting the cation mobility in a manner similar to that of the oxygen sites of ether in polyethylene oxide (PEO).^{5,8} Therefore, PVB polymer would originally not be profitable for the element of the ideal

lithium gel electrolyte. However, it suggests that the polar groups of PVB could be fairly easily substituted by other polar groups in the future. In addition, the OH groups are the cardinal points for cross-linking the polymer chains in the gelation process. Therefore, the research on OH concentration dependence of dynamic properties and the interactive situation of the ionic species of the PVB gel electrolytes is effective for obtaining the fundamental information for gel electrolyte designing. We also prepared the gel electrolytes with other types of polymers, PEO and PVDF-HFP, in order to compare the effects of the structural feature of the polymer on the ion-transport property of the gel.

EXPERIMENTAL SECTION

The PVB polymer was synthesized by the reaction of polyvinyl alcohol (Kuraray Poval, Kuraray Co. Ltd.) and *n*-butyl aldehyde in the presence of hydrochloric acid.⁹ The fundamental chemical structure is represented in Figure 1. With a change

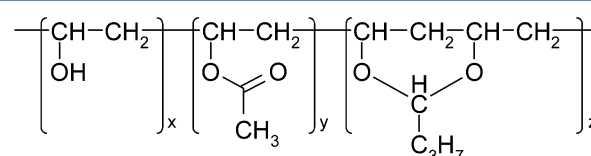


Figure 1. Chemical structure of PVB.

in the amount of *n*-butyl aldehyde, the acetalization grade was controlled. Contents of the OH and OAc groups of the PVB polymer were measured by neutralization titration. The content of the BA (acetal) group was residual, excluding the OH and OAc groups. The fraction of the polar groups of the PVB polymer used in this research is listed in Table 1. The PVB

Table 1. Physical and Chemical Properties of the Polyvinyl Butyral (PVB) Polymers

| | viscosity ^a (mPa s) | fraction of polar group | | |
|-------|--------------------------------|-------------------------|--------------|---------------|
| | | [BA] (mol %) | [OH] (mol %) | [OAc] (mol %) |
| PVB-1 | 50 | 82 | 15 | 3 |
| PVB-2 | 200 | 80 | 18 | 2 |
| PVB-3 | 50 | 72 | 25 | 3 |
| PVB-4 | 210 | 73 | 26 | 2 |
| PVB-5 | 40 | 62 | 35 | 3 |
| PVB-6 | 230 | 63 | 35 | 2 |

^a10 wt % solution of EtOH.

polymer powder was mixed with the lithium electrolyte solution, 1 M LiTFSI/EC/DMC (where EC is ethylene carbonate and DMC is dimethyl carbonate, the wt ratio of EC:DMC = 0:10, 3:7, 7:3), with changing the polymer fraction by 5, 10, 12, 15, and 20 wt %. Each mixture was heated at 60 °C to complete the dissolution to form the homogeneous solutions. In this study, we did not chemically cross-link the polymer chains for gelation of the solutions in order to elucidate the correlation between the OH concentration and ionic mobility quantitatively. The solution samples with the polymer, however, are called gels for convenience herein. Impurities of sodium and chlorine in the polymer were measured by inductively coupled plasma atomic emission spectrometry and confirmed to be less than 200 ppm during the preparation process. Proton content was measured by the

neutralization titration using KOH. As a result, we confirmed that $[\text{Na}]/[\text{Li}]$, $[\text{Cl}]/[\text{Li}]$, and $[\text{H}]/[\text{Li}]$ were 1.9×10^{-3} , 1.3×10^{-3} , and 5.5×10^{-4} , respectively, in the polymer-rich gel with 15 wt % PVB. These results suggest that the contribution of the ionic impurities to conductivity is negligible for the gels in this research.

For comparison, we prepared the different types of gels using PEO (M_n : 20000, Wako Chemicals) and poly(vinylidene fluoride-hexafluoropropylene) (PVDF-HFP) copolymer (Sigma-Aldrich). Electrolyte solution and the polymer of each fraction were mixed while being heated at 60–70 °C to complete the homogeneous solution.

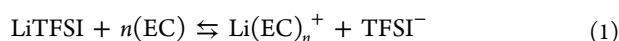
Macroviscosity, η_m , was measured with a digital viscometer (DV-III+, Brookfield) under an air atmosphere at 25 °C. A dielectric constant measurement was performed with a Precision impedance analyzer (4294A, Agilent Technologies) and a Liquid test fixture (16452A, Agilent Technologies) at 25 °C. The dielectric constant (ϵ) was calculated from the ratio of the measured air capacitance (C_0) and measured capacitance of the sample (C_p) according to the relation $\epsilon = C_p/C_0$. Ionic conductivity was measured by the complex impedance technique using the frequency analyzer (SI1250 combined with the 1284 potentiometer, Solartron) in the frequency range from 1 mHz to 65 kHz at 25 °C. The density of the gel was measured based on Archimedes' method at 25 °C.

Diffusion coefficients, D_{Li} , D_{F} , and D_{H} , were measured at 25 °C for the probed nuclear species, ^7Li (116.8 MHz), ^{19}F (282.7 MHz), and ^1H (300.5 MHz), respectively, using the pulsed gradient spin-echo (PGSE) NMR technique with a JNM-ECP300W wide bore spectrometer.¹⁰ D_{H} was obtained using the ^1H peak of the DMC species of the binary solvent. The Hahn-echo pulse sequence was used for measurements. The half-sine-shaped gradient pulse was applied twice in the sequence, after the 90° and 180° pulses, to detect attenuation of echo intensity according to the diffusive migration of the probed species.^{11,12} The typical values of the parameters for the pulse sequence are $g = 2\text{--}4$ T/m for the strength of the gradient pulse, $\delta = 0\text{--}5$ ms for the pulse width, and $\Delta = 50$ ms for the diffusion time corresponding to the interval between the two gradient pulses. Relaxation times ($T_{1\text{Li}}$, $T_{1\text{F}}$, $T_{1\text{H}}$) were measured for each nuclear species using the pulse sequence 180°, τ , 90° at 25 °C.

■ THEORETICAL DERIVATION

Before discussing the correlation between the fundamental parameters responsible for the ion-conduction property and the type of liquid solvent or polymer of polymer gel electrolytes, we will clarify here the theoretical evaluation approach for the fundamental parameters, inherent diffusion coefficient of the ionic species, dissociation degree of the salt, and the microscopic viscosity responsible for the ionic mobility using the measured diffusion coefficients and ionic conductivities.

The lithium salt dissolved in the polar solvent is under the equilibrium state as follows.



Solvation condition of the lithium depends on the mixing ratio of EC to DMC. At the equilibrium situation, observed diffusion coefficients, D_{Li} , D_{F} , and D_{H} , using the probed nuclear species, ^7Li , ^{19}F , and ^1H , respectively, of the electrolyte can be expressed as

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

where x is the dissociation degree of the salt, and D_{cation} , D_{anion} , and D_{pair} are the inherent diffusion coefficients of the cation $[\text{Li}(\text{EC})_n^+]$, anion (TFSI^-), and ion pair (LiTFSI), respectively.¹³ This situation shows that the measured diffusion coefficient does not directly reflect the inherent diffusion value of the individual ionic species. In order to estimate the individual value in eq 2, we can use the Nernst–Einstein equation which represents the relation of the molar conductivity, Λ , and inherent diffusion coefficient^{5,14}

$$\Lambda = \Lambda_{\text{cation}} + \Lambda_{\text{anion}} = \frac{F^2}{RT}x(D_{\text{cation}} + D_{\text{anion}}) \quad (3)$$

Molar conductivity is measured by the impedance technique. The neutral species, ion pair, and solvent DMC species are isolated, and each species follows the Stokes–Einstein relation. Therefore, the diffusion coefficients (D_{pair} and D_{DMC}) and the radii (r_{DMC} and r_{pair}) of these species in a gel are in the relation of

$$\frac{D_{\text{pair}}}{D_{\text{DMC}}} = \frac{r_{\text{DMC}}}{r_{\text{pair}}} \quad (4)$$

where r_{DMC} and r_{pair} are estimated as 2.67 and 4.9 Å, respectively, according to the van der Waals size of the atomic species.^{15,16} Therefore, we can evaluate numerically D_{cation} , D_{anion} , D_{pair} , and x by solving eqs 2–4 with the observed diffusion coefficients, D_{Li} , D_{F} , and D_{H} , and ionic conductivity, Λ , of the gel electrolyte.

Under the equilibrium state of eq 1, the resistance that the ions feel in migration in the solvent is the microviscosity derived from the interactions with the surrounding ions and molecules. We can accept two types of interactions here, the van der Waals interaction and the Coulombic interaction. The van der Waals force, Γ , acts on all presenting species from the surrounding species. It could be assumed that the microviscosity, η , on a species attributed to the interaction, Γ , is almost the same for all species because there is no large difference in the size of the presenting species. On the other hand, the Coulombic force acts between the charged species or polar sites. The interactive force, A , especially, between the closest cation and anion is dominant for ion migration because the Coulombic interaction is inversely proportional to the square of the distance, and the distant ions or polar sites are less effective. Here, we use α to denote the microviscosity attributed to the Coulombic interaction between the cation and anion. As a result, diffusion coefficients of the solvent and ionic species of the electrolyte solution could be represented as follows.

$$\begin{aligned} D_{\text{H}}^0 &= \frac{kT}{6\pi r_{\text{DMC}}\eta^0} \\ D_{\text{anion}}^0 &= \frac{kT}{6\pi r_{\text{anion}}\eta^{0'}} \quad \eta^{0'} = \eta^0 + \alpha^0 \\ D_{\text{cation}}^0 &= \frac{kT}{6\pi r_{\text{cation}}\eta^{0''}} \quad \eta^{0''} = \eta^0 + \frac{r_{\text{anion}}}{r_{\text{cation}}}\alpha^0 \end{aligned} \quad (5)$$

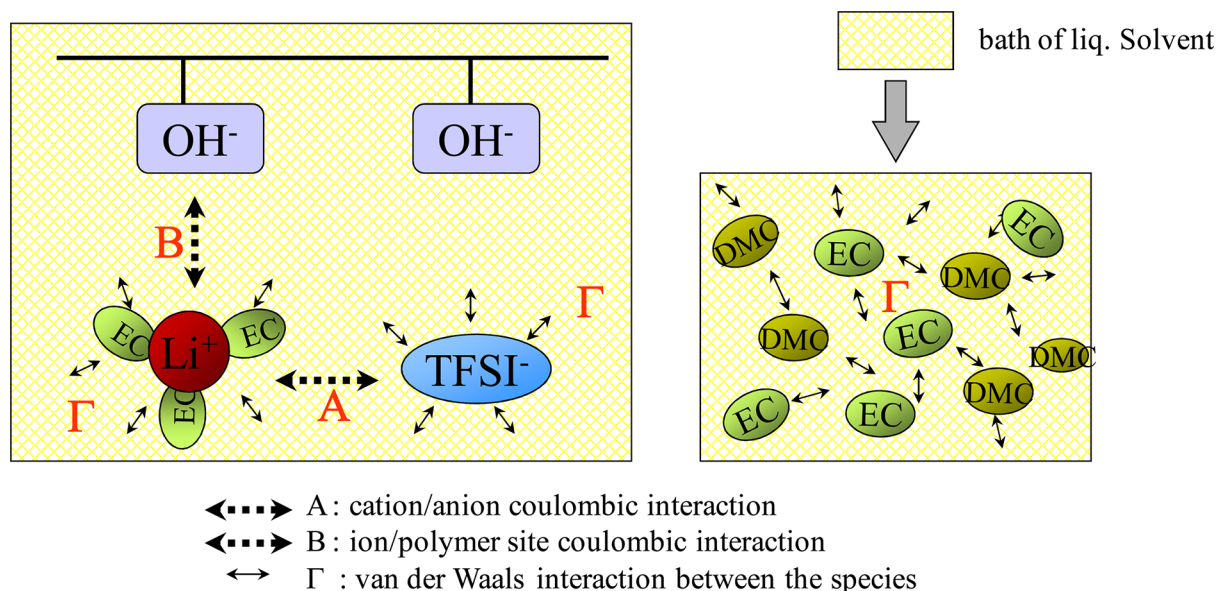


Figure 2. Interactive situation in the PVB gel electrolyte. Γ , van der Waals interaction; A, Coulombic interaction between the cation and anion; B, Coulombic interaction between the cation and OH polar group on the polymer chain. Γ acts on all existing species leading to the microviscosity, η ; A leads to the microviscosity, α , on the ionic species, and B leads to the microviscosity, β , on the cation.

where superscript 0 indicates the solution without polymer. It should be noted that there is the prefactor, $r_{\text{anion}}/r_{\text{cation}}$, for α on D_{cation}^0 . This is because the viscosity is proportional to A/r_{ion} according to the Stokes equation.⁷ Therefore, when we assume $r_{\text{anion}} = r(\text{TFSI}^-) = 0.39$ nm and $r_{\text{DMC}} = 0.33$ nm from the van der Waals size of the ionic and molecular species, we can individually estimate η^0 and α^0 for each electrolyte solution using the estimated diffusion values, D_{H}^0 , D_{cation}^0 , and D_{anion}^0 .¹⁷

In the case of gel electrolytes, the Coulombic force, B, acts between the ion and the polar groups, if they are on the polymer chains, depending on the Lewis basic or acidic feature and its strength. Basic OH groups on the PVB polymer would strongly attract lithium cations in the gel electrolytes. This interaction could be recognized as the microviscosity, β , which leads to reduce the cation mobility selectively. It is also expected that the repulsive force acts between the OH group and anion. However, the observed results of D_{anion} and T_{IF} in the next section reveal that there is no active interaction affecting the anion mobility between the OH group and anion species. Therefore, we do not put the viscosity component, β , in D_{anion} . As a result, the inherent diffusion coefficients of the solvent and ionic species of the PVB gels can be represented as follows.

$$\begin{aligned}
 D_{\text{H}}^i &= \frac{kT}{6\pi r_{\text{DMC}} \eta^i} \\
 D_{\text{anion}}^i &= \frac{kT}{6\pi r_{\text{anion}} \eta^{i'}} \quad \eta^{i'} = \eta^i + \alpha^i \\
 D_{\text{cation}}^i &= \frac{kT}{6\pi r_{\text{cation}} \eta^{i''}} \quad \eta^{i''} = \eta^i + \frac{r_{\text{anion}}}{r_{\text{cation}}} \alpha^i + \beta^i
 \end{aligned} \quad (6)$$

where superscript i represents the gel of the i th polymer fraction. We can also estimate η^i , α^i , and β^i using D_{H}^i , D_{anion}^i , and D_{cation}^i which are derived from the observed diffusion values, D_{H}^i , D_{Li}^i , D_{F}^i , and r_{anion} and r_{cation} that the solvated structure is considered. Figure 2 illustrates the interactive situation between the species of the gel electrolyte.

It is also useful to see the changes of the normalized diffusion coefficients, $D_{\text{cation}}/D_{\text{H}}$ and $D_{\text{anion}}/D_{\text{H}}$, in order to intuitively perceive the Coulombic effect with the polymer fraction or OH content changes of the gel. They are represented as

$$\begin{aligned}
 \frac{D_{\text{cation}}^i}{D_{\text{H}}^i} &= \left(\frac{\eta^i}{\eta^i + \alpha^i + \beta^i} \right) \left(\frac{r_{\text{DMC}}}{r_{\text{cation}}} \right) \quad c = \frac{r_{\text{anion}}}{r_{\text{cation}}} \\
 \frac{D_{\text{anion}}^i}{D_{\text{H}}^i} &= \left(\frac{\eta^i}{\eta^i + \alpha^i} \right) \left(\frac{r_{\text{solv}}}{r_{\text{anion}}} \right)
 \end{aligned} \quad (7)$$

It is recognized, for example, that $D_{\text{anion}}/D_{\text{H}}$ becomes smaller with increasing α because r_{DMC} and r_{anion} are assumed to be constant, independent of the polymer fraction and OH content of the gel. And $D_{\text{cation}}/D_{\text{H}}$ becomes smaller than $D_{\text{anion}}/D_{\text{H}}$ when β is present.

RESULTS AND DISCUSSION

1. Interactive Situation of the Ionic Species of the Electrolyte Solutions. Ionic conductivity is the product of ion concentration and mobility. Ion concentration of the electrolyte solution depends on the dissociation condition of the salt. It is acceptable that the dissociation degree of the salt increases with an increasing dielectric constant of the solvent, and the ionic mobility is inversely proportional to the viscosity of the solution according to the Stokes–Einstein equation. We first plotted in Figure 3 the dissociation degree of the salt, α , and the radius of the lithium cation, r_{cation} , which were calculated from eqs 2, 3, and 5 of the electrolyte solutions as a function of measured dielectric constant, ϵ , of the binary solvent and inherent diffusion coefficients of ions, D_{cation}^0 and D_{anion}^0 , which correspond to the ionic mobilities and were calculated from eqs 2 and 3 as a function of measured macroviscosity, η_{m} , of the binary solvent. As expected, α increased with increasing ϵ of the solvent. EC species in the solvent would selectively coordinate to lithium and form solvated lithium cations as $\text{Li}(\text{EC})_n^+$.¹⁸ However, even in the 0:10 solution without EC, the lithium salt was practically dissociated with low α . In this case, less polar

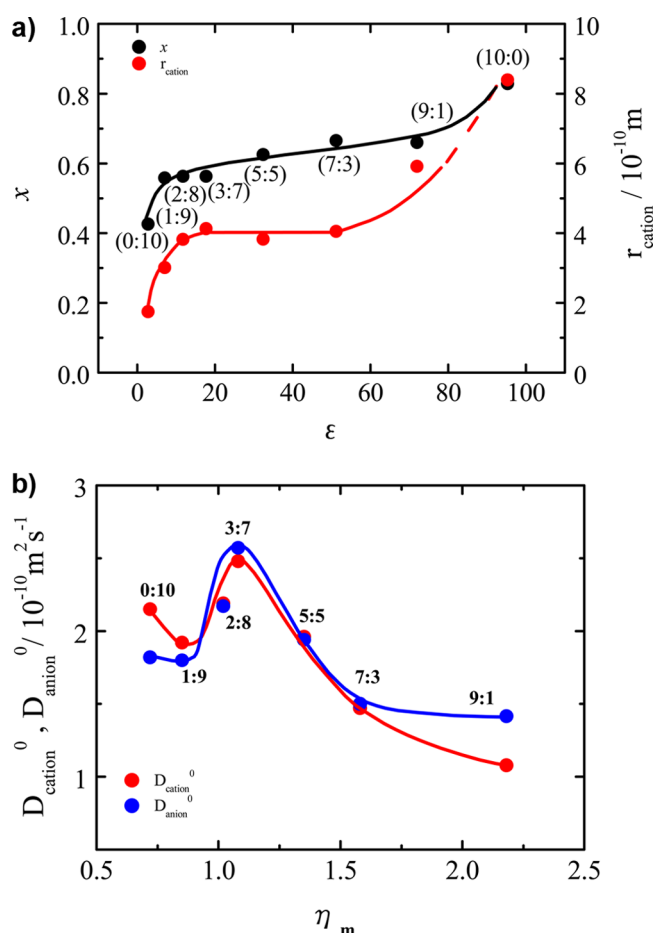


Figure 3. (a) Dissociation degree of the salt, x , and the radius of the cation species, r_{cation} , as a function of the dielectric constant of the binary solvent, EC/DMC, and (b) inherent diffusion coefficients of the cation (D_{cation}^0) and anion (D_{anion}^0) of the electrolyte solution as a function of the macroviscosity of the solvent. x , r_{cation} , D_{cation}^0 , and D_{anion}^0 were calculated using eqs 2, 3, and 5. The dielectric constant and macroviscosity were obtained by measurements. The weight ratios of the binary solvents, EC/DMC, correspond to 0:10, 1:9, 2:8, 3:7, 5:5, 7:3, 9:1, and 10:0.

DMC species would weakly coordinate to the lithium to induce the salt dissociation at the equilibrium state. We can also find the characteristic change of r_{cation} , that is, r_{cation} first increased with ϵ in response to the EC fraction up to the 3:7 solution and then kept constant up to the 7:3 solution and again increased with ϵ in the higher ϵ region. In the first range, the solvation number on a lithium ion increases with an increasing EC content in the solvent. At the 3:7 solution, the molar ratio of EC to Li is estimated to be ~ 3.1 . As confirmed by spectroscopic measurements that $\text{Li}(\text{EC})_3^+$ and $\text{Li}(\text{EC})_4^+$ are the stable structures of the solvated lithium ion, the middle range from 3:7 to 7:3 EC:DMC where r_{cation} is independent of ϵ shows that the stable solvated lithium ions are formed under the equilibrium state of the solutions.^{19,20} Further increase of r_{cation} with ϵ in the 9:1 and 10:0 solutions means that the second and third solvation layers are formed in the EC-rich solvent.

On the other hand, D_{cation}^0 and D_{anion}^0 did not monotonically decrease with η_m contrary to the simple expectation according to the Stokes–Einstein equation. This indicates that the viscosities that the molecular and ionic species feel from the

surrounding species in migration do not directly reflect η_m .⁷ We then plotted the correlation between the calculated microviscosities, η^0 , α^0 , and measured macroviscosity, η_m , in Figure 4.

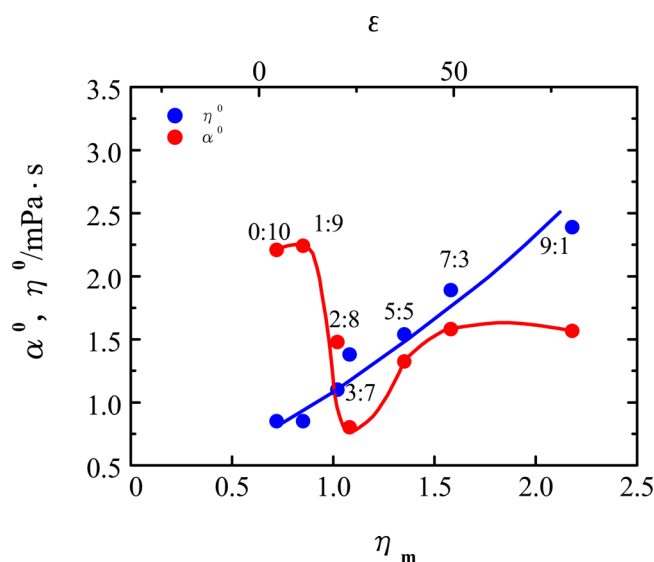


Figure 4. Correlation of the experimental macroviscosity (η_m) and calculated microviscosity components attributed to the van der Waals interaction (η^0) and Coulombic interaction between the cation and anion (α^0) of the electrolyte solutions with different mixing ratio, EC:DMC, of the binary solvents. η^0 and α^0 were calculated according to eq 5.

We can find that η^0 attributed to the van der Waals interaction was almost proportional to η_m . This indicates that the mobility of the neutral species is inversely proportional to η_m . On the other hand, α^0 attributed to the Coulombic interaction showed the change with a minimum in the 3:7 solution. We find that the ionic mobility of the electrolyte solutions strongly reflects α^0 .

Generally, the Coulombic interaction between the species in a solvent decreases with an increasing dielectric constant of the solvent.²¹ The estimated change of α^0 with a minimum, however, indicates that the Coulombic interaction between the ionic species in the solution does not simply follow the generality. It is reasonable to think that α^0 also reflects the equilibrium state of lithium solvation.

As we explained above, the number of solvating EC species would increase with increasing ϵ (EC fraction) of the solvent up to the 3:7 solution. In this region, it is acceptable that α^0 decreases with increasing ϵ according to their general rule. In the 3:7 solution in which $[\text{EC}]/[\text{Li}] = \sim 3.1$, most of all the EC species are located around the lithium to form the stable structure of the solvated lithium, $\text{Li}(\text{EC})_3^+$.¹⁹ This ion would have a long lifetime because there are few residual EC species to exchange with the coordinating EC in the 3:7 solution. Then, the strongly coordinating EC species would be a hard barrier for the approach of TFSI^- anions to the lithium, resulting in the smaller α^0 . In the case of the 7:3 solution in which $[\text{EC}]/[\text{Li}] = \sim 7.8$, on the other hand, the coordination number of EC on a lithium would be 3–4, almost the same as that of the 3:7 solution, due to the same size of r_{cation} in Figure 3a. However, the solvated lithium species are again surrounded by the free EC species in the EC-rich solvent, and the exchange between the coordinating EC and free EC species would be active at the equilibrium state. This situation would also induce

the motility of all species in the solution and give the chance for the TFSI[−] anions, as for the free EC species, to approach the lithium. As a result, the TFSI[−] anion in the EC-rich solutions would be, on average, closer to the lithium cation compared with that of the 3:7 solution, showing larger α^0 . In the case of the EC-poor solutions such as the 1:9 solution, TFSI[−] anions stand, on average, near the lithium cation due to the lower dissociation degree of the salt. Therefore, α^0 would again be larger than that of the 3:7 solution.

2. Gel Electrolytes. PVB Gels: OH Content Dependence.

We first evaluated the interactive effect of the OH groups on the ionic mobility of the gel electrolytes using the PVB polymers with different OH concentration listed in Table 1. We first checked the normalized diffusion values, $D_{\text{cation}}/D_{\text{H}}$ and $D_{\text{anion}}/D_{\text{H}}$, with OH-group content relative to a lithium for each polymer fraction of the gel in Figure 5 to see the presence of

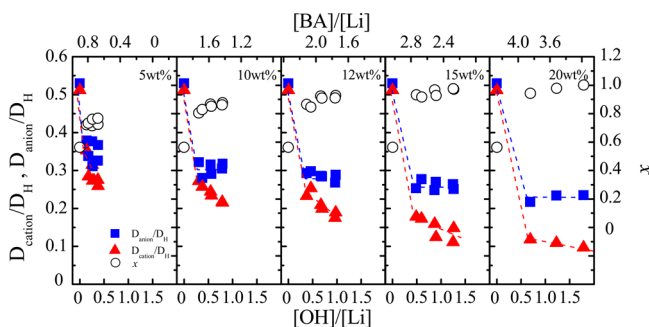


Figure 5. $D_{\text{cation}}/D_{\text{H}}$ and $D_{\text{anion}}/D_{\text{H}}$ and dissociation degree of the salt, α , of the PVB gel electrolytes as a function of $[\text{OH}]/[\text{Li}]$ for each polymer fraction, 5, 10, 12, 15, and 20 wt %. D_{cation} , D_{anion} , and α were estimated using eqs 2 and 3. PVB polymers are listed in Table 1, and the 3:7 EC/DMC solvent was used for gelation. The plots at $[\text{OH}]/[\text{Li}] = 0$ correspond to the values of the electrolyte solution without PVB.

the interactive situation between the ion and OH site. D_{cation} and D_{anion} were calculated from eqs 2 and 3 using the measured D_{Li} , D_{F} , D_{H} , and Λ of the gel electrolyte. It is noted that $D_{\text{cation}}/D_{\text{H}}$ decreased with an increasing OH content of the gel contrary to the independent feature of $D_{\text{anion}}/D_{\text{H}}$ on the OH content. This means that the lithium ions are selectively attracted by the OH site and are restricted in migration. This interactive situation was also proven from the change of the measured relaxation time, T_1 , represented in Figure 6. $T_{\text{Li}}/T_{\text{IH}}$ versus OH content, which reflects the net effect of the OH-group interaction on the relaxation times of the cation species, monotonically decreased with increasing OH content of the gel. On the other hand, $T_{\text{IF}}/T_{\text{IH}}$ of the gels was independent of the OH content except the slight fluctuation of the gels with 20 wt % PVB. This supports the fact that the OH groups selectively attract cation and the TFSI[−] anion is free from the Coulombic effect of the OH groups. We can also find the characteristic difference between the changes of $D_{\text{anion}}/D_{\text{H}}$ and $T_{\text{IF}}/T_{\text{IH}}$. That is, $T_{\text{IF}}/T_{\text{IH}}$ of the gels was same as that of the solution (at $[\text{OH}]/[\text{Li}] = 0$), although $D_{\text{anion}}/D_{\text{H}}$ steeply decreased from the solution to the gel. This suggests that the anion mobility is actually influenced by the PVB dispersion, although the TFSI[−] anion does not directly interact with the OH groups. This situation reveals the presence of the cation–anion interaction, which is another dominant factor of ionic mobility.

Figure 7 represents the calculated microviscosity components, η^i , α^i , and β^i , of the gels with three types of PVB of

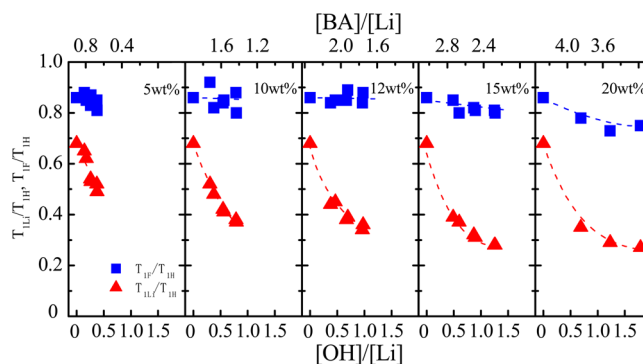


Figure 6. $T_{\text{Li}}/T_{\text{IH}}$ and $T_{\text{IF}}/T_{\text{IH}}$ of the PVB gel electrolytes as a function of $[\text{OH}]/[\text{Li}]$ for each polymer fraction. T_{Li} , T_{IF} , and T_{IH} were obtained by measurements. PVB polymers are listed in Table 1, and the 3:7 EC/DMC solvent was used for gelation. The plots at $[\text{OH}]/[\text{Li}] = 0$ correspond to the values of the electrolyte solution without PVB.

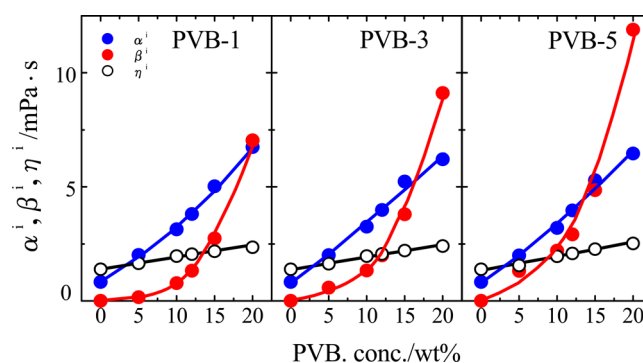


Figure 7. Microviscosities, η^i , attributed to the van der Waals interaction, α^i and β^i from the Coulombic interaction between the cation and anion and between the cation and OH group, respectively, as a function of the PVB fraction of the gel. These values were calculated according to eq 6. The polymers of PVB-1, -3, and -5 and the 3:7 EC/DMC solvent were used for gelation.

different OH concentration. The η^i and α^i values increased with the PVB fraction of the gel independent of the kind of PVB. This means that the η^i and α^i changes are associated with the change of the polymer fraction and not with the change of the content of the attractive OH group. On the other hand, the β^i change with the PVB fraction depended on the kind of PVB. The higher the OH concentration of the PVB, the larger the β^i value that was obtained. This indicates that the cation mobility is restricted in accordance with the OH-site increase in the gel. It is also interesting that α^i originated from the cation–anion interaction increase with the PVB fraction of the gel. This reveals that the cation–anion interaction is really correlated not with the OH content but with the PVB content of the gel, although we do not know the reason now. Anyway, this is the cause of the apparent difference of $D_{\text{anion}}/D_{\text{H}}$ between the solution and gel observed in Figure 5.

PVB Gels: Solvent Polarity Dependence. In order to elucidate the effect of the polarity of the liquid solvent associated with the lithium-solvation condition on the interactive situation between the species in the gels and, consequently, on the ionic mobility, we compared the gels with three different solutions: 0:10, 3:7, and 7:3 EC/DMC solutions and with a polymer, PVB-6. Figure 8 shows the changes of the calculated dissociation degree of the salt, α , inherent diffusion

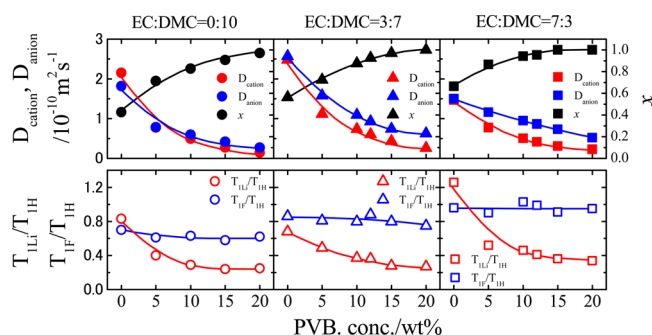


Figure 8. Inherent diffusion coefficients, D_{cation} and D_{anion} , and the dissociation degree of the salt, x , by calculation, and normalized relaxation time, $T_{\text{ILi}}/T_{\text{IH}}$, $T_{\text{1F}}/T_{\text{IH}}$ of the PVB gels with the 0:10, 3:7, and 7:3 EC/DMC solutions as a function of the PVB (PVB-6) fraction.

coefficients, D_{cation} and D_{anion} , and measured relaxation times, $T_{\text{ILi}}/T_{\text{IH}}$ and $T_{\text{1F}}/T_{\text{IH}}$ (normalized values), as a function of the PVB fraction of the gel. The dissociation degree of the salt increased with an increasing PVB fraction for all types of gel. This suggests that the attractive effect of the OH groups on the lithium promoted the salt dissociation in any type of gel. This is also confirmed from the changes of $T_{\text{ILi}}/T_{\text{IH}}$ which decreased with the PVB fraction. On the other hand, $T_{\text{1F}}/T_{\text{IH}}$ was independent of the PVB fraction for all types of gel, indicating that there is no interaction between the anion and OH in any lithium-solvated situation.

Microviscosity components of the gels, η^i , α^i , and β^i , by calculation are shown in Figure 9. We find that the η^i value

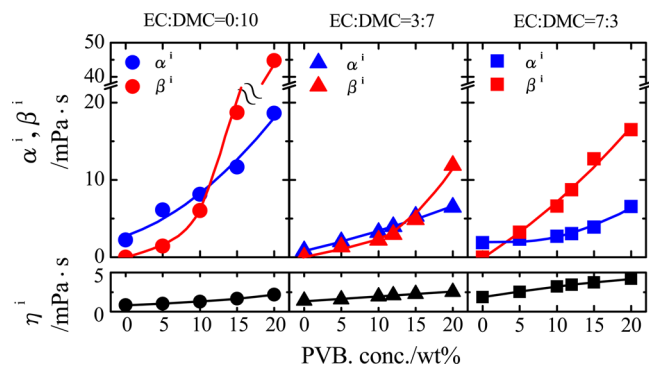


Figure 9. Microviscosities, η^i , α^i , and β^i of the gels with the 0:10, 3:7, and 7:3 EC/DMC solutions as a function of the PVB (PVB-6) fraction. These values were calculated according to eq 6. In order to avoid data overlapping, η^i was plotted at the bottom, independently.

slightly increased with the PVB fraction in the same manner for three types of gel and the contribution to the total viscosity of the gel was small in the PVB-rich region. The α^i and β^i values of the ionic species also increased with the PVB fraction of the gel. However, the changing manner showed the characteristic feature correlated with the polarity of the liquid solvent. It is expected that the increasing rate of β^i , which is attributed to the cation–OH site interaction, reflects the solvation condition of the lithium cation. In the case of the gels with the 3:7 solution, the lithium is stably solvated by three EC species whose exchange rate with other EC species is fairly low as explained previously. As a result, it is difficult for the OH site to approach the lithium, leading to the lowest increasing rate of β^i . On the contrary, the lithium cation in the gels with the 0:10 solution

may be weakly coordinated by the DMC species and could provide the large space or chance for the Lewis basic OH site to attack the lithium. That would be the cause of the largest increasing rate of β^i with the OH content. It is also noted that α^i , attributed to the cation–anion interaction, increased with the PVB fraction for any gels. It seems that the increasing rate of α^i is correlated with that of β^i . However, the results of Figure 7 proved that the α^i increase was independent of the OH-site content. Therefore, the difference of the increasing rate of α^i among the three types of gel would also be associated with the solvation condition of the lithium cation because the solvation number and strength could affect the position of the anion species around a lithium cation.

Polymer Gels with Different Polymers, PVB, PEO, and PVDF-HFP. In order to elucidate the interactive situation between the species and the consequent ionic mobilities in the gel, depending on the kind of polar group and chemical structure of the polymer, we compared the dynamic properties of the gels with PVB, PEO, and PVDF-HFP in Figure 10. It is

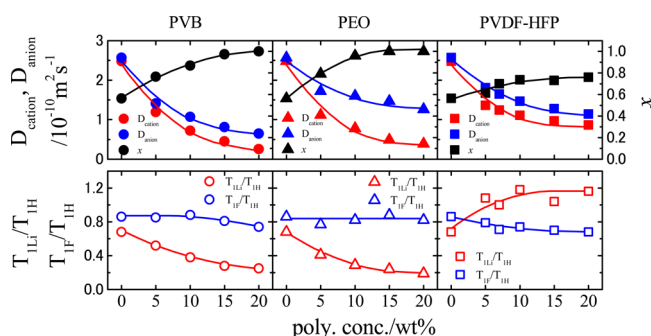


Figure 10. Inherent diffusion coefficients, D_{cation} and D_{anion} , and dissociation degree of the salt, x , by calculation and normalized relaxation time, $T_{\text{ILi}}/T_{\text{IH}}$ and $T_{\text{1F}}/T_{\text{IH}}$, of the gels with the PVB-6, PEO, and PVDF-HFP polymers as a function of the polymer fraction.

characteristic that the dissociation degree of the salt, by calculation of the PVDF-HFP gels, did not increase so much with the polymer fraction compared with those of other gels. This indicates that the interactive situation of the PVDF-HFP polymer with the ions is weak. In practice, $T_{\text{1F}}/T_{\text{IH}}$ was almost constant, independent of the polymer fraction for all kinds of gel, indicating that the TFSI[−] anion was inert with any type of polymer. On the other hand, it is worth noting that $T_{\text{ILi}}/T_{\text{IH}}$ of the PVDF-HFP gels increased with the polymer and, in particular, was larger than unity, contrary to the decreasing manner of the PVB and PEO gels which is attributed to the selective interaction between the lithium and the Lewis basic –OH and –O– sites of the PVB and PEO, respectively. Although we do not know the obvious reason why T_{ILi} and $T_{\text{ILi}}/T_{\text{IH}}$ increased with the PVDF-HFP fraction, which correspondingly liquefies in spite of a viscous polymer increase, it is acceptable that the PVDF-HFP polymer has no attractive effect on the cation to restrict the cation motility.

A comparison of the microviscosities, η^i , α^i , and β^i , of these gels is shown in Figure 11. The value of η^i slightly increased with the polymer fraction in the same way for three types of gel. On the other hand, α^i and β^i changes showed the characteristic feature depending on the kind of polymer. In the case of the PVDF-HFP gels, β^i attributed to the cation–polymer interaction was low and almost constant with the polymer fraction, suggesting that there is no attractive site on the PVDF-

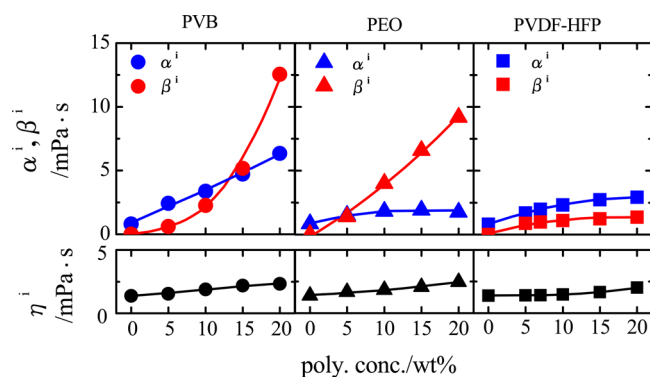


Figure 11. Microviscosities, η^i , α^i , and β^i , of the gels with PVB-6, PEO, and PVDF-HFP polymers as a function of the polymer fraction. These values were calculated according to eq 6. In order to avoid data overlapping, η^i was plotted at the bottom, independently.

HFP, except the physical barrier effect on ion migration in the gel. This noninteractive situation is also reflected in the small change of the dissociation degree of the salt of the PVDF-HFP gels in Figure 10. On the other hand, β^i of the PVB and PEO gels monotonically increased with the polymer fraction. These changes are attributable to the selective interaction between the lithium and the Lewis basic $-\text{OH}$ and $-\text{O}-$ site of the respective PVB and PEO. However, the changes of α^i are different between the PVB and PEO gels. Contrary to the increasing feature of the PVB gels with the polymer fraction, α^i of the PEO gels was almost constant with the polymer similar to the changing manner of α^i of the PVDF-HFP gels. This may be attributable to the polymer structure associated with, for example, the type of polar group and its configuration, molecular structure, network morphology, and molecular weight of the polymer.

In conclusion, we could systematically evaluate the interactive situations which affect the ionic mobility of the electrolytes. In the case of the electrolyte solutions before gelation, the Coulombic interaction between the cation and anion responsible for the microviscosity, α^0 , dominates the ionic mobility. The 3:7 solution showed the smallest α^0 value and highest D_{cation} in the solutions with different EC:DMC mixing ratios. This would be attributed to the stability of the solvated lithium ion. In the 3:7 solution, the $[\text{EC}]/[\text{Li}]$ value is ~ 3.1 , and most of all the EC species are located around the lithium ion to form the stabilized solvated lithium ion such as $\text{Li}(\text{EC})_3^+$. As a result, there are no free EC species for exchange with the coordinating EC. That is, the solvated lithium first prepared has a long lifetime. It is then difficult for the TFSI $^-$ anions to approach the lithium due to the strong barrier of the solvating EC. This would be the reason why α^0 of the 3:7 solution was at a minimum.

In the case of the gel electrolytes, the Coulombic interaction between the ion and polar sites on the polymer, if it is, also affects the ionic mobility. Cation mobility decreased with increasing β^i attributed to the interaction between the lithium and the Lewis basic polar sites of the PVB and PEO. And β^i increased with the polar site content of the gels. It is also characteristic that α^i , attributed to the cation–anion interaction, increased with the polymer fraction of the PVB gels contrary to the independent feature of α^i of the PEO gels with the polymer increase. This difference is due to the difference of the molecular structure of the polymer, especially associated with

the polarity, configuration, concentration of the polar groups, and morphology of the polymer network.

In the process of designing the polymer gel electrolytes, increases of the dissociation degree of the salt and cation mobility would be the dominant evaluation indexes for the practical performance of lithium batteries. Salt dissociation starts with the solvation of the liquid polar-solvent species and, in some cases, the attraction of the polar site of the polymer on the lithium. However, from the aspect of cation mobility enhancement, it is desirable to reduce the cation size by removing the solvating species. The appropriate interactive effect of the polar sites of the polymer could promote the salt dissociation without a change in the cation size. If there are acidic polar groups on the chains, they could attract anions and restrict the anion mobility. This situation is ideal for enhancing the salt dissociation for increasing the cation concentration without enlarging the size. This results in an increase in the cation transport number. We also learned that the control of the cation–anion interaction, which depends on the type of polymer of the gel electrolyte, is significant for the effort of increasing the cation mobility.

AUTHOR INFORMATION

Corresponding Author

*E-mail: yuria-saitou@aist.go.jp. Tel.: +81-72-751-4527. Fax: +81-72-751-9623.

Notes

The authors declare no competing financial interest.

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