Li⁺ Ion Transport in Polymer Electrolytes Based on a Glyme-Li Salt Solvate Ionic Liquid

Ryosuke Kido,[†] Kazuhide Ueno,[†] Kaori Iwata, Yuzo Kitazawa, Satoru Imaizumi, Toshihiko Mandai,
Kaoru Dokko, Masayoshi Watanabe*

Department of Chemistry and Biotechnology, Yokohama National University,

79-5 Tokiwadai, Hodogaya-ku, Yokohama 240-8501, Japan

AUTHOR EMAIL ADDRESS: mwatanab@ynu.ac.jp

TITLE RUNNING HEAD: Polymer Electrolyte of Solvate Ionic Liquids

[†] R. K. and K. U. equally contributed to this work.

CORRESPONDING AUTHOR FOOTNOTE: To whom correspondence should be addressed.

Telephone/Fax: +81-45-339-3955. E-mail: mwatanab@ynu.ac.jp

ABSTRACT

Polymer electrolytes (PEs) have served as the focus of intensive research as new ion-conducting materials, especially for lithium battery applications. A new strategy to develop fast lithium-conducting PEs is reported here. The thermal, ionic transport, and electrochemical properties of polymer solutions in a glyme-Li salt solvate ionic liquid, $[\text{Li}(\text{G4})_1][\text{TFSA}]$, composed of an equimolar mixture of lithium bis(trifluoromethanesulfonyl)amide ($\text{Li}[\text{TFSA}]$) and tetraglyme (G4), were characterized. Poly(ethylene oxide) (PEO), poly(methyl methacrylate) (PMMA), and poly(butyl acrylate) (PBA) were combined with $[\text{Li}(\text{G4})_1][\text{TFSA}]$ in order to explore the effects of polymer structure on the properties. The self-diffusion coefficient ratio of the glyme and Li^+ ions ($D_{\text{G}}/D_{\text{Li}}$) was investigated to evaluate the stability of the complex (solvate) cations. The $D_{\text{G}}/D_{\text{Li}}$ values suggested that the $[\text{Li}(\text{G4})_1]^+$ complex cations underwent a ligand exchange reaction between G4 and PEO in the PEO-based solution, whereas the cations remained stable ($D_{\text{G}}/D_{\text{Li}} = 1$) in the PMMA- and PBA-based solutions. The robustness of the $[\text{Li}(\text{G4})_1]^+$ complex cations in the PMMA- and PBA-based solutions was reflected in high weight-loss temperature, greater Li transference number, and high oxidative stability. Owing to the lower glass transition temperature and low affinity towards Li^+ ions, the PBA-based solutions yielded superior lithium transport properties (ionic conductivity of $10^{-4} \sim 10^{-3} \text{ Scm}^{-1}$ and Li transference number as high as 0.5) among the investigated polymer solutions.

KEYWORDS: solvate ionic liquid, polymer electrolyte, polymer-in-salt, ionicity, glyme

1. Introduction

Polymer electrolytes (PEs) have been the focus of intensive research over the last several decades owing to their potential use as solid-state electrolytes [1-3]. Significant efforts have been focused on the development of lithium-conducting PEs for applications in lithium batteries [4, 5]. The reported lithium-conducting PEs can be divided into the following two categories: (i) solvent-free, dry PEs and (ii) gel PEs. The former consists of a lithium salt and a host polymer that is capable of solvating the lithium salt, and polyethylene oxide (PEO) and its derivatives are predominantly used as the polymer matrix. In dry PEs, the mobility of the Li^+ ions is coupled with the segmental motions of the solvating polymer chains, leading to a relatively low ionic conductivity of $10^{-6}\sim 10^{-4} \text{ Scm}^{-1}$ at ambient temperatures, and a Li^+ transference number of far lower than 0.5. The latter PEs incorporate additional molecular solvents and/or plasticizers [6, 7]. This has been a compromise for enhancing the ionic conductivity of the dry PEs. Unlike with dry PEs, the ions fundamentally travel with the solvents in gel PEs, and Li^+ solvation by the polymer matrix is less significant for ionic transport. While gel PEs provide a high ambient-temperature conductivity of $10^{-4}\sim 10^{-3} \text{ Scm}^{-1}$, they suffer from solvent-derived drawbacks such as high volatility and flammability. The reported Li^+ transference number is lower than 0.5 even for highly conductive gel PEs [5].

Among the reported strategies that do not require volatile additives [8, 9], combining a low-melting salt with the polymer matrix is highly effective for improving the ionic transport properties of PEs. The class of PEs obtained by this method are termed “polymer-in-salt” electrolytes [10], and were independently reported by Angell [11] and one of the authors of this paper [12] in 1993 for the first time. We proposed the use of polymer electrolytes consisting of polymers and ionic liquids (ILs), which are molten salts with melting points lower than 100°C [13-15]. The incorporated ILs serve not only as non-flammable and nonvolatile plasticizers, but also as ionic carriers. The inherently weak coordination of the constituent ions of ILs leads to attenuated polymer-ion interactions and gives rise to translational ionic motion decoupled from the segmental motion of the polymer matrix [16, 17].

1 In order to introduce Li^+ ion transport properties, Li salts must be doped in IL-based PEs [18-20].
2
3 However, the addition of the Li salt results in a higher local viscosity (microviscosity) in the PEs and
4
5 thus decreases the ionic conductivity. Furthermore, the coexistence of organic and Li cations leads to a
6
7 low Li^+ transference number, as reported for liquid electrolytes based on IL and Li salt binary mixtures
8
9 [21]. A simple and effective approach to solving these bottlenecks is to replace the binary system with a
10
11 low-melting Li salt (i.e., lithium IL) [22].
12
13

14
15 Although Li salts generally possess high melting temperatures, recent works have shown that
16
17 certain concentrated mixtures of oligo(ethylene glycol) dimethyl ethers (so-called glymes) and Li salts
18
19 can form low-melting complexes and behave like ILs in the molten state [23]. Strong complexation
20
21 between the glymes and the Li^+ ions yields a long-lived $[\text{Li}(\text{glyme})_1]^+$ cation, where the glyme molecule
22
23 has a crown ether-like conformation [24]. This class of molten complexes are termed “solvate” ILs, and
24
25 are recognized as a new family of ILs in which ligand molecules (as the third species) strongly
26
27 coordinate the cation and/or anion of the salts [25]. As a result, glyme-Li salt molten complexes,
28
29 composed of discrete $[\text{Li}(\text{glyme})_1]^+$ cations and counter anions, can serve as low-melting Li salts for
30
31 polymer-in-salt electrolytes. A representative example of a glyme-Li salt solvate IL is an equimolar
32
33 molten complex of tetraglyme (G4) and lithium bis(trifluoromethanesulfonyl)amide ($\text{Li}[\text{TFSA}]$),
34
35 $[\text{Li}(\text{G4})_1][\text{TFSA}]$ [26]. $[\text{Li}(\text{G4})_1][\text{TFSA}]$ exhibits high ionic conductivity (1.6 mS cm^{-1} at 30°C) and a
36
37 high Li^+ transference number (estimated to be ~ 0.5).
38
39
40
41
42
43
44

45 In this work, we focused on PEs incorporating $[\text{Li}(\text{G4})_1][\text{TFSA}]$ as a low-melting lithium salt. This
46
47 type of PEs was previously reported by Smyrl and coworkers, who utilized polyelectrolytes and a
48
49 glyme-Li salt equimolar complex [27]. Similar to other PEs, the structure of the polymer backbone
50
51 affects the ionic transport properties due to the varying stiffness and polarizability [28]. Here, three
52
53 different host polymers, namely PEO, poly(methyl methacrylate) (PMMA), and poly(butyl acrylate)
54
55 (PBA), were combined with $[\text{Li}(\text{G4})_1][\text{TFSA}]$ to fabricate novel polymer-in-salt-type electrolytes. With
56
57 solvate ILs, the stability of the complex cation dictates the electrolyte properties such as thermal
58
59 stability, electrochemical oxidative stability, and ionic transport properties [29]. Therefore, studies
60
61
62
63
64
65

1 regarding the stability of the $[\text{Li}(\text{G4})_1]^+$ cation in different polymer matrices are crucial for this type of
2
3 PEs. The effects of the polymer matrix on the ionic transport properties were investigated in terms of the
4
5 diffusion coefficients of the ions measured by pulsed-field-gradient (PFG) NMR and ionic conductivity.
6
7 The thermal properties and diffusivity of the glymes and the Li^+ ions were also analyzed in order to
8
9 evaluate the stability of the $[\text{Li}(\text{G4})_1]^+$ cations. To demonstrate the potential application in lithium
10
11 batteries, we also investigated the electrochemical stability of the polymer solutions in $[\text{Li}(\text{G4})_1][\text{TFSA}]$.
12
13
14
15
16
17
18

19 2. EXPERIMENTAL

22 **2.1 Materials** Purified G4 (water content < 50 ppm) was kindly supplied by Nippon Nyukazai Co.,
23
24 Ltd., and battery-grade $\text{Li}[\text{TFSA}]$ was provided courtesy of Solvay. $[\text{Li}(\text{G4})_1][\text{TFSA}]$ was prepared by
25
26 mixing an equimolar amount of $\text{Li}[\text{TFSA}]$ and G4 in an Ar-filled glove box (VAC, $[\text{H}_2\text{O}] < 1$ ppm).
27
28 PEO was purchased from Aldrich and dried under vacuum at elevated temperatures prior to use. PMMA
29
30 and PBA were synthesized by the atom transfer radical polymerization (ATRP) method [30]; the
31
32 detailed synthetic procedure is described in Supplementary Materials. The polymer solutions were
33
34 prepared by mixing the homopolymer and $[\text{Li}(\text{G4})_1][\text{TFSA}]$ in various concentrations. For the PBA- and
35
36 PEO-based solutions, uniform polymer solutions were obtained by directly mixing the homopolymer
37
38 and the solvate IL at 60 °C in the glove box. In the case of the PMMA system, PMMA and the solvate
39
40 ILs were dissolved in a proper amount of dichloromethane to ensure complete mixing. Subsequently,
41
42 dichloromethane was gently evaporated under reduced pressure, and completely removed from PMMA-
43
44 based solutions *in vacuo*.
45
46
47
48
49
50

51 **2.2 Measurements** The thermal stability of the samples was investigated by thermogravimetric (TG)
52
53 analysis on a Seiko Instruments thermogravimetry/differential thermal analyzer (TG-DTA 6200) from
54
55 room temperature to 550 °C at a heating rate of 10 °C min^{-1} under a nitrogen atmosphere. Differential
56
57 scanning calorimetry (DSC) was carried out on a Seiko Instruments DSC 6220. The samples were
58
59 sealed in an Al pan in the glove box. The sample pans were first heated to 100 °C and cooled to -150 °C
60
61
62
63
64
65

1 and then heated again to 100 °C at a heating and cooling rate of 10 °C min⁻¹. The second heating scan
2
3 was recorded as the DSC thermogram to determine the glass transition temperature (T_g). The T_g was
4
5 determined as the onset of the heat flow step.
6

7
8 The ionic conductivity was measured by the complex impedance method using a computer-
9
10 controlled Hewlett-Packard 4192A LF impedance analyzer over the frequency range from 5 Hz to 13
11
12 MHz at an alternative voltage amplitude of 10 mV. A dip-type glass cell equipped with two platinum
13
14 electrodes was used. The cell constant was calibrated by measuring the conductivity of a standard 0.01
15
16 mol dm⁻³ KCl aqueous solution (Kanto Kagaku) at 25 °C. The measurements were conducted in the
17
18 temperature range from 100 to -20 °C in a Tabai Espec SU-220 temperature-controlled chamber. All
19
20 samples were thermally equilibrated at each temperature for 1 h prior to the measurements. The
21
22 reproducibility of all results was confirmed by repeated measurements under the same experimental
23
24 conditions.
25
26
27
28
29

30 The self-diffusion coefficients of the ions in the polymer solutions were determined by PFG-NMR
31
32 measurements using a modified Hahn spin-echo sequence incorporating a PFG in each τ period. The
33
34 measurements were performed on a JEOL-ECX 400 NMR spectrometer with a 9.4 T narrow bore
35
36 superconducting magnet equipped with a PFG probe and current amplifier. ¹H, ⁷Li and ¹⁹F spectra were
37
38 measured for G4, Li⁺ cations, and [TFSA]⁻ anions respectively. In this measurement, the value of the
39
40 interval length between the two gradient pulses (Δ) was set to 50 ms, and the duration of the field
41
42 gradient (δ) was adjusted to a constant value of 3–5 ms. The magnitude of the field gradient (g , 0–13
43
44 T/m) was varied for recording the spin-echo signal intensity (S). The standard deviations of the diffusion
45
46 data were less than 5%. The details of the PFG-NMR measurements are described in Supplementary
47
48 Materials.
49
50
51
52
53

54 The oxidative electrochemical stability of the polymer solutions was evaluated by linear sweep
55
56 voltammetry (LSV) at a scan rate of 1.0 mV s⁻¹. Lithium metal foil was used as the counter and
57
58 reference electrodes and a platinum disk was used as the working electrode. The reductive
59
60 electrochemical stability was investigated using cyclic voltammetry (CV) at a scan rate of 1.0 mV s⁻¹ in
61
62
63
64
65

a three-electrode cell. The counter electrode was lithium metal, and the working electrode was a nickel plate, and lithium metal foil was used as the reference electrode. These electrochemical measurements were performed at 30 °C.

3. RESULTS AND DISCUSSION

Table 1. Number-average molecular weight (M_n), polydispersity index, and glass transition temperature (T_g) of the polymers.

Polymer	$M_n (\times 10^4 \text{ g mol}^{-1})$	$M_w/M_n (-)$	$T_g (^\circ\text{C})$
PEO	2.6	1.4	-57
PMMA	3.0	1.1	119
PBA	1.9	1.1	-53

PMMA and PBA used in this study were synthesized by ATRP, and they had similar molecular weights as commercially available PEO and a narrow polydispersity. The number-average molecular weight (M_n), polydispersity index (M_w/M_n), and glass transition temperature (T_g) of the polymers are listed in **Table 1**. All polymers were compatible with $[\text{Li}(\text{G4})_1][\text{TFSA}]$, and the polymers were dissolved in $[\text{Li}(\text{G4})_1][\text{TFSA}]$ up to 40 wt%. The mixtures were typically not rubbery solid materials, but were viscous polymer solutions in $[\text{Li}(\text{G4})_1][\text{TFSA}]$. We employed these polymer solutions as a simple model to study the ionic transport properties of PEs in the lithium solvate IL. A self-standing PE membrane can be readily obtained by introducing either physical or chemical cross-linking points on the polymers. A polymer gel membrane swollen with ILs (called ion gels) was prepared by the *in situ* polymerization of vinyl monomers [31, 32], by the cross-end coupling reaction of tetra-arm poly(ethylene glycol) [33], or by the self-assembly of ABA-type triblock copolymers where A and B are insoluble and soluble sequences, respectively [33-36].

Figure 1. (a) Thermogravimetric curves for pure G4, [Li(G4)₁][TFSA], and the polymer solutions in [Li(G4)₁][TFSA].

(b) The decomposition temperature, T_d , was defined as a 5 % weight loss in the TG curve as a function of polymer concentration. The solid and broken lines represent the T_d of [Li(G4)₁][TFSA] and pure G4, respectively.

3.1 Thermal properties

As mentioned earlier, the formation of robust [Li(G4)₁]⁺ complex cations plays a pivotal role in the electrolyte properties such as thermal and electrochemical stability as well as ionic transport. **Figure 1a** shows the thermogravimetric (TG) data of the polymer solutions in [Li(G4)₁][TFSA] along with the data for pure G4 and [Li(G4)₁][TFSA]. The TG curves exhibit multi-step weight loss, except for pure G4 which shows a one-step weight loss arising from its vaporization upon heating. The first weight loss of [Li(G4)₁][TFSA] and the polymer solutions is attributed to the volatilization of G4 because the decomposition temperature of pure Li[TFSA] and the polymers are higher than 300 °C. The subsequent weight loss steps are attributed to the further evaporation of G4 and the thermal decomposition of the lithium salt and polymers. In this study, the thermal decomposition temperature (T_d) was defined as the temperature where a 5% weight loss in the thermogravimetric curves occurs: i.e., T_d depends on the first vaporization of G4 in the polymer solutions. In **Figure 1b**, the T_d values are plotted as a function of polymer concentration. The PMMA-based systems exhibit a slightly higher T_d than that of [Li(G4)₁][TFSA] at concentrations greater than 20 wt%, and the change in T_d was less pronounced for the PBA-based solutions. PMMA and PBA would interact poorly with Li⁺ ions because of their low polarity and donor number. Hence, [Li(G4)₁]⁺ cations are stable in these polymer solutions, leading to a

T_d that is comparable to or even higher than that of $[\text{Li}(\text{G4})_1][\text{TFSA}]$ ($> 200\text{ }^\circ\text{C}$) [29]. In contrast, significant decreases in T_d with increasing polymer concentrations were observed for the PEO-based systems. The reduction in T_d suggests that uncoordinated (or only weakly coordinated) G4 molecules are partially evolved in the PEO-based solutions.

Figure 2. Dependency of glass transition temperature (T_g) on polymer concentration in $[\text{Li}(\text{G4})_1][\text{TFSA}]$, as determined by DSC.

The glass transition temperature (T_g) of PE systems is closely related to the ionic mobility (or local viscosity in PEs), and critically affects the ionic conductivity. In the DSC thermograms, only a single T_g was detectable in each polymer solution despite the different components in the binary mixture of the polymers and $[\text{Li}(\text{G4})_1][\text{TFSA}]$. **Figure 2** shows the T_g of the polymer solutions as a function of polymer concentration. The T_g value of a compatible binary system (A and B) locates between the T_g values of the two components (T_{gA} and T_{gB}), as predicted by the Gordon and Taylor equation ($T_g = w_A T_{gA} + k_{GT}(1-w_A)T_{gB}$) [37] and the Fox equation ($1/T_g = w_A/T_{gA} + (1-w_A)/T_{gB}$) [38], where w_A and k_{GT} are the weight fractions of component A and the experimental parameter, respectively. These relationships are likely valid for the PMMA-based solutions. The T_g of the solutions increases with increasing concentrations of PMMA and can be well fitted by the Gordon Taylor equation as shown in Figure S1. For the PBA-based solutions, the change in T_g as a function of polymer concentration is not noticeable because the T_g of PBA ($-53\text{ }^\circ\text{C}$) is very close to that of $[\text{Li}(\text{G4})_1][\text{TFSA}]$ ($-54\text{ }^\circ\text{C}$) [29]. On

the contrary, the T_g values of the PEO-based solutions are lower than the T_g values of parent PEO and [Li(G4)₁][TFSA]; these values cannot be rationalized by the aforementioned equations. It is likely that the uncoordinated G4 (as a third component) decreases the T_g of the PEO-based solutions. Although pure G4 showed only a melting point (T_m) at -30 °C in the DSC measurements, the T_g of pure G4 can be estimated to be -111 °C according to the empirical rule $T_g = (2/3)T_m$, where T_g and T_m are in absolute temperatures [39]. As a consequence, the presence of uncoordinated G4 can explain the decrease in T_g in the PEO-based solutions. As seen in **Figures 1 and 2**, the dependence of the thermal properties (T_d and T_g) on the nature of the polymers suggests a difference in the stability of [Li(G4)₁]⁺ in the polymer solutions.

Figure 3. (a) Arrhenius plot of ionic conductivity for [Li(G4)₁][TFSA] solvate IL and 20 wt% polymer solutions in [Li(G4)₁][TFSA]. Data for [Li(G4)₁][TFSA] was obtained from ref 26. (b) T_g -scaled Arrhenius plot of ionic conductivity.

3.2 Ionic transport properties

Figure 3a shows the Arrhenius plot of ionic conductivity (σ) for [Li(G4)₁][TFSA] solvate IL [26] and 20 wt% polymer solutions in [Li(G4)₁][TFSA]. Although the ionic conductivity decreases upon addition of the polymers to [Li(G4)₁][TFSA], it still exceeds 10^{-4} Scm^{-1} at room temperature. The

1 mixtures were not rubbery solid materials but were viscous polymer solutions. However, we assume that
 2
 3 the ion transport properties can be maintained even in much higher molecular weight polymers and also
 4
 5 in cross-linked networks, which are suitable for practical applications. We understand that critical
 6
 7 molecular weight for entanglement (M_c) of neat molten polymers is lower than 10^4 in most cases [40]. In
 8
 9 the case of PEO, M_c is reported to be 3200; and diffusivity of Li^+ in PEO- LiCF_3SO_3 complexes
 10
 11 measured by PFG-NMR becomes insensitive above M_c , although higher diffusivity is observed when
 12
 13 molecular weight of PEO is lower than the M_c [41]. When polymers having molecular weight higher
 14
 15 than M_c are diluted by solvents, the polymer chains are overlapped together at higher concentration than
 16
 17 critical concentration (c^*). In the case of polymers having molecular weight of 10^4 , c^* is lower than 10
 18
 19 wt% [40] in most cases though c^* depends on the solvent species. From these results, we assume that in
 20
 21 our experimental conditions (molecular weight of PMMA, PBA, and PEO $> 10^4$ and the concentration =
 22
 23 20 wt%) the polymer chains are overlapped together. Therefore, transport property reported in this paper
 24
 25 can be maintained even in much higher molecular weight polymers and also in cross-linked networks.
 26
 27 Actually, we reported self-standing membranes made up of $[\text{Li}(\text{G4})][\text{TFSA}]$ and polystyrene-PMMA-
 28
 29 polystyrene ABA tri-block copolymer (20-30 wt%). That membrane showed conductivity of 0.2
 30
 31 mS cm^{-1} at 30 °C [36], which is comparable to that of the PMMA-polymer solution studied here.

32
 33 Among the polymer solutions, the ionic conductivity is the highest for the PEO-based solution, and
 34
 35 is the lowest for the PMMA-based solution. The PBA-based solution shows an ionic conductivity
 36
 37 equivalent to that of PEO-based solution at lower temperatures, but it becomes slightly lower at higher
 38
 39 temperatures. Ionic conductivity is governed by the carrier concentration and the carrier mobility in PEs.
 40
 41 The difference in conductivity would be primary due to the different mobilities of the ionic carriers
 42
 43 because the number of the ionic carriers seemed to be comparable for these 20 wt% polymer solutions
 44
 45 in $[\text{Li}(\text{G4})_1][\text{TFSA}]$. The larger temperature difference between T_g and the operating temperature T
 46
 47 results in more vigorous motions of the polymers and $[\text{Li}(\text{G4})_1][\text{TFSA}]$. Therefore, the lower T_g is
 48
 49 responsible for the higher conductivity of the PEO- and PBA-based solutions. In **Figure 3b**, the
 50
 51 Arrhenius plot of the ionic conductivity is scaled by the corresponding T_g values. The ionic
 52
 53

conductivities for the polymer solutions exhibit different temperature dependencies, while the high temperature limits seems to reach similar values. The PBA-based solution exhibits the highest conductivity at the same T_g -scaled temperature among the studied polymer solutions.

The temperature dependence of the ionic conductivity can be described using the Vogel–Fulcher–Tamman (VFT) expression:

$$\sigma(T) = \sigma_0 \exp \frac{B}{(T_0 - T)}$$

where σ_0 is the pre-exponent conductivity, B is the adjustable parameter, and T_0 is the vanishing mobility temperature. In addition, B can be replaced by CT_0 , where C is inversely proportional to fragility parameter m in the characterization of glass forming liquids [42]. The obtained parameters are listed in **Table 2**. The parameter C accounts for the curvature of the temperature dependent VFT plots, which deviate from typical Arrhenius behaviors. The values of C for the PBA-based solutions are similar to those of $[\text{Li}(\text{G4})_1][\text{TFSA}]$, implying that the conduction is dictated by the temperature dependent viscosity of $[\text{Li}(\text{G4})_1][\text{TFSA}]$ in the polymer solution. On the other hand, the larger C value of the PEO-based solutions indicates that the conductivity decreases more steeply with temperature. The steeper temperature dependence for the PEO-based solutions suggests an ion conduction process that is different from that in $[\text{Li}(\text{G4})_1][\text{TFSA}]$, and is presumably ascribed to the formation of a PEO- Li^+ ion complex where the motion of the Li^+ ions is coupled to the segmental motion of the PEO chains.

Table 2. VFT fit parameters for ionic conductivity of $[\text{Li}(\text{G4})_1][\text{TFSA}]$ and the polymer solutions.

	σ_0 (S cm ⁻¹)	C (-)	T_0 (K)	R^2 (-)
$[\text{Li}(\text{G4})_1][\text{TFSA}]$	0.226	2.74	195	0.999
20 wt% PMMA	0.172	3.48	200	0.999
20 wt% PBA	0.139	2.99	196	0.999
20 wt% PEO	0.458	4.16	185	0.999

Figure 4. The Stejskal-Tanner plots of $\ln(S/S_0)$ vs $\gamma^2 g^2 \delta^2 (4\Delta - \delta)/\pi^2$ for 20 wt% PEO-based solution in $[\text{Li}(\text{G4})_1][\text{TFSA}]$ at 60 °C.

Figure 5. (a) The diffusivity ratio D_G/D_{Li} and (b) lithium transference number t_{Li} for $[\text{Li}(\text{G4})_1][\text{TFSA}]$ and the polymer solutions in $[\text{Li}(\text{G4})_1][\text{TFSA}]$ at 60 °C. (c) Arrhenius plot of self-diffusion coefficient of lithium D_{Li} . Data for $[\text{Li}(\text{G4})_1][\text{TFSA}]$ was obtained from ref 26.

The difference in the stability of $[\text{Li}(\text{G4})_1]^+$ and the varying ionic transport processes in the polymer solutions were further verified by diffusivity measurements using PFG-NMR. The self-diffusion coefficients of G4, Li^+ , and $[\text{TFSA}]^-$ can be measured individually using ^1H , ^7Li , and ^{19}F nuclei, respectively. The signal decay (S/S_0) of the ^1H spectra in the PEO-based solutions was not monomodal due to the spectral overlap between G4 and PEO. In this case, the data were fitted by a bi-exponential form with two different diffusion coefficients.

$$\frac{S}{S_0} = p \exp(kD_G) + (1-p) \exp(kD_{\text{PEO}})$$

where D_G and D_{PEO} are the self-diffusion coefficients of G4 and PEO, respectively, p is the fraction of the contribution from G4, γ is the gyromagnetic ratio, and $k = -\gamma^2 g^2 \delta^2 (4\Delta - \delta) / \pi^2$. A typical result is shown in **Figure 4** and the detailed procedure was described in Supplementary Materials (Figure S2). The faster value falls in the range of 10^{-6} and 10^{-8} $\text{cm}^2 \text{s}^{-1}$ and can be assigned as D_G whereas the slower diffusion coefficients in the range of 10^{-9} and 10^{-11} $\text{cm}^2 \text{s}^{-1}$ were attributed to PEO.

In an earlier work, we reported that the ratio of the self-diffusion coefficients for glymes and Li^+ ions (D_G/D_{Li}) was a useful metric to evaluate the stability of the complex cations [29]. In typical solvate ILs such as $[\text{Li}(\text{G4})_1][\text{TFSA}]$, the D_G/D_{Li} ratio is unity, indicating that Li^+ and the glyme diffuse together. This can serve as experimental evidence for the formation of long-lived complex $[\text{Li}(\text{G4})_1]^+$ cations. As shown in **Figure 5a**, the D_G/D_{Li} ratio is also unity in the PMMA- and PBA-based solutions, confirming that the complex $[\text{Li}(\text{G4})_1]^+$ cations remain stable. In contrast, the D_G/D_{Li} ratio is apparently larger than unity in the PEO-based solution, indicating the existence of G4 molecules that do not participate in the coordination of Li^+ ions. In other words, Li^+ ions are associated with PEO to some extent. These results are in good agreement with the implication of the stability of $[\text{Li}(\text{G4})_1]^+$, discussed in terms of the thermal properties (T_d and T_g in **Figure 1 and 2**).

The Li^+ transference number (t_{Li}) is an important parameter for characterizing the ionic transport properties of lithium-conducting PEs. The t_{Li} value can be approximated by the equation $t_{\text{Li}} = D_{\text{Li}} / (D_{\text{Li}} + D_{\text{TFSA}})$, using the self-diffusion coefficients of Li^+ (D_{Li}) and $[\text{TFSA}]^-$ (D_{TFSA}), although this value may also be affected by the contribution from transient neutral species [43]. Furthermore, it should be noted here that the glyme complex behaves like an IL consisting of $[\text{Li}(\text{G4})]^+$ and $[\text{TFSA}]^-$ in the bulk; however, desolvation is also possible when electrochemical reactions undergo at the electrolyte/electrode interface. This means that concentration gradient of $\text{Li}[\text{TFSA}]$ is formed when the electrochemical reactions undergo, especially under diffusion-limited conditions. Therefore, t_{Li} obtained by PFG-NMR data may differ from those determined by electrochemical polarization techniques with concentration gradient of $\text{Li}[\text{TFSA}]$. **Figure 5b** shows the estimated t_{Li} for the 30 wt% polymer solutions along with that for $[\text{Li}(\text{G4})_1][\text{TFSA}]$ at 60 °C. For PMMA, the 30 wt% solution was too

viscous for the diffusivity to be measured using PFG-NMR, and was replaced by a 20 wt % solution, as shown in **Figure 5b**. The PMMA- and PBA-based solutions afford nearly the same t_{Li} value of ca. 0.5 to that of $[Li(G4)_1][TFSA]$. The lower t_{Li} observed for the PEO-based solutions supports the notion that some Li^+ ions are coordinated to PEO through the ligand exchange between G4 and PEO, and the translational motion of Li^+ ions is more restricted. **Figure 5c** displays the temperature dependence of D_{Li} for the polymer solutions (20 wt%) and $[Li(G4)_1][TFSA]$. The PBA-based solution yields a higher D_{Li} over the entire temperature range investigated in this study. Moreover, the estimated D_G/D_{Li} and t_{Li} values of the polymer solutions were almost independent of temperature from 10 °C to 80 °C (Figure S3). In light of the high ionic conductivity and high lithium transference number, PBA is a better choice for the polymer matrix of the polymer-in-salt type PEs that incorporate $[Li(G4)_1][TFSA]$.

The different ionic transport process and the stability of $[Li(G4)_1]^+$ discussed above were ascribed to the distinct polymer-ion interactions [44]. G4 and PEO have the same ethylene oxide unit as the solvation site, and it was reported that PEO has a slightly higher complex formation constant with Li^+ ions ($K_{complex}$) than G4 [45]. Therefore, the competition between G4 and PEO to interact with Li^+ ions makes $[Li(G4)_1]^+$ unstable. PMMA and PBA are less polar polymers with lower electron-donating abilities than PEO and G4. The unfavorable ligand exchange between G4 and the polymers hardly takes place because their solvation should be much weaker than that of G4. We previously found that the anionic structure play an important role in the solubility of PMMA in ILs [46]. Among the common anions for ILs, $[TFSA]^-$ has an especially high affinity towards PMMA. Likewise, the interaction between the polymers and $[TFSA]^-$ anions probably accounts for the good compatibility of PMMA and PBA with $[Li(G4)_1][TFSA]$.

Sokolov et al. recently reported a strong correlation between the fragility parameter m of polymers and the decoupling of ionic transport from segmental motion in PEs [47, 48]. It was suggested that ionic transport is strongly coupled to the segmental relaxation of less fragile polymers with well-packed structures, whereas ions may diffuse more freely through loosely packed chains of fragile polymers. PEO is known to be the least fragile polymer with $m = 23$ [49], and we indeed observed the coupled Li^+

ion transport in the PEO-based solutions. On the other hand, PMMA is a fragile polymer with $m = 103$ [49], and PBA was estimated to be more fragile with $m = 180$ from the VFT parameters of the temperature dependent relaxation data [50]. Therefore, the ionic transport decoupled from the polymer segmental relaxation in the PMMA- and PBA-based solutions can be interpreted in terms of Sokolov's notion.

Figure 6. Concentration dependence of ionicity $A_{\text{imp}}/A_{\text{NMR}}$ of $[\text{Li}(\text{G4})_1][\text{TFSA}]$ and 10, 20, and 30 wt% polymer solutions in $[\text{Li}(\text{G4})_1][\text{TFSA}]$ at 30 °C.

In a previous work, ionicity, also known as the molar conductivity ratio ($A_{\text{imp}}/A_{\text{NMR}}$) or reciprocal of the well-known Haven ratio [51], was studied in order to estimate the dissociativity or degree of correlative motion of ions in various ILs ranging from aprotic [52] and protic [53] to solvate ILs [29]. A_{imp} (or A) is the molar conductivity, and A_{NMR} (or A_{NE}) is determined from the ionic self-diffusion coefficients D_{Li} and D_{TFSA} using the Nernst-Einstein equation: $A_{\text{NMR}} = F^2(D_{\text{Li}} + D_{\text{TFSA}})/RT$, where F is the Faraday constant, R is the gas constant, and T is the absolute temperature. The ratio $A_{\text{imp}}/A_{\text{NMR}}$ (or more simply A/A_{NE}) indicates the average proportion of charged species that participate in ionic conduction of all diffusing species on the measurement timescale. In $[\text{Li}(\text{G4})_1][\text{TFSA}]$, the $A_{\text{imp}}/A_{\text{NMR}}$ of 0.63 [29] suggests that the conduction process involves the correlated motions of Li^+ and $[\text{TFSA}]^-$. In **Figure 6**, we estimated the $A_{\text{imp}}/A_{\text{NMR}}$ values for the polymer solutions. Here, ionic concentration was calculated from the density values of $[\text{Li}(\text{G4})_1][\text{TFSA}]$ (1.400 g cm^{-3}) [29] and the polymers, 1.182,

1.064, and 1.119 gcm^{-3} for PMMA [54], PBA [55], and PEO [56] respectively, assuming volumetric additivity.

The change in $A_{\text{imp}}/A_{\text{NMR}}$ values is very small in the PBA-based solutions at different concentrations, suggesting that the conduction process of $[\text{Li}(\text{G4})_1][\text{TFSA}]$ has a similar ionic correlation despite the presence or absence of PBA. This does not conflict with the discussion regarding the VFT parameter of C : similar values of $A_{\text{imp}}/A_{\text{NMR}}$ and C between the PBA-based solutions and $[\text{Li}(\text{G4})_1][\text{TFSA}]$ suggest that the PBA polymer matrix does not affect the manner of conduction of $[\text{Li}(\text{G4})_1][\text{TFSA}]$. More importantly, the $A_{\text{imp}}/A_{\text{NMR}}$ values increase with the addition of PMMA or PEO. The increase of $A_{\text{imp}}/A_{\text{NMR}}$ in the PEO-based solutions can be attributed to the formation of the PEO-Li^+ complex. Because Li^+ ions are partially trapped by PEO chains, it is reasonable that the motion of Li^+ ions and $[\text{TFSA}]^-$ becomes less correlated than that in $[\text{Li}(\text{G4})_1][\text{TFSA}]$. The small increase in $A_{\text{imp}}/A_{\text{NMR}}$ in the PMMA-based solutions may be due to an interplay between $[\text{TFSA}]^-$ and PMMA chains, which can promote the dissociation of $[\text{Li}(\text{G4})_1][\text{TFSA}]$ into discrete ions, $[\text{Li}(\text{G4})_1]^+$ and $[\text{TFSA}]^-$.

3. 3 Electrochemical properties

Figure 7. Linear sweep voltammograms of $[\text{Li}(\text{G4})_1][\text{TFSA}]$ and 20 wt% polymer solutions in $[\text{Li}(\text{G4})_1][\text{TFSA}]$ at a scan rate of 1 mV s^{-1} at 30°C .

The electrochemical oxidation and reduction stabilities of PEs are crucial for electrochemical applications. Typical ether-based liquid electrolytes and PEO-based PEs cannot withstand potentials higher than 4.0 V vs. Li/Li^+ because the ether solvents and PEO are known to be oxidized at around this potential. However, we demonstrated that strong complexation in the stable $[\text{Li}(\text{glyme})_1]^+$ cations lowers the HOMO energy level of the glymes, which in turn improves the anodic stability [24]. **Figure 7** shows the linear sweep voltammogram curves on a Pt electrode of $[\text{Li}(\text{G4})_1][\text{TFSA}]$ and the polymer solutions in $[\text{Li}(\text{G4})_1][\text{TFSA}]$. In the parent $[\text{Li}(\text{G4})_1][\text{TFSA}]$, the oxidative current begins to flow at 4.3 V vs Li/Li^+ , which corresponds to the oxidative decomposition of $[\text{Li}(\text{G4})_1][\text{TFSA}]$. The onset of the oxidative decomposition can also be seen at almost the same potential for the PBA-based solution. However, the current density is higher for the PEO-based solution because of the oxidative decomposition of the uncoordinated G4 and PEO. Interestingly, the oxidative stability of the PMMA-based solution becomes higher than that of $[\text{Li}(\text{G4})_1][\text{TFSA}]$; the anodic current is not detectable even at potentials higher than 4.5 V vs Li/Li^+ . This implies that more robust $[\text{Li}(\text{G4})_1]^+$ cations are formed in the PMMA-based solutions. The good affinity between the PMMA chains and $[\text{TFSA}]^-$ anions may weaken $\text{Li}^+ - [\text{TFSA}]^-$ interactions in $[\text{Li}(\text{G4})_1][\text{TFSA}]$, leading to an increase in the competing $\text{Li}^+ - \text{G4}$ interactions. Indeed, the motions of $[\text{Li}(\text{G4})_1]^+$ and $[\text{TFSA}]^-$ become less correlated in the PMMA-based

solutions, as evidenced by the increased $A_{\text{imp}}/A_{\text{NMR}}$ (**Figure 6**). In addition, the decomposition temperature T_d also slightly improved in the presence of PMMA (**Figure 1**). These results suggest that attractive interactions between the polymer matrix and the counter anions should be considered in the design of PEs based on lithium solvate ILs.

Figure 8. Cyclic voltammograms of 20 wt% PBA solution in $[\text{Li}(\text{G4})_1][\text{TFSA}]$ measured at a scan rate of 1mVs^{-1} at $30\text{ }^{\circ}\text{C}$. Nickel was used as the working electrode.

The cathodic stability was also studied by cyclic voltammetry on a nickel metal working electrode. **Figure 8** shows the cyclic voltammograms of 20 wt% PBA solutions measured at a scan rate of 1 mV s^{-1} at $30\text{ }^{\circ}\text{C}$. The results of the Li deposition/stripping experiments in other polymer solutions are shown in Figure S4. The cathodic current observed at potentials lower than 0 V vs Li/Li^+ corresponds to lithium deposition, and the anodic current in the reverse scan is due to the lithium stripping reaction. We confirmed the reversible Li deposition/stripping in the polymer solutions, suggesting that they are practically stable even at 0 V vs. Li/Li^+ . Consequently, the polymer solutions in $[\text{Li}(\text{G4})_1][\text{TFSA}]$ exhibit a wide electrochemical window of $\sim 4.5\text{ V}$.

4. CONCLUSIONS

In this study, we investigated the effects of polymer structure on the thermal, ionic transport, and electrochemical properties of polymer-in-salt-type PEs based on the lithium solvate IL, [Li(G4)₁][TFSA]. The [Li(G4)₁]⁺ complex cations were stable in PMMA- and PBA-based solutions. However, a ligand exchange between G4 and PEO occurred in PEO-based solutions. The varying stability of the [Li(G4)₁]⁺ complex cations was well correlated to the thermal and electrochemical stability of the polymer solutions as well as the ionic conduction mechanism. We demonstrated that polymer electrolytes employing low-melting solvate ILs can achieve high thermal and electrochemical oxidative stabilities in addition to fast Li⁺ ion transport properties. In terms of lower *T_g* and low affinity towards Li⁺ ions, PBA polymer matrices would show higher lithium transport properties (ionic conductivity and Li transference number) among the polymer electrolytes studied. The PMMA-based solutions provided enhanced thermal and oxidative stability. The high electrochemical stability (wide electrochemical window) against both oxidation and reduction of the polymer solutions in [Li(G4)₁][TFSA], allows for applications in 4V-class lithium ion batteries, and next-generation lithium batteries with high energy densities such as lithium-sulfur and lithium-air cells. The battery performance of PEs containing lithium solvate ILs is currently under investigation and will be published elsewhere.

ACKNOWLEDGMENTS: This study was supported in part by the Advanced Low Carbon Technology Research and Development Program (ALCA) of the Japan Science and Technology Agency (JST) and by the Technology Research Grant Program of the New Energy and Industrial Technology Development Organization (NEDO) of Japan. Y. K. acknowledges a Research Fellowship from the Japan Society for the Promotion of Science for Young Scientists (No. 13J00192).

References

- [1] M. Armand, Solid State Ionics, 9–10, Part 2 (1983) 745-754.
- [2] P.G. Bruce, C.A. Vincent, J. Chem. Soc., Faraday Trans. , 89 (1993) 3187-3203.
- [3] M. Rikukawa, K. Sanui, Prog. Polym. Sci., 25 (2000) 1463-1502.
- [4] E. Quartarone, P. Mustarelli, Chem. Soc. Rev., 40 (2011) 2525-2540.
- [5] J.Y. Song, Y.Y. Wang, C.C. Wan, J. Power Sources, 77 (1999) 183-197.
- [6] I.E. Kelly, J.R. Owen, B.C.H. Steele, J. Power Sources, 14 (1985) 13-21.
- [7] G. Nagasubramanian, S. Di Stefano, J Electrochem Soc, 137 (1990) 3830-3835.
- [8] F. Croce, G.B. Appetecchi, L. Persi, B. Scrosati, Nature, 394 (1998) 456-458.
- [9] A. Nishimoto, M. Watanabe, Y. Ikeda, S. Kohjiya, Electrochim. Acta, 43 (1998) 1177-1184.
- [10] W. Xu, L.-M. Wang, C.A. Angell, Electrochim. Acta, 48 (2003) 2037-2045.
- [11] C.A. Angell, C. Liu, E. Sanchez, Nature, 362 (1993) 137-139.
- [12] M. Watanabe, S.-I. Yamada, K. Sanui, N. Ogata, J. Chem. Soc., Chem. Commun., (1993) 929-931.
- [13] T. Ueki, M. Watanabe, Macromolecules, 41 (2008) 3739-3749.
- [14] M.J. Park, I. Choi, J. Hong, O. Kim, J. Appl. Polym. Sci., 129 (2013) 2363-2376.
- [15] Y.-S. Ye, J. Rick, B.-J. Hwang, J. Mater. Chem. A, 1 (2013) 2719-2743.
- [16] S. Seki, M.A.B.H. Susan, T. Kaneko, H. Tokuda, A. Noda, M. Watanabe, J. Phys. Chem. B, 109 (2005) 3886-3892.
- [17] M. Kofu, T. Someya, S. Tatsumi, K. Ueno, T. Ueki, M. Watanabe, T. Matsunaga, M. Shibayama, V.G. Sakai, M. Tyagi, O. Yamamuro, Soft Matter, 8 (2012) 7888-7897.
- [18] H. Ye, J. Huang, J.J. Xu, A. Khalfan, S.G. Greenbaum, J Electrochem Soc, 154 (2007) A1048-A1057.
- [19] C. Sirisopanaporn, A. Fernicola, B. Scrosati, J. Power Sources, 186 (2009) 490-495.
- [20] J.-H. Shin, W.A. Henderson, S. Passerini, J Electrochem Soc, 152 (2005) A978-A983.
- [21] K. Hayamizu, Y. Aihara, H. Nakagawa, T. Nukuda, W.S. Price, J. Phys. Chem. B, 108 (2004) 19527-19532.
- [22] H. Shobukawa, H. Tokuda, M.A.B.H. Susan, M. Watanabe, Electrochim. Acta, 50 (2005) 3872-3877.

- [23] T. Tamura, K. Yoshida, T. Hachida, M. Tsuchiya, M. Nakamura, Y. Kazue, N. Tachikawa, K. Dokko, M. Watanabe, *Chem. Lett.*, 39 (2010) 753-755.
- [24] K. Yoshida, M. Nakamura, Y. Kazue, N. Tachikawa, S. Tsuzuki, S. Seki, K. Dokko, M. Watanabe, *J Am Chem Soc*, 133 (2011) 13121-13129.
- [25] C.A. Angell, Y. Ansari, Z.F. Zhao, *Faraday Discuss*, 154 (2012) 9-27.
- [26] K. Yoshida, M. Tsuchiya, N. Tachikawa, K. Dokko, M. Watanabe, *J Phys Chem C*, 115 (2011) 18384-18394.
- [27] T.M. Pappenfus, W.A. Henderson, B.B. Owens, K.R. Mann, W.H. Smyrl, *J Electrochem Soc*, 151 (2004) A209-A215.
- [28] O. Buriez, Y.B. Han, J. Hou, J.B. Kerr, J. Qiao, S.E. Sloop, M. Tian, S. Wang, *J. Power Sources*, 89 (2000) 149-155.
- [29] K. Ueno, K. Yoshida, M. Tsuchiya, N. Tachikawa, K. Dokko, M. Watanabe, *J. Phys. Chem. B*, 116 (2012) 11323-11331.
- [30] K. Matyjaszewski, J. Xia, *Chem. Rev.*, 101 (2001) 2921-2990.
- [31] A. Noda, M. Watanabe, *Electrochim. Acta*, 45 (2000) 1265-1270.
- [32] M.A.B.H. Susan, T. Kaneko, A. Noda, M. Watanabe, *J Am Chem Soc*, 127 (2005) 4976-4983.
- [33] K. Fujii, H. Asai, T. Ueki, T. Sakai, S. Imaizumi, U.-i. Chung, M. Watanabe, M. Shibayama, *Soft Matter*, 8 (2012) 1756-1759.
- [34] S. Imaizumi, H. Kokubo, M. Watanabe, *Macromolecules*, 45 (2011) 401-409.
- [35] S. Zhang, K.H. Lee, C.D. Frisbie, T.P. Lodge, *Macromolecules*, 44 (2011) 940-949.
- [36] Y. Kitazawa, K. Iwata, S. Imaizumi, H. Ahn, S.Y. Kim, K. Ueno, M.J. Park, M. Watanabe, *Macromolecules*, 47 (2014) 6009-6016.
- [37] M. Gordon, J.S. Taylor, *J. Appl. Chem.*, 2 (1952) 493-500.
- [38] T.G. Fox, *Bull. Am. Phys. Soc.*, 1 (1956) 123
- [39] H. Kanno, *J. Non-Cryst. Solids*, 44 (1981) 409-413.
- [40] M. Baumgartel, N. Willenbacher, *Rheol. Acta*, 35 (1996) 168-185.
- [41] J. Shi, C.A. Vincent, *Solid State Ionics*, 60 (1993) 11-17.
- [42] R. Böhmer, K.L. Ngai, C.A. Angell, D.J. Plazek, *J. Chem. Phys.*, 99 (1993) 4201-4209.
- [43] S. Zugmann, M. Fleischmann, M. Amereller, R.M. Gschwind, H.D. Wiemhöfer, H.J. Gores, *Electrochim. Acta*, 56 (2011) 3926-3933.
- [44] Y. Saito, M. Okano, T. Sakai, T. Kamada, *J. Phys. Chem. C*, 118 (2014) 6064-6068.
- [45] C.B. Tsvetanov, E.B. Petrova, D.K. Dimov, I.M. Panayotov, J. Smid, *J Solution Chem*, 19 (1990) 425-436.
- [46] K. Ueno, T. Fukai, T. Nagatsuka, T. Yasuda, M. Watanabe, *Langmuir*, 30 (2014) 3228-3235.

- [47] A.L. Agapov, A.P. Sokolov, *Macromolecules*, 44 (2011) 4410-4414.
- [48] Y.Y. Wang, A.L. Agapov, F. Fan, K.L. Hong, X. Yu, J. Mays, A.P. Sokolov, *Phys. Rev. Lett.*, 108 (2012).
- [49] Q. Qin, G.B. McKenna, *J. Non-Cryst. Solids*, 352 (2006) 2977-2985.
- [50] D. Fioretto, A. Livi, P.A. Rolla, G. Socino, L. Verdini, *J. Phys. Condens. Matter*, 6 (1994) 5295.
- [51] J.O. Isard, *J. Non-Cryst. Solids*, 246 (1999) 16-26.
- [52] H. Tokuda, S. Tsuzuki, M.A.B.H. Susan, K. Hayamizu, M. Watanabe, *J. Phys. Chem. B*, 110 (2006) 19593-19600.
- [53] M.S. Miran, H. Kinoshita, T. Yasuda, M.A.B.H. Susan, M. Watanabe, *Chem. Commun.*, 47 (2011) 12676-12678.
- [54] Y. Gotoh, J. Imakita, Y. Ohkoshi, M. Nagura, *Polym. J.*, 32 (2000) 838-844.
- [55] K. Mashita, M. Hirooka, *Polymer*, 36 (1995) 2983-2988.
- [56] N. Vennemann, M.D. Lechner, R.C. Oberthür, *Polymer*, 28 (1987) 1738-1748.