

Manuscript Details

Manuscript number	MOLLIQ_2018_3402_R1
Title	Preparation of polymer electrolytes using ionic liquids and evaluation of physicochemical properties
Article type	Full length article

Abstract

To achieve high safety and good cycle performance of lithium polymer batteries, it is important to develop novel polymer electrolytes based on ionic liquids (ILs). In this study, a number of polymer electrolytes were prepared by applying various ILs to polymethylmethacrylate-type polymers, and the physicochemical properties of the systems were evaluated. The temperature-dependence of the conductivity of the polymer electrolytes obeyed the Arrhenius relation, indicating free migration of the ionic species inside the polymer electrolytes and that ionic conduction proceeded by a conduction mechanism similar to that of the solution system. The conductivity of the phosphonium-type polymer electrolyte at 30 °C was three-fold higher than that of the corresponding ammonium-type polymer electrolyte ([P2225][TFSA] (gel): 1.46×10^{-4} S cm⁻², [N2225][TFSA] (gel): 5.01×10^{-5} S cm⁻², [P4441][TFSA] (gel): 7.94×10^{-5} S cm⁻², [N4441][TFSA] (gel): 2.32×10^{-5} S cm⁻²). For application to the lithium ion battery, the polymer electrolyte containing lithium ions was prepared and the physicochemical properties were evaluated. Even in the presence of a lithium salt, the phosphonium-type polymer electrolytes showed higher conductivity than the corresponding ammonium-type polymer electrolytes. The electrolyte underwent sequential two-stage thermal decomposition. The decomposition of the IL component was observed after thermal decomposition of the polymer component. From analysis of the charge distribution of the phosphonium and ammonium cations by MP2 calculation, the proportion of positive charges in the alkyl chain of the ammonium cation was larger than that of the phosphonium cation. This suggests that the cations in the ammonium-type polymer electrolytes enhance the interaction with the polymer chains and crosslinking sites to a greater extent than the phosphonium cations.

Keywords	Ionic liquid, Physicochemical property, Polymer electrolyte
Manuscript category	Ionic liquids
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Dear Prof. W. Schröer
Editor-in-Chief of Journal of Molecular Liquids

Thank you for sending e-mail and many valuable reviewer comments.
The comments for each reviewer about the revised manuscript were written as follows.
We hope that the revised manuscript will be suitable for the publication.
Sincerely yours.

Dr. Masahiko Matsumiya,
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-Reviewer 1

Thank you for sending many useful comments.

According to your comments, the revised manuscript was corrected as follows.

1. Check the grammar throughout the manuscript.

According to your suggestion, all English expressions were checked and modified by the native speaker in ACN translation company.

2. The abstract is too general. On top of that, there is no any numerical value stated in the abstract.

According to your suggestion, the numerical data was added in the revised manuscript. (p.1L7-L10)

3. Error bar needs to be included for T dependent ionic conductivity studies.

According to your suggestion, the error was estimated from the temperature deviation in measurement system. As a result, the temperature deviation was ± 0.2 K for 30 min after the temperature equilibrium was attained by temperature controller, and it is difficult to show the error bar in the data of ionic conductivity, because the temperature deviation was very small.

4. Under the Results and Discussion part, the discussion are not sufficient enough for a full length article.

According to your advice, we applied the ionic conductivity with temperature dependence for VFT equation. The fitting parameter of VFT equation was added in new Table 2. Moreover, the discussion was also added in the revised manuscript. (p.4L14-L27)

The other revised sentences were marked with red letter in the revised manuscript.

We hope that the revised manuscript will be suitable for the publication.

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Highlights

- A number of polymer electrolytes were prepared using various ILs to polymethylmethacrylate type polymers
- The conductivity of the polymer electrolytes with temperature dependence obeyed Arrhenius type equation.
- Thermal decomposition behavior showed a sequential decomposition behavior in two stages.
- According to the charge distribution analysis by MP2 calculation, the proportion of positive charges of the ammonium cation was larger than that of the phosphonium cation.

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Preparation of polymer electrolytes using ionic liquids and evaluation of physicochemical properties

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1 **ABSTRACT**

2 To achieve high safety and good cycle performance of lithium polymer batteries, it is important to develop
3 novel polymer electrolytes based on ionic liquids (ILs). In this study, a number of polymer electrolytes were prepared
4 by applying various ILs to polymethylmethacrylate-type polymers, and the physicochemical properties of the systems
5 were evaluated. The temperature-dependence of the conductivity of the polymer electrolytes obeyed the Arrhenius
6 relation, indicating free migration of the ionic species inside the polymer electrolytes and that ionic conduction
7 proceeded by a conduction mechanism similar to that of the solution system. The conductivity of the phosphonium-
8 type polymer electrolyte at 30 °C was three-fold higher than that of the corresponding ammonium-type polymer
9 electrolyte ([P₂₂₂₅][TFSA] (gel): 1.46×10^{-4} S cm⁻², [N₂₂₂₅][TFSA] (gel): 5.01×10^{-5} S cm⁻², [P₄₄₄₁][TFSA] (gel):
10 7.94×10^{-5} S cm⁻², [N₄₄₄₁][TFSA] (gel): 2.32×10^{-5} S cm⁻²). For application to the lithium ion battery, the polymer
11 electrolyte containing lithium ions was prepared and the physicochemical properties were evaluated. Even in the
12 presence of a lithium salt, the phosphonium-type polymer electrolytes showed higher conductivity than the
13 corresponding ammonium-type polymer electrolytes. The electrolyte underwent sequential two-stage thermal
14 decomposition. The decomposition of the IL component was observed after thermal decomposition of the polymer
15 component. From analysis of the charge distribution of the phosphonium and ammonium cations by MP2 calculation,
16 the proportion of positive charges in the alkyl chain of the ammonium cation was larger than that of the phosphonium
17 cation. This suggests that the cations in the ammonium-type polymer electrolytes enhance the interaction with the
18 polymer chains and crosslinking sites to a greater extent than the phosphonium cations.

19
20 **Keywords:** Ionic liquid, Physicochemical property, Polymer electrolyte

1 **1. Introduction**

2 An ionic liquid (IL) is a salt in the liquid state and is defined as being limited to a salt whose melting point is
3 lower than an arbitrary temperature such as 373 K [1–6]. **ILs** are sometimes called "designer solvents", because ILs
4 **with** the desired physicochemical properties can be synthesized from various types of ionic species [7]. **ILs that adopt**
5 **the** liquid state at a temperature lower than room temperature are called room temperature ionic liquids (RTILs).
6 **RTILs are potentially** important industrial **solvents** for synthesis, **catalysis**, extraction, and purification due to **their**
7 low vapor pressure and specific catalytic properties [8–10]. **They are** also electrochemically stable **with** high transport
8 **ability**. For this reason, **their** application to various electrochemical devices has **continued to develop** [11–14].

9 **Many** ILs with cations of nitrogen-containing compounds such as quaternary ammonium and imidazolium
10 cations have **been** synthesized and investigated so far. On the other hand, **the phosphonium cation comprising**
11 phosphine is flammable as a raw material and involves a risk of handling. Therefore, **reports on** phosphonium-based
12 ILs are limited in comparison with **those regarding** ILs with nitrogen-containing cations. The **phosphorus-containing**
13 phosphonium-based ILs [15] have been found to have higher transport and thermal stability **than** the corresponding
14 ammonium-based ILs [16,17]. It is also reported that the catalytic activity was improved by using phosphonium-
15 based ILs as a solvent [18]. Thus, phosphonium-based ILs, which have unique physicochemical **properties, have**
16 attracted attention in many fields [19–21].

17 In recent years, **the increasing demand for electronic devices such as tablets has made** it necessary to develop
18 the lithium polymer battery. **The** lithium polymer battery **uses** a polymer electrolyte and has some advantages such
19 as high safety and good cycle performance [22,23]. However, **when** conventional organic solvents **are used as** the
20 electrolyte, it is difficult to maintain high safety due to vaporization of the organic solvent. For this reason, not only
21 phosphonium-based ILs, but also ammonium-based ILs [24–26], are useful as new electrolytes. In this study, polymer
22 electrolytes are prepared by applying various ILs to polymethylmethacrylate-type polymers, and **the** physicochemical
23 properties **of these systems are** evaluated.

24

25 **2. Experimental**

26 **2.1 Preparation**

27 **Using literature methods** [28], tri-*n*-butylalkylphosphonium bromide (Nippon Chemical Industrial Co., Ltd.),
28 tri-*n*-butylalkylammonium bromide, tri-*n*-ethylalkylphosphonium bromide ((Nippon Chemical Industrial Co., Ltd.),

1 and tri-*n*-ethylalkylammonium bromide were synthesized by nucleophilic addition to the corresponding
2 bromoalkanes (Tokyo Chemical Industry Co. Ltd.) under nitrogen atmosphere. Ion exchange reaction was carried
3 out by the metathesis reaction of the phosphonium or ammonium bromide and lithium
4 bis(trifluoromethylsulfonyl)amide (Kanto Chemical Co., Inc.; Li[TFSA]). The resulting crude ILs were purified by
5 washing several times with distilled water until no residual bromide ion was detected with the use of silver nitrate.
6 All the ILs were dried under high vacuum for at least 12 h at 373 K and were stored in a glove box under argon
7 atmosphere. The products obtained were identified by ¹H, ¹³C, ¹⁹F, and ³¹P nuclear magnetic resonance (NMR)
8 [16,17].

9

10 2.2 Polymer electrolytes

11 Methyl methacrylate (96 mol%, Tokyo Chemical Industry Co., Ltd.), benzoyl peroxide (2 mol%, Tokyo
12 Chemical Industry Co., Ltd.), and various crosslinking agents (2 mol%, Shin Nakamura Chemical Co., Ltd.), as
13 shown in Fig. 1, were mixed to prepare a polymerization agent. This polymerization agent and various ILs (Fig. 2)
14 were mixed in a weight ratio of 3:7, heated at 353 K for 24 h, and then heated at 413 K for 30 min [27]. The lithium
15 salt-containing polymer electrolytes were prepared by including Li[TFSA] (Kishida Chemical Co., Ltd.) in the ILs.

16 According to the method of JIS K 0102, using a KCl standard solution, the cell constant was estimated from the
17 thickness of the obtained polymer electrolytes and the conductivity was obtained from the measured resistance. Both
18 ends of the polymer electrolytes were sandwiched between platinum electrodes ($d = 5$ mm), and alternating current
19 impedance measurement (Bio-Logic Science Instruments, SP 150) was carried out. The amplitude fluctuation width
20 was set to 500 mV, and the measurement was performed in the range of 100 mHz to 1 MHz; a Nyquist plot was
21 constructed using a Randles-Ershler type equivalent circuit [29].

22 The thermal decomposition temperature of the polymer electrolytes was measured with a thermogravimetric
23 analyzer (TG/DTA 6300, Seiko Instruments Inc.) under nitrogen atmosphere at a heating rate of 10 K min⁻¹.

24

25 2.3 Computational method

26 All ab initio calculations were carried out by using the software program Gaussian 09 [30]. The Hartree-Fock
27 equation [31–33] was used for geometric structure optimization with the 6-311** [34–37] basis set for cations in the
28 gas phase. The electron correlation was accounted for at the MP2 level [38,39]. The atomic charge distributions of

1 the various cations were calculated by electrostatic potential fitting with the Merz-Singh-Kollman scheme [40,41]
2 using the MP2/6-311G** basis set for isolated ions.

3

4 3 Results and discussion

5 The conductivity of the polymer electrolytes was evaluated using $n = 1$ for the various crosslinking agents, and
6 the behavior was found to follow the Arrhenius model, showing a convex upward trend similar to that of the pure ILs
7 (Fig. 3). This result suggests that the ionic species can freely migrate, even inside the polymer electrolytes, and that
8 ionic conduction would proceed by a conduction mechanism similar to that in the solution system. For all of the
9 polymer electrolytes, the electrical conductivity declined when the ILs were introduced into the polymer. This is
10 presumed to be due to restriction of the movement of the ionic species via the formation of polymer chains. The
11 phosphonium-type polymer electrolytes were found to have higher conductivity than the corresponding ammonium-
12 type polymer electrolytes. It was also confirmed that the decrease in the conductivity was suppressed in the polymer
13 electrolytes employing the phosphonium-based ILs. The phosphonium-type polymer electrolytes were found to have
14 higher thermal stability than the ammonium-type congeners. The conductivity plots could be fitted to the VFT
15 equation, as expressed below [44]:

16

$$\ln\sigma = \frac{k_\sigma}{T - T_0} - \frac{1}{2}\ln T + \ln A_\sigma \quad (1)$$

18

19 where σ is the ionic conductivity, k_σ is a constant related to the Arrhenius activation energy of the conductivity, T_0 is
20 the ideal glass transition temperature, and A_σ is the scaling factor of the conductivity. The fitted parameters and
21 coefficient of determination ($|R|$) are summarized in Table 2. The polymer electrolyte tended to decrease the
22 frequency factor compared with neat the IL. Because this parameter is related to the carrier ion number, it means that
23 the density of the IL in the polymer is lower than that of the neat IL. This may be due to the presence of the polymer
24 chains. Moreover, upon applying the IL to the polymer electrolyte, an increase in the ideal glass transition temperature
25 was confirmed. This parameter influences the curvature of the graph, and it is suggested that the temperature-
26 dependence became more pronounced, especially around room temperature. The activation energy of the polymer

1 electrolyte tended to decrease. The thermal decomposition profile indicated sequential decomposition in two stages;
2 that is, decomposition of the IL component after thermal decomposition of the polymer component (Fig. 4).

3 In order to apply the polymer electrolyte to a lithium ion battery, the polymer electrolyte containing lithium ions
4 was prepared and the physicochemical properties were evaluated. Even when lithium salt was included, the
5 phosphonium-type polymer electrolytes showed higher conductivity than the corresponding ammonium-type
6 polymer electrolytes. However, for all of the polymer electrolytes, the conductivity declined depending on the amount
7 of lithium salt added (Fig. 5). In addition, the decrease in the conductivity was more pronounced for the
8 phosphonium-type polymer electrolytes than the corresponding ammonium-type polymer electrolytes. Umebayashi
9 et al. reported that the TFSA anion forms a complex with lithium ions in a ratio of 2:1 [42]. The stabilization energy
10 associated with complex formation is much larger than that of the interaction between the cation and the anion species
11 originally contained in the ILs [43]. Therefore, depending on the amount of lithium added, most of the ions are likely
12 to undergo complexation. That is, formation of the bulky anion species is presumed to be the cause of the lowered
13 transport ability in the polymer chain. It was also confirmed that high thermal stability was maintained (Fig. 6). A
14 relatively large amount of residue remained in the polymer electrolytes containing lithium in the high temperature
15 region (<773 K). This is presumed to be because the lithium compound precipitated during the thermal decomposition
16 process.

17 When the ILs were applied to the polymer electrolytes, the conductivity decreased, irrespective of the charge of
18 the polymer. Therefore, various crosslinking agents were applied to the polymer electrolytes for the purpose of
19 suppressing the decrease in the conductivity, and the physicochemical properties were evaluated. There was no
20 significant difference in the conductivity for the ammonium-type polymer electrolytes, whereas the conductivity was
21 enhanced for the phosphonium-type polymer electrolytes (Fig. 7). It is believed that by increasing the length of the
22 alkyl chain of the crosslinking agent, the density of the polymer chain decreases, which contributes to the
23 improvement in the conductivity. On the other hand, it was presumed that no improvement in the conductivity was
24 observed for the ammonium type-polymer electrolytes because of the relatively strong positive charge of the side
25 chain of the ammonium-type cation which enhanced the interaction with the polymer chain. From analysis of the
26 charge distribution of the phosphonium and ammonium cations by MP2 calculation, the proportion of positive
27 charges in the alkyl chain of the ammonium cation is larger than that of the phosphonium cation (Fig. 8). This result
28 suggests that the cations in the ammonium-type polymer electrolytes increase the interaction of the polymer chains

1 and crosslinking sites **relative to the** phosphonium cations. This tendency **is similar to that of other** systems containing
2 lithium ions (**Fig. 9**). Finally, the thermal stability of the polymer electrolytes using various crosslinking agents was
3 evaluated, and the thermal stability was maintained **at a high level** (**Fig. 10**).

4 **4. Conclusion**

6 **This study demonstrates** that when radical polymerization is carried out by **introducing** phosphonium-type ionic
7 liquids (ILs) **into** a methacrylate-type monomer, a product in a self-sustained gel state can be obtained, as in **a**
8 nitrogen-containing IL system. The obtained product was referred to **herein** as a 'phosphonium-type polymer
9 electrolyte'. **The product exhibits** higher conductivity and thermal stability than the electrolyte comprising a
10 corresponding ammonium-type IL. The conductivity and thermal stability of the polymer electrolytes were evaluated
11 **in a system containing a lithium salt**. It was confirmed that the thermal stability remained high, even in **the** system
12 containing lithium. It was also revealed that the conductivity decreases in accordance with the amount of lithium salt
13 **added**, in the same manner as in the solution system. **By** applying various crosslinking agents for the purpose of
14 suppressing **the decrease in the** conductivity when **the ILs are applied to** polymer electrolytes, it was found that a
15 crosslinking agent having a slightly longer alkyl chain **could improve the** conductivity. This effect **is** unique to the
16 phosphonium-type polymer electrolytes and **was** not observed for the ammonium-type polymer electrolytes.

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Caption of Figures

Fig. 1 Structures of crosslinking agents in this study.

Fig. 2 Structure of various cations in this study (anion : bis(trifluoromethylsulfonyl)amide (TFSA)).

Fig. 3 Conductivity of various polymer electrolytes. open circles show neat ionic liquids, closed circles show polymer electrolytes. orange plot: [P₂₂₂₅][TFSA], red plot: [P₄₄₄₁][TFSA], green plot: [N₂₂₂₅][TFSA], and blue plot: [N₄₄₄₁][TFSA].

Fig. 4 Thermogravimetric traces for various polymer electrolytes. Orange line: [P₂₂₂₅][TFSA] polymer electrolyte, orange dotted line: neat [P₂₂₂₅][TFSA], red line: [P₄₄₄₁][TFSA] polymer electrolyte, red dotted line: neat [P₄₄₄₁][TFSA], green line: [N₂₂₂₅][TFSA] polymer electrolyte, green dotted line: neat [N₂₂₂₅][TFSA], blue line: [P₄₄₄₁][TFSA] polymer electrolyte, blue dotted line : neat [P₄₄₄₁][TFSA], and black line : neat polymethyl methacrylate.

Fig. 5 Effect of Li⁺ for ionic conductivity. blue plot: [N₄₄₄₁][TFSA], red plot: [P₄₄₄₁][TFSA]. Circle: without lithium salt, triangle: polymer electrolytes including 0.16 mol / kg of lithium salt, cross mark : polymer electrolytes including 0.32 mol / kg of lithium salt

Fig. 6 Effect of Li⁺ on thermal stability. solid line: thermogravimetric trace of polymer electrolyte including lithium salt. dotted line: thermogravimetric trace of polymer electrolyte without lithium salt. blue : [N₄₄₄₁][TFSA], and red : [P₄₄₄₁][TFSA]

Fig. 7 Effect of crosslinking agent on ionic conductivity. closed circle: [P₄₄₄₁][TFSA], open circle: [N₄₄₄₁][TFSA], red: $n=1$, green: $n=3$, and purple: $n=4$

Fig. 8 Atomic charges obtained by electrostatic potential fitting for the cations containing various substituents using Kollman's scheme from the MP2/6-311G** wave functions.

● : hydrogen atom, ● : carbon atom, ● : nitrogen atom, ● : phosphorus atom

Fig. 9 Effect of crosslinking agent on ionic conductivity. blue: [N₄₄₄₁][TFSA], red: [P₄₄₄₁][TFSA], closed circle: $n=3$, and open circle: $n=1$

Fig. 10 Effect of crosslinking agent on thermal stability.

solid line: thermogravimetric trace for polymer electrolytes using a crosslinking agent with a large molecular weight. The dash line is the same as the crosslinking agent. blue: [N₄₄₄₁][TFSA], and red: [P₄₄₄₁][TFSA]

Fig. 1

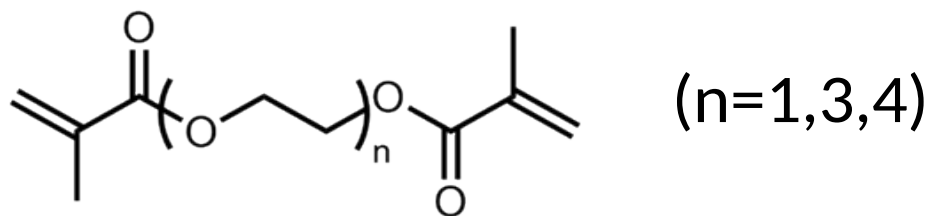


Fig. 2

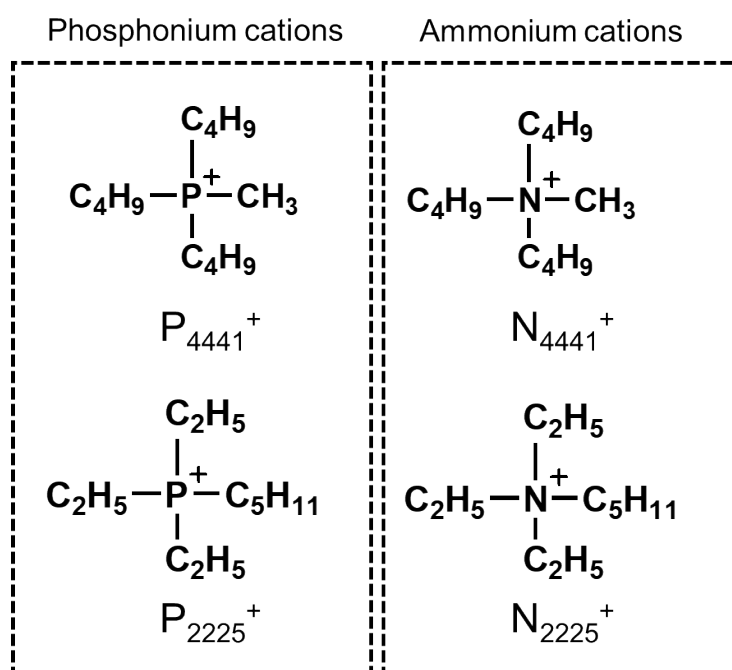


Fig. 3

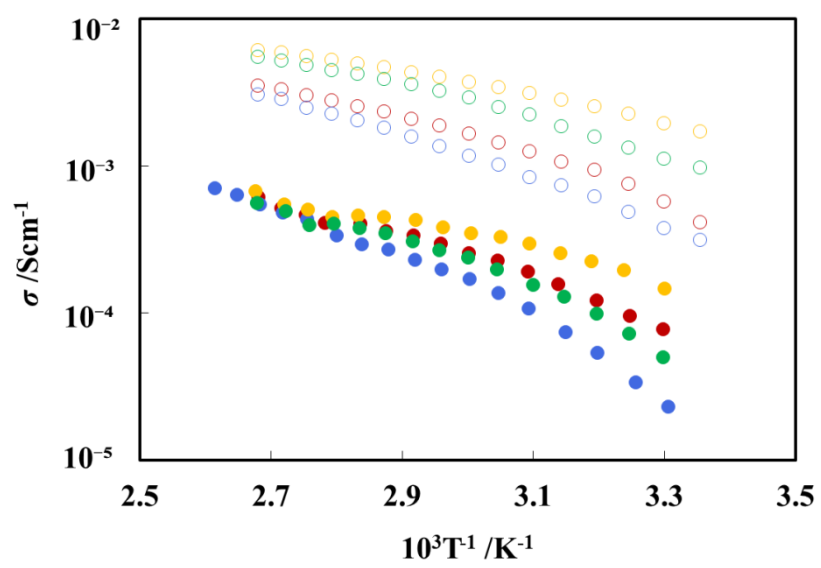


Fig. 4

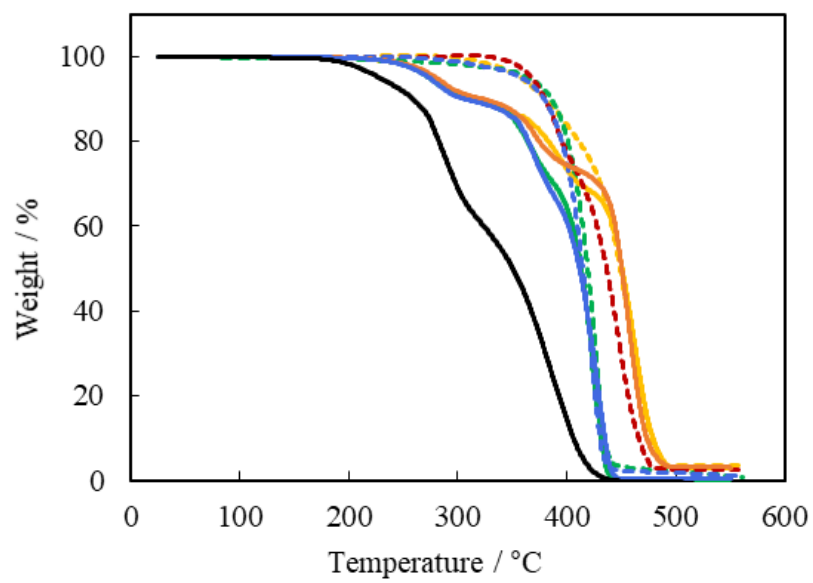


Fig. 5

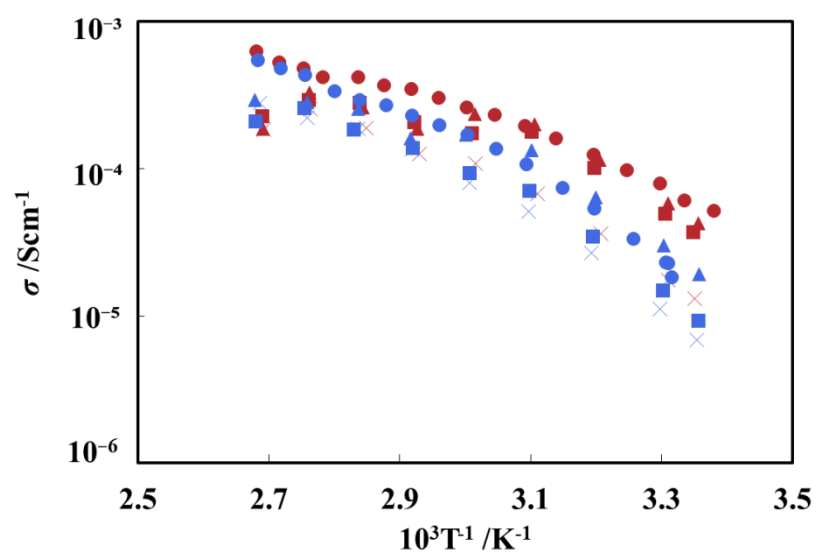


Fig. 6

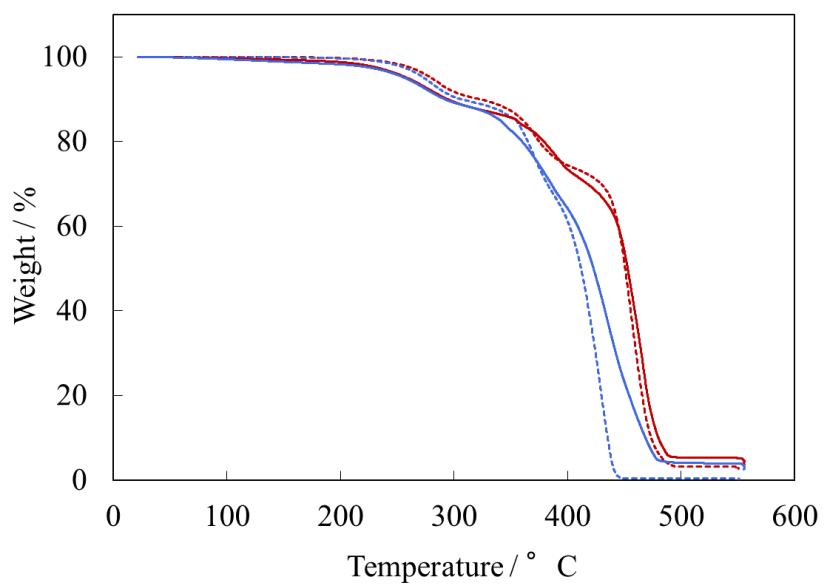


Fig. 7

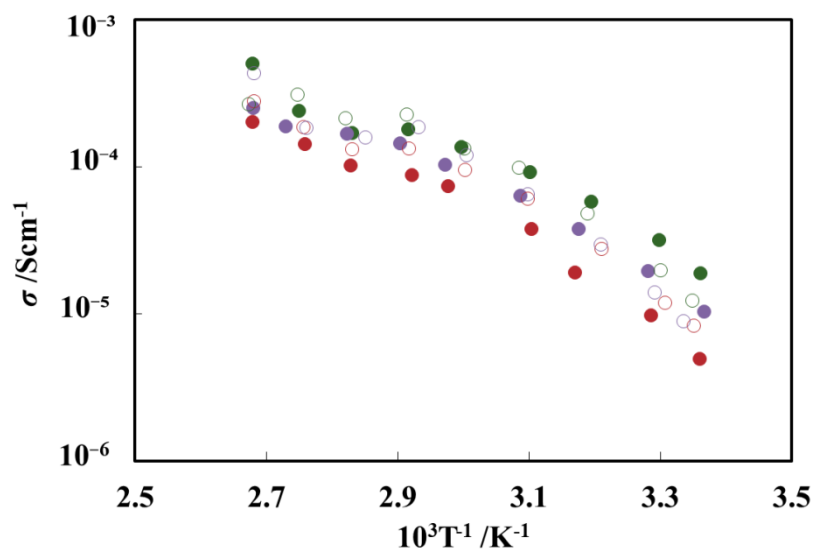


Fig. 8

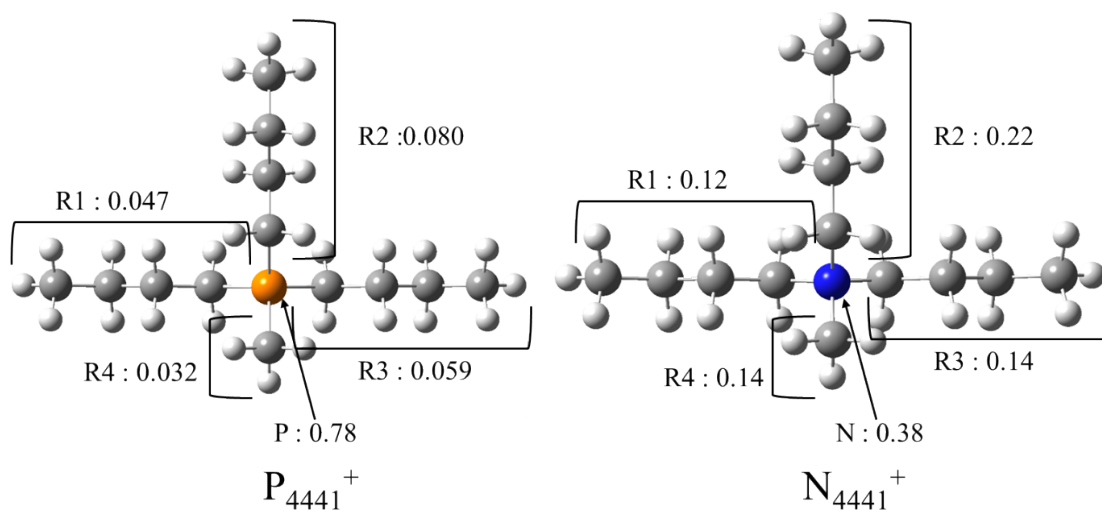


Fig. 9

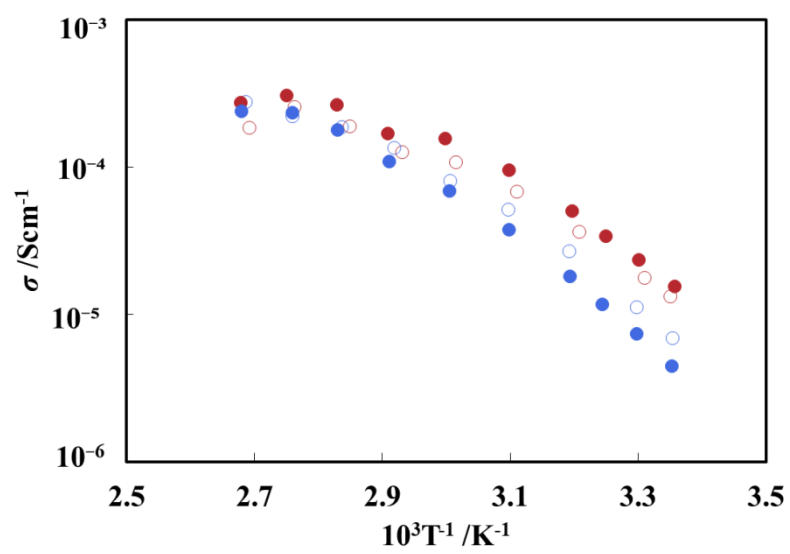


Fig. 10

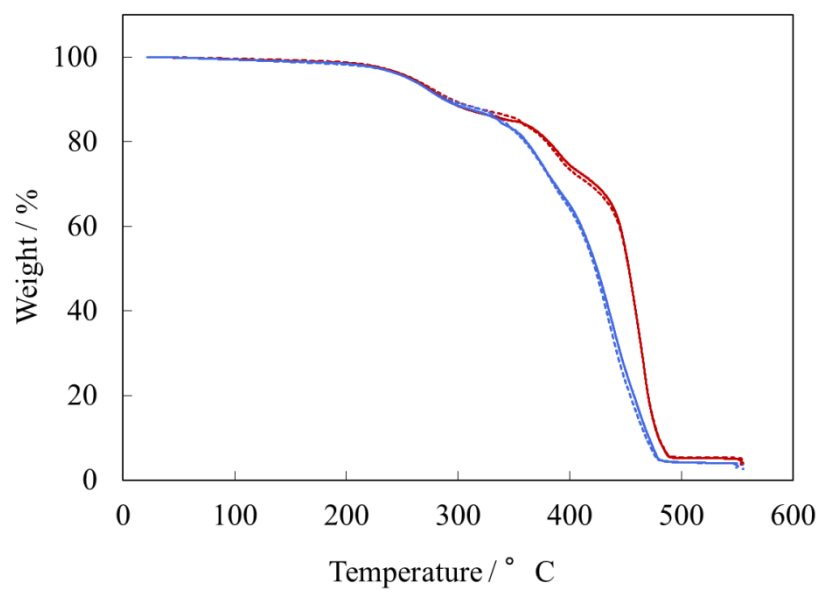


Table 1 Physicochemical property of various ionic liquids (ILs) in this study.

IL	FW ^{a)}	T_m / K ^{b)}	η / mPa·s ^{c)}	σ / mS cm ^{-1d)}	T_{dec} / K ^{e)}	Reference
[P ₄₄₄₁][TFSA]	497.5	289	207	0.42	652	[16]
[N ₄₄₄₁][TFSA]	480.5	296	631	0.31	652	[16]
[P ₂₂₂₅][TFSA]	469.4	290	88	1.73	653	[17]
[N ₂₂₂₅][TFSA]	452.5	<223	172	0.98	658	[17]

- a) Formula weight.
- b) Melting temperature.
- c) Viscosity at 298 K
- d) Ionic conductivity at 298 K
- e) Thermal decomposition temperature of 10% weight loss.

Table 2 Fitted parameters for VFT equation for various IL and polymer electrolyte(gel).

Electrolyte	k_{σ} / K	T_0 / K	$\ln A_{\sigma}$	R	Reference
[P ₄₄₄₁][TFSA](gel)	314.3	231.5	4.67	0.999	this study
[P ₄₄₄₁][TFSA](neat)	295.0	228.5	6.25	0.999	[16]
[P ₂₂₂₅][TFSA](gel)	114.6	254.7	3.33	0.999	this study
[P ₂₂₂₅][TFSA](neat)	352.6	193.0	6.74	1.000	[17]
[N ₄₄₄₁][TFSA](gel)	384.1	241.5	5.34	0.998	this study
[N ₄₄₄₁][TFSA](neat)	843.4	169.4	8.23	1.000	[16]
[N ₂₂₂₅][TFSA](gel)	235.7	249.7	4.28	1.000	this study
[N ₂₂₂₅][TFSA](neat)	395.9	205.7	7.05	0.999	[17]