

Synthesis and Properties of Pyrrolidinium and Piperidinium Bis(trifluoromethanesulfonyl)imide Ionic Liquids with Allyl Substituents

Taeun Yim, Hyun Yeong Lee, Hyo-Jin Kim, Junyoung Mun, Sangmi Kim, Seung M. Oh,* and Young Gyu Kim*

Department of Chemical and Biological Engineering, Research Center for Energy Conversion & Storage, Seoul National University, Seoul 151-744, Korea. *E-mail: seungoh@plaza.snu.ac.kr; ygkim@snu.ac.kr

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New pyrrolidinium and piperidinium bis(trifluoromethanesulfonyl)imide (TFSI) ionic liquids (ILs) having allyl substituents were synthesized and characterized. All of them are liquid at room temperature and stable up to 300 °C. The pyrrolidinium-based ILs showed better conductivities and lower viscosities than the corresponding piperidinium-based ILs. Among them, 1-allyl-1-methylpyrrolidinium TFSI showed the lowest viscosity of 52 cP, the highest conductivity of 5.7 mS cm⁻¹, and the most negative cathodic voltage window of -3.2 V (vs. Fe/Fe⁺) on a platinum electrode, which are the improved results compared to the corresponding analogue having a saturated substituent, 1-methyl-1-propylpyrrolidinium TFSI.

Key Words : Ionic liquid, Pyrrolidinium, Piperidinium, Bis(trifluoromethanesulfonyl)imide (TFSI), Allyl substituent

Introduction

Ionic liquids (ILs) have received a lot of interest recently as ion conductive matrices as well as reaction media because of their unusual properties such as a wide liquid range, high ionic conductivity, a wide voltage window, non-volatility, and non-flammability.¹ In addition, the designability of ILs makes themselves attractive alternatives to the conventional organic electrolytes and solvent systems.

Early ILs containing aluminum chloride anions had serious problems such as corrosiveness and toxicity. Therefore, they were difficult to substitute conventional electrolytes. Since Wilkes and Zaworotko reported the air and water stable imidazolium ILs with a tetrafluoroborate anion,² ILs have attracted much attention as promising candidates for the use in advanced electrochemical applications. Generally, ILs are composed of nitrogen-containing cations and halide or fluorine-containing anions. The representative cations are imidazoliums, pyridiniums, cyclic and acyclic quaternary ammoniums. The anions are halides, PF₆⁻, BF₄⁻ and N(SO₂CF₃)₂⁻ (TFSI). Because imidazolium-based ILs have high ionic conductivity and low viscosity,³ they have been investigated for the use in batteries,⁴ capacitors,⁵ solar cells⁶ and fuel cells.^{4b,7}

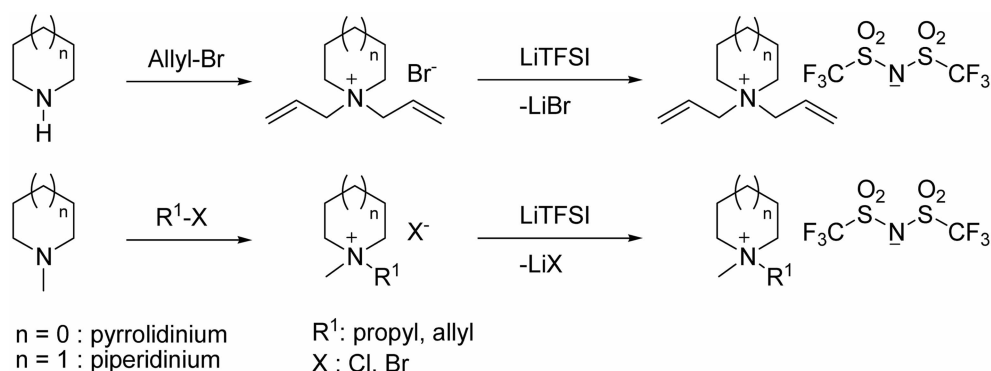
Recently, we have reported the physical and electrochemical properties of several novel imidazolium ILs with olefinic substituents.⁸ They showed lower viscosities, higher ion conductivities and wider electrochemical stability windows than the corresponding ILs with saturated alkyl groups. However, the 1,3-disubstituted imidazolium-based ILs showed poor cathodic stabilities inherently because of an acidic proton at the C-2 position of the imidazolium ring. The cathodic stability window of ILs is one of the crucial requirements when account is taken of their possible application to lithium ion batteries (LIB). That is, as the electrolyte for LIB, the cathodic voltage window of ILs

should be below 0.0 V (vs. Li/Li⁺). Otherwise, electrochemical decomposition of ILs will advance the Li⁺ intercalation to negative electrode materials.

The ILs of quaternary ammoniums could be a solution to overcome this problem because they do not have relatively acidic protons. However, they have rather higher viscosity and lower conductivity.⁹ We have envisioned that introduction of an allyl group into quaternary ammoniums would improve both properties as reported with the imidazolium-based ILs having allyl groups,⁸ while maintaining the cathodic stability. Selection of a bis(trifluoromethanesulfonyl)imide (TFSI) anion would further decrease the viscosity and increase the ionic conductivity of the quaternary ammonium ILs produced. Although pyrrolidinium and piperidinium TFSI ILs having a propyl and a methyl group have been prepared by other groups,⁹ allyl-containing pyrrolidinium and piperidinium TFSI ILs have not been reported yet. Thus, we wish to report the synthesis and physicochemical properties of new pyrrolidinium and piperidinium TFSI ILs with allyl substituents as follows.

Experimental Section

¹H and ¹³C NMR spectra were measured on a JEOL JNM LA-300 spectrometer (300 MHz for ¹H NMR and 75 MHz for ¹³C NMR) using CDCl₃ as solvent. The ¹H NMR data were reported as follows in ppm (δ) from the internal standard (TMS, 0.0 ppm): chemical shift (multiplicity, coupling constant in Hz, integration), and the ¹³C NMR data in ppm (δ) from the internal standard (TMS, 0.0 ppm). Viscosity (η) was measured on a Brookfield DV-II+ cone/plate viscometer. Thermal decomposition temperature (T_d) was determined by using TA instrument SDT Q600 under Ar atmosphere. Heating rate and terminal temperature were set at 10 °C min⁻¹ and 600 °C, respectively. Thermal decomposition temperature was recorded at 10% weight loss



Scheme 1. Preparation of cyclic ammonium bis(trifluoromethanesulfonyl)imides.

temperature. Density was obtained by weighing a measured volume of the ILs. Ionic conductivity was determined by the complex impedance measurements between symmetric platinum electrodes, using a CHI660A electrochemical workstation in the frequency range from 1 Hz to 100 kHz. The cell constant of the cell was 1.6 cm^{-1} , determined with a 1.0 M KCl aqueous solution. Linear sweep voltammetry was performed with a CHI660A electrochemical workstation for the electrochemical stability window measurement at a scan rate of 10 mV s^{-1} by using a micro platinum electrode ($1.96 \times 10^{-3} \text{ cm}^2$) as a working electrode. The working electrode was polished before every measurement. Platinum electrode was used as a counter electrode and silver wire as a quasi-reference electrode. The potential of silver wire reference was calibrated by a ferrocene redox couple. In this work, the cathodic and anodic limits were arbitrarily defined as the potentials at which the current density reached 1 mA cm^{-2} . All the electrochemical measurements were made at room temperature unless otherwise specified.

The target pyrrolidinium and piperidinium TFSI ILs with allyl substituents were prepared according to the same procedure as described in our previous report (Scheme 1),⁸ which is a modification of the procedures reported in literature.^{1a,2,10} Pyrrolidinium and piperidinium TFSI ILs with a methyl and a propyl group were also made here for comparison by using the same synthesis protocol.

General procedure for the preparation of monoallyl-substituted pyrrolidinium and piperidinium halides. To a stirred solution of 1-methylpyrrolidine or 1-methylpiperidine (100.0 mmol) in acetonitrile (70 mL) was added propyl or allyl halide (110.0 mmol) dropwise at 0°C . The reaction mixture was stirred for 24 h at 30°C . Removal of the solvent under reduced pressure afforded crude 1-alkyl-1-methylpyrrolidinium or piperidinium halide. Completion of the reaction was confirmed by ^1H and ^{13}C NMR spectra. The crude product was purified by salting out in a mixture of acetonitrile and ethyl acetate.

General procedure for the preparation of diallyl-substituted pyrrolidinium and piperidinium bromides. To a stirred mixture of pyrrolidine or piperidine (100.0 mmol) and NaHCO_3 (110.0 mmol) in acetonitrile (70 mL) was added allyl bromide (220.0 mmol) dropwise at 0°C . The reaction mixture was stirred for 24 h at room

temperature. Completion of the reaction was confirmed by ^1H and ^{13}C NMR spectra. Filtration of the resulting mixture followed by removal of the solvent under reduced pressure afforded crude 1,1-diallylpyrrolidinium or piperidinium bromide. The crude product was purified by salting out in a mixture of acetonitrile and ethyl acetate.

General procedure for the anion metathesis. To a solution of pyrrolidinium/piperidinium halide (100.0 mmol) in distilled water (70 mL) was added lithium bis(trifluoromethanesulfonyl)imide (100.0 mmol). The reaction mixture was stirred for 24 h at 80°C . After the reaction mixture was cooled to room temperature, distilled water (100 mL) was added to the mixture and the mixture was extracted with dichloromethane ($2 \times 100 \text{ mL}$). The organic layer separated was washed with fresh distilled water ($2 \times 50 \text{ mL}$), dried with MgSO_4 . The crude solution was filtered through neutral aluminum oxide to remove the precipitated lithium salt and its yellowish color. The colorless solution was concentrated by removing the solvent under reduced pressure to afford the desired pyrrolidinium/piperidinium bis(trifluoromethanesulfonyl)imide. The water content of the ILs prepared in the present study was less than 0.005 wt%, measured by Karl-Fischer titration.

1-Methyl-1-propylpyrrolidinium bis(trifluoromethanesulfonyl)imide ([PMPyrr][TFSI] (1)). [PMPyrr]Br: ^1H NMR δ 1.08 (t, $J = 7.3$, 3H), 1.79-1.93 (m, 2H), 2.28-2.36 (m, 4H), 3.33 (s, 3H), 3.61-3.70 (m, 2H), 3.79-3.93 (m, 4H); ^{13}C NMR δ 10.9, 17.6, 21.6, 48.6, 64.5, 65.6.

[PMPyrr][TFSI]: Yield 90%; T_d 417 $^\circ\text{C}$; ^1H NMR δ 1.06 (t, $J = 7.5$, 3H), 1.76-1.89 (m, 2H), 2.20-2.35 (m, 4H), 3.07 (s, 3H), 3.25-3.35 (m, 2H), 3.48-3.59 (m, 4H); ^{13}C NMR δ 10.5, 17.4, 21.6, 48.5, 64.6, 66.2, 119.8 (q, $J_{\text{C-F}} = 319.0$).

1-Allyl-1-methylpyrrolidinium bis(trifluoromethanesulfonyl)imide ([AMPyrr][TFSI] (2)). [AMPyrr]Cl: ^1H NMR δ 2.25-2.34 (m, 4H), 3.32 (s, 3H), 3.74-3.96 (m, 4H), 4.43 (d, $J = 7.1$, 2H), 5.72 (d, $J = 9.9$, 1H), 5.84 (d, $J = 15.8$, 1H), 5.94-6.08 (m, 1H); ^{13}C NMR δ 21.8, 48.8, 63.6, 65.7, 125.4, 129.5.

[AMPyrr][TFSI]: Yield 83%; T_d 321 $^\circ\text{C}$; ^1H NMR δ 2.24-2.34 (m, 4H), 3.06 (s, 3H), 3.46-3.64 (m, 4H), 3.96 (d, $J = 7.1$, 2H), 5.73 (d, $J = 16.7$, 1H), 5.76 (d, $J = 9.5$, 1H), 5.90-6.04 (m, 1H); ^{13}C NMR δ 21.6, 48.8, 63.8, 66.3, 119.8 (q, $J_{\text{C-F}} = 318.9$), 124.7, 129.0.

1,1-Diallylpyrrolidinium bis(trifluoromethanesulfonyl)imide ([AAPyr][TFSI] (3)). [AAPyr]Br: $^1\text{H NMR } \delta$ 2.24–2.34 (m, 2H), 3.86–3.92 (m, 2H), 4.22 (d, $J = 7.1$, 2H), 5.74 (d, $J = 10.1$, 1H), 5.79 (d, $J = 16.8$, 1H), 5.94–6.08 (m, 1H); $^{13}\text{C NMR } \delta$ 21.9, 61.0, 62.1, 124.7, 129.3.

[AAPyr][TFSI]: Yield 81%; T_d 302 °C; $^1\text{H NMR } \delta$ 2.19–2.31 (m, 2H), 3.52–3.57 (m, 2H), 3.87 (d, $J = 7.1$, 2H), 5.70 (d, $J = 16.7$, 1H), 5.74 (d, $J = 9.5$, 1H), 5.88–6.02 (m, 1H); $^{13}\text{C NMR } \delta$ 21.9, 61.3, 62.7, 119.9 (q, $J_{\text{C-F}} = 318.9$), 124.2, 129.3.

1-Methyl-1-propylpiperidinium bis(trifluoromethanesulfonyl)imide ([PMPip][TFSI] (4)). [PMPip]Br: $^1\text{H NMR } \delta$ 1.07 (t, $J = 7.3$, 3H), 1.75–1.93 (m, 8H), 3.38 (s, 3H), 3.61–3.71 (m, 4H), 3.77–3.85 (m, 2H); $^{13}\text{C NMR } \delta$ 10.8, 15.5, 20.2, 20.6, 48.4, 60.8, 64.2.

[PMPip][TFSI]: Yield 94%; T_d 385 °C; $^1\text{H NMR } \delta$ 1.04 (t, $J = 7.3$, 3H), 1.67–1.97 (m, 8H), 3.05 (s, 3H), 3.23–3.29 (m, 2H), 3.36 (t, $J = 5.3$, 4H); $^{13}\text{C NMR } \delta$ 10.4, 15.3, 20.0, 20.7, 47.9, 61.4, 65.6, 119.9 (q, $J_{\text{C-F}} = 318.9$).

1-Allyl-1-methylpiperidinium bis(trifluoromethanesulfonyl)imide ([AMPip][TFSI] (5)). [AMPip]Br: $^1\text{H NMR } \delta$ 1.72–1.97 (m, 6H), 3.34 (s, 3H), 3.73 (t, $J = 5.5$, 4H), 4.50 (d, $J = 7.0$, 2H), 5.75 (dd, $J = 9.7$ and 1.7, 1H), 5.89 (dd, $J = 16.8$ and 1.5, 1H), 5.92–6.08 (m, 1H); $^{13}\text{C NMR } \delta$ 20.1, 20.7, 47.5, 60.3, 65.1, 123.8, 130.1.

[AMPip][TFSI]: Yield 98%; T_d 345 °C; $^1\text{H NMR } \delta$ 1.65–1.98 (m, 6H), 3.03 (s, 3H), 3.36 (t, $J = 5.5$, 4H), 3.94 (d, $J = 7.3$, 2H), 5.75 (d, $J = 16.8$, 1H), 5.78 (d, $J = 9.3$, 1H), 5.88–6.02 (m, 1H); $^{13}\text{C NMR } \delta$ 19.9, 20.6, 47.5, 60.9, 66.3, 119.9 (q, $J_{\text{C-F}} = 318.9$), 123.0, 130.4.

1,1-Diallylpiperidinium bis(trifluoromethanesulfonyl)imide ([AAPip][TFSI] (6)). [AAPip]Br: $^1\text{H NMR } \delta$ 1.85–1.96 (m, 3H), 3.77 (t, $J = 5.3$, 2H), 4.26 (d, $J = 7.1$, 2H), 5.77 (d, $J = 9.9$, 1H), 5.82 (d, $J = 16.9$, 1H), 5.91–6.05 (m, 1H); $^{13}\text{C NMR } \delta$ 20.2, 20.7, 57.8, 60.9, 123.7, 130.1.

[AAPip][TFSI]: Yield 88%; T_d 339 °C; $^1\text{H NMR } \delta$ 1.73–1.79 (m, 1H), 1.88–1.96 (m, 2H), 3.36 (t, $J = 5.7$, 2H), 3.89 (d, $J = 7.1$, 2H), 5.73 (d, $J = 16.5$, 1H), 5.77 (d, $J = 9.9$, 1H), 5.86–6.00 (m, 1H); $^{13}\text{C NMR } \delta$ 19.6, 20.6, 58.3, 61.3, 119.9 (q, $J_{\text{C-F}} = 318.9$), 123.0, 129.9.

Results and Discussion

Thermal and physical properties. Table 1 shows the decomposition temperature (T_d) of the ILs prepared in this

work and some selected TGA charts are represented in Figure 1. All of the pyrrolidinium and piperidinium bis(trifluoromethanesulfonyl)imides with an allyl substituent are liquid at room temperature. They are thermally less stable than the corresponding ILs with a propyl group. The similar results were observed in our previous work that reported the physicochemical properties of several new imidazolium tetrafluoroborates with unsaturated substituents.⁸ The ILs with one allyl group are more thermally stable than the ILs with two allyl groups. However, they are all thermally more stable than the conventional organic carbonate electrolytes such as ethylene carbonate (EC) and propylene carbonate (PC).

Table 1 also lists the densities (d), viscosities (η) and ionic conductivities (σ) of the ILs prepared. As desired, the cyclic quaternary ammonium ILs with one allyl group showed lower viscosities and higher ionic conductivities than their analogues having a saturated propyl substituent (Table 1, entries 1 vs. 2 and 4 vs. 5). In particular, [AMPyr][TFSI] shows the lowest viscosity of 52 cP and the highest ionic conductivity of 5.7 mS cm⁻¹. The lower viscosity of the pyrrolidinium and piperidinium ILs with an allyl group could be explained in terms of their molecular structures. The ILs with an allyl group have relatively planar structures compared to those of the ILs with a saturated propyl substituent because of the presence of the double bond having a planar structure. The planar ILs are known to have relatively low viscosity because the planarity of the mole-

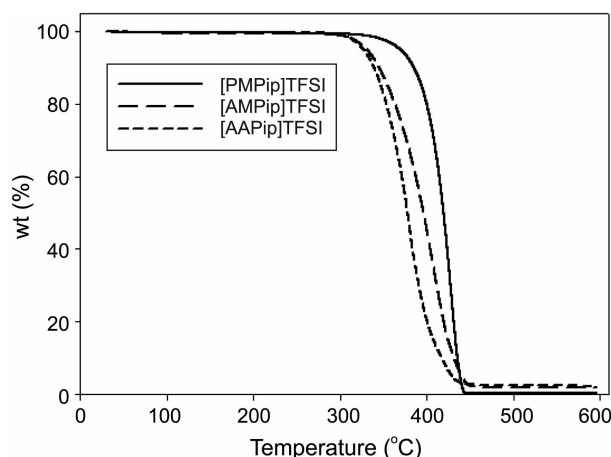
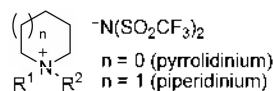


Figure 1. The TGA charts of [Pip][TFSI] ILs.

Table 1. Physicochemical properties of the ionic liquids prepared



No	Ionic liquids	R ¹	R ²	T_d (°C)	d (g/mL)	η (cP)	σ (mS/cm)
1	[PMPyr][TFSI]	Methyl	Propyl	417	1.27	59	4.9
2	[AMPyr][TFSI]	Methyl	Allyl	321	1.43	52	5.7
3	[AAPyr][TFSI]	Allyl	Allyl	302	1.40	57	4.6
4	[PMPip][TFSI]	Methyl	Propyl	385	1.32	141	2.9
5	[AMPip][TFSI]	Methyl	Allyl	345	1.42	108	3.5
6	[AAPip][TFSI]	Allyl	Allyl	339	1.45	113	2.3

cular structure allows rather facile slip between molecules.¹¹ In this work, the more or less planar allyl group can be positioned on the same plane as the pyrrolidinium or piperidinium ring and seems to hold the planarity of the cation itself. However, the diallyl-substituted ILs show slightly higher viscosities than those with monoallyl and methyl substituents probably because of the size difference between the three-carbon allyl group and the one-carbon methyl group.

It is also interesting to note here that the decrease of the viscosity is more significant in the piperidinium-based ILs. The piperidinium-based ILs show the higher viscosities and lower conductivities than the pyrrolidinium-based ILs probably because a piperidine ring has one more carbon than a pyrrolidine ring. In general, larger cations make ILs more viscous because of the increased intermolecular van der Waals interactions.^{10,3,12} Ionic conductivity is proportional to the number of charge carrier ions and their mobility. That is, the bigger piperidinium cations will reduce the rotational freedom of molecules, which leads to higher viscosities and lower ionic conductivities.

The conformational bias of a six-membered ring to a rather stable chair-like conformation in the piperidinium structure seems also to contribute the higher viscosity of the piperidinium-based ILs as is observed with a similar hydrocarbon ring system. Both the lower energy barrier of a ring-flip and the smaller energy difference between the envelope and the half-chair conformations in a five-membered ring make a cyclopentane ring more flexible, leading to the lower mp of cyclopentane than those of cyclohexane and cycloheptane (mp of cyclopentane, cyclohexane and cycloheptane: -95 , $+6.5$ and -12 °C, respectively).¹³

Electrochemical properties. The electrochemical windows of the ILs determined from their linear sweep voltammograms are shown in Table 2 and their linear sweep voltammograms are represented in Figures 2 and 3. As expected, the cathodic stability of the ILs prepared was much improved compared to those of the imidazolium-based ILs that were reported previously by us.⁸ Among them, [AMPyr][TFSI] shows the most negative cathodic stability of -3.2 V (vs. Fc/Fc⁺), which corresponds to 0.2 V (vs. Li/Li⁺). Note that a double bond is more vulnerable to an electrochemical reaction than a saturated one. Recently, Jan and co-workers reported the use of an organic carbonate, allyl ethyl carbonate, containing an unsaturated functional group for an application to lithium secondary batteries as an additive.¹⁴

Table 2. Electrochemical windows of the ionic liquids prepared

No	Ionic liquids	Cathodic limit (V, vs. Fc/Fc ⁺)	Anodic limit (V, vs. Fc/Fc ⁺)	Electrochemical window (V)
1	[PMPyr][TFSI]	-3.0	+2.6	5.6
2	[AMPyr][TFSI]	-3.2	+2.3	5.5
3	[AAPyr][TFSI]	-2.1	+2.6	4.7
4	[PMPip][TFSI]	-2.7	+2.5	5.2
5	[AMPip][TFSI]	-2.5	+2.5	5.0
6	[AAPip][TFSI]	-2.4	+2.5	4.9

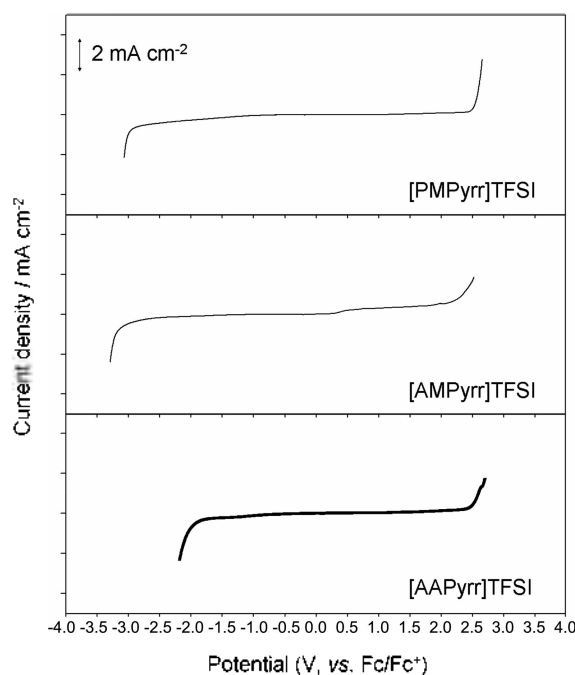


Figure 2. Linear sweep voltammograms of the pyrrolidinium TFSI ILs prepared.

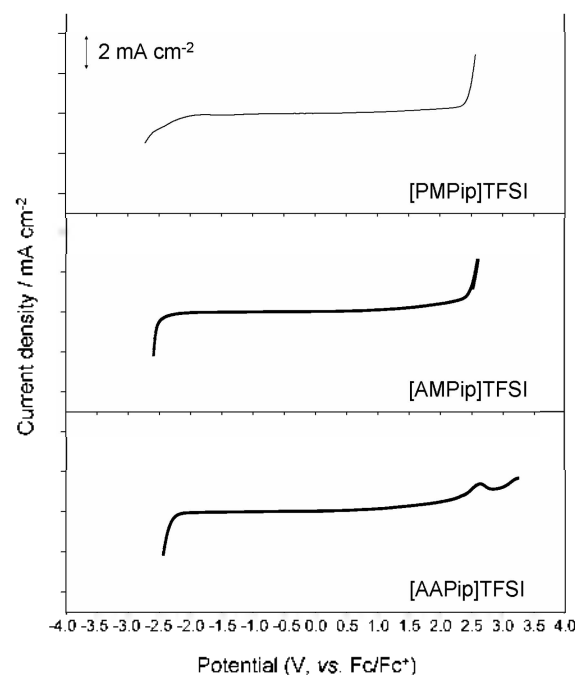


Figure 3. Linear sweep voltammograms of the piperidinium TFSI ILs prepared.

The molecule with a carbon-carbon double bond is easily decomposed to form a passivation layer on the cathode surface so as to inhibit further decomposition of organic electrolytes. The similar behavior of vinylene carbonate is well established for an efficient formation of a solid electrolyte interface (SEI). In this perspective, it seems that a certain type of the passivation layer is developed on the Pt electrode in the present study. Thus, the passivation layer formed on the electrode would suppress the decomposition

of the pyrrolidinium cation to extend the cathodic limit.

It is thus likely that this ionic liquid is usable as the electrolyte for the negative electrodes that are lithiated at >0.2 V (vs. Li/Li^+), for instance, $\text{Li}_4\text{Ti}_5\text{O}_{12}$ that is lithiated at 1.5 V (vs. Li/Li^+). The cathodic stability window of [AMPyr]TFSI is, however, still too high to be applicable for graphite negative electrodes that are lithiated near zero volts (vs. Li/Li^+). The cathodic stability of -1.9 V (vs. Fc/Fc^+) was shown with a similar imidazolium-based IL, 1-allyl-3-methylimidazolium tetrafluoroborate [AMIm]BF₄, as an electrolyte.

Generally, both cathodic and anodic limits would be determined by decomposition of the corresponding cations and anions, respectively. Particularly, the cathodic stability of ILs is decreased mainly by the presence of an acidic proton in cations of ILs, whereas the anodic decomposition is closely associated with the stability of anions of ILs.^{1a,3a} Thus, the ILs with pyrrolidinium or piperidinium cations having no acidic protons showed the wider cathodic limits than the ILs with the 1,3-disubstituted imidazolium cations that have an acidic proton at the C-2 position.

However, the electrochemical stability of the pyrrolidinium or piperidinium TFSI ILs at the anode shows similar or lower limits compared with those of the imidazolium tetrafluoroborate ILs (Table 2). In the previous work,⁸ the electrochemical stability of the imidazolium tetrafluoroborate ILs with unsaturated substituents showed much higher anodic limits by about 1–3 V than those with saturated analogues. This observation reveals that both the unsaturated substituents of the imidazolium ring and the tetrafluoroborate anion play important roles in affecting their anodic limits. It has been proposed that a certain effective passivation layer is developed on the Pt electrode as a result of oxidation of the unsaturated substituents in the case of the imidazolium tetrafluoroborate ILs. When the anion was changed from BF₄ to TFSI, the passivation layer did not seem to form readily on the Pt electrode. To compare an effect of the anions on the anodic stability, we have prepared 1-allyl-3-methylimidazolium bis(trifluoromethanesulfonyl)imide ([AMIm]TFSI) and 1,3-diallylimidazolium bis(trifluoromethanesulfonyl)imide ([AAIm]TFSI). The anodic limit of [AMIm]TFSI was only about +2.0 V and that of [AAIm]TFSI was close to +3.0 V (vs. Ag/Ag^+). Previously, the much higher anodic limits, +4.0 V and +4.2 V (vs. Ag/Ag^+), were shown with [AMIm]BF₄ and [AAIm]BF₄, respectively.⁸ These results indicate importance of the anion on the anodic stability and that the BF₄ anion contributes the anodic stability much more than the TFSI anion does. When the cation was changed from imidazolium to pyrrolidinium or piperidinium, these ILs showed the similar anodic limits (Table 2, entries 2, 3, 5 and 6). Therefore, it seems that the nature of the anion is a major factor to determine the anodic stability of the ILs prepared in the present study.

Conclusions

Four new pyrrolidinium and piperidinium TFSI ILs with

allyl substituents were synthesized, and their physicochemical properties were reported. All of the ILs were liquid at room temperature. All of them with an allyl substituent were thermally less stable than those with a saturated propyl substituent but still more stable than conventional organic carbonate electrolytes such as dimethyl carbonate and ethylene carbonate. The pyrrolidinium-based ILs showed better conductivities and lower viscosities than the corresponding piperidinium-based ILs. Among the pyrrolidinium-based ILs, [AMPyr]TFSI showed the lowest viscosity of 52 cP, the highest conductivity of 5.7 mS cm^{-1} , and the most negative cathodic voltage window of -3.2 V (vs. Fc/Fc^+) on a platinum electrode, which are the improved results compared to the corresponding analogue having a saturated substituent, 1-methyl-1-propylpyrrolidinium TFSI ([PMPyr]TFSI). All of the ILs prepared here showed much wider cathodic voltage windows compared with those of the imidazolium tetrafluoroborate ILs that have been reported in the previous study. However, the anodic limits showed poor results because the anodic stability seems to be related mostly with the anion. The allyl substituent with the TFSI anion did not show any improvement in the anodic stability that was observed with the BF₄ anion. The appropriate combination of a cation and an anion seems to play an important role in the determination of the anodic stability of the ILs.

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