

Synthesis and Physicochemical Properties of Ionic Liquids: 1-Alkenyl-2,3-dimethylimidazolium Tetrafluoroborates

Gwan-Hong Min, 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*

Received May 14, 2007

1-Alkenyl-2,3-dimethylimidazolium tetrafluoroborate ionic liquids having an olefinic substituent were synthesized and characterized. Among them, [AMMIm]BF₄ with an allyl group showed lower viscosity, higher ionic conductivity, and a wider electrochemical window compared with its analogue having a saturated alkyl substituent. An EDLC with [AMMIm]BF₄ showed better performance than that with [PMMIm]BF₄, too.

Key Words : Ionic liquids, 1-Alkenyl-2,3-dimethylimidazolium tetrafluoroborates, Olefinic substituent, Physicochemical properties, Electrochemical window

Introduction

Ionic liquids (ILs) are salts that are liquid at a wide temperature range. ILs have received great interest recently due to their unique properties-wide liquid range, good conductivity, wide electrochemical windows, non-volatility, and non-flammability.¹⁻⁴ Therefore, they have been studied by many researchers as a promising alternative to the conventional organic solvents^{1,2} or organic electrolytes.^{3,4} The widely used cations are imidazoliums and cyclic or acyclic quaternary ammoniums, and the anions are tetrafluoroborate, hexafluorophosphate and bis(trifluoromethanesulfonyl)imide (TFSI). Among these, the ionic liquids containing an imidazolium cation have the potential to be used as electrolytes because of their high conductivity and low viscosity.⁴

Several studies have attempted to control the physicochemical properties of ILs through the novel design of their cations and anions for practical use. One of the problems encountered with the imidazolium-based ILs is the lack of electrochemical stability. It is known that the anodic stability of the ionic liquids is governed by the anionic species. However, we have found that an appropriate substituent on the cation could affect the anodic stability of ILs. That is, the introduction of an olefinic substituent into the 1,3-disubstituted imidazolium tetrafluoroborates resulted in the enhancement of the anodic stability as well as the decrease of viscosity and the increase of ionic conductivity.⁵ However, the ILs bearing the allylic substituent on the imidazolium nitrogen atom still have some problems in an electrochemical application such as Li batteries. The most serious problem is that the imidazolium cation decomposes at about 1 V (vs. Li/Li⁺) mainly due to the presence of an acidic proton at the C-2 position.^{4,6} This urges to reconsider a novel design of the imidazolium-based ILs as an electrolyte or alternative negative electrode material for the practical application of the imidazolium-based ILs to Li batteries.

One of the simplest ways to remove the acidic proton from the imidazolium ring is to substitute the acidic proton with an alkyl group at the C-2 position.⁷ It was reported that 1,2,3-trialkyl substituted imidazolium salts showed an increased cathodic stability and thermal stability. However, their viscosities and the melting points were also increased as a result of the introduction of an alkyl group at the C-2 position of the imidazolium ring. Therefore, we wanted to extend our previous results to the 2-alkyl substituted imidazolium derivatives. It was expected that the introduction of an olefinic substituent would reduce some problems of the 2-alkylimidazolium-based ILs such as the high viscosity and low ionic conductivity, while maintaining the enhanced cathodic stability. Moreover, the anodic stability of the 2-alkylimidazolium-based ILs could be improved due to the olefinic substituent as was the case in our previous work.⁵

As part of an ongoing systematic work to enhance the electrochemical stability of imidazolium-based ILs, we have prepared three new imidazolium tetrafluoroborates with a methyl group at the C-2 position and an olefinic substituent on the nitrogen atom of the imidazolium ring. Herein we wish to report their physical and electrochemical properties as follows.

Experimental Section

¹H and ¹³C NMR spectra were obtained using CDCl₃ as solvent on a JEOL JNM LA-300 spectrometer (300 MHz for ¹H NMR and 75 MHz for ¹³C NMR). 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).

Sodium contents were measured by ICP-AES using a Shimadzu ICPS-1000IV spectrometer. Water contents were determined by Karl-Fischer coulometry using a Mettler Toledo DL39 coulometric titrator.

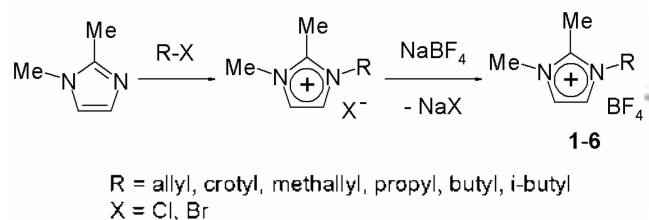
Thermal properties were analyzed by DSC and TGA. Crystallization point and melting point were determined by using TA Instruments Differential Scanning Calorimeter (DSC) Q1000 under N₂ atmosphere. Thermograms were recorded during heating from -80 °C to 100 °C scans at a heating rate of 10 °C min⁻¹ after cooling to -80 °C scans at a cooling rate of 10 °C min⁻¹. Thermal decomposition temperature was recorded by using TA Instruments SDT Q600 under Ar atmosphere. Heating rate and terminal temperature were set at 10 °C min⁻¹ and 800 °C, respectively.

Density was measured by weighing a measured volume of the ILs. Viscosity measurements were carried out on a Brookfield DV-II+ cone/plate viscometer.

Ionic conductivity was determined by the complex impedance measurements with 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 platinum electrode (1.96 × 10⁻³ cm²) as a working electrode. The working electrode was polished before every measurement. Platinum foil was used as a counter electrode and silver wire as a quasi-reference electrode. In this work, the cathodic and anodic limits were arbitrarily defined as the potential at which the current density reached 1 mA cm⁻². All the electrochemical measurements were performed at room temperature unless otherwise specified.

To make the electrodes of an EDLC (electric double-layer capacitor), BP-20 (activated carbon from Kuraray Chemical of which surface area is 2000 m² g⁻¹) was mixed with acetylene black and poly(vinylidene fluoride) (80:10:10 wt. %) and the resulting mixed slurry was coated on an Al current collector and pressed. The 2032 coin cells were assembled with symmetric electrodes and ILs. They were charged and discharged by constant current between 2 V and 0 V. The specific capacitance, *C*, was calculated by $Q = CV$ (*V* is voltage and *Q* was measured from multiplying discharge constant current by discharge time).

Preparation of the ionic liquids. 2-Methyl substituted imidazolium tetrafluoroborates with an olefinic substituent were prepared according to the same procedure described in our previous report,⁵ which is a modified procedure based on the work done by Wilkes and Zaworotko (Scheme 1).⁸ The corresponding 2-methylimidazolium tetrafluoroborates with



Scheme 1. Preparation of 2-methylimidazolium tetrafluoroborates.

Table 1. Maximum content of sodium and water in the ILs prepared

No.	Ionic liquids	R	Na (ppm)	H ₂ O (ppm)
1	[AMMIm]BF ₄	Allyl	133	300
2	[CMMIm]BF ₄	Crotyl	118	312
3	[MaMMIm]BF ₄	Methallyl	147	305
4	[PMMIm]BF ₄	Propyl	130	302
5	[BMMIm]BF ₄	Butyl	131	307
6	[iBMMIm]BF ₄	Isobutyl	131	315

saturated alkyl substituents were also made for comparison following the same synthetic protocol.

General procedure for the preparation of the imidazolium halides. To a stirred solution of freshly distilled 1,2-dimethylimidazole (9.61 g, 100 mmol) in acetonitrile (70 mL) was added requisite alkyl halide (R-X, 110 mmol) dropwise at 0 °C. The reaction mixture was stirred for 24-48 h at 30 °C. Removal of the solvent under reduced pressure afforded crude 1-R-2,3-dimethylimidazolium halide. Completion of the quaternization reaction was confirmed by ¹H and ¹³C NMR spectra. The crude product was used without further purification for the next step, an anion metathesis.

General procedure for the anion metathesis. To a solution of the crude imidazolium halide, obtained from the above reaction, in acetone (70 mL) was added sodium tetrafluoroborate (10.90 g, 100.0 mmol). The reaction mixture was stirred for 24 h at room temperature. The resulting mixture was filtered through a pad of neutral aluminum oxide to remove the sodium salt and color. Evaporation of the solvent under reduced pressure afforded the corresponding imidazolium tetrafluoroborate.

Completion of the anion-exchange reactions was confirmed by ¹H and ¹³C NMR spectra. The Na content of all the imidazolium tetrafluoroborates prepared in the present study was less than 150 ppm by ICP-AES and their water content was below 320 ppm by Karl-Fischer titration (Table 1).

1-Allyl-2,3-dimethylimidazolium tetrafluoroborate ([AMMIm]BF₄) (1). [AMMIm]Br: ¹H NMR δ 2.80 (s, 3H), 4.00 (s, 3H), 4.93 (d, *J* = 5.7, 2H), 5.28 (d, *J* = 17.0, 1H), 5.39 (d, *J* = 10.3, 1H), 5.90-6.02 (m, 1H), 7.53 (d, *J* = 2.0, 1H), 7.70 (d, *J* = 2.0, 1H); ¹³C NMR δ 9.0, 34.1, 48.8, 118.4, 119.6, 120.9, 128.4, 142.2.

[AMMIm]BF₄: Yield 86%; *T*_c -62 °C; *T*_d 381 °C; ¹H NMR δ 2.62 (s, 3H), 3.84 (s, 3H), 4.72 (d, *J* = 5.9, 2H), 5.28 (d, *J* = 17.0, 1H), 5.43 (d, *J* = 10.4, 1H), 5.88-5.99 (m, 1H), 7.19 (d, *J* = 2.0, 1H), 7.28 (d, *J* = 2.0, 1H); ¹³C NMR δ 9.0, 34.9, 50.3, 120.0, 121.1, 122.5, 130.4, 144.5.

1-Crotyl-2,3-dimethylimidazolium tetrafluoroborate ([CMMIm]BF₄) (2). [CMMIm]Cl: ¹H NMR δ 1.76 (d, *J* = 6.4, 3H), 2.82 (s, 3H), 4.04 (s, 3H), 4.83 (d, *J* = 6.4, 2H), 5.52-5.63 (m, 1H), 5.83-5.95 (m, 1H), 7.38 (d, *J* = 2.0, 1H), 7.62 (d, *J* = 2.0, 1H); ¹³C NMR δ 9.5, 17.7, 35.1, 50.3, 120.1,

122.4, 122.5, 133.7, 144.0.

[CMMIm]BF₄: Yield 85%; *T_c* -65 °C; *T_m* -56 °C; *T_d* 254 °C; ¹H NMR δ 1.75 (d, *J* = 6.6, 3H), 2.60 (s, 3H), 3.80 (s, 3H), 4.62 (d, *J* = 6.4, 2H), 5.50-5.60 (m, 1H), 5.79-5.90 (m, 1H), 7.20 (d, *J* = 2.0, 1H), 7.29 (d, *J* = 2.0, 1H); ¹³C NMR δ 9.2, 17.7, 34.9, 50.1, 120.8, 122.4, 122.8, 133.2, 144.1.

1,2-Dimethyl-3-methylimidazolium tetrafluoroborate ([MaMMIm]BF₄) (3). [MaMMIm]Cl: ¹H NMR δ 1.78 (s, 3H), 2.76 (s, 3H), 4.05 (s, 3H), 4.73 (s, 1H), 4.87 (s, 2H), 5.05 (s, 1H), 7.49 (d, *J* = 2.0, 1H), 7.76 (d, *J* = 2.0, 1H); ¹³C NMR δ 10.6, 20.0, 36.0, 54.4, 115.1, 121.9, 123.1, 137.8, 144.5.

[MaMMIm]BF₄: Yield 77%; *T_m* 57 °C; *T_d* 358 °C; ¹H NMR δ 1.76 (s, 3H), 2.59 (s, 3H), 3.85 (s, 3H), 4.63 (s, 2H), 4.71 (s, 1H), 5.07 (s, 1H), 7.20 (d, *J* = 2.2, 1H), 7.34 (d, *J* = 2.2, 1H); ¹³C NMR δ 9.5, 19.7, 35.3, 54.0, 115.2, 121.4, 122.6, 137.7, 144.7.

1,2-Dimethyl-3-propylimidazolium tetrafluoroborate ([PMMIm]BF₄) (4). [PMMIm]Br: ¹H NMR δ 1.02 (t, *J* = 7.4, 3H), 1.84-1.96 (m, 2H), 2.83 (s, 3H), 4.03 (s, 3H), 4.18 (t, *J* = 7.4, 2H), 7.46 (d, *J* = 1.8, 1H) 7.66 (d, *J* = 1.8, 1H); ¹³C NMR δ 10.5, 10.6, 23.1, 35.7, 50.1, 121.3, 122.9, 143.9.

[PMMIm]BF₄: Yield 87%; *T_m* -17 °C; *T_d* 442 °C; ¹H NMR δ 0.99 (t, *J* = 7.3, 3H), 1.79-1.91 (m, 2H), 2.54 (s, 3H), 3.82 (s, 3H), 4.04 (t, *J* = 7.3, 2H), 7.23 (d, *J* = 2.0, 1H), 7.30 (d, *J* = 2.0, 1H); ¹³C NMR δ 9.0, 10.5, 23.0, 34.8, 49.7, 121.0, 122.4, 144.0.

1-Butyl-2,3-dimethylimidazolium tetrafluoroborate ([BMMIm]BF₄) (5). [BMMIm]Br: ¹H NMR δ 0.97 (t, *J* = 7.3, 3H), 1.34-1.47 (m, 2H), 1.77-1.85 (m, 2H), 2.83 (s, 3H), 4.04 (s, 3H), 4.22 (t, *J* = 7.5, 2H), 7.46 (d, *J* = 2.1, 1H), 7.71 (d, *J* = 2.1, 1H); ¹³C NMR δ 11.1, 13.6, 19.6, 31.8, 36.3, 48.8, 121.1, 123.1, 143.8.

[BMMIm]BF₄: Yield 86%; *T_c* -29 °C; *T_m* 21 °C; *T_d* 401 °C; ¹H NMR δ 0.96 (t, *J* = 7.3, 3H), 1.31-1.43 (m, 2H), 1.72-1.82 (m, 2H), 2.61 (s, 3H), 3.81 (s, 3H), 4.06 (t, *J* = 7.5, 2H), 7.23 (d, *J* = 2.0, 1H), 7.30 (d, *J* = 2.0, 1H); ¹³C NMR δ 9.5, 13.5, 19.5, 31.6, 35.2, 48.4, 120.8, 122.6, 143.9.

1,2-Dimethyl-3-isobutylimidazolium tetrafluoroborate ([iBMMIm]BF₄) (6). [iBMMIm]Br: ¹H NMR δ 1.01 (d, *J* = 6.6, 6H), 2.08-2.21 (m, 1H), 2.82 (s, 3H), 4.01 (d, *J* = 7.5, 2H), 4.05 (s, 3H), 7.31 (d, *J* = 2.0, 1H), 7.59 (d, *J* = 2.0, 1H); ¹³C NMR δ 11.3, 19.8, 29.4, 36.4, 56.0, 121.6, 123.0, 144.2.

[iBMMIm]BF₄: Yield 85%; *T_m* 63 °C; *T_c* -50 °C; *T_d* 394 °C; ¹H NMR δ 0.96 (d, *J* = 6.6, 6H), 2.02-2.15 (m, 1H), 2.61 (s, 3H), 3.83 (s, 3H), 3.89 (d, *J* = 7.5, 2H), 7.16 (d, *J* = 2.2, 1H), 7.29 (d, *J* = 2.2, 1H); ¹³C NMR δ 9.9, 19.6, 29.2, 35.4, 55.7, 121.3, 122.5, 144.3.

Results and Discussion

Thermal behaviors. Table 2 lists the crystallization point (*T_c*), melting point (*T_m*), and decomposition temperature (*T_d*) of the ILs prepared in this work. The DSC charts of [AMMIm]BF₄ and [CMMIm]BF₄ are shown in Figure 1. The 2-methylimidazolium salts with an allyl (1) or crotyl group (2) were liquid at room temperature (entries 1 and 2), while the IL having a methyl group was white solid (entry 3). Decomposition temperature of the ILs with an olefinic substituent were beyond 350 °C except for [CMMIm]BF₄ but lower than that of the ILs with saturated alkyl substituents. This observation that an introduction of the olefinic substituent to the imidazolium ring lowers the

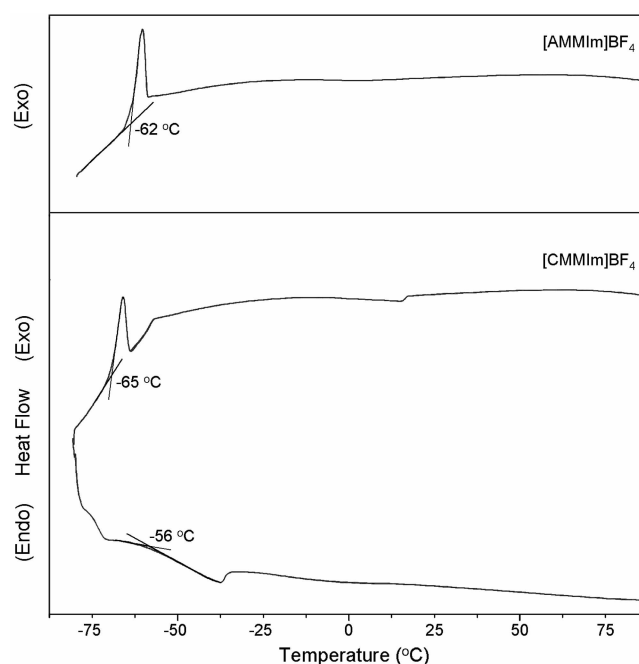
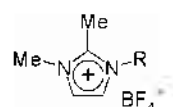


Figure 1. The DSC charts of the ILs with an olefinic substituent.

Table 2. The structures and physicochemical properties of the ILs prepared



No.	Ionic liquids	R	<i>T_c</i> (°C)	<i>T_m</i> (°C)	<i>T_d</i> (°C)	<i>d</i> (g mL ⁻¹)	<i>η</i> (cP)	<i>σ</i> (mS cm ⁻¹)
1	[AMMIm]BF ₄	Allyl	-62	ND ^a	381	1.16	199	3.2
2	[CMMIm]BF ₄	Crotyl	-65	-56	254	1.15	257	1.7
3	[MaMMIm]BF ₄	Methyl	ND	57	358	- ^b	- ^b	5.3 ^c
4	[PMMIm]BF ₄	Propyl	ND	-17	442	1.13	330	1.7
5	[BMMIm]BF ₄	Butyl	-29	21	401	1.03	372	0.7
6	[iBMMIm]BF ₄	Isobutyl	-50	63	394	- ^b	- ^b	10.9 ^d

^aND: not detected. ^bSolid. ^cMeasured at 70 °C. ^dMeasured at 100 °C.

decomposition temperature agrees with our previous results.⁵ However, all of them are more stable than conventional organic carbonate electrolytes.

Physical properties. Table 2 also shows density (d), viscosity (η) and ionic conductivity (σ) of the ILs prepared. As expected, the ILs with the olefinic substituent showed lower viscosity and higher ionic conductivity than their analogues having the saturated alkyl substituents. [AMMIm]BF₄ shows 199 cP of viscosity and 3.2 mS cm⁻¹ of ionic conductivity, which are contrasted by the higher viscosity (330 cP) and lower ionic conductivity (1.7 mS cm⁻¹) of its saturated alkyl analogue [PMMIm]BF₄. The lower viscosity and higher ionic conductivity of the imidazolium salts with the olefinic substituent would be due to their relatively planar structure of an allyl group. A more planar structure would allow relatively facile slip between molecules, resulting in lower viscosity.⁹ In this work, the relatively planar allyl or crotyl group can take a more or less parallel position to the planar imidazolium ring, which seems to hold the planarity of the whole cation itself compared to that having the saturated alkyl substituents.

Electrochemical behavior. The electrochemical stability windows of the ILs determined from their linear sweep voltammograms are listed in Table 3 and a linear sweep voltammogram of [AMMIm]BF₄ is shown together with those of 1-allyl-3-methylimidazolium tetrafluoroborate ([AMIm]BF₄) and [PMMIm]BF₄ in Figure 2. The cathodic limits of the ILs with the olefinic substituent are similar to those of their analogues with saturated alkyl substituents. In particular, the cathodic stability of [AMMIm]BF₄ was better by about 0.1 V than that of [AMIm]BF₄ that has an acidic

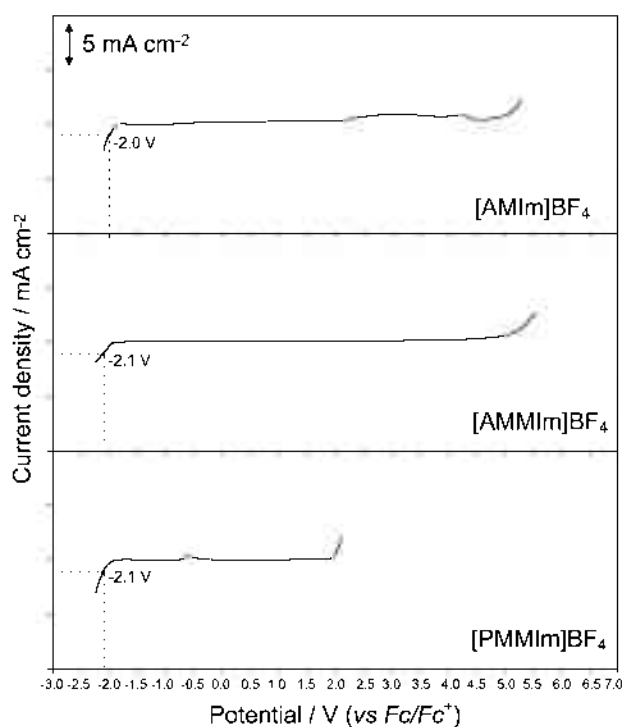


Figure 2. Linear sweep voltammograms of the ILs prepared with a platinum working electrode.

Table 3. The electrochemical windows of the ILs prepared

No.	Ionic liquids	Voltage limit ^a (V)		Electrochemical window (V)
		Cathode	Anode	
1	[AMMIm]BF ₄	-2.1	5.3	7.4
2	[CMMIm]BF ₄	-2.1	2.3	4.4
4	[PMMIm]BF ₄	-2.1	2.2	4.3
5	[BMMIm]BF ₄	-2.1	2.0	4.1
7	[AMIm]BF ₄	-2.0	5.1	7.1

^aPotential vs. Fc/Fc⁺ (Pt working electrode).

proton at the C-2 position (Figure 2, Table 3). It is interesting to note that [AMMIm]BF₄ shows much enhanced anodic stability by about 3.0 V, while the anodic stability of [CMMIm]BF₄ is similar to those of [PMMIm]BF₄ and [BMMIm]BF₄. The anodic limit of [AMMIm]BF₄ was assigned as 5.3 V vs. Fc/Fc⁺, resulting in the widest electrochemical window of 7.4 V. This value is even greater than that of [AMIm]BF₄ that showed the electrochemical window of 7.1 V (Table 3).

At this stage, it was confirmed whether the enhanced electrochemical stability could be obtained under other conditions. Thus, there arose a need for the linear sweep voltammetry by using the other working electrode. Figure 3 shows the linear sweep voltammogram of [AMMIm]BF₄ by using a glassy carbon as a working electrode and a silver wire as a reference electrode. Here, ferrocene was used as an internal reference. An interesting result was obtained under these conditions. [AMMIm]BF₄ exhibited a cathodic limit of -2.9 V and an anodic limit of 6.3 V (vs. Fc/Fc⁺), resulting in an even wider electrochemical window of 9.2 V than that measured with the Pt electrode. This indicates that the enhanced electrochemical stability could be achieved in other electrochemical systems as well, indicating a possibility of application to various electrochemical conditions. Moreover, these observations, along with our previous results, confirm that a simple functionalization on the imidazolium ring can lead to the enhancement of the anodic and/or cathodic stability in linear sweep voltammetry.^{5,10}

Application to an electric double-layer capacitor (EDLC). [AMMIm]BF₄ and [PMMIm]BF₄ were examined as an electrolyte of an EDLC for a practical application. The

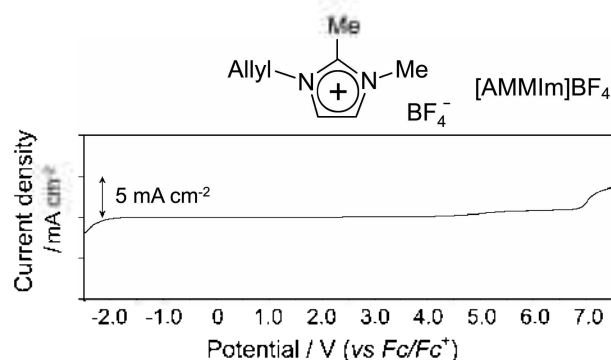


Figure 3. The linear sweep voltammogram of [AMMIm]BF₄ with a glassy carbon working electrode.

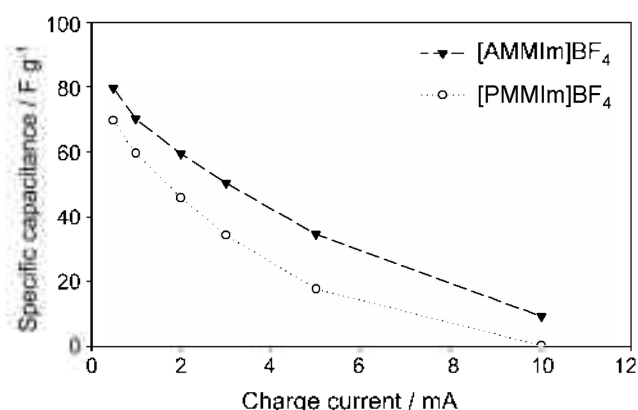


Figure 4. Specific capacitance and current density of an EDLC with the ILs prepared.

specific capacitance of the EDLCs was measured under various charge/discharge current. [AMMIm]BF₄ showed higher specific capacitance compared with [PMMIm]BF₄ (Figure 4) probably because of the higher ionic conductivity of [AMMIm]BF₄ than that of [PMMIm]BF₄ (Table 2). However, [AMMIm]BF₄ showed lower capacitance than the reported ionic liquids such as [EMIm]F(HF)_{2,3} (11.1 F cm³) and DEME-BF₄ (25.5 F g⁻¹).¹¹ The higher conductivity of the IL with an allyl substituent could be explained due to its molecular structure as mentioned above. [AMMIm]BF₄, therefore, could find another application as an electrolyte in electrochemical capacitors in terms of power characteristics.

Conclusions

Three new 2-methyl substituted imidazolium tetrafluoroborates with an olefinic substituent were synthesized, and their physicochemical properties were compared with those of the ILs containing the saturated alkyl substituents. [AMMIm]BF₄ and [CMMIm]BF₄ were liquid at room temperature. All of them were thermally less stable than their analogues with saturated alkyl groups but more stable than conventional organic carbonate electrolytes. [AMMIm]BF₄ and [CMMIm]BF₄ showed lower viscosity and higher ionic conductivity compared with the corresponding ILs containing the saturated alkyl groups. These results could be rationalized by their relatively planar structures. [AMMIm]BF₄ showed a wider electrochemical window on both Pt and glassy carbon electrodes. [AMMIm]BF₄ exhibited the widest electrochemical window of 7.4 V on the Pt electrode. Some enhancement could also be observed when a glassy carbon electrode was used,

showing an even wider electrochemical window of 9.2 V. In an application to a capacitor as an electrolyte, the EDLC using [AMMIm]BF₄ showed higher specific capacitance than that using [PMMIm]BF₄.

Acknowledgement. This work was supported by the Division of Advanced Batteries in NGF Program (Project No. 10016439) and by KOSEF through the Research Center for Energy Conversion and Storage. We also gratefully acknowledge the financial support by the BK 21 Project funded by the Ministry of Education and Human Resources Development of Korea.

References

- (a) Welton, T. *Chem. Rev.* **1999**, *99*, 2071-2083. (b) Anthony, J. L.; Brunnecke, J. E.; Holbrey, J. D.; Maginn, E. J.; Mantz, R. A.; Rogers, R. D.; Trulove, P. C.; Visser, A. E.; Welton, T. In *Ionic Liquids in Synthesis*; Wasserscheid, P.; Welton, T., Eds.; Wiley-VCH Verlag: Weinheim, 2003; pp 41-126. (c) Song, C. E.; Yoon, M. Y.; Choi, D. S. *Bull. Korean Chem. Soc.* **2005**, *26*, 1321-1330. (d) Jorapur, Y. R.; Chi, D. Y. *Bull. Korean Chem. Soc.* **2006**, *27*, 345-354.
- (a) Wasserscheid, P.; Keim, W. *Angew. Chem. Int. Ed.* **2000**, *39*, 3772-3789. (b) Dyson, P. J. *Transition Met. Chem.* **2002**, *27*, 353-358.
- (a) Bonhôte, P.; Dias, A.-P.; Armand, M.; Papageorgiou, N.; Kalyanasundaram, K.; Grätzel, M. *Inorg. Chem.* **1996**, *35*, 1168-1178. (b) Lee, J. S.; Bae, J. Y.; Lee, H.; Quan, N. D.; Kim, H. S.; Kim, H. *J. Ind. Eng. Chem.* **2004**, *10*, 1086-1089.
- (a) Buzzeo, M. C.; Evans, R. G.; Compton, R. G. *ChemPhysChem* **2004**, *5*, 1106-1120. (b) *Electrochemical Aspects of Ionic Liquids*; Ohno, H., ed.; Wiley-Interscience: Hoboken, 2005; pp 173-223. (c) Webber, A.; Blomgren, G. E. In *Advances in Lithium-Ion Batteries*; van Schalkwijk, W. A.; Scrosati, B., Eds.; Kluwer Academic/Plenum Publishers: New York, 2002; pp 185-232.
- Min, G.-H.; Yim, T.; Lee, H. Y.; Huh, D. H.; Lee, E.; Mun, J.; Oh, S. M.; Kim, Y. G. *Bull. Korean Chem. Soc.* **2006**, *27*, 847-852.
- Nakagawa, H.; Izuchi, S.; Kuwana, K.; Nukuda, T.; Aihara, Y. *J. Electrochem. Soc.* **2003**, *150*, A695-A700.
- (a) Gifford, P. R.; Palmisano, J. B. *J. Electrochem. Soc.* **1987**, *134*, 610-614. (b) Koch, V. R.; Nanjundiah, C.; Appetecchi, G. B.; Scrosati, B. *J. Electrochem. Soc.* **1995**, *142*, 1116-1118.
- Wilkes, J. S.; Zaworotko, M. J. *J. Chem. Soc., Chem. Commun.* **1992**, 965-967.
- Sun, J.; MacFarlane, D. R.; Forsyth, M. *Electrochim. Acta* **2003**, *48*, 1707-1711.
- Lee, J. S.; Quan, N. D.; Hwang, J. M.; Bae, J. Y.; Kim, H.; Cho, B. W.; Kim, H. S.; Lee, H. *Electrochem. Commun.* **2006**, *8*, 460-464.
- (a) Ue, M.; Takeda, M.; Toriumi, A.; Kominato, A.; Hagiwara, R.; Itob, Y. *J. Electrochem. Soc.* **2003**, *150*, A499-A502. (b) Sato, T.; Masuda, G.; Takagi, K. *Electrochim. Acta* **2004**, *49*, 3603-3611.