

Ionic Liquids Containing 1,1-Dicyano-1-acetylmethanide Anion as Potential Electrolytes

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Various types of room temperature ionic liquids (RTILs) containing 1,1-dicyano-1-acetylmethanide anion ($[\text{C}(\text{CN})_2(\text{COCH}_3)]^-$, $[\text{DCNAcC}]^-$) were prepared and their physical and electrochemical properties were studied. All of these ILs exhibited high thermal stabilities over 200 °C and relatively high ionic conductivities up to 29.4 mS cm⁻¹ at 80 °C. Although the ionic conductivity of IL containing bis(trifluoromethanesulfonyl)-imide ($[\text{Tf}_2\text{N}]^-$) anion is higher than that of ILs bearing $[\text{DCNAcC}]^-$ anion, the specific capacitance of ILs bearing $[\text{DCNAcC}]^-$ anion are higher than that of IL containing $[\text{Tf}_2\text{N}]^-$ anion and showed high temperature dependence. Such favorable electrochemical properties of these ILs are likely to be attributed to the efficient dissociation of cation and anion at higher temperature and enhanced electrosorption of $[\text{DCNAcC}]^-$ anion at the electrode.

Key Words : Ionic liquid, Electrolyte, Ionic conductivity, Specific capacitance

Introduction

Electrochemical double layer capacitors (EDLCs) have been considered as promising energy storage devices for their long cycle-life, high power density, and very short charging time (within tens of seconds). EDLCs store electric energy by the charge separation of electrolyte at the electrode/electrolyte interface.¹ To achieve high power density, various porous materials with huge surface area^{2,3} and modified carbons as electrodes have been developed.^{1,4,5} However, the operation at high potential and high temperature is restricted because most EDLCs are adopting aqueous or organic electrolyte system.^{6,7} One of the most promising application of EDLCs is in transportation field, especially in hybrid electric vehicles, where the operating temperature higher than 60 °C is required because of the coupling of electrochemical capacitors and fuel cells and hence safety becomes the main concern for this energy storage system.^{6,8,9}

Ionic liquids (ILs), molten salts which have liquid state at below 100 °C, have attractive characteristics such as negligible vapor pressure, non-flammability, wide liquid temperature range, high thermal and electrochemical stability. For this reason, ILs have been considered as promising electrolyte candidates for constructing safe electrochemical devices including EDLC compared with volatile aqueous and organic electrolytes.¹⁰⁻¹⁵ Generally, large surface area of electrode is considered as the necessity to obtain the high capacitance in EDLC. For example, Denshchikov *et al.* reported that the capacitance can be increased from 21 to 111 F g⁻¹ by increasing the surface area of electrode from 190 to 1040 m² g⁻¹.¹⁶ Lazzari *et al.* also showed that the capacitance can be increased from 30 to 160 F g⁻¹ by increasing the surface area from 685 to 1790 m² g⁻¹.¹⁷ However, most ILs showed low specific capacitances 20-40

F g⁻¹ although carbon electrodes have high surface area (2000-2400 m² g⁻¹).^{14,15,18} Generally ILs have relatively higher viscosity than aqueous or organic electrolyte systems and this complicates a good wetting of carbon materials. The performance of the capacitor can be improved by increasing temperature because higher temperature leads to lower viscosity and higher ionic conductivity by the enhanced ion dissociation.¹⁹ Although the relationship between temperature and ion size or shape of ILs has not been studied intensively, the temperature dependence is more profound in larger ion than smaller ion.⁷

In this regard, we have synthesized several ILs containing methanide anion bearing acetyl group and two nitrile groups with a hope that the planar-like structure and smaller size of anion show higher temperature dependence on capacitance compare to the non-planar and larger anion. We report here the preparation, physical and electrochemical properties of a series of ILs containing methanide anion. In addition, the applicability of these ILs for EDLC and the temperature dependence on specific capacitance are also discussed.

Experimental

Synthesis of ILs. All reagents were purchased from Aldrich Chemical Co. and were used as received without further purification. 1-Ethyl-3-methylimidazolium bromide ($[\text{EMIm}]\text{Br}$), 1-butyl-3-methylimidazolium bromide ($[\text{BMIm}]\text{Br}$), *N*-ethyl-*N*-methylmorpholinium bromide ($[\text{EMMor}]\text{Br}$), *N*-ethylpyridinium bromide ($[\text{EPy}]\text{Br}$), *N*-ethyl-*N*-methylpyrrolidinium bromide ($[\text{EMPyr}]\text{Br}$), *N*-ethyl-*N*-methylpiperidinium bromide ($[\text{EMPip}]\text{Br}$), 1-(ethyleneglycol monomethylether)-3-methylimidazolium methanesulfonate ($[\text{E}_1\text{MIm}][\text{MeSO}_3]$), 1-ethyl-3-methylimidazolium bis(trifluoromethylsulfonyl)imide ($[\text{EMIm}][\text{Tf}_2\text{N}]$), and sodium

1,1-dicyano-1-acetylmethanide ($\text{Na}[\text{C}(\text{CN})_2(\text{COCH}_3)]$, $\text{Na}[\text{DCNAcC}]$) were prepared according to the literature procedures.²⁰⁻²⁴

Representative procedure for the preparation of 1-ethyl-3-methylimidazolium 1,1-dicyano-1-acetylmethanide ($[\text{EMIm}][\text{DCNAcC}]$) is as follows. In a 100 mL one-neck flask, a solution of $\text{Na}[\text{DCNAcC}]$ (0.7 g, 5.38 mmol) in acetone (10 mL) and a solution of $[\text{EMIm}]\text{Br}$ (1.03 g, 5.38 mmol) in acetonitrile (25 mL) were mixed. After the mixture was stirred at room temperature for 24 h, white precipitate was filtered off and solvents were removed by rotary evaporation. The crude product was dissolved in dichloromethane (20 mL) followed by filtration to remove the remaining NaBr dissolved in $[\text{EMIm}][\text{DCNAcC}]$. After reducing the volume, $[\text{EMIm}][\text{DCNAcC}]$ was obtained as a light yellow oil by drying under vacuum for 24 h at 80 °C (Yield: 98%). $[\text{BMIm}][\text{DCNAcC}]$, $[\text{E}_1\text{MIm}][\text{DCNAcC}]$, $[\text{EPy}][\text{DCNAcC}]$, $[\text{EMPip}][\text{DCNAcC}]$, $[\text{EMPyr}][\text{DCNAcC}]$, and $[\text{EMMor}][\text{DCNAcC}]$ were prepared in a manner analogous to that used for preparing $[\text{EMIm}][\text{DCNAcC}]$ and the detailed information were shown in the Supporting Information (SI).

Characterization. Thermogravimetric analysis (TGA) was performed using a thermogravimetric analyzer (Shimadzu) in a nitrogen atmosphere between 25 and 800 °C at a ramp rate of 10 °C min^{-1} . The melting temperatures of ILs were determined using a TA Instruments Q10 differential scanning calorimeter (DSC) in the range from -70 to 120 °C at a ramp rate of 5 °C min^{-1} under nitrogen atmosphere. The electrochemical stabilities of ILs were analyzed by cyclic voltammetry (CV) method at an ambient temperature (ASR 2263 potentiostat). A glassy carbon working electrode of 3 mm diameter was used with a carbon rod as a counter electrode and a silver wire as a pseudo-reference electrode. The electrochemical windows were calibrated using the redox potential of ferrocene/ferricenium (Fc/Fc^+) couple measured in each IL. The ionic conductivities were also measured by AC impedance measurement (ASR 2263 potentiostat).

Specific Capacitance Measurement. The EDLC testing cell is schematically shown in Figure 1 where two carbon electrodes divided by separator were assembled between stainless steel current collectors. The carbon electrodes were prepared with the mixture of activated carbon (surface area is 811 $\text{m}^2 \text{g}^{-1}$) 80 wt %, carbon black 10 wt %, and polytetrafluoroethylene 10 wt %. The mixture was ground, pressed at 6 MPa, and dried at 100 °C under vacuum for 8 h

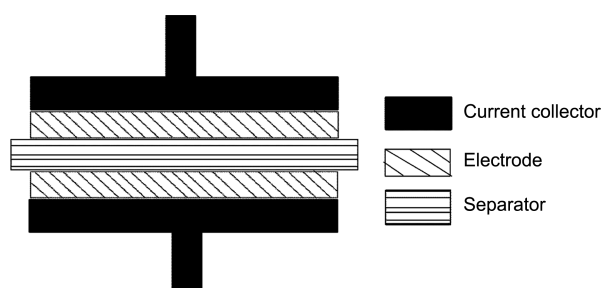


Figure 1. Schematic diagram of EDLC testing cell.

to get the disk electrodes. The electrodes formed in this way were 17 mm in diameter and 0.5 mm in thickness. EDLC was assembled under Ar (g) by placing the separator ($d = 18$ mm) between the two identical electrodes and then wetted with IL which was dried at 80 °C under vacuum for 24 h prior to use. Based on CV experiments under constant sweep rate, capacitance was calculated from equation: $C = i/\nu$, where C represents the capacitance, i is the current density, and ν is the sweep rate.

Results and Discussion

Various ILs containing methanide anion, $[\text{EMIm}][\text{DCNAcC}]$, $[\text{BMIm}][\text{DCNAcC}]$, $[\text{E}_1\text{MIm}][\text{DCNAcC}]$, $[\text{EPy}][\text{DCNAcC}]$, $[\text{EMPip}][\text{DCNAcC}]$, $[\text{EMPyr}][\text{DCNAcC}]$, and $[\text{EMMor}][\text{DCNAcC}]$, have been prepared by the alkylation of *N*-methylimidazole, pyridine, *N*-methylpyrrolidine, *N*-methylmorpholine, *N*-methylpiperidine followed by the anion exchange with sodium 1,1-dicyano-1-acetylmethanide ($\text{Na}[\text{DCNAcC}]$). In a similar way, 1-ethyl-3-methylimidazolium bis(trifluoromethanesulfonyl)imide ($[\text{EMIm}][\text{Tf}_2\text{N}]$) was also prepared. The structures of cations and anions used in this study were shown in Figure 2.

Figure 3 and Figure S1 in SI shows thermogravimetric analysis (TGA) curves of various types of ILs. The thermal stabilities of these ILs were determined in a nitrogen atmosphere between 25 to 80 °C at a ramp rate of 10 °C min^{-1} . As

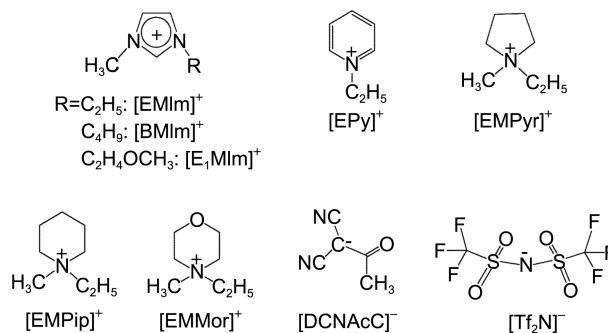


Figure 2. The structures of cations and anions of ILs.

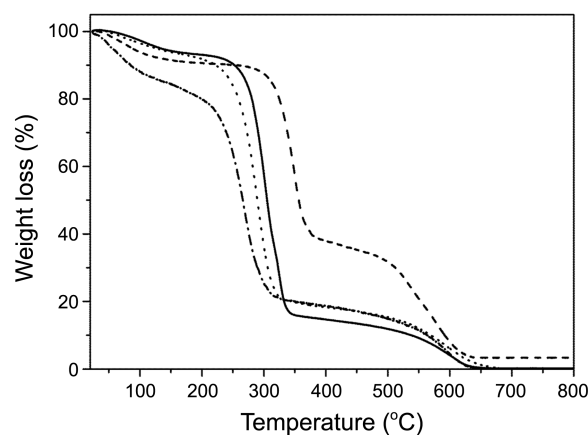
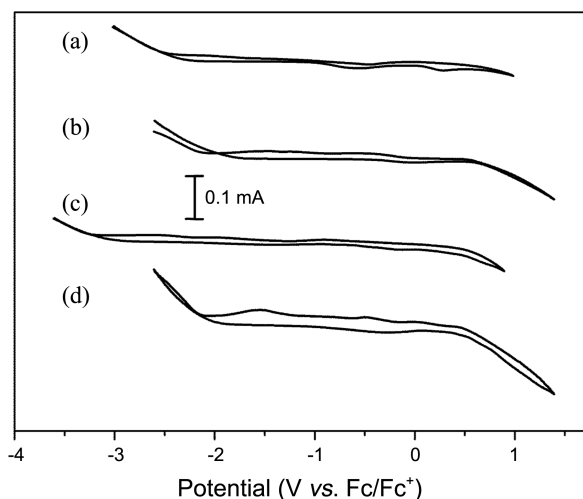


Figure 3. Thermogravimetric analysis (TGA) of selected ILs: (—) $[\text{EMIm}][\text{DCNAcC}]$, (---) $[\text{E}_1\text{MIm}][\text{DCNAcC}]$, (····) $[\text{EMPyr}][\text{DCNAcC}]$, and (-·-·-) $[\text{EMMor}][\text{DCNAcC}]$.

Table 1. Thermal properties of ILs

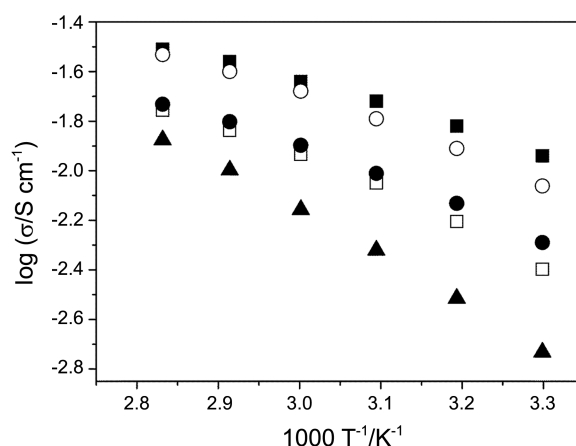
IL	T_m (°C)	$T_{Decomp1}$ (°C)	$T_{Decomp2}$ (°C)
[EMIm][DCNAcC]	-29.3	273	554
[BMIm][DCNAcC]	-29.0	273	554
[E ₁ MIm][DCNAcC]	-29.3	321	504
[EPy][DCNAcC]	-16.2	248	527
[EMPyr][DCNAcC]	-28.5	261	531
[EMPip][DCNAcC]	-4.4	254	572
[EMMor][DCNAcC]	-	239	543

**Figure 4.** Cyclic voltammograms of (a) [EMIm][DCNAcC], (b) [BMIm][DCNAcC], (c) [EMPyr][DCNAcC], and (d) [EMPip][DCNAcC] at a scan rate of 100 mV s⁻¹ at 25 °C.

shown in Table 1 and Figure 3, all ILs are thermally stable over 200 °C and show two decomposition temperatures. The lower decomposition temperature from 239 to 321 °C might be from the methanide anion due to the thermal instability of acetyl group. The melting temperatures of these ILs are lower than room temperature indicating the wide liquid temperature ranges of these ILs (Table 1). The glass transition temperatures of these ILs were not observed from the DSC curves obtained under the experimental condition (see Figure S2 in SI).

The electrochemical stabilities of the prepared ILs were analyzed by using CV at an ambient temperature. Figure 4 shows the cyclic voltammograms for four different ILs containing methanide anion ([EMIm][DCNAcC], [BMIm][DCNAcC], [EMPyr][DCNAcC], and [EMPip][DCNAcC]) at 25 °C. The electrochemical windows of ILs are between 2.6 to 3.9 V. The anodic limits, presumed to be related to the oxidation of anion, start at about 0.6 V (vs Fc/Fc⁺). Meanwhile, the cathodic limits according to the reduction of cations^{20,25-27} are shown in the range of -2.0 ~ -3.3 V (vs Fc/Fc⁺).

The ionic conductivities as a function of temperature are shown in Figure 5 and Figure S3 in SI. In general, the ionic conductivity increases with increasing temperature because the viscosity decreases at elevated temperature. ILs bearing [DCNAcC]⁻ show lower ionic conductivities than that

**Figure 5.** The ionic conductivities of ILs as a function of temperature: (■) [EMIm][Tf₂N], (○) [EMIm][DCNAcC], (□) [BMIm][DCNAcC], (●) [E₁MIm][DCNAcC], (▲) [EMPyr].

of [EMIm][Tf₂N] which has ionic conductivity as 11.5 mS cm⁻¹ at 30 °C. The slopes of the curves of newly prepared ILs with increasing temperature are also greater than [EMIm][Tf₂N]. Activation energies for the ion conduction of [EMIm][Tf₂N], [EMIm][DCNAcC], [E₁MIm][DCNAcC], [BMIm][DCNAcC], and [EMPyr][DCNAcC] are calculated from the slope of the linear Arrhenius plot as 7.7, 9.4, 10.0, 11.3, and 15.3 kJ mol⁻¹, respectively. The higher activation energies of ILs containing [DCNAcC]⁻ may due to the larger ionic interaction between cation and [DCNAcC]⁻ anion than between [EMIm]⁺ cation and [Tf₂N]⁻ anion. Generally, the shorter alkyl substituted imidazolium cations with same anion give the higher ionic conductivities. This may due to the smaller intermolecular dispersion force which gives

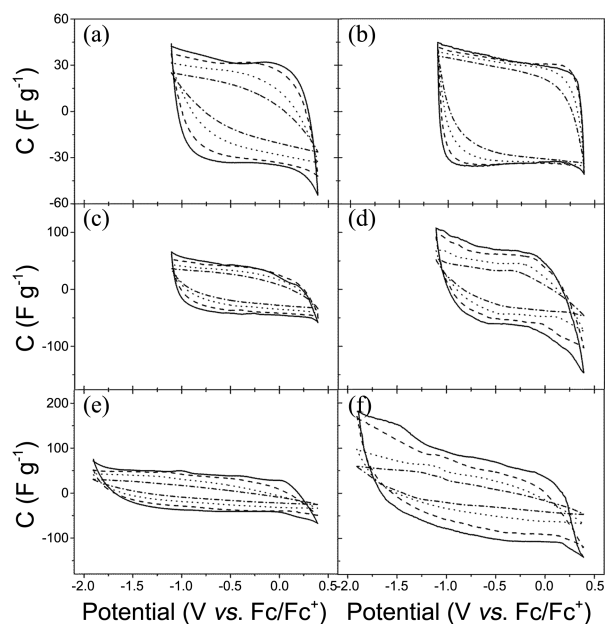
**Figure 6.** The cyclic voltammogram curves of the supercapacitors with electrolytes of [EMIm][Tf₂N] at (a) 25 °C and (b) 80 °C, [EMIm][DCNAcC] at (c) 25 °C and (d) 80 °C, [BMIm][DCNAcC] at (e) 25 °C and (f) 80 °C as a function of sweep rate: (—) 1 mV s⁻¹, (-----) 2 mV s⁻¹, (·····) 5 mV s⁻¹, and (----) 10 mV s⁻¹.

Table 2. Specific capacitances ($F g^{-1}$) of ILs at various temperatures and scan rates

	25 °C				80 °C			
	1 mV/s	2 mV/s	5 mV/s	10 mV/s	1 mV/s	2 mV/s	5 mV/s	10 mV/s
[EMIm][Tf ₂ N]	32.2	31.2	24.0	14.5	33.1	32.8	31.4	27.7
[EMIm][DCNAcC]	42.0	38.6	30.6	23.1	64.9	57.5	44.5	32.8
[BMIm][DCNAcC]	40.4	34.9	23.6	12.3	85.8	64.9	40.8	23.0

lower viscosity.²⁸ Similarly, it can be expected that the ILs containing the smaller anions with same cation give the higher ionic conductivities. The calculated volumes of [DCNAcC]⁻ and [Tf₂N]⁻ are 95.6 and 147.6 Å³, respectively.²⁹ However, the ionic conductivity of [EMIm][DCNAcC] (8.7 mS cm⁻¹ at 30 °C) is lower than that of [EMIm][Tf₂N] (Figure 5). This may be due to the stronger ion association of [EMIm][DCNAcC] than that of [EMIm][Tf₂N]. It is worth to note that the ionic conductivity of [EMIm][DCNAcC] (29.4 mS cm⁻¹) is comparable to that of [EMIm][Tf₂N] (30.9 mS cm⁻¹) at 80 °C. This result implies that the decreased ion association of [EMIm][DCNAcC] at the elevated temperature.³⁰

Figure 6 shows the cyclic voltammograms of [EMIm][Tf₂N], [EMIm][DCNAcC] and [BMIm][DCNAcC] electrolytes using activated carbon as electrode at 25 and 80 °C as a function of sweep rate. The CV curves of ILs are symmetric regardless of the sweep rate, indicating that the electro-sorption and desorption processes are reversible. At slow sweep rates, the cyclic voltammograms are of rectangular shapes, indicating good electrochemical double layer capacitance behavior for these ILs. By choosing the average value at -0.35 V (vs Fc/Fc⁺), the specific capacitances measured at 1 mV s⁻¹ are 32.2, 42.0 and 40.4 F g⁻¹ for [EMIm][Tf₂N], [EMIm][DCNAcC] and [BMIm][DCNAcC], respectively at 25 °C (Table 2). The higher capacitance of [EMIm][DCNAcC] than [EMIm][Tf₂N] may be due to the smaller size of [DCNAcC]⁻ anion. Generally, the electrochemical double layer capacitance is restricted by the ion size because the electro-sorption of small sized ions could be easier than the large sized ions and this gives larger charge separation.^{30,31} However, the effect of the structure of anion is also cannot be ruled out. The [Tf₂N]⁻ anion has more spherical structure than [DCNAcC]⁻ anion and less spherical ion can be packed at the surface of electrode more efficiently. The size and structure effects of anion become more profound at higher temperature. The specific capacitance of [EMIm][Tf₂N] increases only 0.9 F g⁻¹ by elevating temperature from 25 to 80 °C (Table 2). However, the capacitance of [EMIm][DCNAcC] increases from 42.0 to 64.9 F g⁻¹ by elevating temperature from 25 to 80 °C, respectively. The increasing capacitance with temperature is also observed with high-temperature molten salts.³²⁻³⁴ Although several suggestions have been proposed including the increased number of free vacancies in the melt, the accelerated dissociation of complex within the double layer, and the decreasing electrostatic interactions between the ions by theoretical calculation, this behavior is not yet fully explained and those explanations

are difficult to apply for ILs.^{32,35} Recently, V. Lockett proposed that the change of capacitance with varied temperatures might be the result of decreasing ion association in the double layer with increasing temperature. As a result of the dissociation of ion pair in the double layer with increasing temperature, more ions are available for adsorption and they can get closer to the interface.³⁰ As we mentioned previously, because the volume of [DCNAcC]⁻ is much smaller than that of [Tf₂N]⁻, the mobility of [DCNAcC]⁻ increased more than that of [Tf₂N]⁻ by decreasing ion association with increasing temperature. Moreover, the packing of [DCNAcC]⁻ at the surface of electrode could be enhanced by decreasing ion association. This effect is also observed with [BMIm][DCNAcC]. The calculated volumes of [EMIm]⁺ and [BMIm]⁺ are 118.4 and 152.0 Å³, respectively.²⁹ The capacitance of [BMIm][DCNAcC] at 1 mV s⁻¹ and 25 °C are slightly less than that of [EMIm][DCNAcC] for the higher viscosity and larger cation of [BMIm][DCNAcC]. However, the capacitance of [BMIm][DCNAcC] at 80 °C (85.8 F g⁻¹) is higher than that of [EMIm][DCNAcC] although the ionic conductivity of [BMIm][DCNAcC] is still lower than that of [EMIm][DCNAcC] at the same temperature (Table 2 and Figure 5). This result strongly indicates that the ion association of [BMIm][DCNAcC] is lesser than that of [EMIm][DCNAcC] at higher temperature. Further experiments and theoretical calculations are in progress to have a deeper understanding of the temperature dependence on capacitance by varying the shape and size of ions.

Conclusion

The room temperature ionic liquids containing 1,1-dicyano-1-acetylmethanide anion ([DCNAcC]⁻) were prepared and their physical and electrochemical properties were studied. Newly prepared ILs showed high thermal stabilities and wide liquid temperature ranges. Although the ionic conductivity of ILs bearing [DCNAcC]⁻ anion were lower than that of [EMIm][Tf₂N], the specific capacitance of ILs bearing [DCNAcC]⁻ anion were higher than that of [EMIm][Tf₂N]. Interestingly, the ionic conductivities and specific capacitance of [BMIm][DCNAcC] at 25 °C were lower than those of [EMIm][DCNAcC], the capacitance of [BMIm][DCNAcC] at 80 °C was increased upto 85.8 F g⁻¹ in spite of lower ionic conductivity at the same temperature. The higher capacitances of [EMIm][DCNAcC] and [BMIm][DCNAcC] than that of [EMIm][Tf₂N] may be due to the smaller size and non-spherical structure of [DCNAcC]⁻ anion and these effects of ion become more profound for the decreased ion

association at elevated temperature. These results suggest that the ILs containing [DCN₂AcC]⁻ anion can be the promising candidates as the electrolytes for the high temperature operating EDLCs.

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