

# Ionic liquids containing the tetrafluoroborate anion have the best performance and stability for electric double layer capacitor applications

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## Abstract

Fourteen kinds of ammonium salt, including nine ionic liquids, were evaluated for use as the electrolyte (as a solute) of an electric double layer capacitor (EDLC) from the viewpoint of practical performance and thermal stability. For this study, three kinds of anion species were selected for the counter anion: tetrafluoroborate ( $\text{BF}_4$ ), hexafluorophosphate ( $\text{PF}_6$ ) and bis(trifluoromethylsulfonyl)imide (TFSI) anions. A series of EDLCs with only 0.4% deviation in the capacitance of each cell, based on activated carbon and various salts in propylene carbonate (PC), were strictly prepared. The capacitance at room temperature, and the resistance value of the EDLCs at a relatively large direct current at low temperatures were measured. We also examined the durability of these systems by continuous charging at 70 °C and 3.0 V. We report that *N*-(2-methoxyethyl)-*N*-methylpyrrolidinium- $\text{BF}_4$ , a cyclic aliphatic quaternary ammonium with a methoxyethyl functional group, is the preferred ionic liquid for an EDLC electrolyte with respect to capacitance, power density, even at low temperatures and thermal durability.

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**Keywords:** Ionic liquids; Aliphatic quaternary ammonium; Electric double layer capacitor; Durability; Direct current resistance

## 1. Introduction

Ionic liquids are known to be non-volatile, non-flammable and highly conductive [1]. At first, many researchers focused on aromatic type ionic liquids, such as 1-ethyl-3-methylimidazolium tetrafluoroborate ( $\text{EMI-BF}_4$ ), which has a relatively low viscosity and high ionic conductivity [2–5] for use in a variety of applications for electrochemical devices, including batteries and capacitors. However, since aromatic quaternary ammonium cations, such as imidazolium and pyridinium, have relatively low cathodic stability, electrochemical devices using these ionic liquid as electrolyte have not yet been shown to be practical [6]. Recently, we reported that some short chain aliphatic quaternary ammonium cations with a methoxyethyl group on the nitrogen atom formed ionic liquids with a wider potential window compared to the other aromatic type ionic liquids together

with a and relatively high ionic conductivity [7,8]. In particular, *N,N*-diethyl-*N*-(2-methoxyethyl)-*N*-methylammonium tetrafluoroborate ( $\text{DEME-BF}_4$ ), and the same cation paired with the bis(trifluoromethylsulfonyl)imide (TFSI) anion are promising candidates for practical electrolytes to improve the high temperature safety and durability of electrochemical capacitors [7] and lithium ion batteries [9], respectively.

The electric double layer capacitor (EDLC) is an energy storage device based on the operating principle of the electric double-layer that is formed at the interface between an activated carbon material and an electrolyte. Various solvents and salts (solutes in other word) are available, offering specific advantages such as high capacitance and low temperature performances. Generally, an organic electrolyte that is a solid quaternary ammonium salt, such as *N,N,N,N*-tetraethylammonium- $\text{BF}_4$  ( $\text{TEA-BF}_4$ ), dissolved in the high dielectric constant solvent propylene carbonate (PC) has been used for high voltage EDLCs of 2 V or more. This device stores electricity physically, and lacks the chemical reactions found in rechargeable batteries during charging and discharging [10]. Therefore, compared to rechargeable batteries, the EDLC has a remarkably long cycle life and high

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power density. Nisshinbo Industries Inc. in Japan manufactures high performance large size EDLCs using an electrolyte including an ionic liquid, namely DEME- $\text{BF}_4$  diluted with PC. Because a quaternary ammonium type ionic liquid has a higher solubility in the carbonate solvent than the previously investigated solid quaternary ammonium salts, it is possible to make an electrolyte with a high ion concentration, giving the EDLC a high capacitance. In many cases, an electrolyte including an ionic liquid that has a high solubility in PC exhibit high ionic conductivity, even at low temperatures, compared to a traditional solid ammonium salt electrolyte. Hence, Nisshinbo's EDLCs have extremely attractive high charge rate and discharge performance even at  $-40^\circ\text{C}$  [11].

Generally, small sized aliphatic quaternary ammonium cations cannot easily form an ionic liquid; however, by attaching a methoxyalkyl group to the nitrogen atom, many aliphatic quaternary ammonium salts can form ionic liquids with  $\text{BF}_4^-$  and TFSI anions. In this paper, we report that the performance and thermal stability of the EDLCs using various ionic liquids and some solid ammonium salts with methoxyethyl and methoxymethyl groups on the nitrogen atom as an electrolyte. The evaluation was performed using a large size cell with strict quality control at the industrial product manufacturing level.

Of special interest is to determine which ionic liquid or ammonium salt with methoxyalkyl group shows the most attractive performance at low temperature and good thermal and electrochemical stability in a practical large size EDLC. We compare the direct current resistance of EDLCs at a relatively large current at low temperature, and the capacitance deterioration and the internal resistance increase when continuously charging at high temperature. It has been generally thought that a high viscosity of the electrolyte is detrimental to direct current resistance. However, we report that the direct current resistance of the EDLC depends on the size of the solute anion and is independent of the viscosity and the specific conductivity of the electrolyte.

## 2. Experimental

We prepared 14 kinds of ammonium salt that have 6 kinds of cation and 3 kinds of anion species as candidate electrolytes for EDLCs. Nine of these were ionic liquid in nature at  $25^\circ\text{C}$  and some ammonium salts were not liquid at room temperature. The melting temperatures are summarized in Table 1.

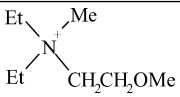
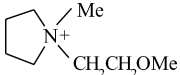
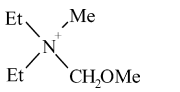
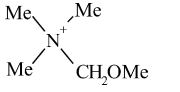
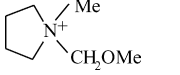
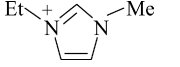
We prepared large size EDLCs using the 14 kinds of salt in Table 1. Because  $\text{PF}_6$  and TFSI salts of *N,N*-diethyl-*N*-methoxymethyl-*N*-methylammonium (DEMM) and *N*-methoxymethyl-*N*-methylpyrrolidinium (MMMP) are expected to have a poor EDLC performance from the results of other experiments, they were not used.

### 2.1. Preparation of quaternary ammonium salts with fluorinated anions

All the ammonium salts of fluorinated anions were synthesized by metathesis reactions between the corresponding quaternary ammonium halides and metal salts. *N,N*-Diethyl-

Table 1

Melting temperature of ammonium salts used in this work at  $25^\circ\text{C}$ 

Code of cation	Cation	Melting temperature ( $^\circ\text{C}$ )		
		$\text{BF}_4$	$\text{PF}_6$	TFSI
DEME		9 <sup>a,b</sup>	23 <sup>a,c</sup>	-91 <sup>a,b,d</sup>
MEMP		18 <sup>a,b</sup>	34 <sup>a,c</sup>	-95 <sup>a,b,d</sup>
DEMM		45 <sup>a,b</sup>	—	—
MMTM		51 <sup>a,b</sup>	204 <sup>a,c</sup>	-2 <sup>a,b</sup>
MMMP		-5 <sup>a,b</sup>	—	—
EMI		11 <sup>a,b</sup>	60 <sup>a,c</sup>	-16 <sup>a,b</sup>

<sup>a</sup> One molar of propylene carbonate solution was tested for EDLC electrolyte in this work.

<sup>b</sup> Melting temperature was measured by DSC.

<sup>c</sup> Melting temperature was measured by the microscope with heating plate for melting point measurement.

<sup>d</sup> Glass transition temperature was measured by DSC.

*N*-(2-methoxyethyl)-*N*-methylammonium (DEME) iodide and *N*-(2-methoxyethyl)-*N*-methylpyrrolidinium (MEMP) iodide were synthesized according to the procedures described in our patent application [8] and previous paper [7]. Methoxymethyl-chloride was reacted with corresponding amines in tetrahydrofuran to yield *N,N*-diethyl-*N*-methoxymethyl-*N*-methylammonium (DEMM) chloride, *N*-methoxymethyl-*N,N,N*-trimethylammonium (MMTM) chloride and *N*-methoxymethyl-*N*-methylpyrrolidinium (MMMP) chloride. All of these salts are white solids and could be prepared in a very pure state. All of these salts were extremely hygroscopic and were used without further purification except for MMTM, which was recrystallized from acetonitrile. 1-Ethyl-3-methyl-imidazolium bromide was purchased from Kanto Chemical Co. Inc. and used after recrystallization from acetonitrile.

#### 2.1.1. General procedure for the preparation of $\text{BF}_4$ salts

A suitable quaternary ammonium salt was dissolved in acetonitrile, and the solution was stirred and cooled with ice. An equivalent amount of silver tetrafluoroborate dissolved in acetonitrile was added and the mixture stirred for more than 10 h. The resulting solid was filtered off, and the reaction mixture was concentrated, dried in vacuum for more than 3–7 h at  $70$ – $80^\circ\text{C}$ . Except for MMTM- $\text{BF}_4$  and DEMM- $\text{BF}_4$ , the remaining liquid was again filtered, this time with a polytetrafluoroethylene membrane (PTFE-membrane) with a pore

size of 0.45  $\mu\text{m}$ , to remove silver halide which appears after the acetonitrile was removed. MMTM- $\text{BF}_4$  and DEMM- $\text{BF}_4$  were both solids and were recrystallized several times from acetonitrile-tetrahydrofuran to produce pure crystals.

### 2.1.2. General procedure for the preparation of $\text{PF}_6$ salts

A suitable quaternary ammonium salt was dissolved in milliQ water, and the solution was stirred and cooled with ice. An equivalent amount of lithium hexafluorophosphate ( $\text{LiPF}_6$ ) dissolved in milliQ water was added and the solution was again stirred for more than 4 h. The solid that appeared was filtered off to obtain the  $\text{PF}_6$  salt. All the  $\text{PF}_6$  salts were recrystallized from milliQ water except for MEMP- $\text{PF}_6$  which was recrystallized from methanol.

### 2.1.3. General procedure for the preparation of TFSI salts

A suitable quaternary ammonium salt was dissolved in milliQ water, and the solution was stirred and cooled with ice. An equivalent amount of lithium (trifluoromethylsulfonyl)imide ( $\text{LiTFSI}$ ), dissolved in milliQ water, was added and the mixture stirred for more than 4 h. After standing, the reaction mixture was divided into two layers, the bottom layer being the ionic liquid. The bottom layer was separated, and methylenechloride or chloroform was used to extract the water layer and the extract was combined with the bottom layer. The TFSI salts used in this work dissolved in some organic halide solvents. The combined liquid was washed with milliQ water several times, concentrated and dried in vacuum for 3–7 h at 70–80  $^\circ\text{C}$  to obtain the ionic liquid of the TFSI anion.

The NMR spectra data summarized below was obtained using a JEOL JNM-AL400 spectrometer, with dimethylsulfoxide- $d_6$  as a solvent. Chemical shift values are reported in ppm with respect to a tetramethylsilane (TMS) internal reference for  $^1\text{H}$  and  $\alpha,\alpha,\alpha$ -trifluorotoluene as an external reference for  $^{19}\text{F}$ .

DEME- $\text{BF}_4$ ;  $^1\text{H}$  NMR(DMSO)  $\delta$  = 1.20(t,6H), 2.95(s,3H), 3.29(s,3H), 3.33(q,4H), 3.45(m,2H), 3.71(m,2H);  $^{19}\text{F}$  NMR(DMSO)  $\delta$  = -151.60(s).

DEME- $\text{PF}_6$ ;  $^1\text{H}$  NMR(DMSO)  $\delta$  = 1.20(t,6H), 2.95(s,3H), 3.29(s,3H), 3.33(q,4H), 3.45(m,2H), 3.71(m,2H);  $^{19}\text{F}$  NMR(DMSO)  $\delta$  = -72.77(d).

DEME-TFSI;  $^1\text{H}$  NMR(DMSO)  $\delta$  = 1.21(t,6H), 2.95(s,3H), 3.30(s,3H), 3.34(q,4H), 3.45(m,2H), 3.71(m,2H);  $^{19}\text{F}$  NMR(DMSO)  $\delta$  = -81.47(s).

MEMP- $\text{BF}_4$ ;  $^1\text{H}$  NMR(DMSO)  $\delta$  = 2.07(m,4H), 3.01(s,3H), 3.30(s,3H), 3.48(m,4H), 3.55(m,2H), 3.74(m,2H);  $^{19}\text{F}$  NMR(DMSO)  $\delta$  = -151.37(s).

MEMP- $\text{PF}_6$ ;  $^1\text{H}$  NMR(DMSO)  $\delta$  = 2.07(m,4H), 3.01(s,3H), 3.30(s,3H), 3.48(m,4H), 3.55(m,2H), 3.74(m,2H);  $^{19}\text{F}$  NMR(DMSO)  $\delta$  = -73.03(d).

MEMP-TFSI;  $^1\text{H}$  NMR(DMSO)  $\delta$  = 2.09(m,4H), 3.03(s,3H), 3.31(s,3H), 3.50(m,4H), 3.56(m,2H), 3.75(m,2H);  $^{19}\text{F}$  NMR(DMSO)  $\delta$  = -81.75(s).

DEMM- $\text{BF}_4$ ;  $^1\text{H}$  NMR(DMSO)  $\delta$  = 1.20(t,6H), 2.86(s,3H), 3.25(q,4H), 3.56(s,3H), 4.56(s,2H);  $^{19}\text{F}$  NMR(DMSO)  $\delta$  = -151.60(s).

MMTM- $\text{BF}_4$ ;  $^1\text{H}$  NMR(DMSO)  $\delta$  = 2.98(s,9H), 3.62(s,3H), 4.57(s,2H);  $^{19}\text{F}$  NMR(DMSO)  $\delta$  = -151.47(d).

MMTM- $\text{PF}_6$ ;  $^1\text{H}$  NMR(DMSO)  $\delta$  = 2.98(s,9H), 3.62(s,3H), 4.56(s,2H);  $^{19}\text{F}$  NMR(DMSO)  $\delta$  = -72.49(d).

MMTM-TFSI;  $^1\text{H}$  NMR(DMSO)  $\delta$  = 2.97(s,9H), 3.60(s,3H), 4.57(s,2H);  $^{19}\text{F}$  NMR(DMSO)  $\delta$  = -81.74(s).

MMMP- $\text{BF}_4$ ;  $^1\text{H}$  NMR(DMSO)  $\delta$  = 2.07(m,4H), 2.99(s,3H), 3.30(s,3H), 3.41(m,4H), 3.59(m,3H), 4.61(s,2H);  $^{19}\text{F}$  NMR(DMSO)  $\delta$  = -151.37(d).

EMI- $\text{BF}_4$ ;  $^1\text{H}$  NMR(DMSO)  $\delta$  = 1.42(t,3H), 3.85(s,3H), 4.19(q,2H), 7.67(t,1H), 7.76(t,1H), 9.05(1H);  $^{19}\text{F}$  NMR(DMSO)  $\delta$  = -151.91(d).

EMI- $\text{PF}_6$ ;  $^1\text{H}$  NMR(DMSO)  $\delta$  = 1.42(t,3H), 3.85(s,3H), 4.19(q,2H), 7.65(t,1H), 7.74(t,1H), 9.07(1H);  $^{19}\text{F}$  NMR(DMSO)  $\delta$  = -72.11(d).

EMI-TFSI;  $^1\text{H}$  NMR(DMSO)  $\delta$  = 1.42(t,3H), 3.85(s,3H), 4.19(q,2H), 7.65(t,1H), 7.74(t,1H), 9.07(1H);  $^{19}\text{F}$  NMR(DMSO)  $\delta$  = -81.51(s).

To prepare the EDLC electrolytes, all of the ionic liquids and ammonium salts were dissolved in electrochemical device grade propylene carbonate purchased from Kishida Chemical Co. and used without further purification. The PC solutions were then dried to less than 100 ppm (w/w) of moisture, as measured by a Karl Fischer titration in a dry atmosphere (dew point of air  $< -40^\circ\text{C}$ ). To ensure that none of the PC solutions contained more than 200 ppm impurity of metal and halogen ions, these levels were checked by inductively coupled plasma spectrometer and ion-chromatography, respectively.

## 2.2. Fabrication of EDLC

The following procedure was used for the preparation of the electrodes. To prepare the electrode active layer we first mixed an ink suspension containing carbonized palm shell charcoal (surface area 2000  $\text{m}^2 \text{g}^{-1}$ , average pore diameter 20 nm, average particle size 8  $\mu\text{m}$ , prepared by Nisshinbo Ind. Inc.), acetylene black, poly(vinylidene fluoride) [PVDF; average  $M_w$  ca. 534,000, purchased from Sigma-Aldrich Fine Chemicals Co. Ltd.] and *N*-methyl-2-pyrrolidone (NMP). We then spread this mixture onto both sides of an aluminum oxide foil (30  $\mu\text{m}$  thick) with a blade and dried it at 140  $^\circ\text{C}$  for 72 h in vacuum to remove NMP and moisture. At this point, the dried electrode was pressed by a roll press at 30 MPa and dried again at 120  $^\circ\text{C}$  in vacuum for 15 h. The electrode thus obtained, which was composed of 89 wt.% of palm shell charcoal, 5 wt.% of acetylene black and 6 wt.% of PVDF, was cut into 45 mm  $\times$  73 mm with an activated layer 150  $\mu\text{m}$  thick. The electrodes were arranged with a paper separator (Nippon Kodoshi Corporation) sandwiched between them, and in all, 37 sheets of electrodes were stacked. The resultant stack of electrodes was pressed between polypropylene sheets and fixed onto a tape; then, the electrode assembly was inserted into a bag made of thermoplastic film laminated to an aluminum sheet. The electrolyte was allowed to penetrate the electrode assembly in the bag by keeping it under reduced pressure for 8 h; afterward the bag was sealed by hot pressing

under reduced pressure. All of this fabrication process was performed in a dry atmosphere (dew point of air  $<-40^{\circ}\text{C}$ ). The differences of the capacitance and the internal cell resistance at 1 kHz in two 265 F EDLCs prepared with 1 M DEME- $\text{BF}_4/\text{PC}$  were 1 F and  $0.2\text{ m}\Omega$ , respectively. The prepared EDLC with 1 M DEME- $\text{BF}_4$  in PC had  $44\text{ F g}^{-1}$  of the specific capacitance per electrode weight.

### 2.3. Measurements

The specific conductivity measurements of the  $1\text{ mol L}^{-1}$  solution of an ionic liquid or salt in PC were performed with a conductivity meter (HM-30R, DKK-TOA Corporation). The dynamic viscosity was determined at varying temperatures with a programmable Brookfield RVDV-III viscometer with a CP-40 spindle. The melting temperature was determined by differential scanning calorimetry (DSC) with a EXSTAR 6000 (Seiko Instruments Inc.) instrument for  $\text{BF}_4$  and TFSI, and by a microscope with a heating plate for melting point analysis (Yanaco Model MP-J3 micro melting point apparatus, Yanagimoto-Seisakusho Co. Ltd.). All of melting temperature measurements were performed by heating at a rate of  $10^{\circ}\text{C min}^{-1}$ .

The assembled cell was charged in a constant current (CC) mode from  $V=0\text{--}3.0\text{ V}$  at a constant current  $I=0.2\text{ A}$ , and then further charged to keep a constant voltage ( $3.0\text{ V}$ ) for 30 min (i.e. constant voltage, or CV, mode). It was then discharged to  $0\text{ V}$  at a given temperature  $T$  in a CC mode at a current varying from  $I=0.2\text{--}5\text{ A}$ . To carry out the EDLC testing, we used a HJ1010SM8 charge-discharging system, from HOKUTO DENKO Co. Ltd. The capacitance  $C$  was calculated from the relation  $C=2WV^{-2}$ , in which the energy output  $W$  was calculated from the discharge curve via the relation  $W=\int IV\text{ d}t$  [7]. The direct current resistance (DCIR) was calculated from the  $IR$  drop on the discharge curve at a discharge current of  $5\text{ A}$  at various temperatures. The internal resistance of cells (equivalent series resistance (ESR)) was also measured by using a HIOKI BATTERY HITESTER 3550 impedance analyzer at  $1\text{ kHz}$  at various temperatures.

The thermal stability of an EDLC – a life test – was performed by continuous charging at  $3.0\text{ V}$  at  $70^{\circ}\text{C}$ , and the cell deterioration was monitored by measuring its capacitance and internal resistance at  $25^{\circ}\text{C}$  at given intervals. All data were the average value of two measurements from two similar cells.

## 3. Results and discussion

### 3.1. Comparison of EDLC capacitance and internal resistance

We evaluated the cell performance and durability of EDLCs using all 14 types of ammonium salts, including 9 ionic liquids. The capacitance of the EDLCs using various ammonium salts with a methoxyalkyl group on nitrogen atom, and some imidazolium salts, in a 1 M propylene carbonate solution was determined by charge–discharge cycling from  $0$  to  $3.0\text{ V}$  at  $25^{\circ}\text{C}$ . Fig. 1 shows the variation of the cell capacitance in the 10th cycle as a function of the total molecular weight of the

salts (a), and as a function of the molecular weight of the separate cations (b) and anions (c).

In general, it has been thought that an ion with a high molecular weight shows lower cell capacitance than a small size ion. However, we have previously observed that the EDLC using 1 M DEME- $\text{BF}_4$ , which a molecular weight of  $233.05$ , has an approximately 10% higher capacitance than a cell using a 1 M solution of a conventional ammonium salt, tetraethylammonium

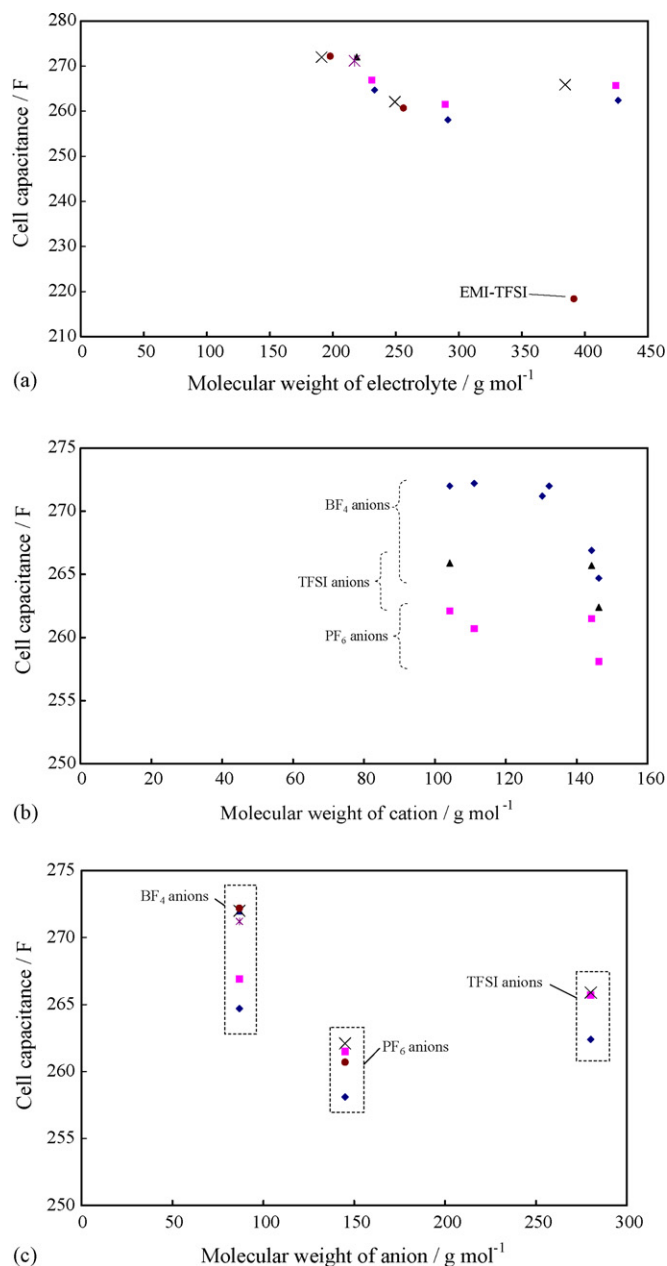


Fig. 1. The discharge capacitance of EDLCs containing various electrolytes. The test cell was discharged at a constant current  $I=0.2\text{ A}$  from  $V=3.0\text{--}0\text{ V}$  at  $25^{\circ}\text{C}$ . Cell capacitance is plotted against the molecular weight of salts, cations and anions for (a), (b) and (c), respectively. The electrolyte concentration was  $1\text{ M}$  in PC: (◆) DEME-cation species; (■) MEMP-cation species; (▲) DEMM-cation species; (×) MMTM-cation species; (✕) MMMP-cation species; (●) EMI-cation species in figure (a) and (c). In (b): (◆)  $\text{BF}_4$ -anion species; (■),  $\text{PF}_6$ -anion species; (▲) TFSI-anion species. The prepared EDLC with 1 M DEME- $\text{BF}_4$  in PC had  $44\text{ F g}^{-1}$  of the specific capacitance per electrode weight.

tetrafluoroborate (TEA-BF<sub>4</sub>), which has a molecular weight of 217.6 [12]. However, in the results shown in Fig. 1(a), the cell capacitance with a 1 M EMI-TFSI propylene carbonate solution exhibited an exceptionally very low value, and a clear correlation cannot be found between the molecular weights of the salts and cations and the cell capacitance based on the data in Fig. 1(a and b). We did not observe a large difference in the cell capacitance with the cation used even though the molecular weights of the cations varied by approximately 1.4 times. However, we realized from the data shown in Fig. 1(c) that the capacitance of the cell depends not on the total molecular weight of the salt or that of the cation, but on that of the anion. EDLCs using the BF<sub>4</sub> anion species had higher capacitances than those using other anion species. Because the deviation in the measured capacitance of each tested EDLC was only about 0.4%, the 2 F or more differences in capacitance found between different cells are significant. The ammonium salts with a methoxymethyl group show somewhat larger capacitance than ones with methoxyethyl group. In addition, it is undoubtedly the case that the state of the ammonium salt itself at room temperature, namely whether it is an ionic liquid or not, is irrelevant to the EDLC capacitance when used in PC solution.

We also understand that the kind of anion species used also influences the internal resistance (ESR) of an EDLC. Fig. 2 shows the ESR of EDLCs using various electrolytes at 1 kHz, 25 °C. Those EDLCs using the BF<sub>4</sub> anion in PC have the practicable value of ESR of 2.5 mΩ. On the other hand, the ESR associated with the use of TFSI anions is twice or more than that of BF<sub>4</sub>. The EDLC using the PF<sub>6</sub> anion showed a poor ESR value below a practical level. It seems that the ESR value of EDLCs significantly increased with an increase of the molecular weight of anion. As a result, we suggest that the use of solutes other than those containing BF<sub>4</sub> as electrolytes is unpractical for high voltage EDLCs.

### 3.2. Comparison of DCIR for EDLCs at low temperature

Fig. 3 shows the DCIR of EDLCs using various 1 M solutions as an electrolyte at (a) 25 °C and (b) –30 °C.

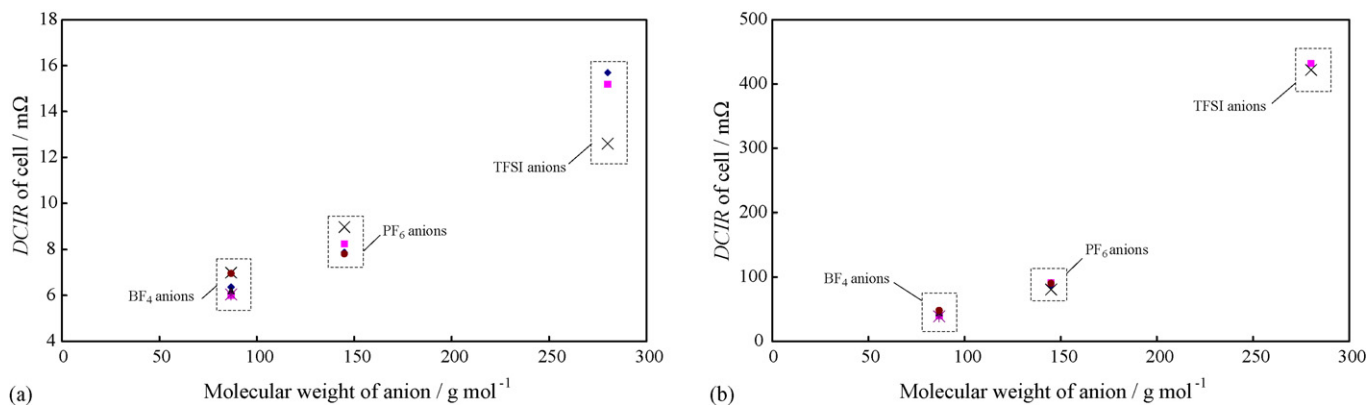


Fig. 3. The direct resistance (DCIR) of EDLCs containing various electrolytes at 5 A discharge. Measurement temperature: (a) 25 °C, (b) –30 °C. The electrolyte concentration was 1 M in PC: (♦) DEME-cation species; (■) MEMP-cation species; (▲) DEMM-cation species; (×) MMTM-cation species; (×) MMMP-cation species; (●) EMI-cation species.

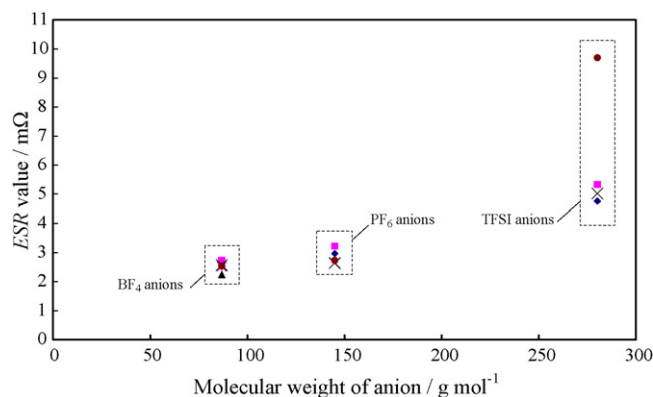


Fig. 2. The internal resistance (ESR) of EDLCs containing various electrolytes at 1 kHz, 25 °C. The electrolyte concentration was 1 M in PC: (♦) DEME-cation species; (■) MEMP-cation species; (▲) DEMM-cation species; (×) MMTM-cation species; (×) MMMP-cation species; (●) EMI-cation species.

The major advantage of an EDLC versus a battery is long cycle life and high power density. Therefore, because a high power density is achieved by a low DCIR, an EDLC that has lower DCIR is desirable. It is obvious that cells using electrolytes including BF<sub>4</sub> have a significantly lower DCIR at room temperature than cells using other anion species. Cells using solutes with a large molecular weight anion have a high DCIR and ESR. The DCIR at the very low temperature of –30 °C increased between six to seven times compared to the room temperature value for BF<sub>4</sub> solutes, from ten to twelve times for PF<sub>6</sub> solutes, and for TFSI solutes by a factor of 30 or more. In the case of EDLCs using EMI-TFSI and DEME-TFSI, the cells could not discharge because the cell resistance was too large at low temperatures, and so they are not plotted in the figure. As it is generally considered that, since ionic liquids have high solubility in PC, an EDLC using an ionic liquid as a solute in the electrolyte should have a good performance compared to a cell using solid ammonium salts. However, based on our results, we suggest that not only should an ionic liquid be used as an electrolyte to obtain an EDLC with a high power density at low temperatures, but in particular, the ionic liquid

Table 2

DCIR value of EDLCs and specific conductivity of 1 M ionic liquids including BF<sub>4</sub> anion in PC solution at 25 and −30 °C

Code of cation	Cation	DCIR <sup>a</sup> (mΩ)		Specific conductivity (mS cm <sup>−1</sup> )	
		25 °C	−30 °C	25 °C	−30 °C
DEME		6.6	42.9	11.2	1.7
MEMP		6.4	40.0	11.2	1.8
DEMM <sup>b</sup>		6.2	45.1	n.m. <sup>c</sup>	n.m. <sup>c</sup>
MMTM <sup>b</sup>		7.0	38.8	11.4	1.9
MMMP		6.0	39.3	12.8	2.3
EMI		7.0	48.0	n.m. <sup>c</sup>	n.m. <sup>c</sup>

<sup>a</sup> DCIR was calculated from the IR drop on the discharge at 5 A.<sup>b</sup> Solid state at room temperature.<sup>c</sup> Not measured.

should contain the BF<sub>4</sub> anion. However, MMTM-BF<sub>4</sub> in PC had a low DCIR at both temperatures, even though it was not an ionic liquid. Possibly, the very compact nature of the cation in this case was responsible for its good performance.

The DCIR values of various electrolytes containing BF<sub>4</sub>-type ionic liquids are summarized in Table 2. There was little difference in the DCIR values among BF<sub>4</sub> ionic liquids with methoxyethyl or methoxymethyl groups on the cation nitrogen. On the other hand, aliphatic quaternary ammonium type ionic liquids have lower DCIR values than aromatic ones such as EMI-BF<sub>4</sub>, and cyclic aliphatic ionic liquids, such as those containing methylpyrrolidinium, have slightly lower values than do linear alkyl ammonium type ionic liquids. It is generally thought that the ionic conductivity of the electrolyte solution has an influence on the DCIR of an EDLC, namely, a high ionic conductive electrolyte gives a low DCIR value. The ionic conductivity ( $\sigma$ ) for various electrolytes below 30 °C is shown in Fig. 4.

Even though the nature of the anion and cation varied widely, the ionic conductivities of the various electrolytes were quite similar at a given temperature, over a range of temperatures from −30 °C to room temperature. There is essentially no difference among the six electrolytes' temperature dependence. The difference of ionic conductivity between BF<sub>4</sub> and TFSI at 25 °C was only 1.1 and 1.5 mS cm<sup>−1</sup> in the MEMP and DEME series, respectively. It is not reasonable to suppose that a large difference in a DCIR value was caused by a small difference in ionic conductivity. It was surprising that at −30 °C, the DCIR difference between the BF<sub>4</sub> and TFSI anion combined with DEME or MEMP is ten times or more, yet the difference in ionic

conductivity between BF<sub>4</sub> and TFSI was only 0.3 mS cm<sup>−1</sup> at the same temperature.

The dynamic viscosity ( $\eta$ ) of 1 M solutions of DEME-BF<sub>4</sub>, DEME-TFSI, MEMP-BF<sub>4</sub> and MEMP-TFSI in PC at various temperatures are displayed in Fig. 5.

We focus attention first on the viscosity of DEME-BF<sub>4</sub> and its TFSI anion at −30 °C. If the viscosity of the electrolyte has a big influence on DCIR, due to a highly viscous electrolyte decreasing the mobility of the ionic species, then an electrolyte

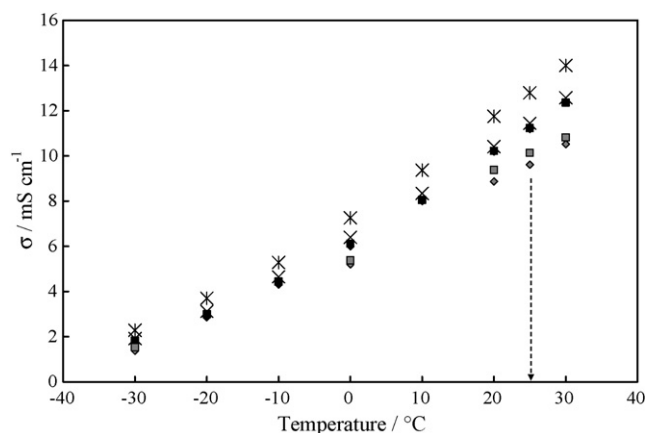


Fig. 4. The specific conductivity ( $\sigma$ ) vs. temperature plots the various electrolytes containing a 1 M concentration of ammonium salts. The electrolyte concentration was 1 M in PC: (◆) DEME-BF<sub>4</sub>; (◐, half-tone) DEME-TFSI; (■) MEMP-BF<sub>4</sub>; (◑, half-tone) MEMP-TFSI; (×) MMTM-BF<sub>4</sub>; (✱) MMMP-BF<sub>4</sub>.

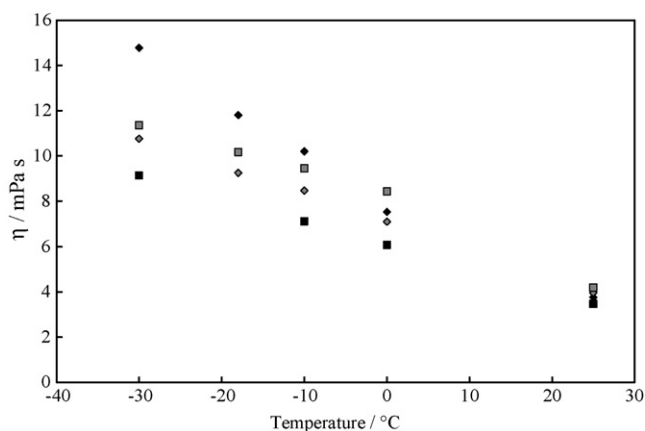


Fig. 5. Dynamic viscosity ( $\eta$ ) as a function of temperature for the various electrolytes containing a 1 M concentration of ammonium salts. The electrolyte concentration was 1 M in PC: (◆) DEME- $\text{BF}_4$ ; (◆, half-tone) DEME-TFSI; (■) MEMP- $\text{BF}_4$ ; (■, half-tone) MEMP-TFSI.

using DEME- $\text{BF}_4$  should have a large DCIR value compared to one using DEME-TFSI. However, an EDLC using DEME- $\text{BF}_4$  in PC had a remarkably small DCIR value compared with a DEME-TFSI cell. In fact, the EDLC using a DEME-TFSI electrolyte could not discharge as a result of having too large a value of DCIR at  $-30^\circ\text{C}$ . In the case of MEMP, the large difference of DCIR that existed between cells using  $\text{BF}_4$  and TFSI anions seemed to overcome the difference of the viscosity. In a dilute PC system, the dynamic viscosity and the ionic conductivity of electrolyte did not much influence the DCIR of EDLCs with the same molar concentration. This suggests that the kind of anion species has the most significant effect on the DCIR at low temperatures. It seems that the molecular weight of the anion or the molecular size of the solvated anion most influences the DCIR value. In designing cells with such ions, it will be necessary to pay attention to the specific ion species used, especially for the anion, because the ease of ion adsorption and desorption in the confined space of porous activated carbon may influence the cell's ultimate DCIR. The compounds MEMP- $\text{BF}_4$ , MMMP- $\text{BF}_4$  and DEMM- $\text{BF}_4$  in PC are more attractive candidates than DEME- $\text{BF}_4$  for use as an EDLC electrolyte from the view point of capacitance and DCIR.

### 3.3. Practical stability of EDLCs using various electrolytes

In contrast to batteries, the cycling test is less important for an EDLC, because deterioration mostly occurs at the maximum operating voltage. So, as a more useful life test we continuously operated the cell at 3.0 V,  $70^\circ\text{C}$ . Presumably, a good response to this test will indicate good durability at room temperature. The ESR and maintenance ratio of the capacitance after 500 and 1000 h operation are summarized in Table 3. Fig. 6 also demonstrates that the EDLCs using MEMP- $\text{BF}_4$  and DEME- $\text{BF}_4$  showed a good practical level of durability after 1000 h of use.

After 1000 h, the capacity loss was just 15 and 20% for EDLCs using MEMP- $\text{BF}_4$  and DEME- $\text{BF}_4$ , respectively. On the other hand, MMMP- $\text{BF}_4$  and DEMM- $\text{BF}_4$  had good capacitance and DCIR value at low temperature, but their durabil-

Table 3

The results of stability test of EDLC using various electrolytes by continuous charging at 3 V,  $70^\circ\text{C}$

Code of cation	Anion	ESR ( $\text{m}\Omega$ )			Maintenance ratio of capacitance (%)	
		0 h	500 h	1000 h	500 h	1000 h
DEME	$\text{BF}_4$	2.7	4.5	7.0	87.9	80.1
DEME	$\text{PF}_6$	2.9	6.8	12.1	77.9	57.7
DEME	TFSI	4.7	10.3	n.m.	10.3	n.m.
MEMP	$\text{BF}_4$	2.7	4.4	6.2	90.5	84.6
MEMP	$\text{PF}_6$	3.2	5.9	14.9	84.9	56.6
MEMP	TFSI	5.3	126	n.m.	47.2	n.m.
DEMM	$\text{BF}_4$	2.2	7.3	15.1	75.9	63.4
TMMM	$\text{BF}_4$	2.6	4.5	11.3	84.8	73.7
TMMM	$\text{PF}_6$	2.6	7.0	26.8	83.3	53.3
TMMM	TFSI	5.0	n.m.	n.m.	n.m.	n.m.
MMMP	$\text{BF}_4$	2.5	6.7	24.6	83.4	52.9
EMI	$\text{BF}_4$	2.5	12.9	37.5	80.1	40.9
EMI	$\text{PF}_6$	2.7	35.9	n.m.	n.m.	n.m.
EMI	TFSI	9.7	35.6	28.3	n.m.	n.m.

n.m.: not measurable due to unstable cell performance caused by gas generation.

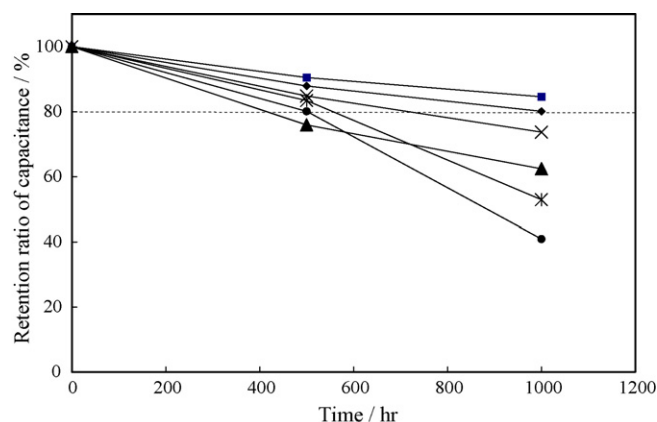


Fig. 6. Life test of EDLCs using various electrolytes including  $\text{BF}_4$  anion. The cell was continuously charged at 3.0 V,  $70^\circ\text{C}$  for 1000 h. The electrolyte concentration was 1 M in PC: (◆) DEME- $\text{BF}_4$ ; (■) MEMP- $\text{BF}_4$ ; (▲) DEMM- $\text{BF}_4$ ; (×) MMTM- $\text{BF}_4$ ; (✕) MMMP- $\text{BF}_4$ ; (●) EMI- $\text{BF}_4$ .

ity at high temperatures was inferior to that of DEME- and MEMP- $\text{BF}_4$  cells. Our conclusion is that ammonium salts with a methoxyethyl group have higher stability than those with a methoxymethyl group. Therefore, we recommend MEMP- $\text{BF}_4$  in PC as the preferred electrolyte for an EDLC in terms of capacitance, low temperature performance and thermal durability in practical use.

## 4. Conclusions

We have evaluated various kinds of ammonium salt with a methoxyalkyl group on the nitrogen atom, including several kinds of ionic liquids, as electrolytes for an EDLC. A cell using an electrolyte containing the  $\text{BF}_4$  anion had a higher capacitance at  $25^\circ\text{C}$ , 3 V than those including  $\text{PF}_6$  and TFSI anions. The capacitance of an EDLC at room temperature depends on the

nature of the anion, rather than the cation, species or whether the solute is an ionic liquid or is a solid itself at room temperature. The values of the resistance that are most relevant to the power density performance of an EDLC also differed greatly with different ionic species. At room (25 °C) and low (−30 °C) temperatures, both the resistance parameters, ESR and DCIR, followed the same trend that the cell resistance increased in the order of BF<sub>4</sub>, PF<sub>6</sub> and TFSI. This order corresponds to the ranking of the molecular weights of the anion. Even in the ionic liquids, those including the PF<sub>6</sub> and TFSI anions had cell resistances that would make the practical performance of the cell such as to make it unusable. Of the ionic liquids tested, MEMP-BF<sub>4</sub> and DEME-BF<sub>4</sub>, compounds that possess an aliphatic ammonium group including a methoxyethyl group, performed well at continuous charging at 70 °C. The aromatic type of ionic liquids of the EMI series were inferior to the aliphatic ones in terms of their practical long life stability. Our tests show that MEMP-BF<sub>4</sub> is the preferred ionic liquid for use as an electrolyte solute in an EDLC.

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