Application of sulfonium-, thiophenium-, and thioxonium-based salts as electric double-layer capacitor electrolytes

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ABSTRACT

The purpose of this paper is to develop novel molten salts based on sulfonium, thiophenium, and thioxonium cations as electrolytes for EDLCs. We evaluated various kinds of the salts, with tetrafluoroborate (BF_4) and bis(trifluorometanesulfonyl)amide (TFSA) anions, including several kinds of ionic liquids. The cell using the electrolyte containing diethylmethylsulfonium (DEMS)–BF_4 salt had the higher capacitance and the lower DC-IR value than those containing conventional salts such as 1-ethyl-3-methylimidazolium (EMI)–BF_4 and N,N,N-triethyl-N-methylammonium (TEMA)–BF_4 at 243 K and 2 V. The capacitance and DC-IR at low temperature depended strongly on the structure, particularly on the size of each ion. We also examined the durability of cells by continuous charging at 333 K and 2.5 V. The stabilities of sulfonium-, thiophenium-, and thioxonium-based electrolytes were much inferior to that of EMI–BF_4.

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1. Introduction

Ionic liquids (ILs) are organic salts with melting points lower than 373 K, often lower than the room temperature. ILs have been increasingly researched as the substitutes for the organic solvents traditionally used as the chemical reaction media because they are known to be non-volatile, non-flammable and highly conductive [1–4]. The common ILs are imidazolium and pyridinium derivatives [5,6]. Phosphonium and tetraalkylammonium compounds can be also used for the same purpose [7,8].

The recent research has focused on the ILs for electric double-layer capacitors (EDLCs), known as the supercapacitors or ultracapacitors [9]. Various solvents and salts are available, offering specific advantages of the high capacitance and the low temperature performances. Generally, the organic electrolyte that is the solid quaternary ammonium salt dissolved in the high dielectric constant solvent has been used for high voltage EDLC of 2 or higher than 2 V. Here, the salt is N,N,N,N-tetraethylammonium–BF_4 (TEA–BF_4) or N,N,N-triethyl-N-methylammonium–BF_4 (TEMA–BF_4) and the solvent is propylene carbonate (PC). EDLCs charge physically, not chemically, in contrast with the rechargeable batteries [10]. So, EDLCs have attracted much attention recently because of the power delivery performance that

perfectly fills the gap between dielectric capacitors and traditional batteries. Recently various salts for EDLCs have been reported, such as salts composed of asymmetric ammonium [8], pyrrolidinium [11], piperidinium [12], spiro-type quaternary ammonium [13–15], and phosphonium [16,17]. ILs containing imidazolium-type, such as 1-ethyl-3-methylimidazolium (EMI) have been hardly researched because of its low viscosity, high ionic conductivity, and low melting point [18]. And the use of solvent-free ILs enabled the high cell voltages required for increasing capacitor energy up [19], and it also suppressed the self-discharge of EDLC cells and a cycling durability [20].

We recently reported the sulfonium cation-based room temperature ionic liquids and the performance of the lithium-ion battery using them [21–23]. The properties of the $Li/LiMn_2O_4$ cell containing Li-bis(trifluorometanesulfonyl)amide (LiTFSA)/buthyldimethylsulfonium (BDMS)–TFSA electrolyte were studied and the cycle performances were compared to those with the conventional organic electrolyte (1 mol L^{-1} LiPF$_6$ in dimethylcarbonate (DMC)/ethylenecarbonate (EC)) at room temperature. Electrochemical impedance spectroscopy (EIS) and X-ray diffraction (XRD) were conducted to analyze the mechanisms affecting the cell performances at different temperatures. The lithium secondary battery system, using the abovementioned ionic liquid electrolyte material, showed excellent cycle performances, and is worthwhile to further investigate so as to find out the potential application. In this paper, we report on the physical properties of various sulfonium-, thiophenium-, or thioxonium-based salts and
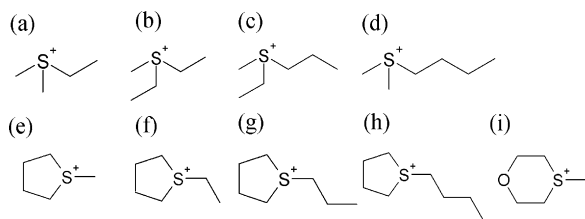

Fig. 1. Chemical structures of cations used in this study. (a) DMES (dimethylethylsulfonium), (b) DEMS (diethylethylsulfonium), (c) EMPS (ethylmethylpropylsulfonium), (d) BDMS (buthyldimethylsulfonium), (e) MTT (1-methyltetrahydrothiophenium), (f) ETT (1-ethyltetrahydrothiophenium), (g) PTT (1-propyltetrahydrothiophenium), (h) BTT (1-butyltetrahydrothiophenium), (i) MOT (1-methyl-[1,4]-thioxonium).

their application to EDLCs. We also report the initial performance at 243–298 K and the life performance at the constant voltage of 2.5 V and 333 K.

2. Experimental

2.1. Preparation of sulfonium-, thiophenium-, and thioxonium-based salts

Fig. 1 shows the chemical structures of cations studied. TFSA, PF$_6$, and BF$_4$ were chosen as the anion. The salts were synthesized and dried before use according to the standard procedures reported previously [24–26]. For example, we synthesized the sulfonium-based salts with TFSA anion, by the alkylation of the secondary sulfide with alkylhalide, followed by the exchange reaction with LiTFSA in water. The high-grade salt of sulfonium–TFSA was obtained after washing with excess purified water repeatedly for cleaning up, followed by the evacuation at 433 K for 3 h for dehydration. In the case of thiophenium-base salts, tetrahydrothiophene was used as the starting material. The structures of synthesized salts were confirmed by 1H NMR (AV400M, Bruker Biospin) and the purities of the salts were measured by the ion chromatography (DX-100 and DX-120, DIONEX Co., Ltd.).

1-Methyl-[1,4]-thioxonium–BF$_4$ (MOT–BF$_4$) salt was prepared as follows; at the first step, MOT–I was obtained by the alkylation of 1,4-thioxane with iodemethane in acetinitrile at 343 K for 5 h, followed by washing with excess acetinitrile. Then, the obtained MOT–I was reacted with silver tetrafluoroborate in methanol at 298 K for 1 h. MOT–BF$_4$ was obtained as the product of the reaction after filtration. The high-grade MOT–BF$_4$ was obtained by the recrystallization repeated three times using methanol followed by the evacuation at 433 K for 3 h. MOT–BF$_4$: 1H NMR (DMSO-d$_6$, δ/ppm relative to TMS): 4.17–4.11 (m, 2H), 3.96–3.90 (m, 2H), 3.55–3.48 (m, 2H), 3.20–3.14 (m, 2H), 3.00 (s, 3H).

2.2. Preparation of electrolytes

The electrolytes were prepared by dissolving the salts in propylene carbonate (PC) All electrolytes were prepared in a glove box of Ar atmosphere. 1.4 M EMI–BF$_4$, EMI–TFSA, and TEMA–BF$_4$ typically used as electrolytes were on the commercial market.

2.3. Characterization of salts and electrolytes

The viscosity values of each ionic liquid and electrolyte were got by using viscometer (Tokyo Keiki Inc.), and the ionic conductivities were tested by the conductivity meter (CM-201, DKK-TOA Co., Ltd.) with a pair of Pt-black electrodes. The melting points were analyzed by using the differential scanning calorimeter (DSC, Perkin-Elmer Pyris 1) in the temperature range of 243 and 373 K. The sample was sealed in aluminum pan, and then heated and cooled at scan rate of

10 K min^{-1} under a flow of nitrogen. The thermal data of the second heating–cooling scan were collected.

The PGSE-NMR measurement was conducted in the similar way reported previously [27]. The measurements were carried with JEOL JNM-AL 400 spectrometer equipped with 9.4-T narrow-bore superconducting magnet, JEOL pulse field gradient probe and current amplifier. The cationic and anionic self-diffusion coefficients in each room temperature ionic liquids were measured by using the 1H (399.7 MHz) and 19F (376.1 MHz) nuclei at 303 K, respectively.

2.4. EDLC performance measurements

Two types of activated carbons whose average particle sizes are large or small were prepared by the carbonization of phenolic resin, followed by KOH-activation and the pulverization. The BET specific surface area and the average pore diameter were calculated from the nitrogen adsorption isotherm at 77 K using surface area analyzer (AUTOSORB-1, Quantachrome Instruments) and the particle size distribution was measured using laser diffraction particle size analyzer (SALD-3000J, Shimazu Co., Ltd.). To prepare the electrode with active layer, we first mixed the ink suspension containing activated carbon, acetylene black, acrylic binder solution of N-methyl-2-pyrrolidon. We then spread the mixture onto the aluminum foil of 20 μm thick with blade, dried at 353 K for 3 h in air and evacuated it at 353 K for 3 h. The electrode thus obtained, had the activated layer of 50 μm thick whose composition is 85 wt% of activated carbon, 9 wt% carbon black, 3 wt% of carboxymethylcellulose, and 3 wt% of polytetrafluoroethylene, and was cut into circles of 15 mm diameter.

The coin-type capacitor cells were assembled in a glove box of Ar atmosphere. The cell was constructed by setting a couple of electrodes face to face, with a paper separator (Nippon Kodoshi Co., Ltd.) inserted between them. 1.4 M EMI–TFSA, EMI–BF$_4$, and TEMA–BF$_4$/PC solutions were used as references.

The assembled cell was charged in a constant current (CC) mode from V = 0–2.0 V at a constant current I = 320 mA g^{-1}, and then charged further to keep a constant voltage (2.0 V) for 2 h. It was then discharge to 0 V at a given temperature, 243–298 K, in a CC mode at a current I = 320 mA g^{-1}. To carry out the EDLC testing, we used a TOSCAT charge–discharging system, from Toyo System Co., Ltd. The capacitance C was calculated from the relation $C = It/V$, where t indicates discharging time [28]. Capacitance was normalized by the mass of a single electrode active layer including the carbon black, CMC, and PTFE. The direct current resistance (DC-IR) was calculated from the IR drop on the discharge curve at various temperatures.

The thermal stability (=life test) of EDLC was performed by continuous charging at 2.5 V at 333 K, and the cell deterioration was monitored by measuring the capacitance and DC-IR at 2.0 V at 243–298 K. All data was the average value of two cells.

3. Results and discussion

3.1. Physicochemical properties of TFSA-based salts

At first we evaluated TFSA-based electrolytes, because we were able to synthesize high-grade salts repeatedly by a simple method in the case of TFSA-based salts. Afterwards the effect of anions was examined. Table 1 shows the melting points of salts based on a TFSA anion. DMES–TFSA, DEMS–TFSA, EMPS–TFSA, and BDMS–TFSA are room temperature ionic liquids and the detail of the investigation about the melting points has been already described [14]. In the case of thiophenium-based salts, MTT–, ETT–, and PTT–TFSA are solid, and BTT–TFSA was ionic liquid at room temperature (298 K). The difference of behavior between sulfonium- and thiophenium-based salts might be explained by the poor cationic motion and the

Table 1
Melting point of salts and fundamental properties of salts of various sulfonium and thiophenium cations at 298 K.

Electrolyte	Melting point (K)	Viscosity (mPa s)	Ionic conductivity (mPa s)
DMES–TFSA	279	81	3.7
DEMS–TFSA	253	51	5.3
EMPS–TFSA	<243	42	4.7
BDMS–TFSA	271	63	5.2
MTT–TFSA	368	–	–
ETT–TFSA	340	–	–
PTT–TFSA	304	–	–
BTT–TFSA	<243	74	2.3
EMI–TFSA	258	31	8.9

strong interaction between cation and anion of thiophenium-based salts due to the cyclic structure in contrast to that of sulfonium. In general, the increase in the size of ion in salt decreases the electrostatic interaction between the cation and anion and lowers the melting point. Therefore, the low melting points of EMPS–, BDMS–, PTT–, and BTT–TFSA may be explained by the larger size of cations than others. The asymmetricity may also affect the melting point of salt because of the instabilization of the sequence, and the reason of much lower melting point of EMPS than that of BDMS may be explained by the degree of asymmetricity, although the correlation of asymmetricity with melting point is still discussing [29,30].

The viscosities of ionic liquids based on sulfonium and thiophenium cations, were 42–81 mPa s at 298 K and higher than that of EMI–TFSA (31 mPa s at 298 K). This may be explained by the contribution of the delocalization of the positive charge on imidazolium ring, which lowers the interaction between EMI and TFSA. The other reasons may concern with the difference of dissociation degree of ions between the sulfonium- or thiophenium-based ionic liquid and imidazolium-based ionic liquid, because the existence of ion-pair would increase the viscosity. It was reported that the dissociation degree of EMI–TFSA was estimated to be 0.75 based on the results of pulsed gradient spin-echo NMR studies [31]. Our corresponding result of dissociation degree of DEMS–TFSA obtained using the similar method was so low as 0.45 and suggested that it might also affect the ionic conductivity. The viscosities of ionic liquids containing sulfonium cations with three different alkyl groups are 42–81 mPa s at 298 K and higher than that of triethylsulfonium–TFSA whose cation had three same alkyl groups and viscosity of 33 mPa s at 298 K [32,33]. We obtained the different viscosities compared to our previous report [22]. For example, the viscosity of DMES at this report was 81 mPa s and that at the previous report was 81 mPa s. This may be explained by the difference of the purities of ionic liquid, although we did not measure the purity of every ionic liquids and we should measure the purities of ionic liquids for details.

The viscosity and ionic conductivity of 1.4 M electrolytes of sulfonium and thiophenium cations at 298 K are shown in Figs. 2 and 3. Comparing with 1.4 M EMI–TFSA/PC solution whose viscosity and ionic conductivity are 4.3 mPa s and 13.5 mS cm^{-1}, the electrolytes of sulfonium and thiophenium cations showed higher viscosity and lower ionic conductivity. In the description of classical electrolyte solutions, the mobility of charged carrier is related to the diffusion coefficient D through the Nernst–Einstein equation (1) [2]:

$$\text{molar conductivity } \Lambda = \frac{N_A z^2 e_0^2 D}{k_B T} = \frac{z^2 F^2 D}{k_B T} \tag{1}$$

where z is the valence of the charge carrier, e_0 is the elementary charge, N_A is the Avogadro number, k_B is the Boltzmann constant and F is the Faraday constant. The diffusion coefficient D, of a model spherical species of an effective radius r depends on the medium
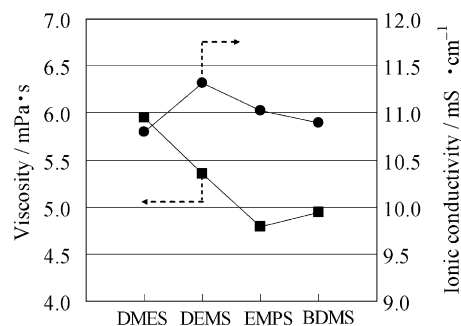

Fig. 2. Viscosity and ionic conductivity of electrolyte containing sulfonium-based cations, TFSA, and PC. The electrolyte concentration was 1.4 M in PC at 298 K.

viscosity, η, according to Stokes–Einstein equation:

$$D = \frac{k_B T}{6\pi r \eta} \tag{2}$$

As the conductivity $\sigma = \Lambda c = \Lambda n/V$ where c and n are the molar concentration and number of moles of the charge carrier and N ($=nN_A$) is the number of charge carriers present in the volume V, the following equation of conductivity is derived:

$$\sigma = \frac{z^2 e_0^2}{6V\pi r} \frac{N}{\eta} \tag{3}$$

As shown by Eq. (3), the conductivity σ of the electrolyte solution is proportional to the number of charge carriers N and inversely proportional to the medium viscosity η and the effective radius r. However, the classical model assuming that the system consists entirely of ions causes the conceptual problem regarding the distinction of individual ionic species formed in the melt. If some ions of opposite sign are sufficiently close to form relatively stable aggregates, they may be regarded as neutral species which cannot be charge carriers. The mobility of ions which may be affected by the ion size, may also contribute to the ionic conductivity.

As shown in Fig. 2, it seems that there may be an optimum ionic size because the viscosity of the electrolyte composed of EMPS was the lowest among the sulfonium-based electrolytes, and the ionic conductivity of that of DEMS was the highest. The similar result was reported in the case of neat sulfonium ionic liquid [34]. The increase in the ionic size may lead to the decrease in the coulomb interaction between cations and anions, and the increase in the entanglement of ions. So, the moderate size of cation may provide the low viscosity and high conductivity. The reason why the optimum cation for the lowest viscosity was different from that for the highest conductivity may be explained using Eq. (3). As shown in Eq. (3), the ionic conductivity is not only inversely proportional to viscosity (η) but also inversely proportional to ion size (r) and proportional to the number of charge carriers (N). According to the abovementioned interpretation, the number of carriers of DEMS–TFSA/PC solution
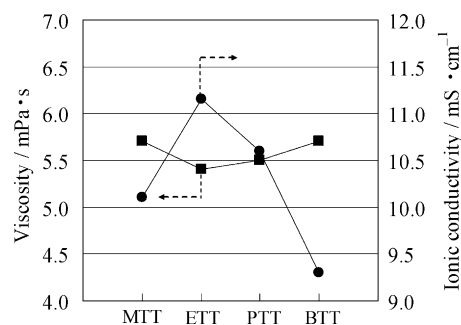

Fig. 3. Viscosity and ionic conductivity of electrolyte containing thiophenium cations, TFSA, and PC. The electrolyte concentration was 1.4 M in PC at 298 K.

Table 2
Pore structure parameters of activated carbon studied.

Carbon	Surface area ($m^2 g^{-1}$)	Average pore diameter (nm)	Average particle size ($D50$) (μm)
A	2400	1.73	10.8
B	2300	1.82	3.9

might be higher than that of EMPS–TFSA/PC solution, although the viscosity of DEMS–TFSA/PC solution was higher.

In the case of electrolyte of thiophenium cation, as shown in Fig. 3, ETT cation showed the lowest viscosity and the highest ionic conductivity. The result suggests that the size of ETT is moderate not only for lower viscosity but also for higher ionic conductivity in PC solution, being affected by the size of the coulomb interaction, ion size, and the number of charge carriers.

3.2. Comparison of EDLC capacitance and DC-IR

Table 2 shows the properties of activated carbons studied which have been well established for EDLC performance [35,36]. We properly used two kinds of activated carbons (A; bigger particle size, B; smaller particle size) depending on the situation. In the case of the initial characterization of EDLC, we used activated carbon A which expands the difference between various electrolytes. In the case of the life test, we used activated carbon B which is able to eliminate the effect of the degradation of activated carbon itself and shows the better life performance of EDLC at 2 V, 243–298 K.

Fig. 4 shows the temperature dependence of the capacitance of EDLCs using various electrolytes of 1.4 M in PC. As shown in the figure, there was little difference among electrolytes at 298 K. However, the decreasing behavior of capacitance at low temperature depended on the kind of cation. The decrease in capacitance at low temperature may be explained by the size of TFSA which is so big that the penetration of anion into the pore of activated carbon is restrictive.

The use of DEMS cation led to the highest capacitance in the series of electrolytes based on sulfonium cations and it was superior to that of EMI–TFSA/PC. This is likely because of the high ionic conductivity and the compact ion size of DEMS, although the ion size was not calculated. The electrolyte containing DMES cation showed the higher capacitance than those of EMPS and BDMS although the ionic conductivities of EMPS–TFSA/PC and BDMS–TFSA/PC were higher than that of DMES–TFSA/PC. The key factor may be, in this case, the compact ion size of DMES which causes the easy ion adsorption and desorption at the inside of pores of activated car-
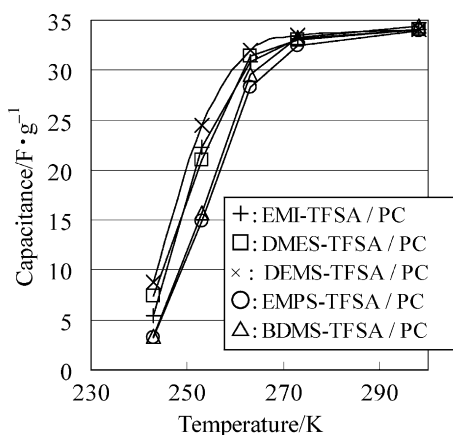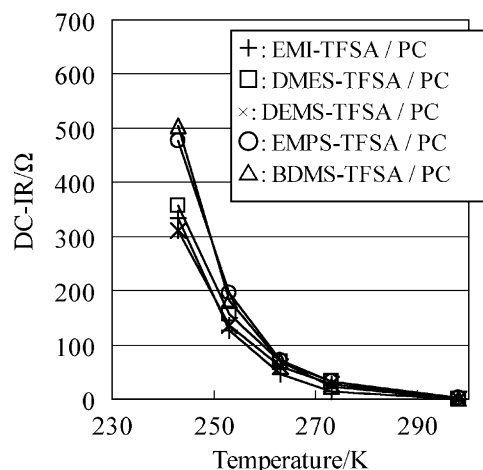

Fig. 5. DC-IR as a function of temperature for various electrolytes containing sulfonium cations and EMI.

bon. The importance of the ion size agreed with the result of EDLC using spiro-type quaternary ammonium salt [13].

Fig. 5 shows DC-IR data of salts/PC at 243–298 K. As show in the figure, the resistances were very high at low temperature and decreased rapidly with increasing temperature. The high resistance at low temperature may be due to the poor penetrating ability of the ion into pores. DC-IR values at 298 K were too low to discuss the difference of salts. It is interesting that the resistance of DEMS–TFSA/PC is lower than that of EMI–TFSA/PC. As same as the case of capacitance, the compact DEMS cation might lead to the better performance.

Fig. 6 shows the temperature dependence of capacitances of thiophenium cations/PC. It is obvious that ETT–TFSA/PC, which had the highest ionic conductivity in Fig. 3, showed the best performance (the highest capacitance). However, comparing with DEMS–TFSA/PC, the capacitor performance was not so high, although the ionic conductivity and viscosity are almost same. The reason is likely explained by the difference in the cation size. That is, the cation size of DEMS–TFSA/PC may be smaller than ETT.

While, MTT–TFSA/PC provided the better performance than PTT–TFSA and BTT–TFSA/PC although the ionic conductivity was lower. The result may also be explained with the small compact cation size of MTT–TFSA/PC as discussed above.
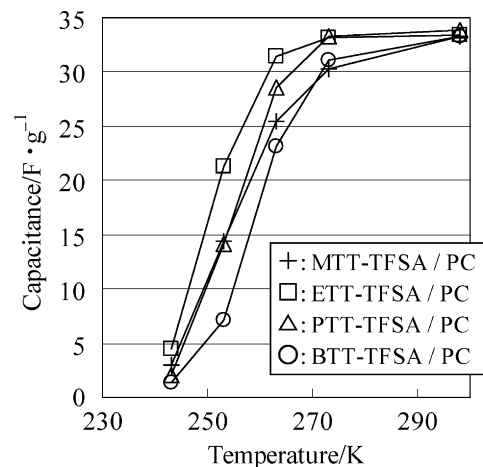

Fig. 4. Capacitance as a function of temperature for various electrolytes containing sulfonium cations and EMI.

Fig. 6. The temperature dependence of DC-IR of 1.4 M various type-electrolytes in PC solutions at 298 K.
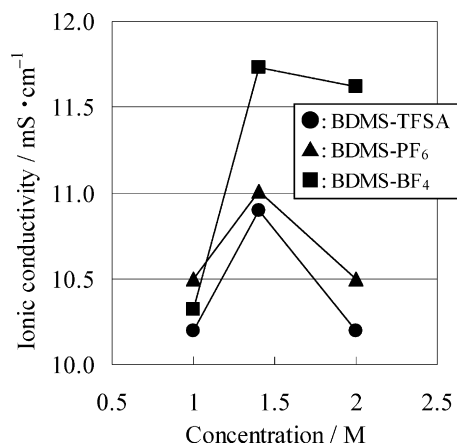
Fig. 7. Ionic conductivities of BDMS–BF$_4$, PF$_6$, and TFSA/PC solutions at 298 K.

3.3. The effect of anions on the physicochemical properties and EDLC performance

We investigated the effect of anions in the case of BDMS-based salts, because we could synthesis high-grade BDMS-based salts easily. The viscosity of BDMS salts/PC increased monotonically to the concentration of salts (see Fig. B in the supplemental data). The salts of BF$_4$ showed the lowest viscosity at the high concentration of 2.0 M. Fig. 7 shows the ionic conductivity at 298 K of BDMS salts/PC. The ionic conductivity of BF$_4$-based electrolyte was higher than the other electrolytes at the concentration of 1.4 and 2.0 M. The results agreed with the previously works [18,37]. As Van der Waals volumes for BF$_4$, PF$_6$, and TFSA were reported to be 48, 68, and 143 Å^3, respectively [37], the small ion size of BF$_4$ may play the main role of the higher ionic conductivity, although the influence of solvation on the apparent size should be taken into account [38].

Fig. 8 shows the temperature dependence of capacitance of BDMS salts/PC. The capacitance increased sharply with temperature and that of BDMS–BF$_4$ was the highest among the salts. But, the difference was little at 298 K as reported previously [39]. The simple model of the electrified interface was proposed by Helmholtz [40]. The interface consists of two plates of opposite charge, as in a parallel-plate capacitor. The capacitance is given by [40,41]

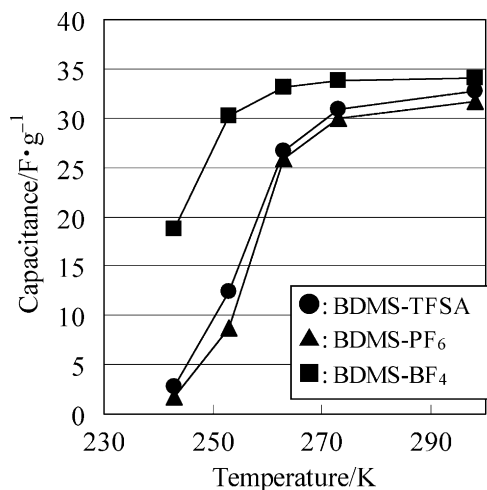$$C = \frac{\varepsilon_0 \cdot \varepsilon_r}{d} \tag{4}$$

Fig. 8. The temperature dependence of capacitance of BDMS–BF$_4$, PF$_6$, and TFSA/PC solutions at 243–298 K.

Table 3
Melting points of salts and fundamental properties of 1.4 M electrolytes including BF$_4$ anion in PC solutions at 298 K.

Salt of electrolyte	Melting point (K)	Viscosity (mPa s)	Ionic conductivity (mS cm^{-1})
BDMS–BF$_4$	342	5.0	11.7
ETT–BF$_4$	337	5.3	14.1
DEMS–BF$_4$	330	3.9	13.8
EMI–BF$_4$	288	3.8	15.3
TEMA–BF$_4$	357	4.3	14.3
MOT–BF$_4$	>373	6.5	9.6

where ε_0 is the permittivity of free space, ε_r is the dielectric constant of the material between the plates, and d is the distance between the plates. Thus, as the first approximation, the double-layer capacitance depends on the thickness of the double layer and the dielectric constant of the electrolyte. Additional variables are considered in more sophisticated models [42]. When an ion was small, distance d may be small, and then capacitance would increase. But, it is reported that capacitance of EDLC using BF$_4$, PF$_6$, and TFSA anion species was the following order, BF$_4$ > TFSA > PF$_6$ [39]. The result suggests that capacitance does not always depend on ion sizes of anions. The high capacitance retention of BDMS–BF$_4$/PC at the wide range of temperature observed in Fig. 8, can be said to be suggestive of the moderate compact cation which leads to the excellent performance of EDLC probably at the negative electrode. This may be caused by the easy diffusion of compact BF$_4$ inside narrow pores of activated carbon, for example, mesopores (2–50 nm width). It is reported that mesopores are mostly responsible for the rate performance of EDLCs [43], and it is also expected that mesopores effect strongly on the low temperature performance of EDLCs. In other words, it seems that a molecular size of a solvated anion most influences a capacitance at low temperature because the ease of ion adsorption and desorption in the confirmed space of porous activated carbon may influence it. So, the sizes of solvated cation and anion are both very important for EDLC performance. The best ion should be as small as possible, and at the same time, the ionic conductivity must be high. Therefore, the balance of the molecular size of solvated ion and the ionic conductivity may be very important.

In the case of the BDMS–BF$_4$, the DC-IR was very low at wide range of temperature comparing with the BDMS–TFSA and BDMS–PF$_6$ (see Fig. C in the supplemental data). As mentioned above, the compact nature and high ionic conductivity referred to BF$_4$ anion were also responsible for the low DC-IR at low temperature.

Table 3 shows the melting points of BF$_4$ salts and fundamental properties of 1.4 M electrolytes at 298 K. At room temperature (around 298 K), only EMI–BF$_4$ is liquid, while the salts of sulfonium or thiophenium cations with BF$_4$ anion are solid. It is of note that the comparison of melting points of salts is in reverse in the case of TFSA salt, that is, the melting point of DEMS–TFSA is lower than that of EMI–TFSA. These results indicate that the order of arrangement and the degree of interaction of ions depend strongly on the kind and combination of ions as reported in the previous study [44].

Fig. 9 shows the capacitance of EDLC using the BF$_4$-based salts. As shown in Fig. 9, DEMS–BF$_4$ maintained the high capacitance even at the low temperature of 243 K and showed the better performance than commercially available TEMA–BF$_4$ and EMI–BF$_4$. This is probably because of the compact DEMS cation leading to the high ionic conductivity, and the improvement of diffusion inside pores of negative electrode. It seems that diffuseness inside pores is more important than an ionic conductivity which reflects the ease of diffusion in the bulk electrolyte.
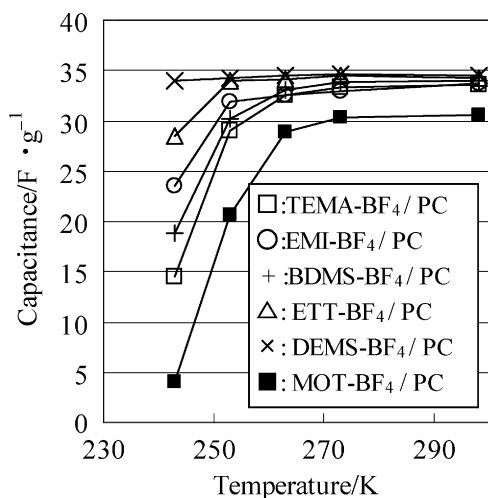
Fig. 9. The temperature dependence of capacitance of TEMA–BF$_4$, EMI–BE$_4$, BDMS–BF$_4$, ETT–BF$_4$, DEMS–BF$_4$, and MOT–BF$_4$/PC solutions at 243–298 K.

3.4. The life test for EDLCs comprising of BF$_4$-based electrolytes

In contrast with batteries, the cycling test is less important for an EDLC, because mostly the deterioration occurs at the maximum operating voltage. So, as the more useful life test, we continuously operated the cell at 2.5 V, 333 K and then evaluated the capacitance and the DC-IR operating at 2.0 V, 243–298 K. The activated carbon B shown in Table 2 and BF$_4$-based electrolytes were used for the life test. TFSA anion was not used, because it causes the corrosion of the Al current collector [45,46].

The capacitances at 243 and 298 K after 50 and 100 h operation are summarized in Fig. 10(a) and (b). And the DC-IRs at 243 and 298 K are also summarized in Fig. 11(a) and (b). After 100 h, the capacitance losses of EDLC using sulfonium– and thiophenium–BF$_4$ were higher than that of EMI–BF$_4$ cell at both 298 and 243 K. DC-IR values of EDLCs using sulfonium–BF$_4$ and thiophenium–BF$_4$ were considerably higher than that of EMI–BF$_4$ cell. The result indicates that sulfonium–BF$_4$ and thiophenium–BF$_4$ decompose easily at 2.5 V, 333 K. We observed the lower capacities of sulfonium–BF$_4$ and thiophenium–BF$_4$ electrolytes at 3.0 V, 298 K than those at 2.0, 298 K. The capacitances of BDMS–BF$_4$ and EMI–BF$_4$ were 18 and 36 F g^{-1} at 3.0 V, 298 K even in the first cycle. The reason of easy decomposition may be that sulfonium and thiophenium cations have unshared pairs of electron onto sulfur atoms which play the main role of oxidization. However, according to the previous study concerning the electrochemical stability, the cathodic limit of triethylsulfonium–TFSA ionic liquid shifts about 1.0 V positively from that of aliphatic quanternary ammonium–TFSA, but that of EMI–TFSA is the almost same [34]. Thus, the electrochemical stability of neat ionic liquid may directly affect on the durability of the EDLC.

DC-IR values at 298 K of EDLCs using BDMS– and DEMS–BF$_4$ after 100 h operation were higher than those at 243 K although the capacitances at 243 and 298 K were almost the same. So, it may be said that BDMS–BF$_4$ and DEMS–BF$_4$ decomposed at the external surface of activated carbon and the surface area of activated carbon differs little from that before the decomposition. But, the deposition of degradation products onto the external surface of activated carbon may lead to the increase of DC-IR value even at 298 K. Whether a cation decomposes inside pores or at external surface may depend on the structure of cations.

The abovementioned result shows the possibility of the specific sulfonium–BF$_4$ or thiophenium–BF$_4$ to be a viable way to improve
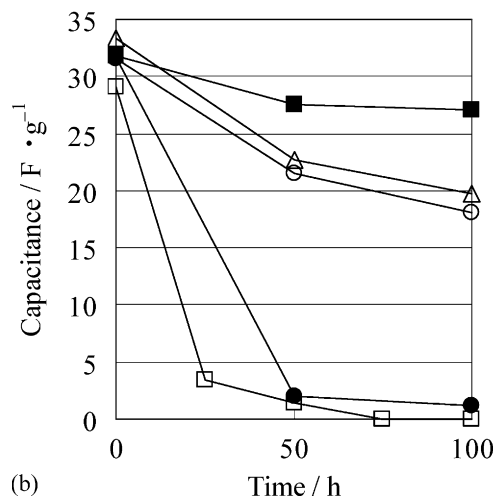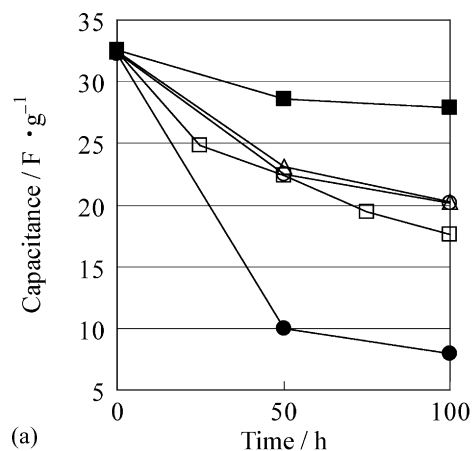

(a)

(b)

Fig. 10. Capacitance operating at 2.0 V, (a) 298 K and (b) 243 K of various electrolytes including BF$_4$ anion after the operation of continuously charging at 2.5 V, 333 K for 100 h. The electrolyte concentration was 1.4 M in PC: (■) EMI–BF$_4$; (○) BDMS–BF$_4$; (●) ETT–BF$_4$; (△) DEMS–BF$_4$; (□) MOT–BF$_4$.

the performance of EDLC at low operating voltage and temperature. The issue to be solved is the poor stability comparing with the conventional salts such as EMI–BF$_4$. The energy stored in a capacitor is expressed by the equation $E = CV^2/2$. So, the further studies are necessary to improve the operating voltage of EDLC using sulfonium–BF$_4$ or thiophenium-salts.

3.5. Physicochemical properties and EDLC performance of thioxonium-based salts

We synthesized MOT–BF$_4$ whose structure was shown in Fig. 1 as the novel salt to improve the life. The key point of MOT is the adoption of the alkyl ether group to cation, referring to the previous report about the improvement of life [18]. The melting point of MOT–BF$_4$ is higher than 373 K and easily crystallized indicating the strong interaction between MOT and BF$_4$ and the poor diversity of the conformation of MOT cation. Table 3 shows the physicochemical properties of ETT, DEMS, and MOT–BF$_4$/PC solutions. As shown in Table 3, the viscosity of MOT–BF$_4$ is high and the ion conductivity is fairly low, suggesting the strong interaction between MOT and BF$_4$ and the poor dissociation of the salt in PC solution.

Fig. 9 shows the temperature dependence of capacitance of ETT, DEMS, and MOT–BF$_4$/PC. MOT–BF$_4$/PC resulted in the lower capacitance, suggesting that the extent of dissociation is not satisfactory.
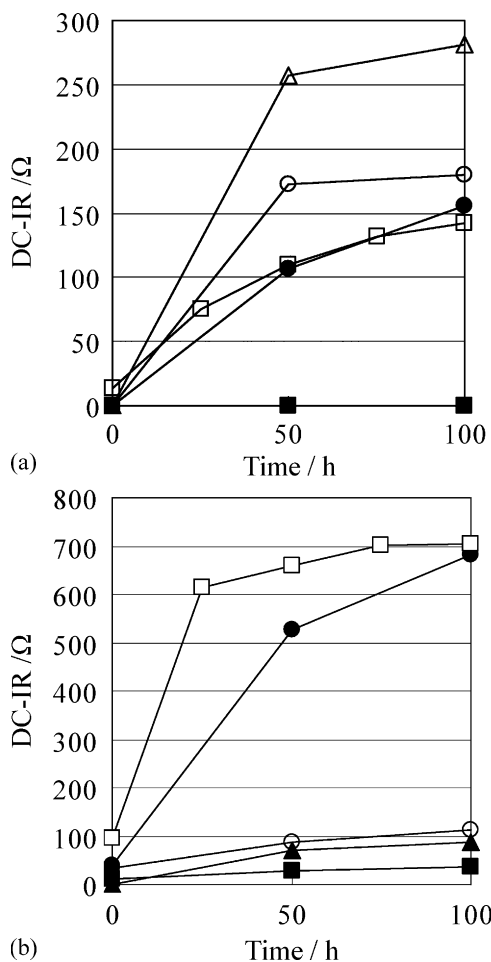
Fig. 11. DC-IR operating at 2.0 V, (a) 298 K and (b) 243 K using various electrolytes including BF_4 anion after the operation of continuously charging at 2.5 V, 333 K for 100 h. The electrolyte concentration was 1.4 M in PC: (■) EMI–BF_4; (○) BDMS–BF_4; (●) ETT–BF_4; (△) DEMS–BF_4; (□) MOT–BF_4.

Fig. 11(a) and (b) shows the capacitance and DC-IR during the life test up to 100 h. The extent of decrease of capacitance and the increase of DC-IR of MOT–BF_4 cell were similar to that of ETT–BF_4. So, the effect of ether group onto the durability at high voltage and temperature was not proven. The result suggested that ether group which has electron-donating property has little effect on the inhibition of decomposition of MOT–BF_4.

4. Conclusions

In this paper, the properties for EDLC of sulfonium- and thiophenium-based salts were studied. DEMS–TFSA/PC showed the highest ionic conductivity among the TFSA salts, suggesting that the ion size and the coulomb interaction between ions of the salt may be moderate for the easy diffusion. The study of the effect of anion showed that the ionic conductivity of DEMS–BF_4/PC is highest among DEMS salts. The cell using the electrolyte containing DEMS–BF_4 salt showed higher capacitance at 243 K and 2 V than those containing conventional EMI–BF_4 and TEMA–BF_4. The capacitance and DC-IR at low temperature were thought to depend strongly on the structure, in particular, the size of cation and anion. But, the life of DEMS–BF_4 salt was shorter than the conventional EMI–BF_4. The instability of DEMS–BF_4 salt was thought to come from the existence of the unshared electrons on ions. The adoption of the ether group did not improve the stability.

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