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Ionic Liquids for the Electric Double Layer Capacitor Applications

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1. Introduction

The properties of ionic liquids (ILs) include non-volatility, non-flammability, and relatively high ionic conductivity (Rogers & Seddon, 2001). As novel green, reusable solvents that can substitute for organic solvents, ionic liquids have attracted much attention as good media in organic synthesis and other chemical processes (Zhao et al., 2009, 2011). At the same time, some studies have been reported which aim to improve the high-temperature safety and durability of such electrochemical devices as lithium rechargeable batteries (Sato et al., 2004), electric double layer capacitors (EDLC) (Sato et al., 2004), and titanium oxide dye-sensitized solar cells (Papageorgiou et al., 1996).

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 otherword) 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 tetrafluoroborate (TEA-BF₄), dissolved in the high dielectric constant solvent propylene carbonate (PC) has been used for high voltage EDLCs of 2V or more. This device stores electricity physically, and lacks the chemical reactions found in rechargeable batteries during charging and discharging (Zheng et al., 1997). Therefore, compared to rechargeable batteries, the EDLC has a remarkably long cycle life and high power density. Such devices are now widely used in power electronics for peak power saving and back up memories, and in electronic power supplies for automated guided vehicle systems and construction equipment. One of their most promising applications is for use in transportation, especially in hybrid electric vehicles (HEVs). However, some issues in the development of EDLCs remain.

1. A lower energy density compared with lithium ion secondary batteries.
2. Flammable electrolytes raise safety concerns.
3. Low cycle durability in the high temperature region.
4. Poor charge-discharge properties at low temperatures.

In order to overcome these challenges, we are actively pursuing research and development in the use of ionic liquids for the electrolyte of EDLCs.

The energy E stored in an EDLC is proportional to its capacity, C , as well as the voltage V applied between the positive and the negative electrodes:

$$E = (CV^2) / 2 \quad (1)$$

In order to increase the energy density of EDLCs, it is necessary to increase C and V . A higher ionic concentration in the electrolyte is required for the improvement of the C value. And, since the energy density is proportional to the square of the cell voltage, increasing the cell voltage is a very important development target for EDLCs. Conventional electrolytes for EDLCs are solutions in which a certain type of solid ammonium salt is dissolved in an organic solvent. In this case, a high ionic concentration level is not achieved due to the restriction of the solubility of the ammonium salt; many kinds of solid ammonium salt have solubilities of only about 2M. On the contrary, ionic liquids are composed of dissociated cations and anions with a high concentration, and it is possible to use them alone as an electrolyte for EDLCs, that is to say, the ionic liquid electrolyte is both the solute and solvent. In this case, a high capacity can be expected because there are extremely high concentrations (3-5 M) of ion species that contribute to double layer formation in the ionic liquid. Furthermore, the non-flammability of the ionic liquid should be an attractive feature for the enhanced safety of EDLCs.

An ionic liquid with a wide electrochemical stability window is needed for the achievement of a high energy density EDLCs. Some cations of ionic liquids that have been the subjects of many previous studies are shown in Fig. 1.

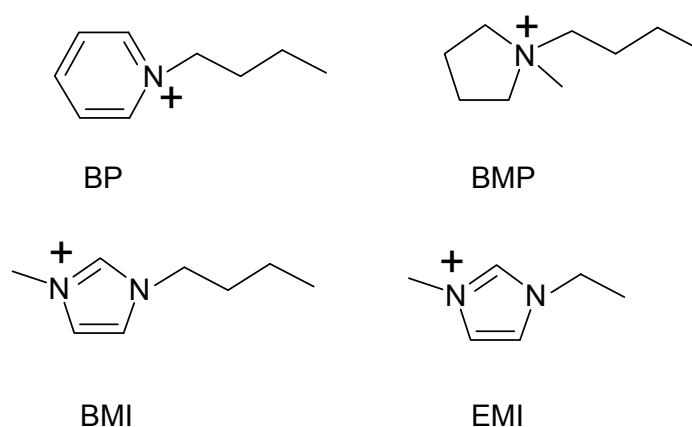


Fig. 1. Some cation structures of ionic liquids. BP: butylpyridinium, BMP: butylmethylpyrrolidinium, BMI: 1-butyl-3-methylimidazolium, EMI: 1-ethyl-3-methylimidazolium.

At first, many researchers focused on aromatic type ionic liquids, such as 1-ethyl-3-methylimidazolium tetrafluoroborate (EMI- BF_4), which has a relatively low viscosity and high ionic conductivity (Koch et al.,1995; Koch et al.,1994; McEwen et al.,1999; McEwen et al.,1997) 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 (Ue et al.,2002). On the other hand, some papers have been published on the use of aliphatic quaternary ammonium-based ionic liquids, which would be expected to have a higher cathodic stability; this is due to the fact that the small size aliphatic quaternary ammonium-based ionic liquid has a relatively high melting temperature, compared with the aromatic ones. MacFarlane and co-workers reported that aliphatic quaternary ammonium cations which had relatively short (C1-C4) alkyl chains could not easily form an ionic liquid near room temperature (Sato, 2004, as cited in Sun et al.,1997,1998a,1998b & MacFarlane et

al.,1999,2000). However, Angell and co-workers and Matsumoto et al. reported that some asymmetric and short-chain aliphatic quaternary ammonium cations with a methoxyethyl or methoxymethyl group on the nitrogen atom formed ionic liquids below room temperature (Cooper & Angell,1986; Emanuel et al.,2003) (Matsumoto et al.,2000,2001,2002). Recently, the major advances in research and development of ionic liquid electrolytes have mainly concerned quaternary ammonium-based ionic liquids where the anion has a relatively high anodic stability, such as BF_4^- , bis(trifluoromethanesulfonyl)imide ($-\text{N}(\text{SO}_2\text{CF}_3)_2$: TFSI) and other fluorinated anions.

2. Neat ionic liquid electrolytes for EDLC application

2.1 Aliphatic quaternary ammonium type ionic liquids having a methoxyethyl group on the nitrogen atom

Generally, small sized aliphatic quaternary ammonium cations cannot easily form an ionic liquid, however, by attaching a methoxyethyl group to the nitrogen atom, many aliphatic quaternary ammonium salts can form ionic liquids with BF_4^- and TFSI anions. For instance, DEME- BF_4 and DEME-TFSI are novel ionic liquids whose liquid state covers a wide temperature range (Fig. 2) (Maruo et al.,2002).

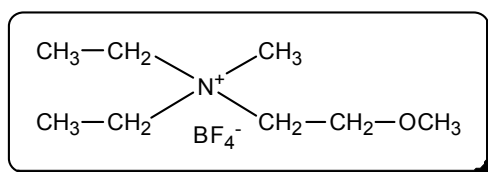


Fig. 2. Schematic illustration of the molecular structure of the DEME cation.

Since the electron donating feature of an oxygen atom in a methoxyethyl group weakens the cation's positive charge, the electrostatic binding between the ammonium cation and anion weakens, and an ionic liquid forms. The limiting reduction and oxidation potentials (E_{red} and E_{oxd}) on platinum of the ionic liquids were measured by cyclic voltammetry at room temperature as shown in Fig. 3.

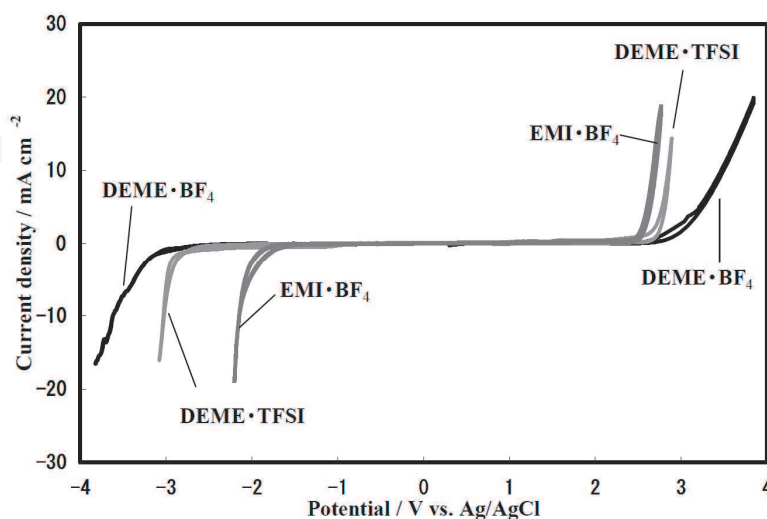


Fig. 3. Cyclic voltammogram of the ionic liquids based on the DEME cation and EMI- BF_4 at 25 °C. Scan rate: 1mVs^{-1} , working and counter electrode: platinum, reference electrode: Ag/AgCl electrode.

The E_{red} and E_{oxd} were defined as the potential where the limiting current density reached 1mAcm^{-2} . The potential window between the onset of E_{red} and E_{oxd} was 6.0V for the DEME- BF_4 and 4.5V for the EMI- BF_4 , respectively. Since the E_{red} of the DEME-based ionic liquid was approximately 1V lower than that of the EMI- BF_4 , we realized that DEME had a higher cathodic stability than aromatic type ionic liquids since it does not have a π -electron conjugated system. Compared with DEME-TFSI, DEME- BF_4 is a little more stable in the limiting reduction potential. Since DEME- BF_4 has the largest potential window so far reported, it should be suitable as an electrolyte for a high operating voltage EDLC.

2.2 The electric double layer capacitor using DEME- BF_4 as an electrolyte

The EDLC is an energy storage device based on charge storage between an activated carbon and an electrolyte solution. It may be possible to improve the safety and durability at high temperatures using an ionic liquid instead of an inflammable organic solvent. However, a typical ionic liquid, EMI- BF_4 cannot be used for an EDLC operating at a high voltage because of decomposition on the anode. We tried to prepare a test cell for the EDLC which would be stable at high temperature using DEME- BF_4 as an electrolyte. The cell configuration of a demonstration EDLC is shown in Fig.4.

Table 1 summarizes the capacitance C of the EDLC using various electrolytes at temperatures higher than room temperature. The capacity and the Coulombic efficiency between the charged and discharged capacity were obtained from the charge and discharge curves. As Table 1 shows, the EDLCs using ionic liquids showed higher discharge capacities than those using the standard electrolyte TEA- BF_4 in PC solution at all the temperatures tested. Within high ionic concentration electrolyte, the double layer might be specifically formed on the surface, while ion adsorption does not occur at a low ionic concentration, although the reason for this behavior is not clear.

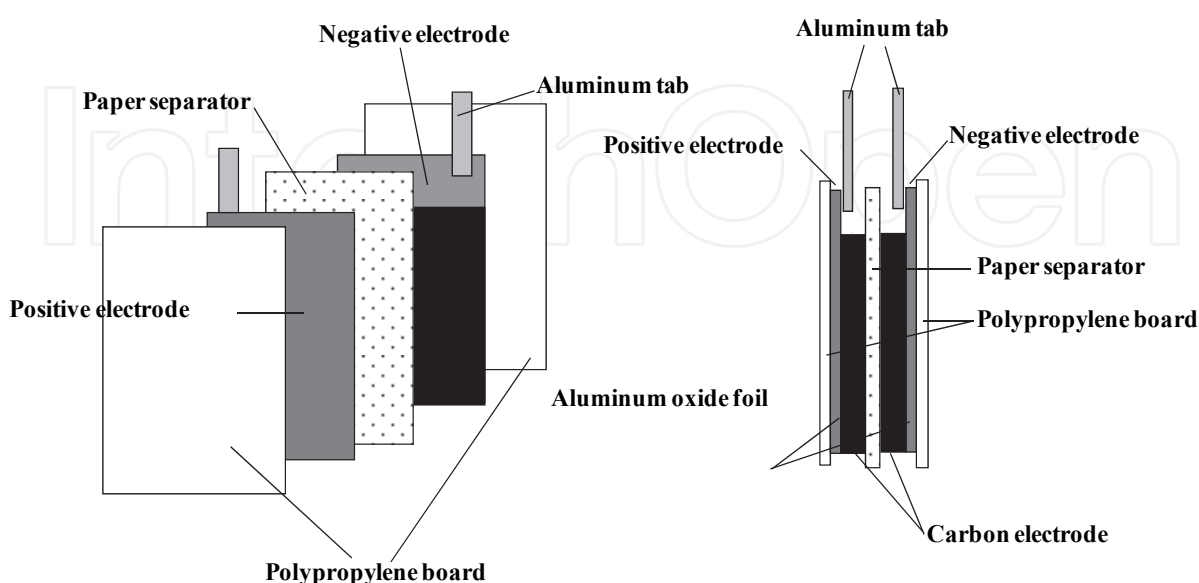


Fig. 4. EDLC test cell configuration.

Measurement temperature, T (°C)	Electrolytes		
	DEME-BF ₄	EMI-BF ₄	1M TEA-BF ₄ in PC
	Discharge capacitance C^a (Fg ⁻¹) and coulombic efficiency ^b (%)		
25	25.4(98.5)	26.3(90.5)	21.3(98.3)
40	25.5(96.0)	26.6(84.7)	20.2(90.1)
70	25.7(88.9)	23.9(60.9)	20.1 (68.7)
100	23.7(78.5)	n.m. ^c (n.m.)	20.1 (40.0)
130	21.3(58.7)	n.m. (n.m.)	n.m. (n.m.)
150	17.5(33.7)	n.m. (n.m.)	n.m. (n.m.)

^a C was calculated by $C = 2WV^{-2}$. ^b Coulombic efficiency: [discharged capacity (mA h)/charged capacity (mA h)] \times 100. Values of coulombic efficiency. ^c n.m., not measurable due to unstable cell performance caused by gas evolution.

Table 1. Double layer capacitance of EDLC with various electrolytes above room temperature.

However, for the EDLC using EMI-BF₄ we observed both, the generation of gas from the decomposition of the ionic liquid and a remarkable drop in the capacity at 70°C. In the case of TEA-BF₄ in PC, the large drop in capacity was observed at 100 °C. On the other hand, the EDLC using DEME-BF₄ exhibited little gas generation and did not show such a large capacity drop at 100°C and capacity could be observed even at 150°C. These results indicate that the cell using DEME-BF₄ is more stable compared to the EDLC using the general organic electrolyte TEA-BF₄/PC. At high temperatures, the cell using DEME-BF₄ has the highest relative Coulombic efficiency of the tested electrolytes. Fig. 5 demonstrates that, even at 100 °C, the EDLC using DEME-BF₄ showed a practical good level of durability over cycles of charging and discharging. After 500 charge and discharge cycles, the capacity loss was just 15% of the initial discharge capacity. It is possible that an EDLC using DEME-BF₄ may be a practical energy storage device, which can stably charge and discharge at high temperature.

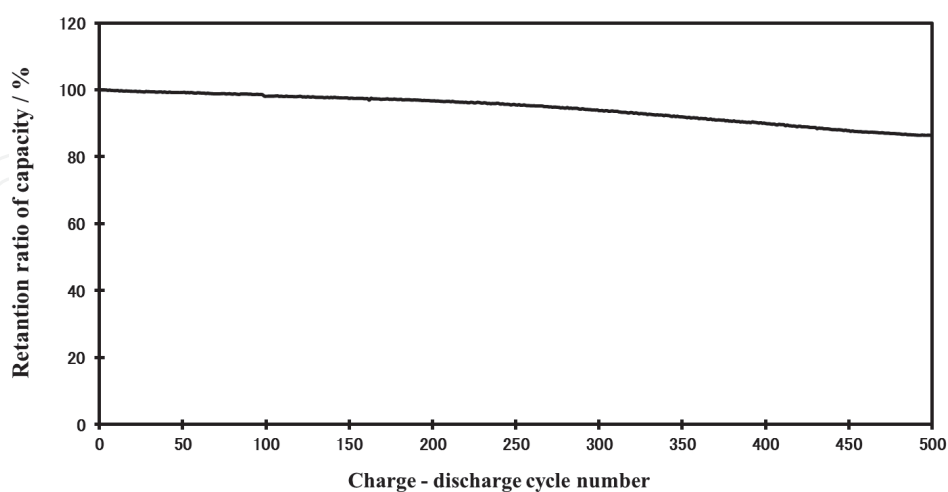


Fig. 5. Cycle test of an EDLC using DEME-BF₄ as an electrolyte at 100 °C. The test cell was charged by a constant current-constant voltage mode from $V = 0$ to 2.5V at a constant current (CC) $I = 15$ mA and then charged to keep constant voltage (2.5 V) for 15 min and discharged to 0V by CC mode.

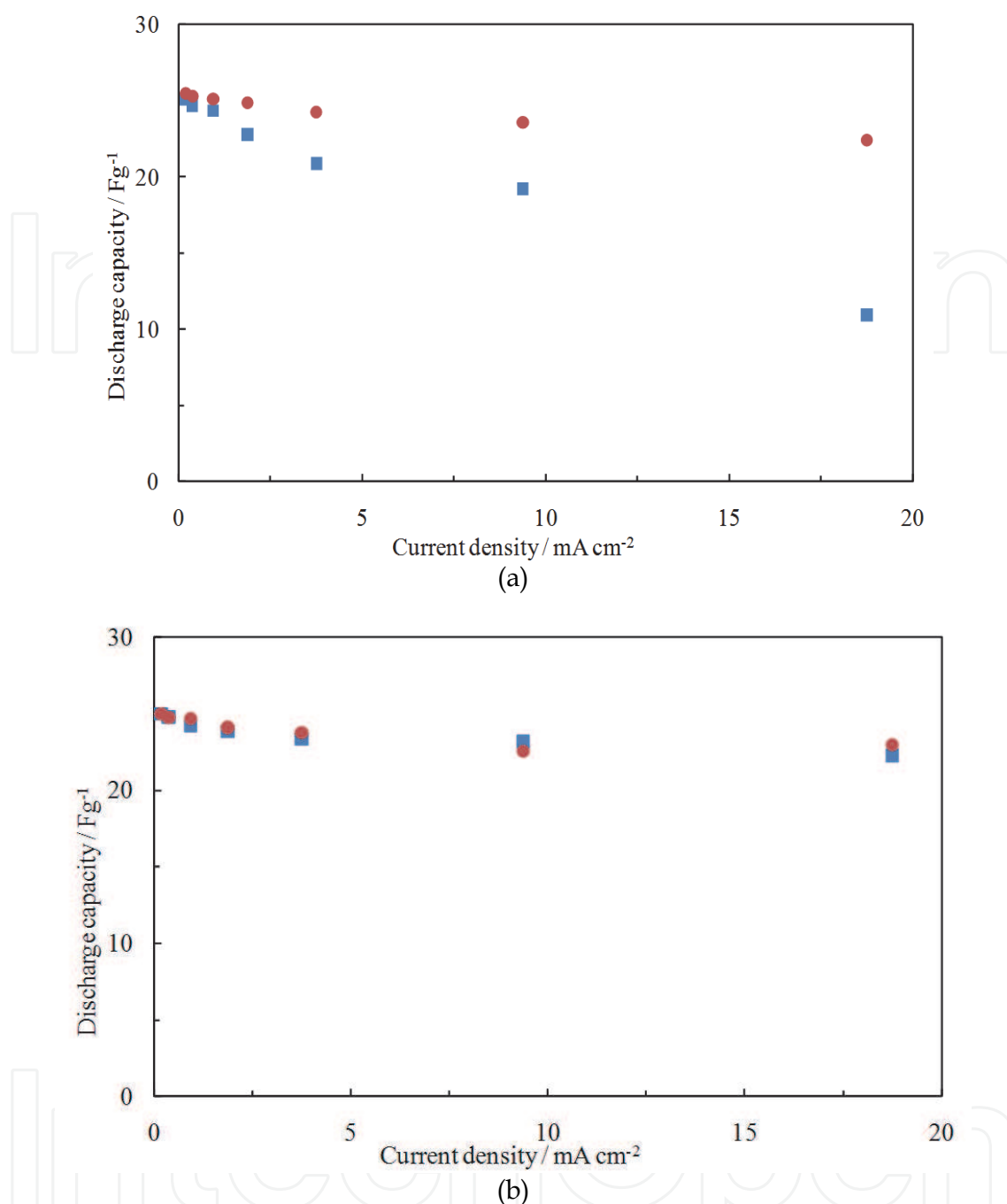


Fig. 6. The discharge capacity at various discharge currents for an EDLC using DEME-BF₄ (square) and 1M TEA-BF₄ (circle) as an electrolyte; (a) at 25 °C, (b) at 40 °C.

The relation between the capacity C and the discharge current I is shown in Fig. 6. At 25°C the discharge capacity of the EDLC using DEME-BF₄ decreased significantly faster than that using TEA-BF₄ as the discharge current increased. It is probable that the larger decrease in C at discharge currents using DEME-BF₄ resulted from the large internal resistance of the EDLC cell when using this high viscosity electrolyte. In the case of an EDLC using an ordinary electrolyte the discharge capacity decreased only by 15% for a 100 times large current. The high viscosity of the ionic liquid decreases the mobility of ionic species. However, in operation at 40 °C shown in Fig. 6b, the capacity of the EDLC using DEME-BF₄

is remarkably improved. In this case the capacity of the ionic liquid cell is higher than that of a cell using TEA-BF₄/PC. A slight elevation of the temperature has decreased the viscosity of the ionic liquid, since the effect of a temperature change on the viscosity of ionic liquids is known to be large. We suggest that, at temperatures of 40 °C or above, an EDLC using DEME-BF₄ has a practical useable performance comparable to that of a conventional EDLC using an organic electrolyte. Furthermore, the durability at high temperatures of such an ionic liquid cell is higher than that of a conventional EDLC. However, below room temperature, the capacity of an EDLC using this ionic liquid was inferior to that of the conventional EDLCs using solid-ammonium salt / PC system due to the high viscosity of the ionic liquid and the fact that the charge and discharge operation of our demonstration cell might be compromised around 0°C.

On the other hand, Japanese researchers (Ishikawa et al., 2006 and Matsumoto et al., 2006) reported that ILs containing bis(fluorosulfonyl)imide (FSI) had a quite low viscosity and high ionic conductivity when compared with those based on the TFSI anion, and various ILs containing the FSI anion had some suitable properties for use as the electrolyte of a lithium ion battery. Also, Handa et al., (2008) reported the application of an EMI-FSI ionic liquid as an electrolyte for an EDLC, and found that demonstration cell showed excellent capabilities comparable to one using a solid ammonium salt / PC electrolyte. Further, Senda et al. (2010) reported that fluorohydrogenate ionic liquids (FHILs) exhibit a low viscosity, high ionic conductivity and low melting point compared to other ionic liquids. Their EDLCs using some FHILs were operable even at -40 °C, exhibiting a capacitance higher than that of TEA-BF₄ / PC. The use of the ionic liquids with these new fluorine system anions as the electrolyte of various electrochemical devices will probably develop in the future, because the structure of the anion has a big influence on the viscosity of the ionic liquid.

3. Practical use of ionic liquid as a solute for an EDLC electrolyte

3.1 Use of ionic liquids for EDLC performance improvement at low temperatures

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. Some solid ammonium salts might be precipitated by recombination of dissociated ions in the low temperature region due to their low solubility. As a result, an EDLC including a solid ammonium salt solute will suffer a large drop in capacitance at low temperatures. In many cases, an electrolyte including an ionic liquid that has a high solubility in propylene carbonate (PC) exhibit a high ionic conductivity, even at low temperatures, compared to a traditional solid ammonium salt electrolyte. Also, DEME-BF₄ can be homogeneously mixed with PC to produce a uniform electrolyte solution and it does not cause precipitation of the salt, even at temperatures below -40 °C. Figure 7 shows the relation between the ionic liquid concentration in PC and the solution viscosity at room temperature.

Many ionic liquids cause a remarkable viscosity decrement for just a small amount of solvent addition. It is the simplest method by which the problem of the high viscosity of the ionic liquid can be eased. Nisshinbo Industries Inc. in Japan manufactures successful large size EDLCs that have an extremely attractive high charge rate and discharge performance even at -40 °C by the use of an electrolyte including DEME-BF₄ diluted with PC (http://www.nisshinbo.co.jp/english/r_d/capacitor/index.html).

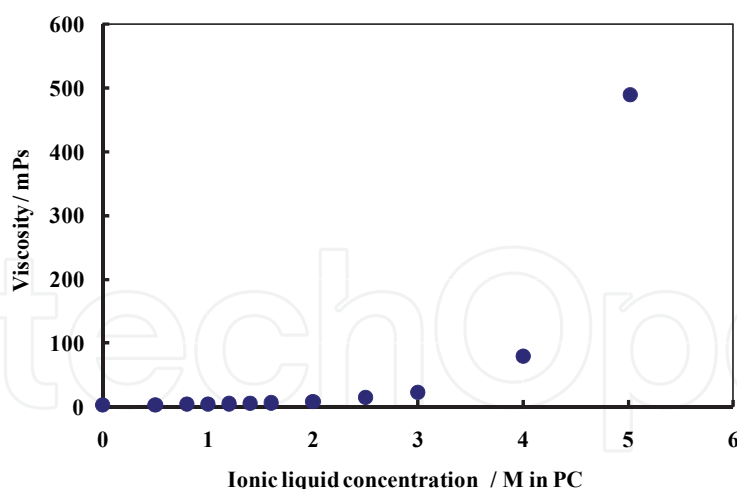


Fig. 7. Viscosity of ionic liquid / PC solution.

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

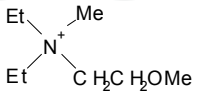
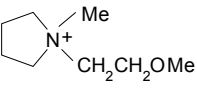
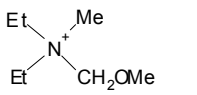
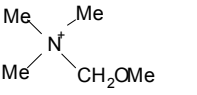
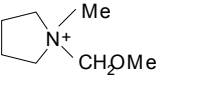
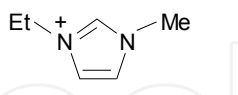
3.2.1 Ionic liquids having a methoxyalkyl group on the nitrogen atom as a solute

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 BF_4^- and TFSI anions. In this section, we report on 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 a solute in an electrolyte. The evaluation was performed using a large size cell (265F) 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. We prepared 14 kinds of ammonium salt that have 6 kinds of cation and 3 kinds of anion species as candidate electrolytes for EDLCs (Yuyama et al. 2006). Nine of these were ionic liquid in nature at 25 °C and some ammonium salts were not liquid at room temperature. The melting temperatures are summarized in Table 2. We prepared large size EDLCs using the 14 kinds of salt in Table 2. Because 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.

3.2.2 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 1M propylene carbonate solution was determined by charge–discharge cycling from 0 to 3.0V at 25 °C. Fig. 8 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).

Code of cation	cation	Melting temperature / °C		
		BF ₄	PF ₆	TFSI
DEME		9 ^{a,b)}	23 ^{a,c)}	-91 ^{a,b,d)}
MEMP		18 ^{a,b)}	34 ^{a,c)}	-95 ^{a,b,d)}
DEMM		45 ^{a,b)}	--	--
MMTM		51 ^{a,b)}	204 ^{a,c)}	-2 ^{a,b)}
MMMP		-5 ^{a,b)}	--	--
EMI		11 ^{a,b)}	60 ^{a,c)}	-16 ^{a,b)}

a 1M of propylene carbonate solution was tested for EDLC electrolyte in this work.

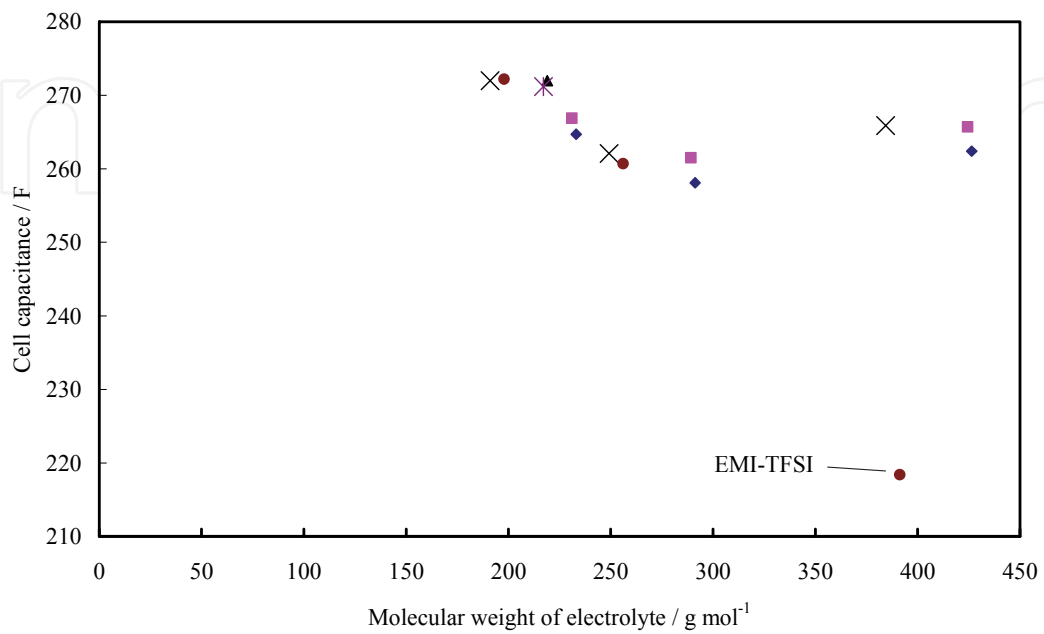
b Melting temperature was measured by DSC.

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

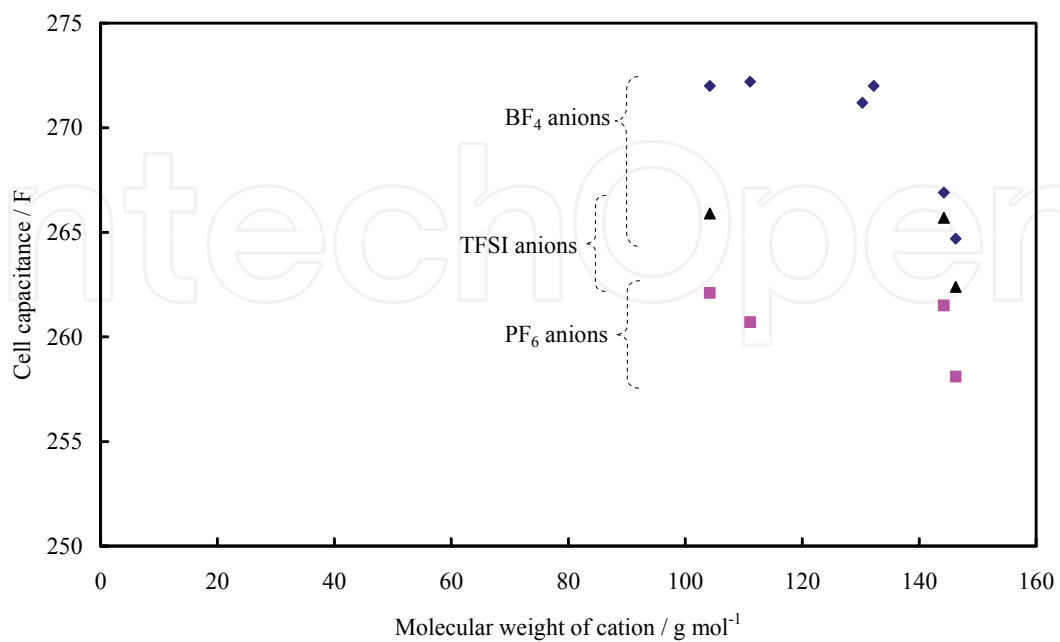
d Glass transition temperature was measured by DSC.

Table 2. Melting temperature of ammonium salts used in this work.

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 1M DEME-BF₄, which a molecular weight of 233.05, has an approximately 10% higher capacitance than a cell using a 1M solution of a conventional ammonium salt,



(a)



(b)

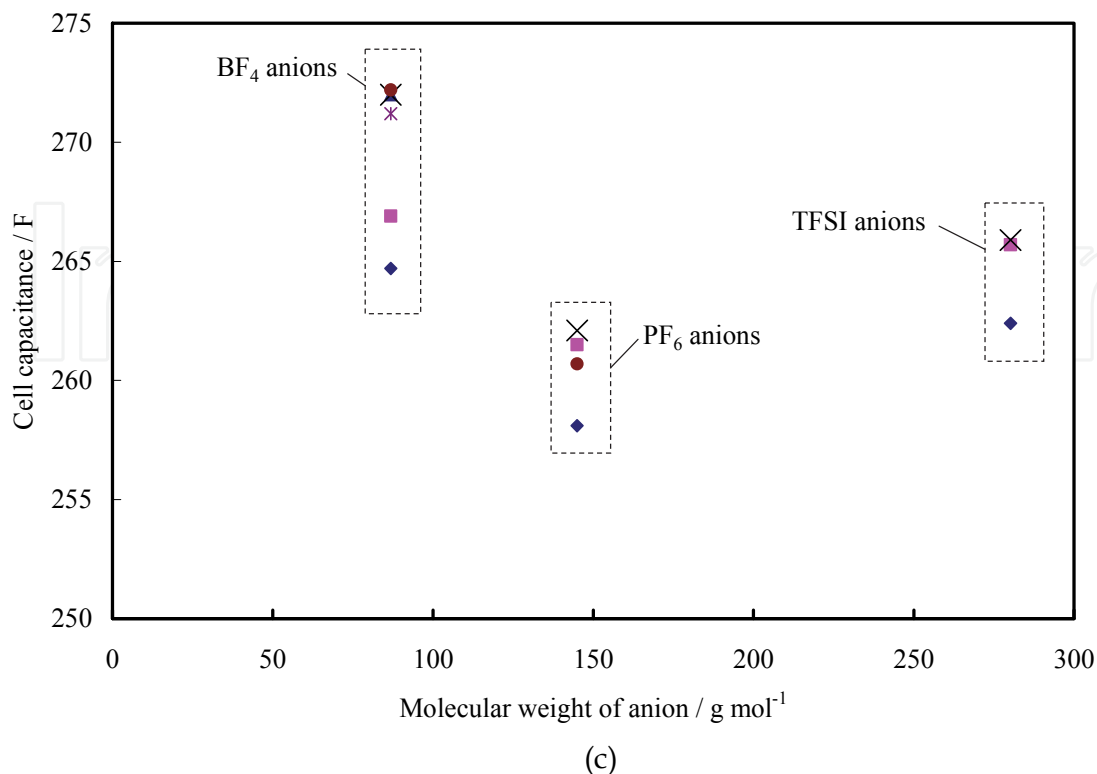


Fig. 8. The discharge capacitance of EDLCs containing various electrolytes. The test cell was discharged at a constant current $I = 0.2$ A from $V = 3.0$ to 0 V at 25 °C. Cell capacitance is plotted against the molecular weight of salts, cations and anions for (a), (b) and (c), respectively. The electrolyte concentration was 1M in PC: (♦) DEME-cation species; (■) MEMP-cation species; (▲) DEMM-cation species; (x) MMTM-cation species; (*) MMMP-cation species; (●) EMI-cation species in figure (a) and (c). In figure (b): (♦) BF₄-anion species; (■), PF₆-anion species; (▲) TFSI-anion species. The prepared EDLC with 1M DEME-BF₄ in PC had 44 F g⁻¹ of the specific capacitance per electrode weight.

tetraethylammonium tetrafluoroborate (TEA-BF₄), which has a molecular weight of 217.6 (Kim et al. 2005). However, in the results shown in Fig. 8(a), the cell capacitance with a 1M 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. 8(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. 8(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 BF₄ 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.

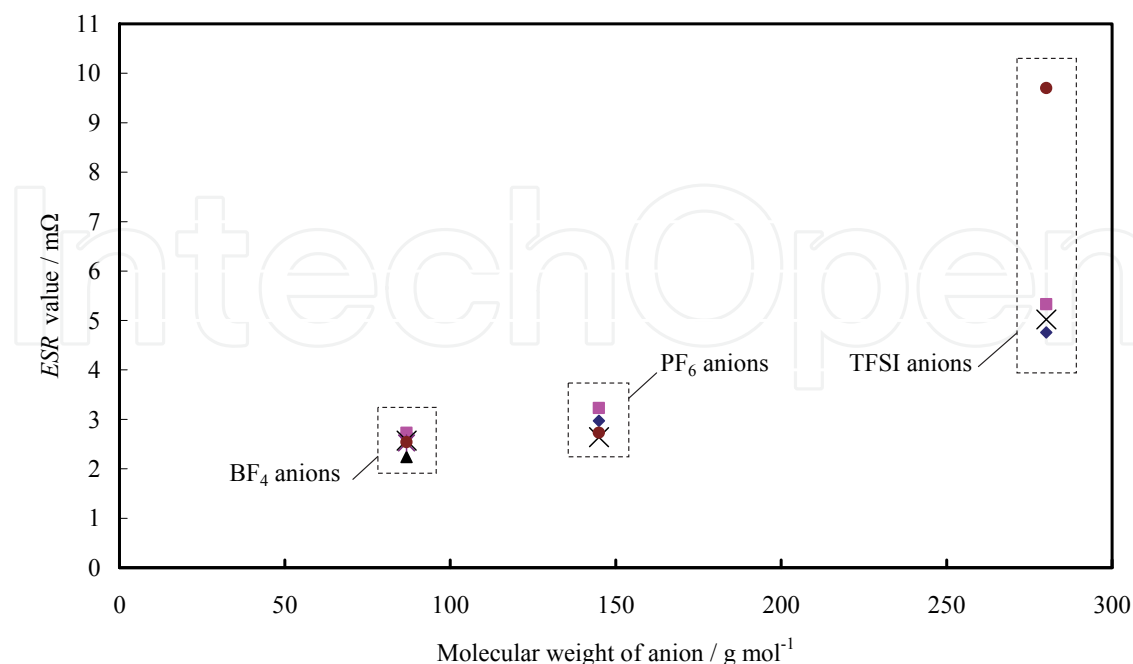


Fig. 9. The internal resistance (*ESR*) of EDLCs (265F) containing various electrolytes at 1kHz, 25 °C. The electrolyte concentration was 1M in PC: (◆) DEME-cation species; (■) MEMP-cation species; (▲) DEMM-cation species; (x) MMTM-cation species; (*) MMMP-cation species; (●) EMI-cation species.

We also understand that the kind of anion species used also influences the internal resistance (*ESR*) of an EDLC. Fig. 9 shows the *ESR* of EDLCs using various electrolytes at 1 kHz, 25 °C. Those EDLCs using the BF₄ anion in PC have the practicable value of *ESR* of 2.5mΩ. On the other hand, the *ESR* associated with the use of TFSI anions is twice or more than that of BF₄. The EDLC using the PF₆ 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 BF₄ as electrolytes is unpractical for high voltage EDLCs.

3.2.3 Comparison of DCIR for EDLCs at low temperature

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 BF₄ 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 BF₄ solutes, from ten to twelve times for PF₆ solutes, and for TFSI solutes by a factor of 30 or more. Fig. 10 shows the DCIR of EDLCs using various 1M solutions as an electrolyte at -30 °C. 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.

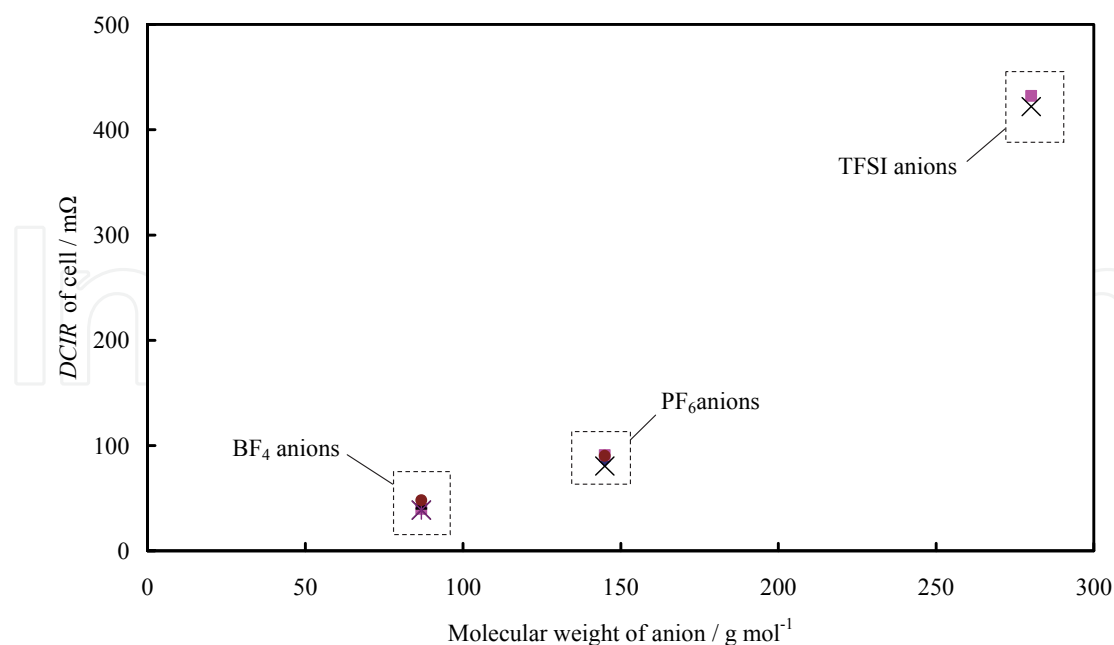


Fig. 10. The direct resistance (*DCIR*) of EDLCs containing various electrolytes at 5A discharge at $-30\text{ }^{\circ}\text{C}$. The electrolyte concentration was 1M in PC: (♦) DEME-cation species; (■) MEMP-cation species; (▲) DEMM-cation species; (x) MMTM-cation species; (*) MMMP-cation species; (●) EMI-cation species.

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 should contain the BF_4 anion. However, MMTM- BF_4 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.

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 (σ) for various electrolytes below $30\text{ }^{\circ}\text{C}$ is shown in Fig. 11. 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 $-30\text{ }^{\circ}\text{C}$ to room temperature. There is essentially no difference among the six electrolytes' temperature dependence. The difference of ionic conductivity between BF_4 and TFSI at $25\text{ }^{\circ}\text{C}$ was only 1.1 and 1.5 mS cm^{-1} 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 $-30\text{ }^{\circ}\text{C}$, the DCIR difference between the BF_4 and TFSI anion combined with DEME or MEMP is ten times or more, yet the difference in ionic conductivity between BF_4 and TFSI was only 0.3 mS cm^{-1} at the same temperature.

The dynamic viscosity (η) of 1M solutions of DEME- BF_4 , DEME-TFSI, MEMP- BF_4 and MEMP-TFSI in PC at various temperatures are displayed in Fig. 12. We focus attention first on the viscosity of DEME- BF_4 and its TFSI anion at $-30\text{ }^{\circ}\text{C}$. If the viscosity of the electrolyte

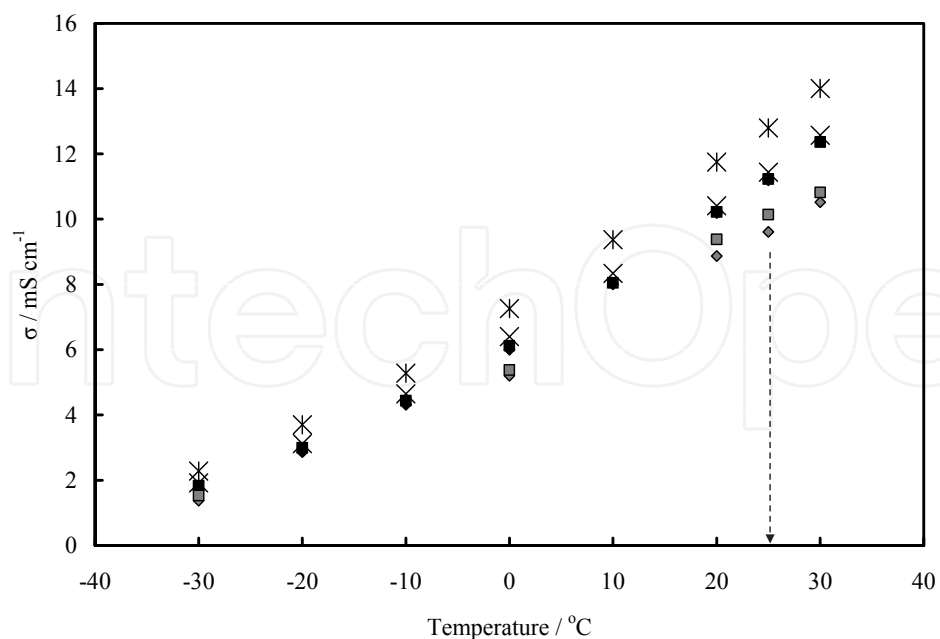


Fig. 11. The specific conductivity (σ) vs. temperature plots the various electrolytes containing a 1M concentration of ammonium salts. The electrolyte concentration was 1M in PC: (♦) DEME-BF₄; (◐, half-tone) DEME-TFSI; (■) MEMP-BF₄; (◑, half-tone) MEMP-TFSI; (x) MMTM-BF₄; (*) MMMP-BF₄.

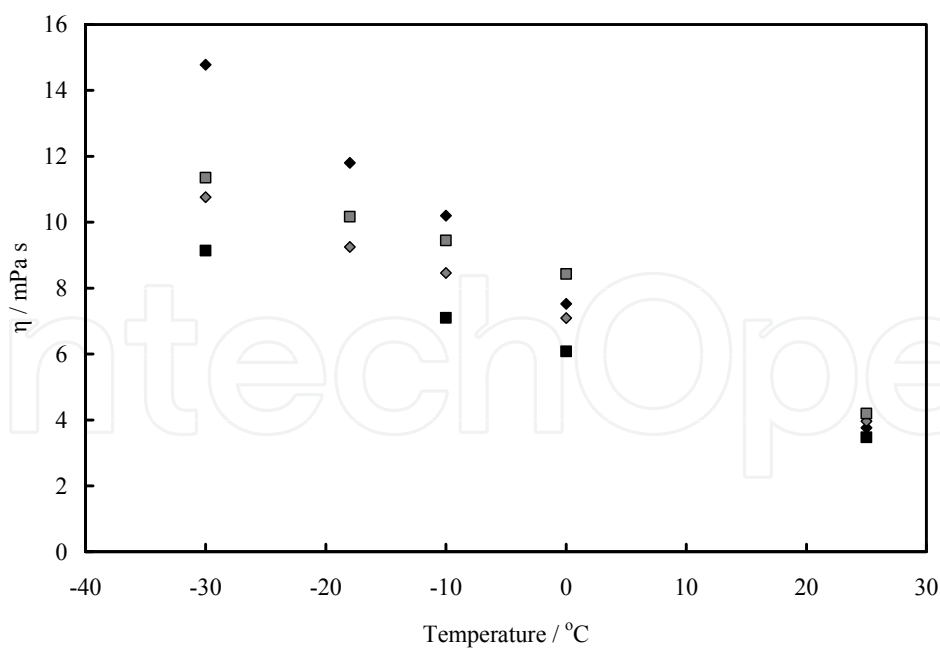


Fig. 12. Dynamic viscosity (η) as a function of temperature for the various electrolytes containing a 1M concentration of ammonium salts. The electrolyte concentration was 1M in PC: (♦) DEME-BF₄; (◐, half-tone) DEME-TFSI; (■) MEMP-BF₄; (◑, half-tone) MEMP-TFSI.

has a big influence on DCIR, due to a highly viscous electrolyte decreasing the mobility of the ionic species, then an electrolyte using DEME-BF₄ should have a large DCIR value compared to one using DEME-TFSI. However, an EDLC using DEME-BF₄ 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 °C. In the case of MEMP, the large difference of DCIR that existed between cells using BF₄ 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-BF₄, MMMP-BF₄ and DEMM-BF₄ in PC are more attractive candidates than DEME-BF₄ for use as an EDLC electrolyte from the view point of capacitance and DCIR.

3.2.4 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 3.0V, 70 °C. Presumably, a good response to this test will indicate good durability at room temperature. Fig. 13 demonstrates that the EDLCs using MEMP-BF₄ and DEME-BF₄ 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-BF₄ and DEME-BF₄, respectively. On the other hand, MMMP-BF₄ and DEMM-BF₄ had good capacitance and DCIR value at low temperature, but their durability at high temperatures was inferior to that of DEME- and MEMP-BF₄ cells. Our conclusion is that ammonium salts with a methoxyethyl group have higher stability than those with a methoxymethyl group. Therefore, we recommend MEMP-BF₄ in PC as the preferred electrolyte for an EDLC in terms of capacitance, low temperature performance and thermal durability in practical use. The detailed ESR and maintenance ratio of the capacitance after 500 and 1000 h operation are summarized in literature (Yuyama et al. 2006).

We developed a new 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 BF₄ anion had a higher capacitance at 25 °C, 3V than those including PF₆ 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 BF₄, PF₆ and TFSI. This order corresponds to the ranking of the molecular weights of the anion. Even in the ionic liquids, those including the PF₆ 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-BF₄ and DEME-BF₄, 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-BF₄ is the preferred ionic liquid for use as an electrolyte solute in an EDLC.

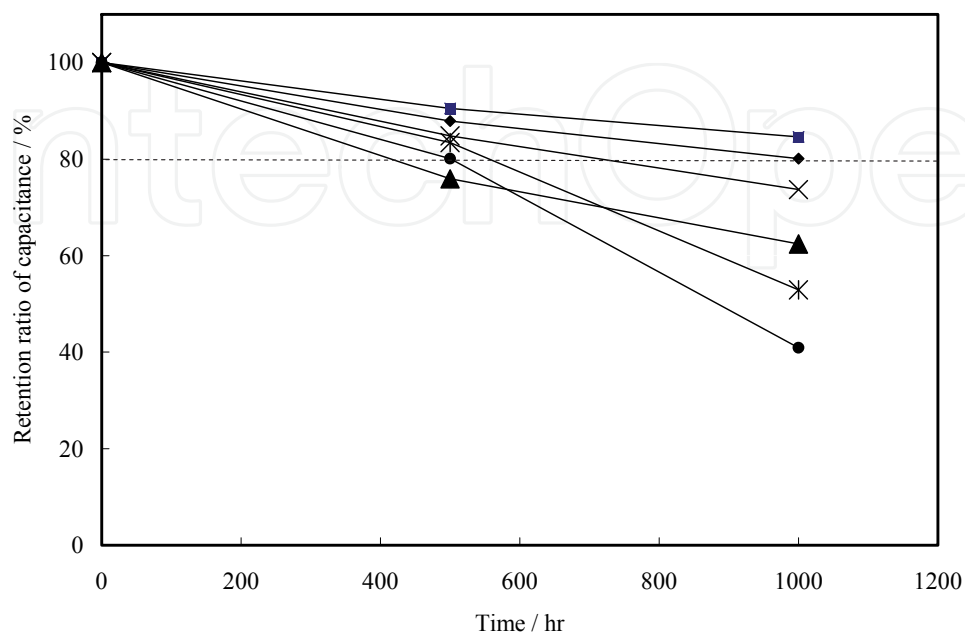


Fig. 13. Life test of EDLCs using various electrolytes including BF₄ anion. The cell was continuously charged at 3.0V, 70 °C for 1000 hrs. The electrolyte concentration was 1M in PC: (◆) DEME-BF₄; (■) MEMP-BF₄; (▲) DEMM-BF₄; (x) MMTM-BF₄; (*) MMMMP-BF₄; (●) EMI-BF₄.

4. A thin layer including a carbon material improves the rate capability of an electric double layer capacitor

The discussion above showed that ionic liquids have very high potential as practicable EDLC electrolytes. However, the dilution of the ionic liquid with organic solvent is an indispensable step in order that such EDLCs may have a high power performance that is equal or better than cells with a conventional electrolyte such as the solid ammonium salt/PC solution system. While the addition of the organic solvent brings about a spectacular high power performance of the EDLC at low temperatures, at the same time it also has negative implications for the safety of the cells.

On the other hand, we develop a new method to improve the rate capability of an electric double layer capacitor (EDLC) using a thin polymer layer having a high concentration of carbon material on a current collector (CLC) (Sato et al., 2011). A novel thermocuring coating composed of a glycol-chitosan, a pyromellitic acid and a conductive carbon powder can form stable CLC on a metal foil current collector simply by spreading and curing at 160 °C for a couple of minutes. We compared the performance of some demonstration EDLC cells using three kinds of current collector: a conventional aluminum oxide foil for EDLC, an aluminum foil and an aluminum foil with CLC. The cell with the CLC had a much higher rate capability than the cell without CLC. Only the CLC cell was able to discharge at a current density of 500C. This cell shows a slight deterioration in capacity in a high

temperature, continuous charging, life test, and the CLC has a suppressing effect on the internal resistance increase of EDLCs. The use of a CLC film current collector is one of the most effective and simple methods for the improvement of EDLC rate performance. In particular, a current collector consisting of aluminum foil coupled with a CLC promises to be a low cost alternative to the aluminum oxide foil commonly used in EDLCs. Also, these effects of a CLC have been confirmed in an EDLC with an undiluted ionic liquid as an electrolyte. In this connection, we note the use of a combination of undiluted aliphatic cyclic ammonium type ionic liquid, MEMP-BF₄ (Fig.14), which has a relatively low viscosity, with an aluminum collector, coupled with a CLC.

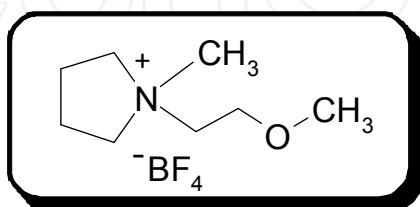


Fig. 14. Molecule structure of *N*-(2-methoxyethyl)-*N*-methylpyrrolidinium tetrafluoroborate (MEMP-BF₄).

4.1 Thermocuring coating on the current collector of an EDLC electrode

To improve rate performance, we have prepared cells containing a carbon layer on the current collector (CLC). This consists of a thin layer having a high concentration of conductive carbon material, situated between the activated carbon electrode layer and the current collector. We have found that a hydroxyalkylated chitosan (glycol-chitosan) derivative and 1,2,4,5-benzene-tetracarboxylic acid (pyromellitic acid) mixture acts as a thermally activated binder that adheres strongly to metal foil was very effective in improving the rate capability of EDLC cells.

Chitosan is a natural and low cost biopolymer prepared by the deacetylation of chitin, the most abundant polymer after cellulose, and is mainly obtained from crab shells (Fig. 15). Due to its unique physicochemical properties such as non-toxicity, chemical and thermal stability, hydrophilicity, remarkable affinity towards certain substances and film formation with relatively high physical strength, it has been extensively studied and is used in many fields (Rinaudo,2006; Mourya,2008) We found that we could form a stable coating layer on the metal substrate by spreading and heating an ink composed of a glycol-chitosan and a polycarboxylic acid compound. Because it is well known that the secondary amino group of the chitosan forms an imide linkage by reacting with two carboxylic acids, we propose that such cross-linkage between chitosan molecules can be formed by use of a tetracarboxylic compound. It is probable that a stable three-dimensional polymer network had been formed by the synergistic effect of combining a chitosan with a relatively rigid backbone with a chemically stable imide crosslinkage (Fig. 15). In addition the amino group of the chitosan has a strong affinity to carboxylic and hydroxyl groups on the surfaces of inorganic materials. Because the conductive carbon material used here, such as acetylene black and Ketjen black, has a lot of carboxylic acid and hydroxyl groups on the powder surface, it is likely that the chitosan binds strongly to them.

The chitosan dissolves easily in aqueous acids, though it does not dissolve in the NMP conventionally used as a solvent in electrode making. However, the chitosan can be converted into the amphipathic partially hydroxyalkylated derivative obtained on reacting

the hydroxyl and amino groups in the glucosamine unit with epoxide compounds such as ethylene oxide, propylene oxide and butylene oxide. We developed a novel coating to use as a conductive layer on a metal current collector by reacting glycolchitosan and pyromellitic acid.

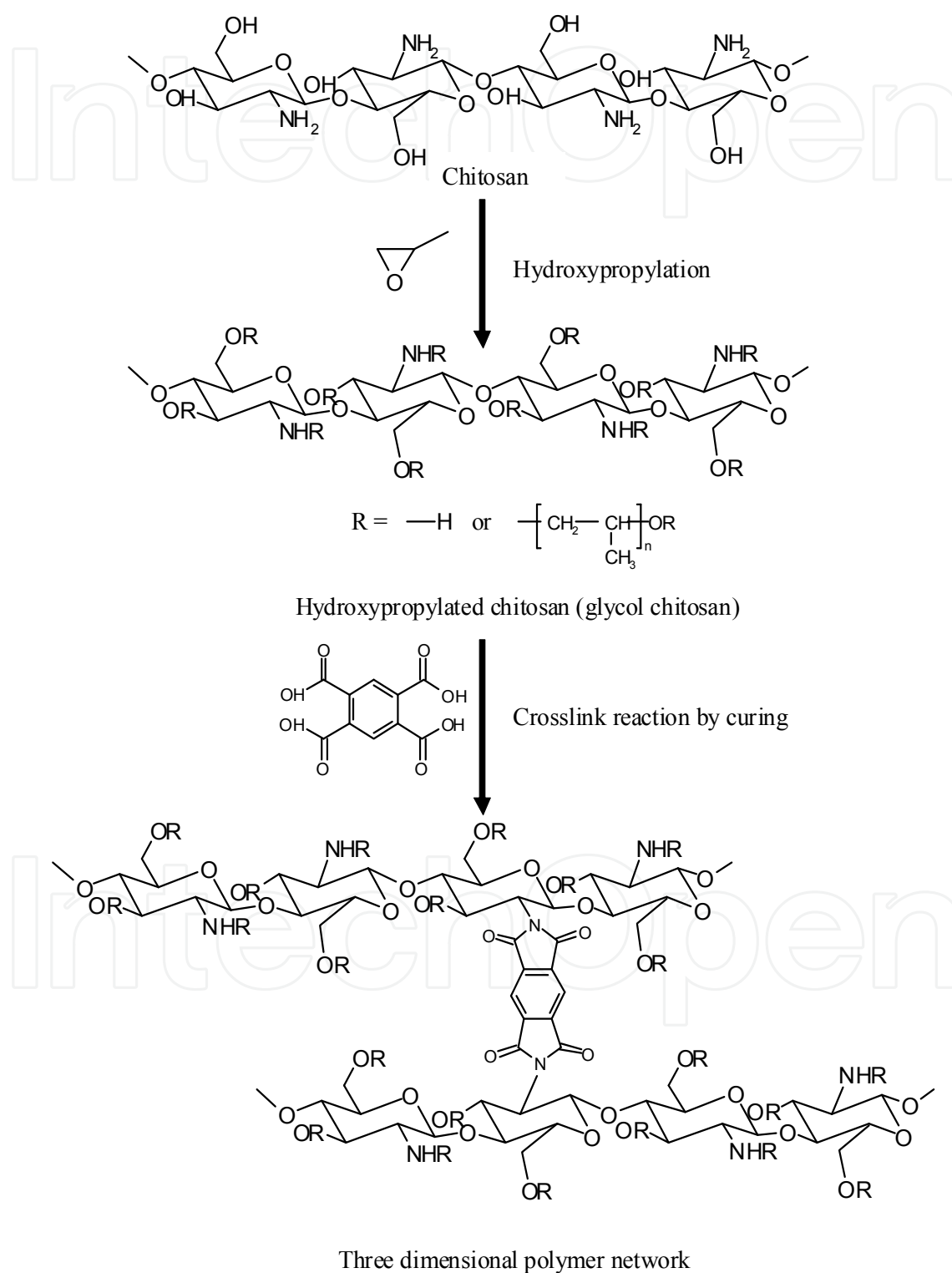


Fig. 15. Thermosetting chitosan / pyromellitic acid binder in this study.

4.2 CLC effect on EDLC cells

In this study, we assumed that the cell impedance could be decreased by decreasing the contact resistance between the activated carbon electrode layer and the current collector. The method we employed simply places stable, thin carbon layer composed of acetylene black and glycol-chitosan (CLC) between the activated carbon electrode and the current collector. The rate performance of demonstration EDLCs at 25 °C with, and without, a CLC on the current collector and various electrolytes are summarized in Table 3.

The EDLC cell with an aluminum oxide current collector showed a slightly higher capacitance at low discharge current values. The pores present on the aluminum oxide foil surface might be contributing to a small capacity increase. The conventional aluminum foil cell has the lowest capacitance of the examined cells, resulting from the large internal resistance of the cell, even for low rate discharging, such as that at 1C. On the other hand, the cell with a thin carbon layer on both positive and negative conventional aluminum foil collectors (CLC) showed an excellent discharge rate character for an EDLC. Evidently, this cell has about the same capacitance as a common EDLC cell at 20C discharging, and at 50C, the discharging capacity of the CLC cell surpassed that of the common cell. The capacitance of the CLC cell at 300C discharging was five times larger than that of the common cell, and was thirty times for a 500C discharging process.

At 500C discharging, corresponding to approximately 94 mAcm⁻² of current density to the electrode surface area, the EDLC with an aluminum oxide could not discharge. However, the CLC cell maintained 40% of the capacitance at 1C discharging. A remarkable improvement in the rate characteristic of an EDLC was also observed with a CLC using neat ionic liquid as an electrolyte. Such a cell showed almost the same output capacity as an aluminum oxide collector cell with diluted PC system as an electrolyte, although the viscosity at room temperature of the MEMP-BF₄ IL used is 72 mPa s, higher by a factor of 20 times or more compare with that of the conventional PC-diluted electrolyte. Fig. 16 shows discharging profiles of demonstration EDLCs at various discharge rates. In the discharge with a relatively large current, such as 300C and 500C, it is clear that the CLC cell has better rate character than the conventional EDLC. These results indicate that the installation of a CLC had an extremely positive effect on the rate performance of the cell.

Nyquist plots for a demonstration cell in the frequency range from 10mHz to 20 kHz are shown in Fig. 17. They consist of a semicircle at high frequency followed by an inclined line and a vertical line in the low frequency region. The intercept with the real axis at high frequency gives an estimate of the solution resistance (R_s). The diameter of semi-circle, namely the difference between the high frequency intercept (R_s) and low frequency intercept, indicates the interfacial resistance (R_i), which is attributed to the impedance at the interface between the current collector and carbon particles, as well as that between the carbon particles themselves.

The R_s value is different because of a difference in the ionic conductivity of the electrolyte. The most important conclusion is that the diameters of the semicircles were different in each cell. The cell with a CLC has a very small semicircle compared with AlOx cells. The cell with the largest semi-circle was that with a conventional aluminum current collector (not displayed in the figure). In the case of the cell with neat ionic liquid, the R_i value is small, similar to that of a CLC cell with diluted electrolyte. The activated carbon layer was prepared by the same methods and materials in each case, so the diameter of a semi-circle indicates the difference in the interfacial resistance between the activated carbon layer and current collector. The installation of a CLC has the effect of decreasing the interfacial

Electrolyte	Current collector ^a		Discharge capacity C (Fg ⁻¹) in various discharging rates ^b					
	Positive electrode	Negative electrode	1C	20C	50C	100C	300C	500C
1M DEME-BF ₄ in PC	AlOx	AlOx	25.2	21.3	16.9	11.6	2.4	0.3
1M DEME-BF ₄ in PC	Al	Al	21.3	14.3	7.9	3.4	0.1	0.2
1M DEME-BF ₄ in PC	Al+CLC	Al+CLC	22.5	20.8	19.1	17.6	12.3	9.1
Neat MEMP-BF ₄	Al+CLC	Al+CLC	21.2	18.0	14.6	11.3	4.3	1.2

^a Al + CLC, aluminum foil (20 μ m) with 2.5 μ m of CLC; Al, aluminum foil; AlOx, aluminum oxide foil (30 μ m). ^b Constant discharging current of 1.5mA corresponds to 1C and 0.19mAcm⁻².

*preparation of CLC: To form a CLC on a current collector, XSC-1N carbon ink suspension (Kyoritsu Chemical & Co., Ltd.) was spreaded by use of a gravure printing method. The thickness of the printed layer was approximately 5 μ m. After printing, the foil was dried at 160 °C in an oven to react chitosan and pyromellitic acid and evaporate the NMP solvent.

Table 3. Double layer capacitance of EDLCs with various current collectors at different discharging rate.

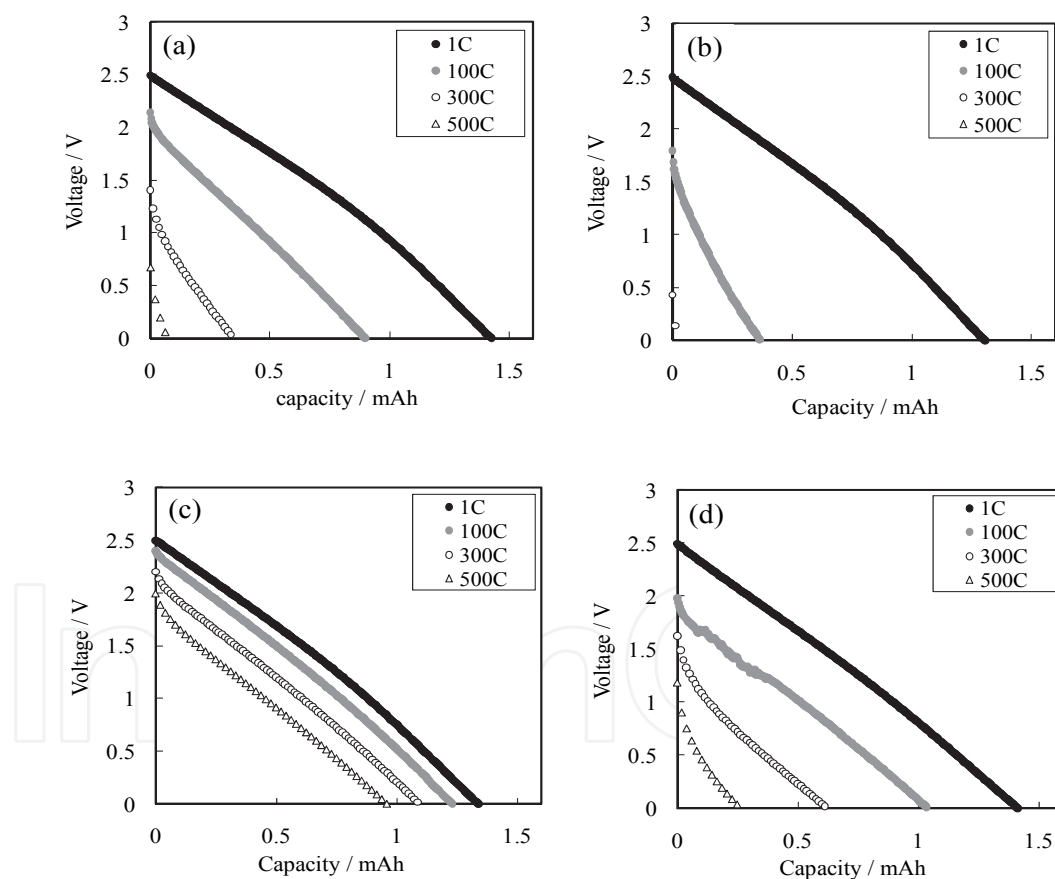


Fig. 16. Discharge curves of demonstration EDLCs using various current collectors at various current densities at 25 °C. (a) EDLC cell using aluminum oxide; (b) cell using aluminum foil; (c) cell using aluminum with CLC on both electrodes; (d) cell using aluminum with CLC on both electrodes and neat ionic liquid electrolyte. The discharging rate of 1C corresponds to 0.15mA of discharge current.

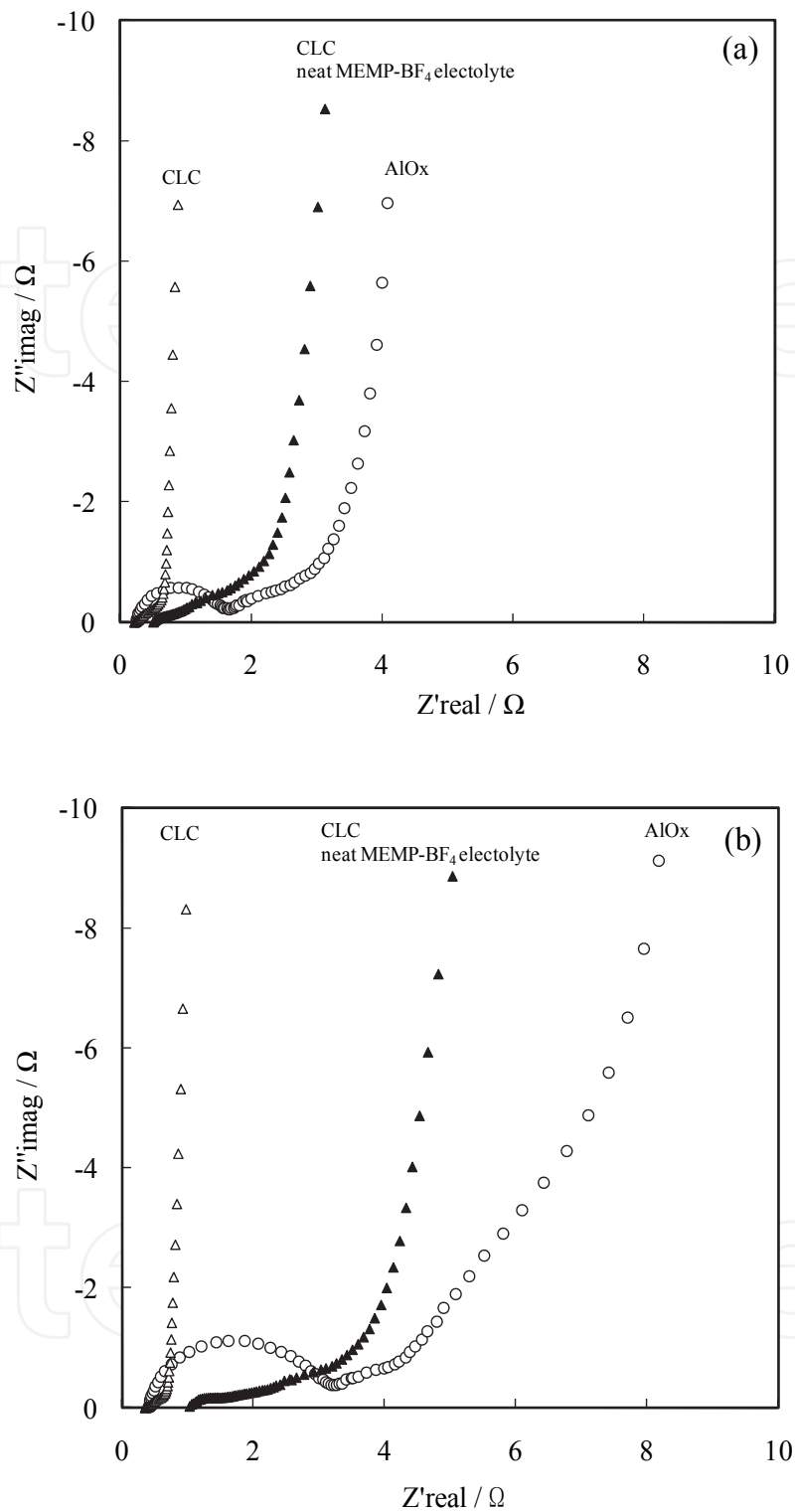


Fig. 17. Experimental Nyquist plots of demonstration EDLCs using various current collectors and electrolyte at 25 °C. (a) Fresh cell; (b) cell after life test, continuous charging at 2.5 V, 60 °C for 500 h. (CLC) = cell with aluminum foil with CLC on both electrodes; (AlOx) = cell with aluminum oxide foil on both electrodes. Unless otherwise indicated, 1M DEME-BF₄ in PC was used as an electrolyte.

resistance between the electrode layer including the active material and the collector. Of course, the viscosity of the ionic liquid does not decrease by employing a CLC, however, it is possible to improve the performance of a cell using neat ionic liquid to be similar to that of a conventional EDLC available on the market. It should be possible to develop nonflammable and high durability EDLCs by the combination of CLC technology and low viscosity ionic liquids including FSI or FH anions.

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 2.5 V, 60 °C. Presumably, a good response to this test will indicate good durability at room temperature. The maintenance of capacity of demonstration cells after 500 h operation is summarized in Fig. 18. All cells showed a good practical level of durability, the capacity loss being just 8%, regardless of the presence of a CLC in diluted electrolyte. In the case of the neat IL cell, the capacity loss from 100 to 500 hours was only 3%, though some deterioration was seen in the first 100 hours of operation. However, the interfacial impedance R_i of cells with neat ionic liquid cell and aluminum oxide collectors small increased after continuous charging at 60 °C, as shown in Fig.17(b).

We opened the demonstration CLC cell after the continuous charging examination and investigated the bonding between the electrode and current collector by rubbing the electrode surface with paper. The activated carbon layer of both electrodes with both the aluminum collector and aluminum oxide collector were peeled off easily by rubbing one or

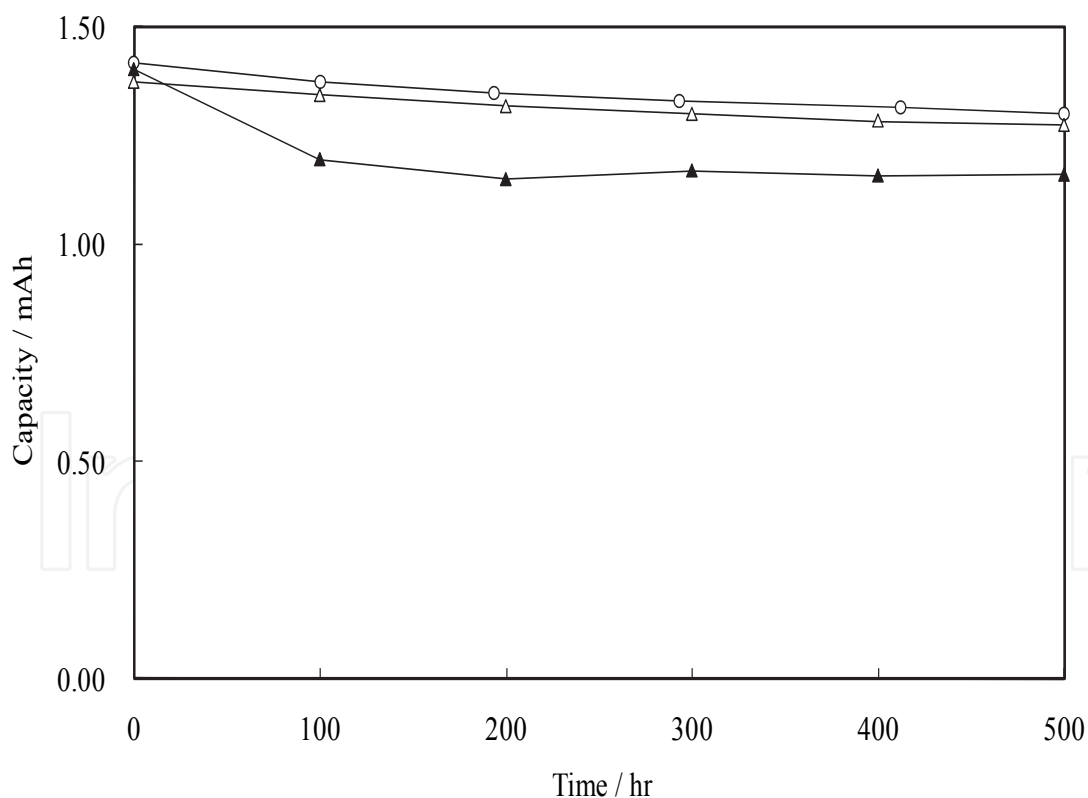


Fig. 18. Life test of demonstration EDLCs using various current collectors. The cell was continuously charged at 2.5 V, 60 °C for 500 h. The current collector used are: (open circle) aluminum oxide foil; (open triangle) aluminum foil with CLC; (filled triangle) aluminum foil with CLC and neat ionic liquid electrolyte.

two times. However, that on the CLC did not separate even after rubbing more than 20 times in both diluted and neat ionic liquid cells. Both the interfacial bonding between the CLC and aluminum foil, and between the CLC and the carbon electrode remained completely intact. The scanning electron micrograph observation data are summarized elsewhere (Sato. et.al 2011). We can conclude that the CLC acted as a long-lasting internal adhesive layer that improves durability.

5. Conclusion

1. The DEME-based ionic liquids have relatively high conductivities and remarkably wider potential windows compared to the other aromatic type ionic liquids that have been reported.
2. An EDLC using DEME-BF₄ as the electrolyte exhibits excellent stability and cycle durability even at temperatures over 100°C. Although below room temperature the capacity of an EDLC using this ionic liquid was inferior to that of a conventional EDLC using TEA-BF₄/PC due to the high viscosity of the ionic liquid, the ionic liquid EDLC showed a higher capacity for the discharge of a large current at temperatures of 40°C or above.
3. The major problem for the practical use of ionic liquids has been their high viscosity. Ionic liquids with relatively low viscosity with new type of anions, such as bis(trifluorosulfonyl)imide and fluorohydrogenate have been developed recently, leading to the hope that the problem of the viscosity will be soon overcome.
4. The viscosity of many kinds of ionic liquids decreases markedly on adding an organic solvent. In this way, it is possible to make an electrolyte with a high ion concentration, giving the EDLC a high capacitance. Ionic liquids never precipitate and crystallize even at low temperatures. EDLCs made with PC diluted ionic liquid (DEME-BF₄) have an extremely attractive high charge rate and discharge performance even at -40 °C
5. We have evaluated various kinds of ammonium salt with a methoxyalkyl group on the nitrogen atom, including several kinds of ionic liquids, as solutes in PC for an EDLC. A cell using an electrolyte containing the BF₄ anion had a higher capacitance at 25 °C, 3V than those including PF₆ 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.
6. The value of the resistance that is most relevant to the power density performance of an EDLC, the cell resistance, increased in the order of BF₄, PF₆ and TFSI. Of the ionic liquids tested, MEMP-BF₄ and DEME-BF₄, both of which have a methoxyethyl group on nitrogen atom, showed the highest durability in a continuous charging life test. We conclude that ionic liquids containing the tetrafluoroborate anion have the best performance and stability for electric double layer capacitor applications.
7. We have developed a new method that improves the rate capability of EDLCs. It comprises a very simple method of creating a thin polymer film containing a high concentration of carbon material (CLC) on the current collector that makes high power discharging at 500C possible. It was revealed from impedance analysis that a CLC that was only 2.5 μm thick was effective in decreasing the interfacial impedance between the current collector and the electrode layer. The CLC technique was extremely effective

also for EDLCs with a neat ionic liquid. We anticipate that the use of a CLC will be one of the effective technologies to master the difficulties of using high viscosity ionic liquids.

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7. References

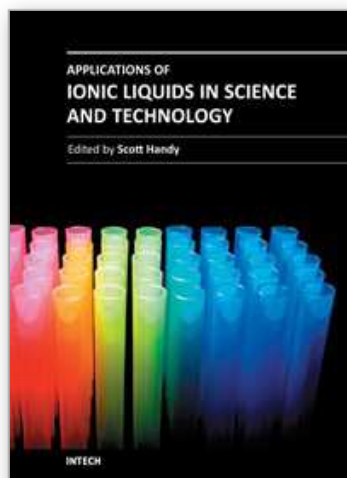
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This volume, of a two volume set on ionic liquids, focuses on the applications of ionic liquids in a growing range of areas. Throughout the 1990s, it seemed that most of the attention in the area of ionic liquids applications was directed toward their use as solvents for organic and transition-metal-catalyzed reactions. Certainly, this interest continues on to the present date, but the most innovative uses of ionic liquids span a much more diverse field than just synthesis. Some of the main topics of coverage include the application of RTILs in various electronic applications (batteries, capacitors, and light-emitting materials), polymers (synthesis and functionalization), nanomaterials (synthesis and stabilization), and separations. More unusual applications can be noted in the fields of biomass utilization, spectroscopy, optics, lubricants, fuels, and refrigerants. It is hoped that the diversity of this volume will serve as an inspiration for even further advances in the use of RTILs.

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