Application of Ionic Liquids Based on 1-Ethyl-3-Methylimidazolium Cation and Fluoroanions to Double-Layer Capacitors

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Abstract. Ionic liquids based on 1-ethyl-3-methylimidazolium cation (EMI^+) and inorganic or organic anions containing fluorine atoms were applied to electrolyte materials for double-layer capacitors. The double-layer capacitors composed of a pair of activated carbon electrodes and an ionic liquid selected from $EMIBF_4$, $EMINbF_6$, $EMITaF_6$, $EMICF_3SO_3$, $EMI(CF_3SO_2)_2N$, and $EMI(C_2F_5SO_2)_2N$ showed inferior low-temperature characteristics to those of a conventional nonaqueous electrolyte based on propylene carbonate (PC) solvent. On the other hand, the capacitor using $EMIF \cdot 2.3HF$ showed excellent low-temperature characteristics due to its high conductivity at low temperatures, however, it had a lower working voltage (~2 V) than the conventional nonaqueous counterpart (~3 V).

Key words : Ionic liquid, 1-Ethyl-3-Methylimidazolium, Fluoroanion, Double-layer capacitor, Electrolyte material

1. Introduction

Ionic liquids (or room temperature molten salts) have a long history as electrolytes. The first ionic liquid, a mixture of alkylpyridinium halide and aluminum chloride was found in 1948 by Hurley and Wier[1,2]. After that 1-ethyl-3-methylimidazolium cation (EMI^+) was found to be the best one from the viewpoint of conductivity and these chloroaluminate systems have been applied to metal electrodeposition and rechargeable battery[3-5]. However, the advent of air- and moisture-stable ionic liquids with high conductivities such as $EMICF_3SO_3$ and $EMIBF_4$[6-8] have attracted more attention to their applications for lithium rechargeable cell[9,10], titanium oxide wet solar cell[11,12], and carbon double-layer capacitor[13-16].

The double layer capacitor (DLC) is an energy storage device, which accumulates electric charges at the interface between an electrode (electronic conductor) and an electrolyte (ionic conductor)[17,18]. The DLC based on a pair of activated carbon electrodes and a nonaqueous electrolyte solution[19-21] is regarded as one of the most promising energy storage devices for hybrid electric vehicles. Even though the power density of DLC is higher than those of Ni-MH and Li ion batteries, its energy density is still lower than others, and further improvements to increase the energy density are required.

The DLC consisting of activated carbon cloth electrodes (SpectraCarb 2220 yarn) and an ionic liquid ($EMI(CF_3SO_2)_2N$) was proposed by Covalent Associates, Inc., however, its detailed performances were not disclosed except a moderate capacitance and poor cycleability at 3 V[15]. Therefore, we have examined the performances of DLC composed of a pair of activated carbon electrodes and an ionic liquid selected from

$EMIBF_4$, $EMINbF_6$, $EMITaF_6$, $EMIF \cdot 2.3HF$, $EMICF_3SO_3$, $EMI(CF_3SO_2)_2N$, and $EMI(C_2F_5SO_2)_2N$ in comparison with the conventional nonaqueous electrolyte (1 M Et_3MeNBF_4/PC[22-24])[25-28].

2. Experimental

2.1. Preparation of ionic liquids

$EMIBF_4$, $EMICF_3SO_3$, $EMI(CF_3SO_2)_2N$, and $EMI(C_2F_5SO_2)_2N$ were prepared by the neutralization of $EMICO_3Me$ (1-ethyl-3-methylimidazolium methylcarbonate) with the corresponding acid; HBF_4, CF_3SO_3H, $(CF_3SO_2)_2NH$, and $(C_2F_5SO_2)_2NH$, respectively. A methanol solution of $EMICO_3Me$ was prepared by the reaction between 1-ethylimidazole and dimethyl carbonate in methanol at 145°C for 13 h[29]. $EMINbF_6$[26], $EMITaF_6$[26], and $EMIF \cdot 2.3HF$[30,31] were prepared according to the methods described elsewhere.

2.2. Measurement of electrochemical properties of ionic liquids

The electrolytic conductivity κ was measured by a conductivity meter (Toa Electronics, CM-50S/CGT-511B). The electrochemical window was measured by an automatic polarization system (Hokuto Denko Corp., HZ-3000) and a cell equipped with a 3 mmϕ Pt working electrode, a Pt wire counter electrode, and a reference electrode consisting of Pt/0.1 M Et_4NI + 0.05 M I_2 in $EMIBF_4$.

2.3. Fabrication of double-layer capacitors

Coconut shell charcoal (average pore diameter 2.0 nm, surface area 1700 m^2g^{-1}, average particle size 10 μm) 80 wt%, acetylene black conductor 10 wt%, and polytetrafluoroethylene binder 10 wt% were mixed and ground, and pressed at 6

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MPa to form a disk composite 10 mm in diameter and 0.55 mm thick. A pair of these disk composite electrodes were dried at 300°C below 7.5×10^{-3} Pa for 3 h, afterward they were cooled in an argon atmosphere and an electrolyte was immersed in them under reduced pressure. By sandwiching a non-woven polypropylene separator with the two identical immersed electrodes, a 2032 coin cell was assembled with a stainless steel spacer.

2.4. Measurement of double-layer capacitance

The assembled cell was charged for $t = 50$ min by constant current (CC)-constant voltage (CV) mode from $V = 0$ to 2.8 V (or 2.0 V for EMIF·2.3HF) at a constant current $I = 5$ mA, and discharged by CC mode to 0 V at a given temperature T. The capacitance C was calculated by $C = 2WV^{-2}$, where energy output W was calculated from the discharge curve by $W = \int IV \mathrm{d}t$ [21]. The volumetric capacitance was obtained by dividing the above capacitance by the total volume of a pair of the disk electrodes. The internal resistance R was calculated from IR drop on the discharge curve. All data were the average values of the three identical cells.

2.5. Life test of double-layer capacitors

The cell was continuously charged at 3.0 V (or 2.0 V for EMIF·2.3HF) and 70°C, and its deterioration was monitored by measuring its capacitance at 70°C at given intervals.

3. Results and Discussion

A typical DLC is composed of a pair of activated carbon electrodes, an electrolyte, and a separator as main components as shown in Figure 1. The energy W and power P of the DLC are represented in the following equations, when it is discharged at a constant current I from initial voltage V_i to final voltage V_f.
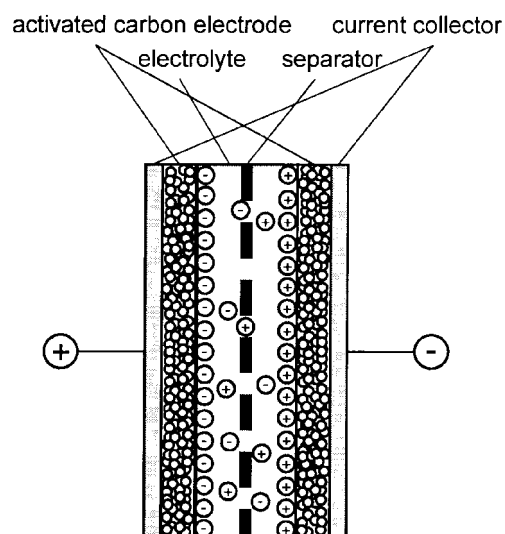
$$W = 1/2\ C(V_i^2 - V_f^2) = 1/2\ C[(V_0 - IR)^2 - V_f^2]$$

Fig. 1. Configuration of double-layer capacitor.

$$P = 1/2\ I(V_i + V_f) = 1/2\ I[(V_0 - IR) + V_f]$$

where C, V_0, and R are capacitance, open circuit voltage, and internal resistance, respectively.[21] Therefore, the electrolyte requires the following fundamental properties in order to achieve high energy density and power density[19-21].

1) High electrolytic conductivity κ
2) High decomposition voltage V_s
3) High double-layer capacitance C_d
4) Wide operational temperature range ΔT
5) High safety

3.1. Electrochemical properties of ionic liquids

Table 1 lists physicochemical properties of almost all EMI salts published in journals[25,32,33], where T_{mp}, d, η, E_{red}, and E_{ox} are melting point, density, viscosity, limiting reduction potential, and limiting oxidation potential, respectively. If the ionic liquid is defined as a molten salt whose melting point is below 25°C, the kind of anion which forms an ionic liquid is not so many. They are $AlCl_4^-$, $F^-\cdot2.3HF$, BF_4^-, NbF_6^-, TaF_6^-, $CH_3CO_2^-$, $CF_3CO_2^-$, $CF_3SO_3^-$, $(CF_3SO_2)_2N^-$, $(C_2F_5SO_2)_2N^-$, and $(CN)_2N^-$. All ionic liquids with fluoroanions were selected as electrolyte candidates for DLC, except $EMICF_3CO_2$ which does not have enough oxidation stability.

Ionic liquids have intrinsic good safety properties because these are non-flammable and non-volatile. However, the following disadvantages are expected compared with the conventional nonaqueous electrolyte (1 M Et_3MeNBF_4/PC):

1) Inferior low-temperature characteristics due to low electrolytic conductivities at low temperatures: Figure 2 shows the change of electrolytic conductivities of the above seven ionic liquids when the temperature was decreased from 25 to -20°C. The electrolytic conductivities of the ionic liquids were too low at -20°C compared with the conventional nonaqueous electrolyte except EMIF·2.3HF which has extremely high conductivity at low temperatures (one order of magnitude).

2) Lower working voltage due to narrow electrochemical window: Figure 3 shows the electrochemical windows of $EMIBF_4$ measured by linear sweep voltammetry in (a) neat ionic liquids and (b) propylene carbonate. From the comparison of these results, it is evident that ionic liquids based on the EMI cation have narrower electrochemical window than the conventional nonaqueous electrolyte, because the EMI skeleton is weak for not only reduction but also oxidation due to the existence of π-electron conjugated system. Most ionic liquids showed the same cathodic limit. EMIF·2.3HF was a little bit weak to reduction probably due to the existence of acidic protons. Anodic limits were generally restricted by EMI cation, and they shifted slightly dependent on the kind of anion.
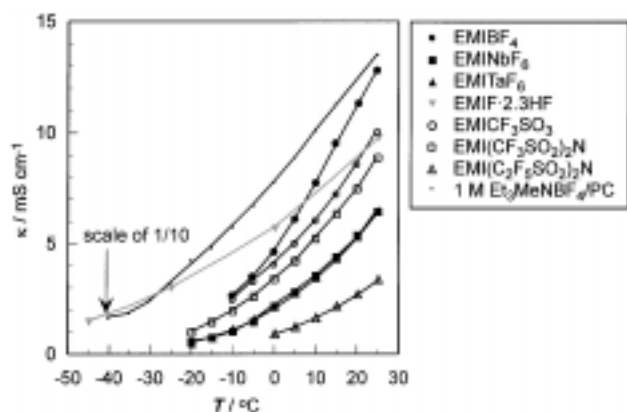
3.2. Performances of double-layer capacitors with ionic liquids

The capacitances of the cells were around 13 F cm^{-3} at 25°C and no remarkable difference was observed between the ionic liquids and 1 M Et_3MeNBF_4/PC except EMIF·2.3HF, which showed almost two times capacitance of those of

Table 1. Physicochemical properties of EMI salts at 25℃.

Salt	T_{mp} /℃	d /gcm^{-3}	η /mPa·s	κ /mScm^{-1}	E_{red} /V vs. Li$^+$/Li^c	E_{ox}	Ref.
EMIAlCl$_4$	8	1.29	18	22.6	1.0	5.5	6,34,35
EMIAl$_2$Cl$_7$	nc	1.39	14	14.5	3.0	5.5	6,34,35
EMIF·HF	51	1.26					36
EMIF·2.3HF	-90	1.14	5	100	1.5	5.3	31
EMINO$_2$	55	1.27^a					7
EMINO$_3$	38	1.28^a					7
EMIBF$_4$	11	1.24	43	13.0	1.0	5.5	7,37,38
EMIPF$_6$	62	1.56					8,38
EMIAsF$_6$	53						38
EMISbF$_6$	?						39
EMINbF$_6$	-1	1.67	49	8.5			40
EMITaF$_6$	2	2.17	51	7.1	1.0	5.7	40
EMICH$_3$CO$_2$	-45		162^a	2.8^a			7,11
EMICF$_3$CO$_2$	-14	1.29^b	35^a	9.6^a	1.0^d	4.6^d	11
EMIC$_3$F$_7$CO$_2$	nc	1.45^b	105^a	2.7^a			11
EMICH$_3$SO$_3$	39	1.25	160	2.7	1.3^d	4.9^d	6
EMICF$_3$SO$_3$	-10	1.38	43	9.3	1.0	5.3	6,37
EMIC$_4$F$_9$SO$_3$	28						11
EMI(CF$_3$SO$_2$)$_2$N	-15	1.52^b	28	8.4	1.0	5.7	11,37,38
EMI(C$_2$F$_5$SO$_2$)$_2$N	-1		61	3.4	0.9	5.8	38,41
EMI(CF$_3$SO$_2$)$_3$C	39		181	1.7	1.0	6.0	11,37,42
EMI(CN)$_2$N	-21	1.06	21				43
EMIVOCl$_4$	?			2^a			44

nc:not crystallized, ^{a}20℃, ^{b}22℃, ^{c}GC, 1 mA cm^{-2}, 20 mVs^{-1}(^{d}Pt, 50 mVs^{-1}).

Fig. 2. Temperature dependence of electrolytic conductivities of various electrolytes.

other ionic liquids as shown in Table 2. Lower capacitance of EMI(C$_2$F$_5$SO$_2$)$_2$N might be attributed to low C_{dl} due to its large anion size.[45] All ionic liquids showed higher internal resistances than 1 M Et$_3$MeNBF$_4$/PC.

    Figure 4 shows the change of the capacitances of the DLCs using various electrolytes, when operating temperature was varied from 25 to -25°C. The capacitance of all ionic liquids decreased rapidly compared with the conventional nonaqueous electrolyte due to the increase of internal resistance. We have recognized this behavior is a fatal disadvantage of the ionic liquids, and EMIF·2.3HF is only one exception which afforded enough capacitance even at low
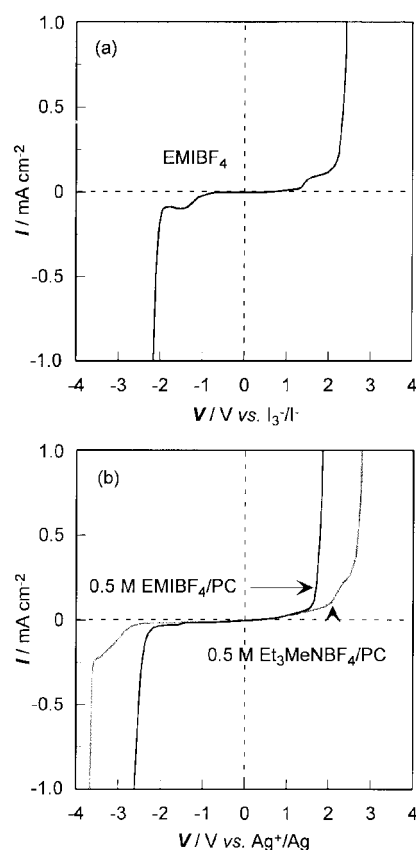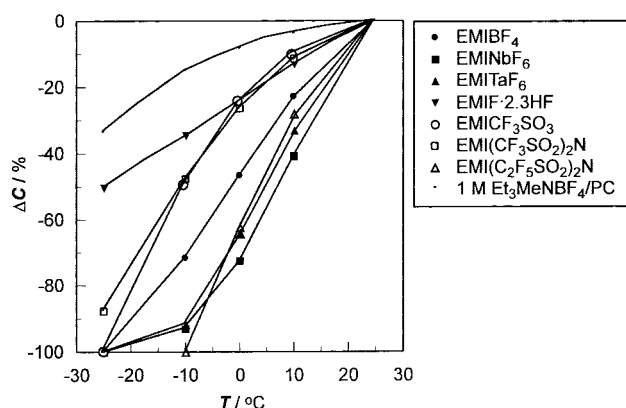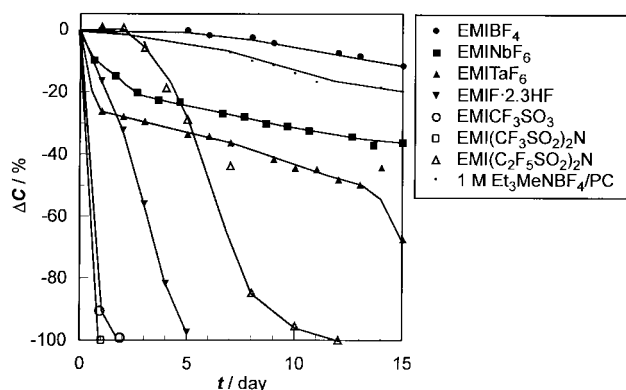

Fig. 3. Linear sweep voltammograms for EMIBF$_4$ on a Pt electrode at 5 mVs^{-1} and 25°C. (a) neat EMIBF$_4$, (b) EMIBF$_4$ in PC.

Table 2. Physicochemical properties of electrolytes and capacitances of DLCs.

Electrolyte	κ/mScm^{-1} (25°C)	η/mPa·s (25°C)	C/F cm^{-3} (25°C)	R/Ω (25°C)	C/F cm^{-3} (70°C)	R/Ω (70°C)
EMIBF$_4$	13	43	12.8	43	14.6	31
EMINbF$_6$	8.5	49	12.0	93	17.1	33
EMITaF$_6$	7.1	51	13.6	71	15.9	42
EMIF·2.3HF	100	4.9	24.7	43	36.2	53
EMICF$_3$SO$_3$	9.3	43	14.6	37	14.0	53
EMI(CF$_3$SO$_2$)$_2$N	8.4	28	13.6	39	16.1	19
EMI(C$_2$F$_5$SO$_2$)$_2$N	3.4	61	10.7	80	15.7	24
1M Et$_3$MeNBF$_4$/PC	13	3.5	13.1	24	13.3	18

Fig. 4. Temperature dependence of capacitances of DLCs using various electrolytes.

Fig. 5. Life test of DLCs using various electrolytes at 3 V (2 V for EMIF·2.3HF) and 70°C.

temperatures reflecting its high electrolytic conductivity.

Different from batteries, the cycling test is not so important for double-layer capacitors, because the deterioration mostly occurs at maximum operating voltage. Figure 5 shows the deterioration with time when 3 V (or 2 V for EMIF·2.3HF) was continuously applied to the cells at 70°C. The capacitance generally deteriorated with time. EMIBF$_4$ showed good life (time stability) similar to the conventional liquid electrolyte. EMINbF$_6$ and EMITaF$_6$ were not as stable as EMIBF$_4$, however, they were more stable than any of the organic fluoroanion compounds, EMICF$_3$SO$_3$, EMI

(CF$_3$SO$_2$)$_2$N, and EMI(C$_2$F$_5$SO$_2$)$_2$N. EMIF·2.3HF did not have enough stability at 70°C even at 2 V. The increase in internal resistance from 25 to 70°C shown in Table 2 is the sign of the decomposition of the ionic liquid. This behavior can be attributed to the inferior anodic stability of EMIF·2.3HF and organic fluoranions.[46]

4. Conclusion

1) DLCs using ionic liquids generally showed similar capacitances with the conventional nonaqueous electrolyte at 25°C.

2) DLCs using ionic liquids generally showed higher internal resistances than the conventional nonaqueous electrolyte.

3) DLCs using ionic liquids generally lost the capacitance at -25°C due to the high internal resistance.

4) DLC using EMIF·2.3HF was only one exception which afforded higher capacitance than the conventional nonaqueous electrolyte even at -25°C.

5) DLC using EMIF·2.3HF had a lower working voltage around 2 V than the conventional nonaqueous electrolyte or EMIBF$_4$ (~ 3 V).

6) DLCs using EMI salts with inorganic fluoroanions had better life than those with organic counterparts.

Acknowledgment

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