



Short communication

Effects of the cationic structures of fluorohydrogenate ionic liquid electrolytes on the electric double layer capacitance

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ABSTRACT

Electric double layer capacitance of an activated carbon electrode has been measured for fluorohydrogenate ionic liquids (FHILs) based on five different cations (1,3-dimethylimidazolium (DMIm⁺), 1-ethyl-3-methylimidazolium (EMIm⁺), 1-butyl-3-methylimidazolium (BMIm⁺), 1-ethyl-1-methylpyrrolidinium (EMPy⁺), and 1-methoxymethyl-1-methylpyrrolidinium (MOMMPyr⁺)) at 25 °C. For all the FHILs, the capacitance increases with increase in charging voltage, and exhibits the maximum value around 2.7 V. The capacitances for FHILs are higher than those for EMImBF₄ or 1 M tetraethylammonium tetrafluoroborate in propylene carbonate (TEABF₄/PC) in the measured range (1.0 < V < 3.2). For the three imidazolium-based FHILs, the maximum capacitance decreases with increase in the size of the cation in the order, DMIm(FH)_{2,3}F (178 F g⁻¹) > EMIm(FH)_{2,3}F (162 F g⁻¹) > BMIm(FH)_{2,3}F (135 F g⁻¹). On the other hand, the maximum capacitance observed for MOMMPyr(FH)_{2,3}F (152 F g⁻¹) is larger than that for EMPyr(FH)_{2,3}F (134 F g⁻¹) in spite of the larger size of MOMMPyr⁺ than EMPyr⁺, which is derived from introduction of the methoxy group. Some FHILs with low melting points exhibit a sufficient capacitance even at -40 °C (64 F g⁻¹ for EMIm(FH)_{2,3}F).

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1. Introduction

Electric double layer capacitors (EDLCs) have recently received much attention as energy-storage devices for energy regeneration or data back-up owing to their high power density and long cycle life [1–4]. Activated carbon is used as the electrode material in EDLCs combined with aqueous or organic electrolytes due to their high surface area, and the relationship between the pore size and the ion diameter was discussed in previous literature [5,6]. While aqueous electrolytes have a high conductivity, the low breaking-up voltage (<~1.0V) is a major drawback. Non-aqueous electrolytes, typically, organic electrolytes, have a higher electrochemical stability compared to the aqueous electrolytes, but their low conductivity leads to the high internal resistance [7,8].

Room temperature ionic liquids (RTILs) are potential electrolytes to replace the electrolytes in the present electrochemical devices. Non-flammability, low vapor pressure, and high electrochemical stability are the properties often observed for RTILs and are attractive to construct safe electrochemical devices including EDLCs [9–18]. However, low conductivity is a major drawback for conventional RTILs. On the other hand, we found that fluorohydrogenate ionic liquids (FHILs) exhibit a high ionic con-

ductivity and low melting point compared to other ionic liquids (100 mS cm⁻¹ and -65 °C for EMIm(FH)_{2,3}F (EMIm = 1-ethyl-3-methylimidazolium)) [19–23]. Here, the high conductivity leads to the low internal resistance and the low melting point enables the low temperature operation. According to our previous study, EMIm(FH)_{2,3}F exhibits a high capacitance at room temperature, although the breaking-up voltage is smaller than usual ionic liquid electrolytes [23]. The present study reports the effect of the cationic structure of FHILs on the electric double layer capacitance. The capacitance was evaluated by using a two-electrode cell with a pair of activated carbon electrodes, and compared with that of a typical RTIL, EMImBF₄, or a typical organic electrolyte, TEABF₄/PC. Low temperature performance of EDLCs using FHILs was also investigated since some FHILs exhibit a sufficient ionic conductivity even at -40 °C.

2. Experimental

2.1. Reagents and preparation of ionic liquids

The starting chlorides, 1,3-dimethylimidazolium chloride (DMImCl), EMImCl, 1-butyl-3-methylimidazolium chloride (BMImCl), and 1-ethyl-1-methylpyrrolidinium chloride (EMPyCl) were prepared as previously described [19,20], while 1-methoxymethyl-1-methylpyrrolidinium chloride (MOMMPyrCl, Otsuka Chemical Co., Ltd.) was used as supplied. Fluorohydro-

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genate ionic liquids were prepared by the reaction of a large excess of anhydrous HF and the corresponding chloride [19,20]. For comparison, 1-ethyl-3-methylimidazolium tetrafluoroborate (EMImBF₄, Kanto Kagaku) and 1 M tetraethylammonium tetrafluoroborate (Aldrich) in propylene carbonate (Aldrich) (TEABF₄/PC) were used as typical IL and organic electrolyte, respectively.

2.2. Fabrication of electric double layer capacitors

Sheet electrodes (10 mm in diameter and 21 mg in weight, 85 wt% activated carbon of which the surface area is 2000 m² g⁻¹, 10 wt% PTFE, and 5 wt% carbon black) were dried at 180 °C under vacuum and were immersed in the electrolyte under vacuum prior to use. The EDLC cell was assembled with a pair of the sheet electrodes, glassy carbon current collectors (BAS Inc., 2 mm in thickness and 30 mm in diameter), and a PTFE separator (ADVANTEC H100A013A, 35 μm in thickness and 13 mm in diameter) in a glove box filled with dry argon. The entire cell was evacuated for half an hour to degas residual gaseous species.

2.3. Electrochemical measurements

The assembled cell was charged for 1 h by a constant voltage (CV) mode, and discharged by a constant current (CC) mode of $I = 5 \text{ mA}$ to 0 V. The capacitance, C , was calculated by $C = \Delta Q/V$, where the charge, ΔQ , was calculated from I and time, Δt , using the equation, $\Delta Q = I\Delta t$. The energy density, W , was calculated by $W = 1/2CV^2$. Measurements were carried out by using a Solartron 1480A Multi-Channel Potentiostat. Electrochemical window of MOMMPyr(FH)_{2,3}F was measured as described in a previous study [22].

2.4. Quantum mechanical calculations

Geometries were optimized at the MP2 level of theory combined with the cc-pVTZ basis set for all atoms using the program Gaussian 03 [24]. Molecular volumes were calculated using the Monte Carlo method as implemented in Gaussian 03.

3. Results and discussion

3.1. Physical properties of FHILs

Table 1 shows physical properties of FHILs used in the current study. Among them, DMIm(FH)_{2,3}F exhibits the highest ionic conductivity of 110 mS cm⁻¹ at 25 °C. The new FHIL, MOMMPyr(FH)_{2,3}F, has a high conductivity of 75 mS cm⁻¹ at 25 °C and does not exhibit a melting point above -128 °C. The electrochemical window of MOMMPyr(FH)_{2,3}F on a glassy carbon electrode has been determined to be 4.4 V, the cathodic and anodic limits being observed at -1.6 and 2.8 V vs. Fc⁺/Fc, respectively (Fig. S1 in Supplementary Content). The volume of the cations calculated at MP2/cc-pVTZ level is listed in Table 1 to see the effect

Table 1
Physical and structural properties^a of selected fluorohydrogenate ionic liquids.

System	T_m (K)	T_g (K)	ρ (g cm ⁻³)	η (mPa s)	σ (mS cm ⁻¹)	MV (cm ³ mol ⁻¹)	V_{cat} (Å ³)	Ref.
DMIm(FH) _{2,3} F	272	–	1.17	5.1	110	138	132	[19]
EMIm(FH) _{2,3} F	208	148	1.13	4.9	100	156	156	[19]
BMIm(FH) _{2,3} F	– ^b	154	1.08	19.6	33	189	202	[19]
EMPyrr(FH) _{2,3} F	– ^b	– ^b	1.07	11.5	75	167	173	[20]
MOMMPyr(FH) _{2,3} F	– ^b	– ^b	1.13	7.91	75	173	186	This work

^a T_m : Melting point, T_g : glass transition temperature, ρ : density, η : viscosity, σ : ionic conductivity, MV: molecular volume, V_{cat} : volume of the cation calculated at MP2/cc-pVTZ.

^b These transition temperatures were not detected under the present experimental condition (>145 K).

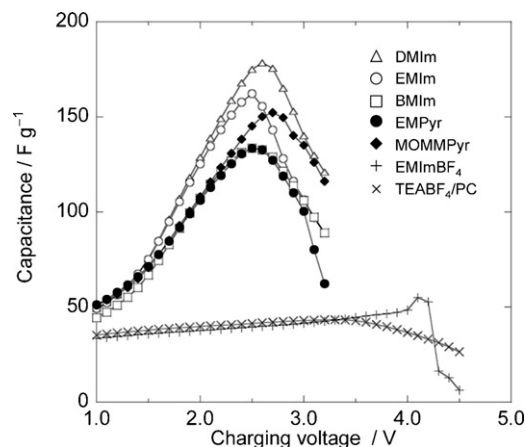


Fig. 1. Voltage dependence of capacitance for the EDLCs using DMIm(FH)_{2,3}F, EMIm(FH)_{2,3}F, BMIm(FH)_{2,3}F, EMPyr(FH)_{2,3}F, MOMMPyr(FH)_{2,3}F, EMImBF₄, and TEABF₄/PC at 25 °C.

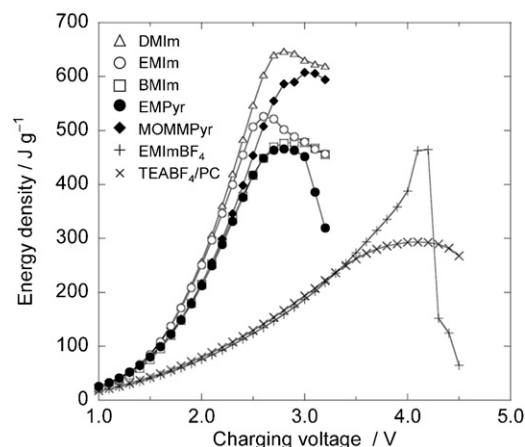


Fig. 2. Voltage dependence of energy density for the EDLCs using DMIm(FH)_{2,3}F, EMIm(FH)_{2,3}F, BMIm(FH)_{2,3}F, EMPyr(FH)_{2,3}F, MOMMPyr(FH)_{2,3}F, EMImBF₄, and TEABF₄/PC at 25 °C.

of the size of the cation on the physical and electrochemical properties of the FHILs. For the imidazolium-based cations, the volume increases in the order, DMIm⁺ (132 Å³) < EMIm⁺ (156 Å³) < BMIm⁺ (202 Å³) as the alkyl chain is extended. For the pyrrolidinium-based cations, the volume of EMPyr⁺ (173 Å³) is smaller than that of MOMMPyr⁺ (186 Å³). The size of the cation reflect the molar volumes observed for the FHILs well.

3.2. Effect of the cation on capacitance

Figs. 1 and 2 show voltage dependence of capacitance and energy density for the present EDLCs at 25 °C, respectively. The

Table 2
Performance of electrolytes in EDLCs at 25 and -40°C .

System	C_{25} (F g^{-1})	C_{-40} (F g^{-1})	E_{25} (J g^{-1})	E_{-40} (J g^{-1})
DMIm(FH) _{2,3} F	178	–	647	–
EMIm(FH) _{2,3} F	162	64	526	270
BMIm(FH) _{2,3} F	133	45	478	155
EMPyrr(FH) _{2,3} F	134	–	466	–
MOMMPyrr(FH) _{2,3} F	152	62	608	285
EMImBF ₄	42	–	187	–
TEABF ₄ /PC	43	20	193	88

C_{25} : Capacitance at 25°C , C_{-40} : capacitance at -40°C , E_{25} : energy density at 25°C , E_{-40} : energy density at -40°C . The capacitance and energy density values are at V_{max} for FHILs and at 3.0 V for EMImBF₄ and TEABF₄/PC.

results for EMImBF₄ and TEABF₄/PC are also plotted for comparison. Capacitance and energy density obtained in the current work are summarized in Table 2.

Capacitance for FHILs shows a significant voltage dependence, that is, the capacitance increases with increase in charging voltage. Such a voltage dependence of capacitance was not observed for EMImBF₄ or TEABF₄/PC. The voltage where FHILs show the maximum capacitance, V_{max} , ranges between 2.5 and 2.7 V. Electric double layer capacitors using FHILs show higher capacitances ($133\text{--}178 \text{ F g}^{-1}$ at V_{max}) than those using EMImBF₄ (42 F g^{-1} at 3.0 V) and TEABF₄/PC (43 F g^{-1} at 3.0 V), where the highest capacitance of 178 F g^{-1} was observed for DMIm(FH)_{2,3}F. Capacitance for the three imidazolium-based FHILs decreases with increase in the size of the cations in the order, DMIm(FH)_{2,3}F (178 F g^{-1}) > EMIm(FH)_{2,3}F (162 F g^{-1}) > BMIm(FH)_{2,3}F (133 F g^{-1}). This observation is simply explained by considering the sizes of the cations and the resulting number of ions per unit area of the electrode. On the other hand, the larger capacitance observed for MOMMPyrr(FH)_{2,3}F (152 F g^{-1}) than that for EMPyrr(FH)_{2,3}F (134 F g^{-1}) does not follow the same trend, since the size of MOMMPyrr⁺ is larger than that of EMPyrr⁺ as described above. Introduction of an ether oxygen atom to the side chain changes the charge distribution in the cation, which may result in the different arrangement of the adsorbed cations on the electrode.

The evolution of hydrogen gas from the fluorohydrogenate anion at the cathode limit is considered to narrow the breaking-up voltage of FHILs compared to EMImBF₄ and TEABF₄/PC [21]. The slightly larger V_{max} for MOMMPyrr(FH)_{2,3}F than the other FHILs probably arises from the difference in anodic limit potential. The higher energy densities for FHILs ($466\text{--}647 \text{ J g}^{-1}$ at V_{max}) compared to those for EMImBF₄ (187 J g^{-1} at 3.0 V) and TEABF₄/PC (193 J g^{-1} at 3.0 V) in spite of the smaller breaking up voltages arise from the high capacitance of FHILs.

3.3. Low temperature performance

One of the attractive points in use of FHILs as electrolytes for EDLC is their low temperature performance, since some FHILs exhibit a sufficient ionic conductivity at low temperatures. Fig. 3 shows the voltage dependence of capacitance for EDLC using EMIm(FH)_{2,3}F between -40 and 25°C . The capacitance decreases and voltage dependence of capacitance becomes less remarkable with decrease in the temperature. Nevertheless, the maximum capacitances are still high, 119 F g^{-1} at 0°C and 64 F g^{-1} at -40°C .

Figs. 4 and 5 show the voltage dependence of capacitance and energy density at -40°C for EDLCs using EMIm(FH)_{2,3}F, BMIm(FH)_{2,3}F, MOMMPyrr(FH)_{2,3}F, and TEABF₄/PC that are liquid at -40°C . Although the capacitance of the EDLCs at -40°C is smaller than that at 25°C for all the electrolytes, the EDLCs using FHILs at -40°C ($45\text{--}64 \text{ F g}^{-1}$) have much larger capacitances than that for TEABF₄/PC at -40°C (20 F g^{-1}) and even larger than the value at 25°C (43 F g^{-1}). As shown in Fig. 4, the voltage dependence of

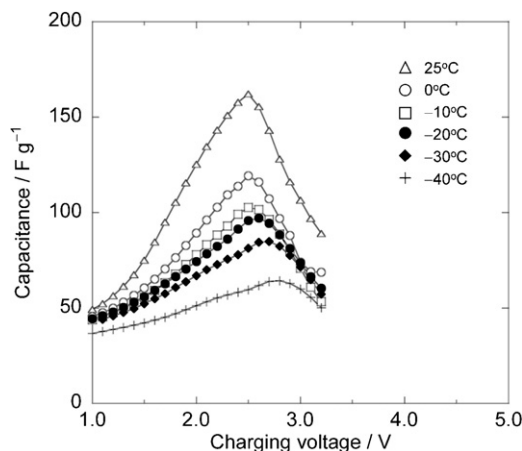


Fig. 3. Voltage dependence of capacitance for the EDLC using EMIm(FH)_{2,3}F at 25, 0, -10 , -20 , -30 , and -40°C .

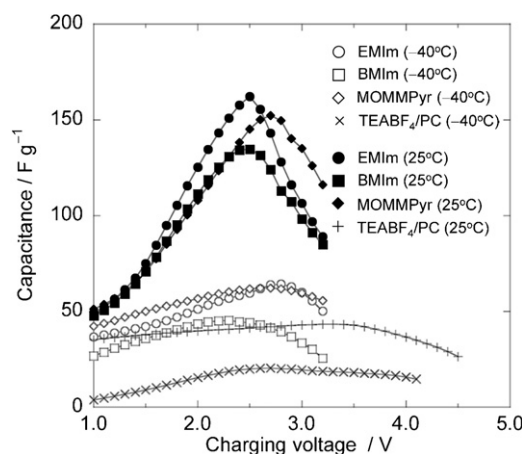


Fig. 4. Voltage dependence of capacitance for the EDLCs using EMIm(FH)_{2,3}F, BMIm(FH)_{2,3}F, MOMMPyrr(FH)_{2,3}F, and TEABF₄/PC at 25 and -40°C .

capacitance becomes smaller at -40°C compared to that at 25°C for all the FHILs, whereas V_{max} for some ILs shifts by decreasing temperature because the Faradaic reaction that determines V_{max} is also influenced by temperature. The large drop in capacitance for BMIm(FH)_{2,3}F by decreasing temperature arises from its high viscosity. Although the energy density also decreases with decrease in

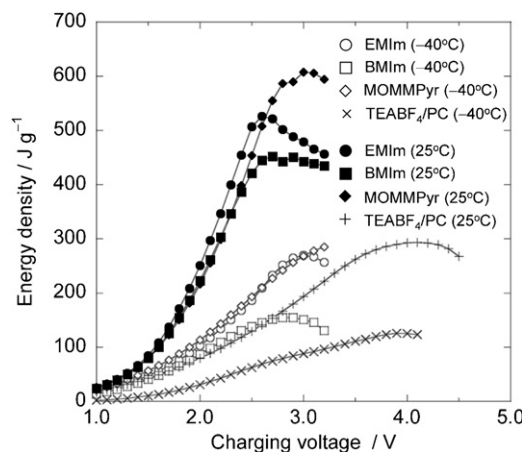


Fig. 5. Voltage dependence of energy density for the EDLCs using EMIm(FH)_{2,3}F, BMIm(FH)_{2,3}F, MOMMPyrr(FH)_{2,3}F, and TEABF₄/PC at 25 and -40°C .

temperature, the maximum energy density at -40°C , 270 J g^{-1} for EMIm(FH)_{2.3}F for example, is much higher than that for TEABF₄/PC (88 J g^{-1}). Although these FHILs lose HF at high temperatures, the HF-deficient FHILs such as EMIm(FH)_nF ($n < 2.3$) are stable over a wide temperature range below and above room temperature [25] and are interesting candidates as electrolytes for EDLCs.

4. Conclusions

This study reported the electric double layer capacitance for FHILs with five different cationic structures in a two-electrode test cell using activated carbon electrodes. The capacitances obtained for FHILs are higher than those for EMImBF₄ or TEABF₄/PC and exhibit significant voltage and cationic structure dependences. Introduction of the methoxymethyl group changes the charge distribution on the cation and causes a change in the capacitance. Electric double layer capacitors using some FHILs are operable even at -40°C , exhibiting the capacitance higher than that for TEABF₄/PC. Direct evidence for the reason of the high capacitance and voltage dependence requires further study using a three-electrode cell to see the behavior of the cathode and anode independently, which is under way.

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Appendix A. Supplementary data

Supplementary data associated with this article can be found, in the online version, at doi:10.1016/j.jpowsour.2010.01.055.

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