

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

Atsushi Senda, Kazuhiko Matsumoto, Toshiyuki Nohira, Rika Hagiwara\*

Graduate School of Energy Science, Kyoto University, Sakyo-ku, Kyoto 606-8501, Japan

\* E-mail: [hagiwara@energy.kyoto-u.ac.jp](mailto:hagiwara@energy.kyoto-u.ac.jp), Tel: +81-75-753-5822, Fax: +81-75-753-5906

## 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<sup>+</sup>), 1-ethyl-3-methylimidazolium (EMIm<sup>+</sup>), 1-butyl-3-methylimidazolium (BMIm<sup>+</sup>), 1-ethyl-1-methylpyrrolidinium (EMPyr<sup>+</sup>), and 1-methoxymethyl-1-methylpyrrolidinium (MOMMPyr<sup>+</sup>)) 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 EMImBF<sub>4</sub> or 1M tetraethylammonium tetrafluoroborate in propylene carbonate (TEABF<sub>4</sub>/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)<sub>2,3</sub>F (178 F g<sup>-1</sup>) > EMIm(FH)<sub>2,3</sub>F (162 F g<sup>-1</sup>) > BMIm(FH)<sub>2,3</sub>F (135 F g<sup>-1</sup>). On the other hand, the maximum capacitance observed for MOMMPyr(FH)<sub>2,3</sub>F (152 F g<sup>-1</sup>) is larger than that for EMPyr(FH)<sub>2,3</sub>F (134 F g<sup>-1</sup>) in spite of the larger size of MOMMPyr<sup>+</sup> than EMPyr<sup>+</sup>, 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<sup>-1</sup> for EMIm(FH)<sub>2,3</sub>F).

Keywords: Ionic liquid; Electric double layer capacitor; Fluorohydrogenate

## 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 ( $< \sim 1.0$  V) 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. Nonflammability, 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 conductivity and low melting point compared to other ionic liquids ( $100 \text{ mS cm}^{-1}$  and  $-65^\circ\text{C}$  for  $\text{EMIm}(\text{FH})_{2,3}\text{F}$  (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,  $\text{EMIm}(\text{FH})_{2,3}\text{F}$  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, EMImBF<sub>4</sub>, or a typical organic electrolyte, TEABF<sub>4</sub>/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 liquid

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. Fluorohydrogenate 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 (EMImBF<sub>4</sub>, Kanto Kagaku) and 1M tetraethylammonium tetrafluoroborate (Aldrich) in propylene carbonate (Aldrich) (TEABF<sub>4</sub>/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 m<sup>2</sup> g<sup>-1</sup>, 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  $\mu\text{m}$  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  $I = 5$  mA to 0 V. The capacitance,  $C$ , was calculated by  $C = \Delta Q/V$ , where the charge,  $\Delta Q$ , was calculated from  $I$  and time,  $\Delta t$ , 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)<sub>2,3</sub>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, DMIIm(FH)<sub>2,3</sub>F exhibits the highest ionic conductivity of 110 mS cm<sup>-1</sup> at 25°C. The new FHIL, MOMMPyr(FH)<sub>2,3</sub>F, has a high conductivity of 75 mS cm<sup>-1</sup> at 25°C and does not exhibit a melting point above -128°C. The electrochemical window of MOMMPyr(FH)<sub>2,3</sub>F on a glassy carbon electrode has been determined to be 4.4 V, the cathodic and anodic limits being observed at -1.6 V and 2.8 V vs. Fc<sup>+</sup>/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 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, DMIIm<sup>+</sup> (136 Å<sup>3</sup>) < EMIIm<sup>+</sup> (157 Å<sup>3</sup>) < BMIm<sup>+</sup> (208 Å<sup>3</sup>) as the alkyl chain is extended. For the pyrrolidinium-based cations, the volume of EMPyr<sup>+</sup> (178 Å<sup>3</sup>) is smaller than that of MOMMPyr<sup>+</sup> (190 Å<sup>3</sup>). The size of the cation reflect the molar volumes observed for the FHILs well.

(TABLE 1)

### 3.2 Effect of the cation on capacitance

Figures 1 and 2 show voltage dependence of capacitance and energy density for the present EDLCs at 25°C, respectively. The results for EMIImBF<sub>4</sub> and TEABF<sub>4</sub>/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 EMImBF<sub>4</sub> or TEABF<sub>4</sub>/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 - 178 F g<sup>-1</sup> at  $V_{\max}$ ) than those using EMImBF<sub>4</sub> (42 F g<sup>-1</sup> at 3.0 V) and TEABF<sub>4</sub>/PC (43 F g<sup>-1</sup> at 3.0 V), where the highest capacitance of 178 F g<sup>-1</sup> was observed for DMIm(FH)<sub>2,3</sub>F. Capacitance for the three imidazolium-based FHILs decreases with increase in the size of the cations in the order, DMIm(FH)<sub>2,3</sub>F (178 F g<sup>-1</sup>) > EMIm(FH)<sub>2,3</sub>F (162 F g<sup>-1</sup>) > BMIm(FH)<sub>2,3</sub>F (133 F g<sup>-1</sup>). 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 MOMMPyr(FH)<sub>2,3</sub>F (152 F g<sup>-1</sup>) than that for EMPyr(FH)<sub>2,3</sub>F (134 F g<sup>-1</sup>) does not follow the same trend, since the size of MOMMPyr<sup>+</sup> is larger than that of EMPyr<sup>+</sup> 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 EMImBF<sub>4</sub> and TEABF<sub>4</sub>/PC [21]. The slightly larger  $V_{\max}$  for MOMMPyr(FH)<sub>2,3</sub>F than the other FHILs probably arises from the difference in anodic limit potential. The higher energy densities for FHILs (466 - 647 J g<sup>-1</sup> at  $V_{\max}$ ) compared to those for EMImBF<sub>4</sub> (187 J g<sup>-1</sup> at 3.0 V) and TEABF<sub>4</sub>/PC (193 J g<sup>-1</sup> at 3.0 V) in spite of the smaller breaking up voltages arise from the high capacitance of FHILs.

(TABLE 2)

(FIGURES 1 AND 2)

### 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. Figure 3 shows the voltage dependence of capacitance for EDLC using EMIm(FH)<sub>2,3</sub>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<sup>-1</sup> at 0°C and 64 F g<sup>-1</sup> at -40°C.

(FIGURE 3)

Figures 4 and 5 show the voltage dependence of capacitance and energy density at -40°C for EDLCs using EMIm(FH)<sub>2,3</sub>F, BMIm(FH)<sub>2,3</sub>F, MOMMPyr(FH)<sub>2,3</sub>F, and TEABF<sub>4</sub>/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 – 64 F g<sup>-1</sup>) have much larger capacitances than that for TEABF<sub>4</sub>/PC at -40°C (20 F g<sup>-1</sup>) and even larger than the value at 25°C (43 F g<sup>-1</sup>). As shown in Figure 4, the voltage dependence of 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)<sub>2.3</sub>F by decreasing temperature arises from its high viscosity. Although the energy density also decreases with decrease in temperature, the maximum energy density at  $-40^{\circ}\text{C}$ ,  $270 \text{ J g}^{-1}$  for EMIm(FH)<sub>2.3</sub>F for example, is much higher than that for TEABF<sub>4</sub>/PC ( $88 \text{ J g}^{-1}$ ). Although these FHILs lose HF at high temperatures, the HF-deficient FHILs such as EMIm(FH)<sub>*n*</sub>F ( $n < 2.3$ ) are stable over a wide temperature range below and above room temperature [25] and are interesting candidates as electrolytes for EDLCs.

<FIGURES 4 AND 5>

#### 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 EMImBF<sub>4</sub> or TEABF<sub>4</sub>/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  $-40^{\circ}\text{C}$ , exhibiting the capacitance higher than that for TEABF<sub>4</sub>/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.

## **Acknowledgement**

The chloride, MOMMPyrCl, was kindly supplied by Otsuka Chemical Co., Ltd. This work was supported by a Grant-in-Aid for Scientific Research for Priority Area “Science of Ionic Liquids” of Ministry of Education, Culture, Sports, Science and Technology.

## References

- [1] B. E. Conway, *Electrochemical Supercapacitors*, p. 29, Kluwer Academic/Picnum Publishers, New York (1999).
- [2] B. E. Conway, *J. Electrochem. Soc.* 138 (1991) 1539.
- [3] R. F. Service, *Science* 313 (2006) 902.
- [4] P. Simon, Y. Gogotsi, *Nature Materials* 7 (2008) 845.
- [5] M. Endo, T. Maeda, T. Takeda, Y. J. Kim, K. Koshiba, H. Hara, M. S. Dresselhaus, *J. Electrochem. Soc.* 148 (2001) A910.
- [6] C. Largeot, C. Portet, J. Chmiola, P. L. Taberna, Y. Gogotsi, P. Simon, *J. Am. Chem. Soc.* 130 (2008) 2730.
- [7] M. Ue, K. Ida, S. Mori, *J. Electrochem. Soc.* 141 (1994) 2989
- [8] M. Ue, M. Takeda, M. Takehara, S. Mori, *J. Electrochem. Soc.* 144 (1997) 2684
- [9] R. T. Carlin, H. C. De Long, J. Fuller, P.C. Trulove, *J. Electrochem. Soc.* 141 (1994) L73.
- [10] V. R. Koch, C. Nanjundiah, G. B. Appetecchi, B. Scrosati, *J. Electrochem. Soc.* 142 (1995) L116.
- [11] P. Bonhôte, A.-P. Dias, N. Papageorgiou, K.Kalyanasundaram, M. Grätzel, *Inorg. Chem.* 35 (1996) 1168.
- [12] N. Papageorgiou, Y. Athanassov, M.Armand, P. Bonhote, H. Pettersson, A. Azam, M. Grazel, *J. Electrochem.Soc.* 143 (1996) 3099.
- [13] V. R. Koch, L. A. Dominey, C. Nanjundiah, M. J. Ondrechen, *J. Electrochem. Soc.* 143 (1996) 798.
- [14] C. Nanjundiah, S. F. McDevin, and V. R. Koch, *J. Electrochem. Soc.* 144, (1997) 3392.
- [15] H. Ohno, in: H. Ohno (Ed.), *Electrochemical Aspects of Ionic Liquids*, John Wiley & Sons,

Inc., Hoboken, NJ, 2005.

[16] S. Shiraishi, T. Miyauchi, R. Sasaki, N. Nishina, A. Oya, R. Hagiwara, *Electrochemistry* 75 (2007) 619.

[17] K. Yuyama, G. Masuda, H. Yoshida, T. Sato, *J. Power Sources* 162 (2006) 1401.

[18] N. Handa, T. Sugimoto, M. Yamagata, M. Kikuta, M. Kono, M. Ishikawa, *J. Power Sources* 185 (2008) 1585.

[19] R. Hagiwara, K. Matsumoto, Y. Nakamori, T. Tsuda, Y. Ito, H. Matsumoto, K. Momota, *J. Electrochem. Soc.* 150 (2003) D195.

[20] K. Matsumoto, R. Hagiwara, Y. Ito, *Electrochem. Solid-State Lett.* 7 (2004) E41.

[21] M. Yamagata, S. Konno, K. Matsumoto, R. Hagiwara, *Electrochem. Solid-State Lett.* 12 (2009) F9.

[22] S. Kanematsu, K. Matsumoto, R. Hagiwara, *Electrochem. Commun.* 11 (2009) 1312.

[23] M. Ue, M. Takeda, A. Toriumi, A. Kominato, R. Hagiwara, Y. Ito, *J. Electrochem. Soc.* 150 (2003) A499.

[24] M. J. Frisch, G. W. Trucks, H. B. Schlegel, G. E. Scuseria, M. A. Robb, J. R. Cheeseman, V. G. Zakrzewski, J. A. Jr. Montgomery, R. E. Stratmann, J. C. Burant, S. Dapprich, J. M. Millam, A. D. Daniels, K. N. Kudin, M. C. Strain, O. Farkas, J. Tomasi, V. Barone, M. Cossi, R. Cammi, B. Mennucci, C. Pomelli, C. Adamo, S. Clifford, J. Ochterski, G. A. Petersson, P. Y. Ayala, Q. Cui, K. Morokuma, P. Salvador, J. J. Dannenberg, D. K. Malick, A. D. Rabuck, K. Raghavachari, J. B. Foresman, J. Cioslowski, J. V. Ortiz, A. G. Baboul, B. B. Stefanov, G. Liu, A. Liashenko, P. Piskorz, I. Komaromi, R. Gomperts, R. L. Martin, D. J. Fox, T. Keith, M. A. Al-Laham, C. Y. Peng, A. Nanayakkara, M. Challacombe, P. M. W. Gill, B. Johnson, W. Chen, M. W. Wong, J. L. Andres, C. Gonzalez, M. Head-Gordon, E. S. Replogle, J. A. Pople, *Gaussian 03* Revision E.01, Gaussian, Inc., Pittsburgh, PA, 2003.

[25] R. Hagiwara, Y. Nakamori, K. Matsumoto, Y. Ito, *J. Phys. Chem. B* 109 (2005) 5445.

## Figure captions

Fig. 1 Voltage dependence of capacitance for the EDLCs using DMIm(FH)<sub>2.3</sub>F, EMIm(FH)<sub>2.3</sub>F, BMIm(FH)<sub>2.3</sub>F, EMPyr(FH)<sub>2.3</sub>F, MOMMPyr(FH)<sub>2.3</sub>F, EMImBF<sub>4</sub>, and TEABF<sub>4</sub>/PC at 25°C.

Fig. 2 Voltage dependence of energy density for the EDLCs DMIm(FH)<sub>2.3</sub>F, EMIm(FH)<sub>2.3</sub>F, BMIm(FH)<sub>2.3</sub>F, EMPyr(FH)<sub>2.3</sub>F, MOMMPyr(FH)<sub>2.3</sub>F, EMImBF<sub>4</sub>, and TEABF<sub>4</sub>/PC at 25°C.

Fig. 3 Voltage dependence of capacitance for the EDLC using EMIm(FH)<sub>2.3</sub>F at 25, 0, -10, -20, -30, and -40°C.

Fig. 4 Voltage dependence of capacitance for the EDLCs using EMIm(FH)<sub>2.3</sub>F, BMIm(FH)<sub>2.3</sub>F, MOMMPyr(FH)<sub>2.3</sub>F, and TEABF<sub>4</sub>/PC at 25 and -40°C.

Fig. 5 Voltage dependence of energy density for the EDLCs using EMIm(FH)<sub>2.3</sub>F, BMIm(FH)<sub>2.3</sub>F, MOMMPyr(FH)<sub>2.3</sub>F, and TEABF<sub>4</sub>/PC at 25 and -40°C.

Table 1 Physical and structural properties<sup>a</sup> of selected fluorohydrogenate ionic liquids.

System	$T_m$ / K	$T_g$ / K	$\rho$ / g cm <sup>-3</sup>	$\eta$ / mPa·s	$\sigma$ / mS	MV / cm <sup>3</sup> mol <sup>-1</sup>	$V_{cat}$ / Å <sup>3</sup>	Ref.
DMIm(FH) <sub>2,3</sub> F	272	–	1.17	5.1	110	138	132	19
EMIm(FH) <sub>2,3</sub> F	208	148	1.13	4.9	100	156	156	19
BMIm(FH) <sub>2,3</sub> F	– <sup>b</sup>	154	1.08	19.6	33	189	202	19
EMPy <sub>r</sub> (FH) <sub>2,3</sub> F	– <sup>b</sup>	– <sup>b</sup>	1.07	11.5	75	167	173	20
MOMMPy <sub>r</sub> (FH) <sub>2,3</sub> F	– <sup>b</sup>	– <sup>b</sup>	1.13	7.91	75	173	186	This work

<sup>a</sup>  $T_m$ : melting point,  $T_g$ : glass transition temperature,  $\rho$ : density,  $\eta$ : viscosity,  $\sigma$ : ionic conductivity, MV:

molecular volume,  $V_{cat}$ : volume of the cation calculated at MP2/cc-pVTZ. <sup>b</sup> These transition temperatures were not detected under the present experimental condition (> 145 K).

Table 2 Performance of electrolytes in EDLCs at 25°C and –40°C.<sup>a</sup>

System	$C_{25}$ / F g <sup>-1</sup>	$C_{-40}$ / F g <sup>-1</sup>	$E_{25}$ / J g <sup>-1</sup>	$E_{-40}$ / J g <sup>-1</sup>
DMIm(FH) <sub>2,3</sub> F	178	-	647	-
EMIm(FH) <sub>2,3</sub> F	162	64	526	270
BMIm(FH) <sub>2,3</sub> F	133	45	478	155
EMPy <sub>r</sub> (FH) <sub>2,3</sub> F	134	-	466	-
MOMMPy <sub>r</sub> (FH) <sub>2,3</sub> F	152	62	608	285
EMImBF <sub>4</sub>	42	-	187	-
TEABF <sub>4</sub> /PC	43	20	193	88

<sup>a</sup>  $C_{25}$ : 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 EMImBF<sub>4</sub> and TEABF<sub>4</sub>/PC.











