



Short communication

A neat ionic liquid electrolyte based on FSI anion for electric double layer capacitor

Norihisa Handa^a, Toshinori Sugimoto^{a,b}, Masaki Yamagata^{a,c},
Manabu Kikuta^b, Michiyuki Kono^b, Masashi Ishikawa^{a,c,*}

^a Department of Chemistry and Materials Engineering, Faculty of Chemistry, Materials and Bioengineering, Kansai University, 3-3-35 Yamate-cho, Suita 564-8680, Japan

^b Dai-ichi Kogyo Seiyaku Co., Ltd., 5 Ogawa-cho, Kisshoin, Minami-ku, Kyoto 601-8391, Japan

^c Research Center for Business Academia Collaboration, Kansai University, 3-3-35 Yamate-cho, Suita 564-8680, Japan

ARTICLE INFO

Article history:

Received 28 July 2008

Received in revised form 28 August 2008

Accepted 28 August 2008

Available online 6 September 2008

Keywords:

Ionic liquid

Electric double layer capacitor

1-Ethyl-3-methyl imidazolium

bis(fluorosulfonyl)imide

ABSTRACT

An ionic liquid, 1-ethyl-3-methyl imidazolium bis(fluorosulfonyl)imide (EMI-FSI), has been applied to an electrolyte for electric double layer capacitors (EDLCs). The electrolyte exhibited high ionic conductivity comparable to that of a conventional organic electrolyte. EDLC prepared with EMI-FSI showed excellent rate capability although the electrolyte is a neat ionic liquid; this performance was observed irrespective of the presence of a binder in an activated carbon-based electrode. The self-discharge was suppressed by using EMI-FSI. A cycling durability test showed that the cell with EMI-FSI kept over 90% of the initial capacitance even after 10,000 cycles.

© 2008 Elsevier B.V. All rights reserved.

1. Introduction

Ionic liquids have attracted a lot of attention as electrolyte for electric double layer capacitors (EDLCs) from the viewpoints of their high ionic carrier number and non-flammable property. Many researchers have reported on EDLCs prepared with ionic liquid electrolytes [1–9]. However, ionic liquids generally have high viscosity so that the ionic conductivity is lower than that of common organic electrolytes composed of a quaternary ammonium salt and organic solvent, and hence cause the deterioration of power density in EDLCs. The decrease in viscosity of ionic liquids is, therefore, essential for improvement of EDLC performance.

Recently, ionic liquids based on imidazolium salts have been widely investigated because they have relatively low viscosity and high ionic conductivity [1–4,10–12]. Our group as well as Matsumoto et al. reported on ionic liquids based on bis(fluorosulfonyl)imide (FSI) for rechargeable Li batteries [13,14]. The ionic liquids were found to have quite low viscosity and high ionic conductivity when compared with those based on

bis(trifluoromethylsulfonyl)imide (TFSI). EMI-FSI-based electrolyte containing Li ions exhibited practical ionic conductivity, and a graphite/Li cell with the electrolyte showed excellent cycleability [14]. Their systems inevitably need a Li salt, which causes considerable deterioration of the ionic conductivity when compared to that of the corresponding ionic liquids without a Li salt. On the other hand, we can enjoy the intrinsic high ionic conductivity of FSI-based ionic liquids in EDLC because it does not need a Li salt.

In this paper, we report on the application of neat EMI-FSI to EDLC. The key performance was evaluated by using a two-electrode cell, and compared with that of other electrolytes including a typical organic-solvent electrolyte. More specifically, we investigated the discharge capacitance at various current densities, self-discharge behavior, and cycle durability.

2. Experimental

EMI-FSI (Dai-ichi Kogyo Seiyaku Co.) and EMI-TFSI (Kanto Chemical Co.) were used as ionic liquid electrolytes. For comparison, 1.96 M triethylmethylammonium tetrafluoroborate dissolved in propylene carbonate (TEMABF₄/PC: Tomiyama industries) was used as typical organic electrolyte.

Activated carbon fiber cloths (ACFCs: Nippon Kynol ACC-5092-20 SSA: ca. 1800 m² g⁻¹) were used as electrode material. Activated carbon powder sheets (AC sheets: Japan Gore-Tex MSP-2000) were

* Corresponding author at: Department of Chemistry and Materials Engineering, Faculty of Chemistry, Materials and Bioengineering, Kansai University, 3-3-35 Yamate-cho, Suita 564-8680, Japan. Tel.: +81 6 6368 0952; fax: +81 6 6368 0952.

E-mail address: masashi@ipcku.kansai-u.ac.jp (M. Ishikawa).

Table 1
Characteristics of various electrolytes at 298 K

| Electrolyte | Viscosity (mPa s) | Ionic conductivity (mS cm ⁻¹) | Molar concentration (mol dm ⁻³) |
|-------------------------|-------------------|---|---|
| EMI-FSI | 17.9 | 15.5 | 4.94 |
| EMI-TFSI | 28.0 | 8.4 | 3.88 |
| TEMABF ₄ /PC | 4.2 | 15.3 | 1.96 |

also used as electrode material including a binder. Their electrode materials were cut into disks of 1.13 cm² and then were adhered to aluminum foils using carbon paste. The resulting electrodes were dried in a vacuum at 393 K for 12 h in order to remove residual moisture. Two-electrode cells made of stainless steel cases were then assembled with a pair of the electrodes and separator (GB-100R: Toyo Roshi Kaisha) in a grove box filled with argon (dew point: below 213 K).

Charge–discharge tests were performed in the range from 2.5 to 50 mA cm⁻² between 1 and 2 V using HJ1001-SM8 (Hokuto Denko Co.); the current was changed every 10 cycles. Discharge capacitance specified as a gravimetric value of each electrode (C) was calculated from the equation: $C = 2It(Vw)^{-1}$, where I is the current value, t is the discharge time, V is the applied cell voltage, and w is the mass of a single electrode. After cycling, the cells were kept at 2 V for 3 h and then self-discharge characteristics were obtained on an open circuit. Long cycle tests (10,000 cycles) were performed at a constant-current density of 20 mA cm⁻² between 1 and 2 V. AC impedance measurements were carried out using a Solartron SI 1260 impedance analyzer; the applied AC amplitude was 10 mV and the frequency range was from 20 kHz to 10 mHz. All measurements were carried out at an ambient temperature, 298 ± 2 K.

3. Results and discussion

Table 1 lists the viscosity, ion conductivity and molar concentration of EMI-FSI, EMI-TFSI and TEMABF₄/PC. EMI-FSI has considerably low viscosity and high conductivity when compared to those of EMI-TFSI, and the conductivity is comparable to that of a typical organic electrolyte, TEMABF₄/PC. Ionic liquids generally have high molar concentration. Besides the common property, EMI-FSI has relatively low viscosity, and hence high ion conductivity.

Fig. 1 shows charge–discharge curves at 10th cycle with a current density of 2.5 mA cm⁻² for EDLCs containing ACFC electrodes

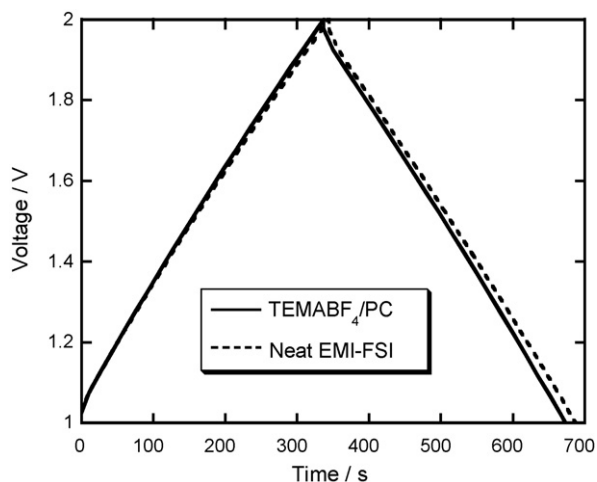


Fig. 1. Charge–discharge curves of EDLCs with ACFC electrodes and electrolytes: TEMABF₄/PC and neat EMI-FSI at 10th cycle.

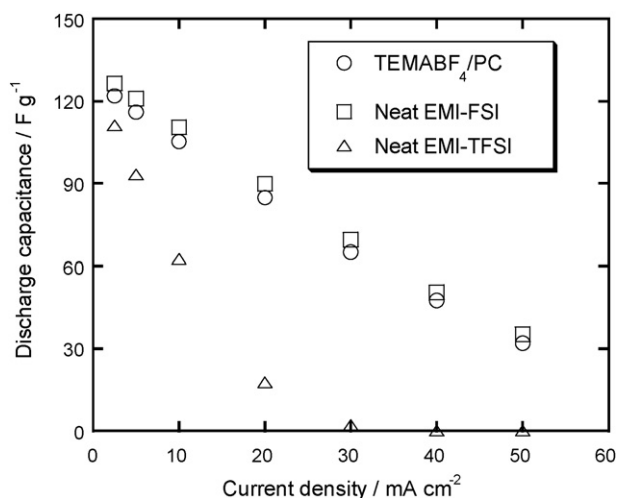


Fig. 2. Rate capability of EDLCs with ACFC electrodes and various electrolytes.

and TEMABF₄/PC or neat EMI-FSI as an electrolyte. In the present study, we applied 2.0 V as a maximum cell voltage because the self-discharge from 2.5 V for a cell with EMI-FSI was relatively fast. Although the origin has not so far been clear, this might be due to some impurities in EMI-FSI or minor decomposition of EMI-FSI. When we operated 3 or more cells between 1 and 2 V, however, variability in their capacitance and internal resistance was within 5%, suggesting that obtained data in 1–2 V cycling are reliable.

The cell with EMI-FSI exhibited a typical charge–discharge curve of EDLC in the almost same way observed for the cell with TEMABF₄/PC as shown in Fig. 1, where their coulombic efficiencies were above 99%. Fig. 2 shows discharge capacitance (F g⁻¹) at various current densities, i.e., rate capability, of EDLCs containing the above electrolytes together with neat EMI-TFSI. Although the cell with EMI-TFSI could not operate over 40 mA cm⁻² due to its large IR drop, the cell containing EMI-FSI exhibited excellent rate capability despite a neat ionic liquid, and the performance was comparable to that for TEMABF₄/PC because of the high ionic conductivity of EMI-FSI.

Nonetheless, there is a further issue that we must not ignore. That is the affinity of electrolytes for electrodes, which is a crucial factor for EDLC performance [15–18]. ACFCs are composed of only carbonaceous material while AC sheets contain a binder to keep AC particles in the electrode. When the electrodes containing a binder are used, EMI-FSI might lack the affinity for the electrode due to the presence of a binder. Thus, we should investigate the influence of the binder for the cell performance. Figs. 3 and 4 show Nyquist plots and rate capability for AC sheet electrodes, respectively. As presented in Fig. 3, the behaviors for EMI-FSI and TEMABF₄/PC were almost the same, suggesting that EMI-FSI has good affinity similar to TEMABF₄/PC for AC sheet electrodes. As can be expected from this result, the rate capability for EMI-FSI was comparable to that of TEMABF₄/PC (Fig. 4), suggesting that the cell with a neat EMI-FSI also has good rate capability even in the presence of the binder. To the best of our knowledge, EMI-FSI is an exclusive ionic liquid that can exhibit an excellent rate capability comparable to a practical EDLC electrolyte, e.g., TEMABF₄/PC, among neat ionic liquid electrolytes that have ever been reported.

To check the reliability of cells with EMI-FSI, self-discharge behavior was investigated. As shown in Fig. 5, the voltage decay of the cells with ionic liquid electrolytes was lower than that of TEMABF₄/PC, suggesting that self-discharge is suppressed by using ionic liquid electrolytes. There have been several reports about the causes of self-discharge [19,20]. Conway [19] suggested that a major

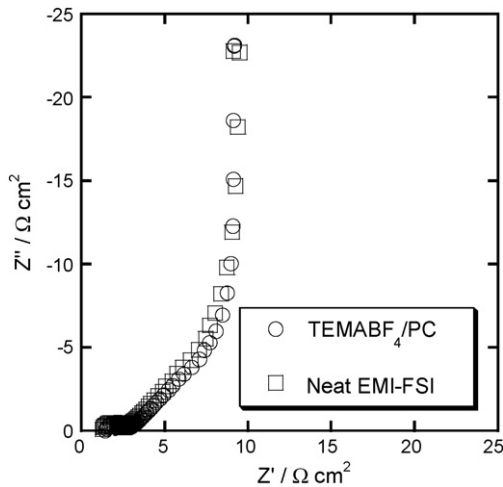


Fig. 3. Nyquist plots of EDLCs with AC sheet electrodes.

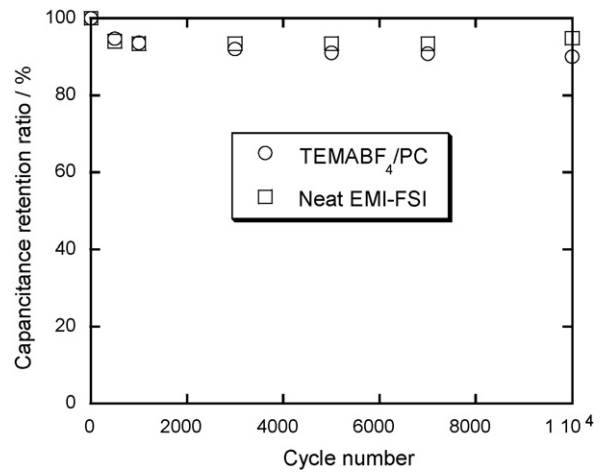


Fig. 6. Capacitance retention ratio as a function of cycle number.

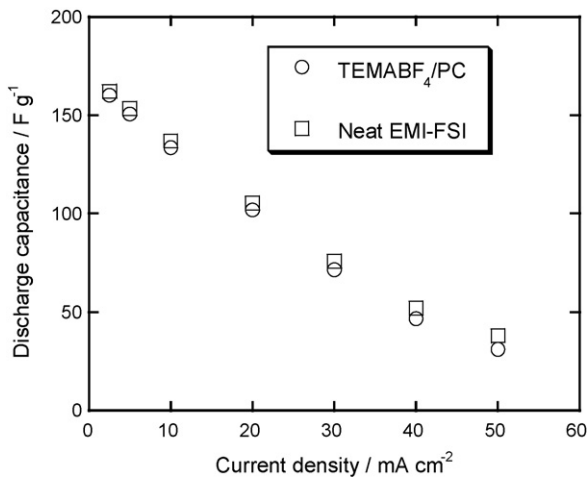


Fig. 4. Rate capability of EDLCs with AC sheet electrodes.

cause is some shuttle reaction of slight impurities such as water. When water is decomposed to generate O₂, the resulting O₂ would diffuse for a negative electrode and be reduced to reproduce water. As a result, the shuttle reaction could cause self-discharge. The water content (w/w) of EMI-FSI and TEMABF₄/PC were 32.2 and

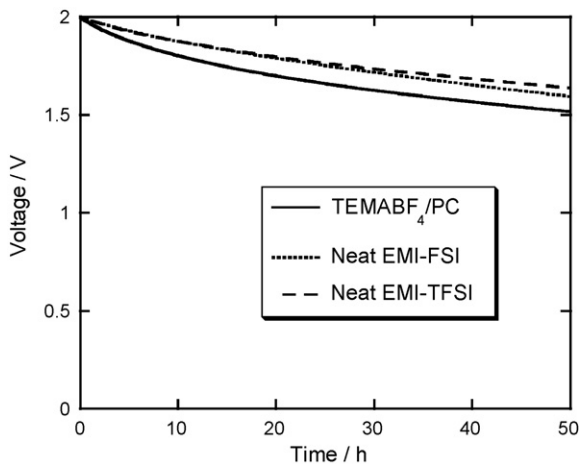


Fig. 5. Self-discharge behaviors of EDLCs with various electrolytes.

18.7 ppm, respectively. As can be seen in Table 1, the viscosity of ionic liquids is much higher than that of TEMABF₄/PC. The high viscosity would, therefore, prevent reactive species causing a shuttle reaction between electrodes.

Long cycling tests were performed to evaluate the cycle durability and then we calculated the capacitance retention ratio using the following formula: $C_x/C_0 \times 100$, where C_x is discharge capacitance at each cycle and C_0 is that at the first cycle. Fig. 6 shows the capacitance retention ratio for EMI-FSI and TEMABF₄/PC, respectively. After 10,000 cycles, both of the cells retained a capacitance of over 90%, suggesting that the neat EMI-FSI electrolyte is as stable as, or rather better than TEMABF₄/PC over the long cycling.

4. Conclusions

An ionic liquid, EMI-FSI, was applied to an electrolyte for EDLC. It has high ionic conductivity comparable to a conventional organic electrolyte, TEMABF₄/PC, without any solvent. This EDLC showed excellent rate capability comparable to that with TEMABF₄/PC. Such an excellent performance was obtained for electrodes both with and without a binder. Furthermore, self-discharge was rather suppressed by using EMI-FSI. EDLCs with EMI-FSI as well as TEMABF₄/PC retained over 90% of the initial discharge capacitance even after 10,000 cycles. From the present results, EMI-FSI can be regarded as a promising electrolyte for EDLC.

References

- [1] A.B. McEwen, S.F. McDevitt, V.R. Koch, J. Electrochem. Soc. 144 (1997) L84–L86.
- [2] B. McEwen, H.L. Ngo, K. LeCompte, J.L. Goldman, J. Electrochem. Soc. 146 (1999) 1687–1695.
- [3] Z.B. Zhou, M. Takeda, M. Ue, J. Fluorine Chem. 125 (2004) 471–476.
- [4] M. Ue, M. Takeda, A. Toriumi, A. Kominato, R. Hagiwara, Y. Ito, J. Electrochem. Soc. 150 (2003) A499–A502.
- [5] Y.J. Kim, Y. Matsuzawa, S. Ozaki, K.C. Park, C. Kim, M. Endo, H. Yoshida, G. Masuda, T. Sato, M.S. Dresselhaus, J. Electrochem. Soc. 152 (2005) A710–A715.
- [6] T. Sato, G. Masuda, K. Takagi, Electrochim. Acta 49 (2004) 3603–3611.
- [7] K. Yuyama, G. Masuda, H. Yoshida, T. Sato, J. Power Sources 162 (2006) 1401–1408.
- [8] A. Lewandowski, M. Galiński, J. Phys. Chem. Solids 65 (2004) 281–286.
- [9] C.O. Ania, J. Pernak, F. Stefaniak, E. Raymundo-Piñero, F. Béguin, Carbon 44 (2006) 3126–3130.
- [10] R. Hagiwara, T. Hirashige, T. Tsuda, Y. Ito, J. Electrochem. Soc. 149 (2002) D1–D6.
- [11] Y. Yoshida, O. Baba, G. Saito, J. Phys. Chem. B 111 (2007) 4742–4749.
- [12] V. Lockett, R. Sedev, J. Ralston, J. Phys. Chem. C 112 (2008) 7486–7495.
- [13] H. Matsumoto, H. Sakaebe, K. Tatsumi, M. Kikuta, E. Ishiko, M. Kono, J. Power Sources 160 (2006) 1308–1313.

- [14] M. Ishikawa, T. Sugimoto, M. Kikuta, E. Ishiko, M. Kono, J. *Power Sources* 162 (2006) 658–662.
- [15] S. Yamazaki, K. Obata, Y. Okuhama, Y. Matsuda, M. Ishikawa, *Electrochemistry* 75 (2007) 592–594.
- [16] D. Lozano-Castelló, D. Cazorla-Amorós, A. Linares-Solano, S. Shiraishi, H. Kurihara, A. Oya, *Carbon* 41 (2003) 1765–1775.
- [17] Y. Honda, M. Takeshige, H. Shiozaki, T. Kitamura, M. Ishikawa, *Electrochemistry* 75 (2007) 586–588.
- [18] Y. Fukuda, R. Tanaka, M. Ishikawa, *Electrochemistry* 75 (2007) 589–591.
- [19] B.E. Conway, *Electrochemical Supercapacitors*, Kluwer Academic/Plenum Publishers, New York, 1999.
- [20] B.W. Ricketts, C. Ton-That, J. *Power Sources* 89 (2000) 64–69.