Electrochemistry Communications 11 (2009) 1996–1999

Contents lists available at ScienceDirect

Electrochemistry Communications

journal homepage: www.elsevier.com/locate/elecom

Application of novel room temperature ionic liquids in flexible supercapacitors

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ARTICLE INFO

Article history:
Received 6 August 2009
Received in revised form 20 August 2009
Accepted 20 August 2009
Available online 27 August 2009

Keywords:
EDLC flexible supercapacitors
Room temperature ionic liquids (RTILs)

ABSTRACT

This paper studied application of different types of room temperature ionic liquids (RTILs) into flexible supercapacitors. Typical RTILs including 1-buthyl-3-methyl-imidazolium [BMIM][Cl], trioctylmethylammonium bis(trifluoromethylsulfonyl)imide [OMA][TFSI] and triethylsulfonium bis(trifluoromethylsulfonyl)imide ([SET_3][TFSI]) were studied. [SET_3][TFSI] shows the best result as electrolyte in electrochemical double-layer (EDLC) supercapacitors with very high specific capacitance of 244 F/g at room temperature, overceiling the performance of conventional carbonate electrolyte such as dimethyl carbonate (DMC) with more stable performance and much larger electrochemical window.

1. Introduction

Supercapacitors (or ultracapactiors) store energy either by a pure electrostatic attraction occurring between the ions and the charged surface of the electrode (e.g. carbon) which is known as electrochemical double-layer capacitor (EDLC), or by fast surface Faradaic redox reactions (pseudocapacitors) [1]. Electrode materials with pseudocapacitance properties are generally metal oxides (RuO_2, MnO_2, etc.) or conducting polymers [2,3]. To get genuine information on the electrolyte property per se, the supercapacitors discussed in this paper are all EDLCs with mesoporous and activated carbon as electrodes. Supercapacitors based on EDLC capacitance differ from conventional physical capacitors in the action of the dielectric medium. In a normal capacitor the bulk phase of the dielectric medium defines the capacitance, but in an EDLC the charges are stored in the electrode/electrolyte interface.

Room temperature ionic liquids (RTILs) are promising electrolytes in EDLC supercapacitors due to their large electrochemical windows, higher ionic conductivities, stable, non-flammable and non-volatile properties. Application of low-viscosity RTILs as electrolyte of EDLC has been tried by many groups [4–7]. An irreversible cationic intercalation into graphene interlayers has been a significant and common problem with usual RTILs, it was found that RTILs containing bis(trifluoromethylsulfonyl)imide [TFSI] anion with the Li cation can prevent such an irreversible reaction and provide reversible Li cation intercalation into graphene interlayers [8]. In the meanwhile, the [TFSI] electrolytes have been shown to cycle well with Li metal, offering a dramatic increase in possible energy densities and simpler technology for high-performance batteries and even hybrid supercapacitor-batteries [9]. This is the reason why the majority of RTILs chosen are with [TFSI] anions and the lithium salt, LiTFSI was selected to add to the electrolytes for comparison studies.

For high EDLC capacitance, the carbon electrodes should have a high specific surface area that can be easily accessed by electrolytes. Specific capacitance for supercapacitors made of carbon-nanotube electrodes and imidazolium ionic liquid gel is generally in the range of 22–40 F/g [10–12]. When the substrate is changed to activated carbon, the value was reported to be 52 F/g and increased to 107 F/g with modification of mesoporous carbons [13], which is comparable with the hybrid (pseudo-EDLC) supercapacitors with active carbon and conducting polymers [14]. A significant increase in the capacitance values up to 140 F/g at 75 centigrade was observed for the trigeminal tricationic RTIL whereas it only gives ca. 40 F/g at room temperature [15]. The improvement of specific capacitance may be mainly due to the decrease of viscosity of RTIL by elevating the operation temperature. As discussed above, because of the benefits of [TFSI] anion and common use of imidazolium cation, typical RTILs including [BMIM][Cl], [OMA][TFSI] and [SET3][TFSI] are studied and compared in the flexible supercapacitors at room temperature in this paper. In addition, possible degradation of imidazolium cations at larger electrochemical windows and higher-temperatures makes it meaningful to study non-imidazolium RTILs with [TFSI] anions.

2. Experimental

All the RTILs and salt of lithium bis(trifluoromethylsulfonyl)imide (LiTFSI, 99.95%) were purchased from solvent innovation (Merck) GmbH. Dimethyl carbonate (DMC, ⩾99%), polyvinylidene

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doi:10.1016/j.elecom.2009.08.037

fluoride (PVdF) and N-methyl-2-pyrrolidinon (NMP) were from Sigma–Aldrich.

The coating slurry for supercapacitor electrodes was made by mixing 80% mesoporous and activated carbon with 10% carbon black and 10% polyvinylidene fluoride (PVdF) binder in N-methyl-2-pyrrolidinon (NMP) solvent to form homogeneous slurry. The slurry was spread onto aluminium (Al) foil substrate. The coated electrodes were dried in a vacuum oven at 100 centigrade for 24 h and then pressed. Subsequently, the electrodes were cut to a 1 * 2 cm^2 size to assemble the supercapacitors.

The electrochemical properties of the assembled supercapacitors were studied by cyclic voltammetry and galvanostatic measurement using Autolab (PGSTAT 302 N).

3. Results and discussion

Supercapacitors are very attractive for portable electronics as well as automotive applications due to their high specific power and durability. The supercapacitor reported here is a completely flexible electrochemical device that you can bend easily. A high-fiber cellulose paper as separator is sandwiched between the two-electrodes, between which are filled with RTILs. Unlike organic electrolytes, which are easy to evaporate, the non-volatile RTILs are able to retain in the device even without packaging. The picture of the flexible supercapacitor is shown in Fig. 1A. The electrodes are made of Al foil coated with mesoporous and activated carbon. Fig. 1B shows the SEM image of the electrode surface.

Physical properties and chemical structures of RTILs including [BMIM][Cl], [OMA][TFSI] and [SET3][TFSI] are illustrated in Table 1. [BMIM][Cl] has a high melting temperature, which makes it a solid at room temperature but gives high ionic conductivity when dissolved in water. In the meanwhile, both [OMA][TFSI] and [SET3][TFSI] are liquids at room temperature, and [SET3][TFSI] shows as high conductivity as 0.1 M [BMIM][Cl] aqueous solution (Table 1). RTILs based on triethylsulfonium cation ($[SET3]^+$) show low melting point (−35 °C) and the lowest viscosity (30 mPs at 25 °C) of all the [TFSI] based RTILs reported so far. The conductivity of 7.1 mS cm^{-1} at 25 °C is the highest of all the non-chloroaluminate RTILs based on aliphatic onium cations [16].

Three supercapacitors have been assembled based on these three types of RTILs. Results from cyclic voltammetry and galvanostatic charge–discharge measurements are shown in Fig. 2A and B. [BMIM][Cl] is in form of solid salt at room temperature but melts when heated over 60 °C and the paper separator can be easily im-

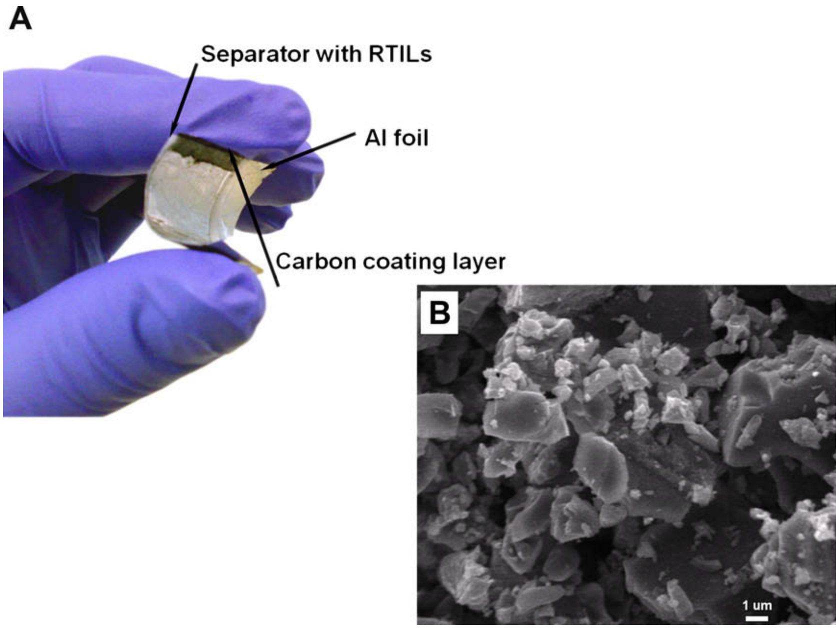
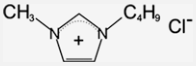
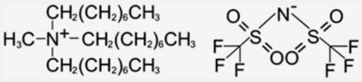
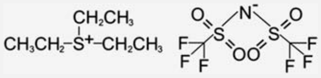


Fig. 1. (A) Picture of the flexible supercapacitor assembled and (B) SEM image of mesoporous activated carbon paste on the Al foil for the supercapacitor electrodes.

Table 1
Physical properties and different chemical structures of RTILs.

RTILs		Melting point (°C)	Conductivity (mS cm^{-1})
[BMIM]Cl Butyl-3-methylimidazolium chloride		60	6.92 (0.1 M in H_2O)
[OMA][TFSI] (Also known as [OMA][Tf_2N]) Trioctyimethylammonium bis(trifluoromethylsulfonyi)imide		<−65	0.074
[SET_3][TFSI] (Also known as[TES] [Tf_2N]) Triethyisulfoniumbis(trifluoromethyisulfonyl)imide		About −35	6.89

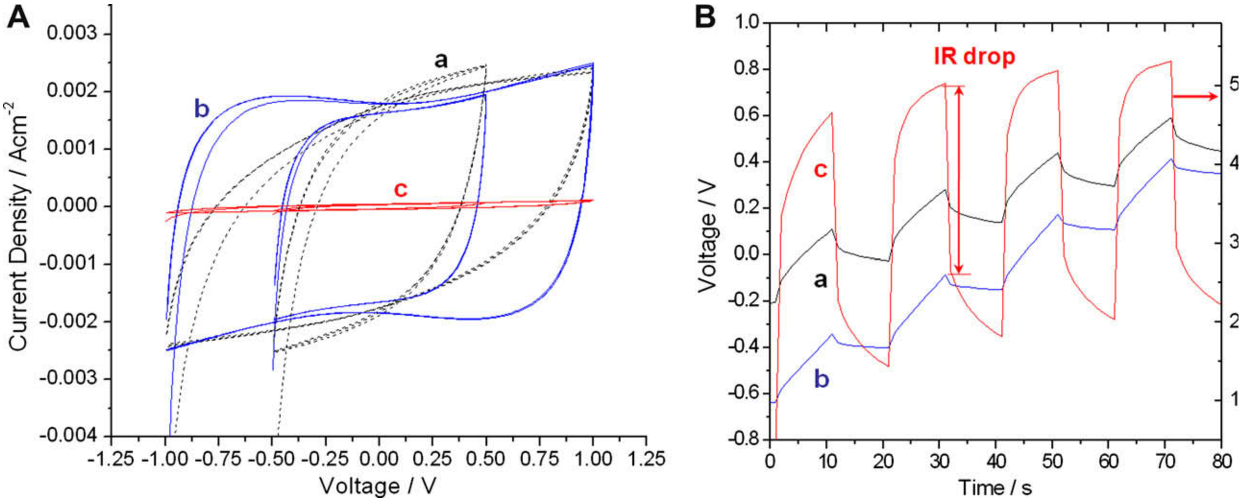


Fig. 2. (A) Cyclic voltammogram curves of supercapacitors assembled from different RTILs on activated carbon electrode in the range of −0.5 to 0.5 V and −1 to 1 V with scan rate of 50 mV/s. (a) [BMIM][Cl] (dash line), (b) [SET3][BTA], (c) [OMA][BTA]. (B) Galvanostatic charge–discharge measurement of these supercapacitors at constant current of 1 mA.

merged within. As Fig. 2A shows, supercapacitor based on [SET3][TFSI] shows the best performance with rectangular shape over the other two. [BMIM][Cl] also shows good capacitive current, a little inferior to the one from [SET3][TFSI]. Supercapacitors containing [OMA][TFSI] does not show any comparable capacitive current and this may be due to the low conductivity ($0.074 \ll 6.9$ mScm^{-1}) as Table 1 lists. Galvanostatic charge–discharge measurements were used to evaluate the specific capacitance and the internal resistance of the devices in the two-electrode configuration. The charge–discharge behaviour was measured at a constant current of 1 mA. Internal resistance (iR) drop can be observed in each pulsing measurement in Fig. 2B. This is due to the equivalent series resistance of electrodes, RTIL electrolytes and the contact resistance between the electrodes. The internal resistance of supercapacitors based on [OMA][TFSI] is the highest, which correlates the low conductivity of this RTIL and explains its cyclic voltammogram.

The slope of the discharge curve (dV/dt) from the Galvanostatic measurement can be used to calculate the specific capacitance. Specific capacitance, C_{spec} (F/g), can be calculated from the following equation [17]:

$$C_{\mathrm{spec}} = \frac{i}{dV/dt}\left(\frac{1}{m}\right)$$

where i is the constant discharging current, m is the mass of the active materials within the electrodes, and dV/dt is the rate of voltage change.

The specific capacitance of the supercapacitors based on [OMA][TFSI], [BMIM][Cl] and [SET3][TFSI] is 7.9, 94.1 and 243.9 F/g, respectively calculated from Fig. 2B. The value from [BMIM][Cl] is comparable with what literature reported on supercapacitor electrolyte based on imidazolium ionic liquid [13].

LiTFSI salt, which has the same anion of [TFSI] with [OMA][TFSI] and [SET3][TFSI] was added to the RTIL of [SET3][TFSI] and the performances were compared with that of dimethyl carbonate (DMC), a common organic liquid electrolyte that serves as a bench mark. Fig. 3A shows that the performance of pristine [SET3][TFSI] is similar to DMC with 5 wt.% of LiTFSI. When same amount of lithium salt was added to [SET3][TFSI], the capacitive current improves a little. The iR drop also becomes smaller when adding the salt to [SET3][TFSI] as Fig. 3B shows. At constant current of 10 mA, the device requires approximately 30 s to charge/discharge when 5 wt% LiTFSI was added, whereas it takes approximately 20 s when pure [SET3][TFSI] was used. The electrochemical window was kept from −1 to 1 V with scan rate of 50 mV/s during the cyclic voltammetry. When the electrochemical window is enlarged from 3 V (−1.5 to 1.5 V) to 5 V (−2.5 to 2.5 V), the benefit of using RTIL is

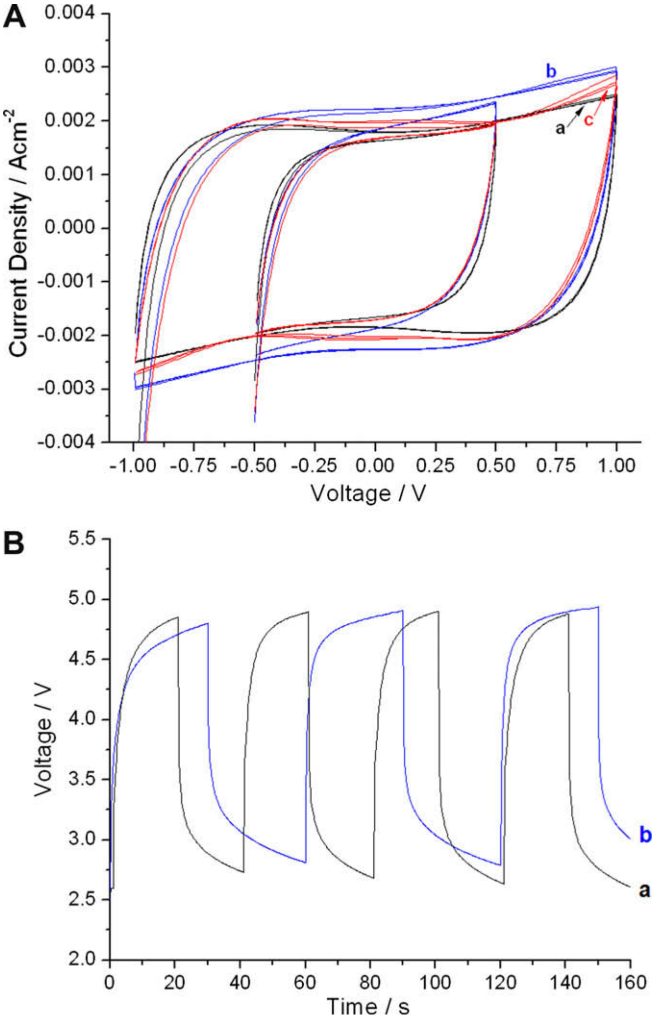


Fig. 3. A. The cyclic voltammogram curves of the supercapacitors with electrolytes of (a) [SET$_3$][TFSI], (b) [SET$_3$][TFSI] with 5 wt% LiTFSI salt and (c) DMC with 5 wt% LiTFSI dissolved. B. Galvanostatic charge–discharge performance of supercapacitors based on [SET$_3$][TFSI] electrolytes at constant current of 10 mA.

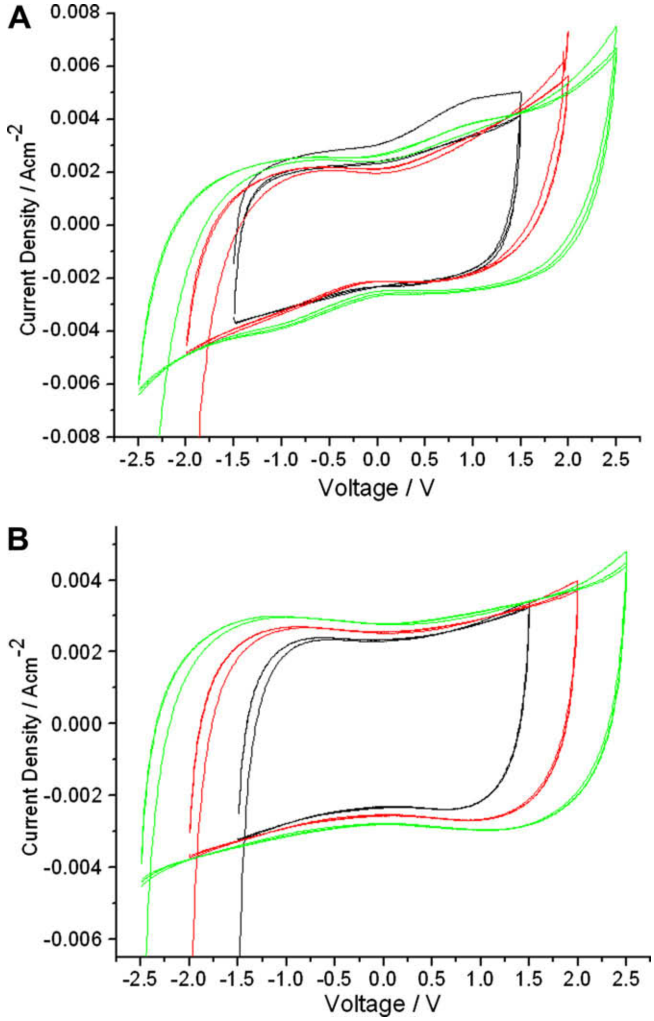


Fig. 4. The cyclic voltammogram curves of the supercapacitors with electrolytes of (A) 5 wt% LiTFSI in DMC (B) 5 wt% LiTFSI in [SET3][TFSI]. Electrochemical window is in the range of −1.5 to 1.5 V, −2.0 to 2.0 V and −2.5 to 2.5 V with scan rate of 50 mV/s.

obvious as Fig. 4 shows. Faradaic current can be observed in DMC containing 5 wt.% of LiTFSI (Fig. 4A), while [SET3][TFSI] containing 5 wt.% of LiTFSI (Fig. 4B) still maintains perfect square-shape capacitive current. The addition of LiTFSI salt to [SET3][TFSI] gave a little improved performance and a better square-shape of the cyclic voltammogram.

In summary, a supercapacitor with the mechanical flexibility has been fabricated using RTIL electrolyte and the mesoporous and activated carbon electrodes coated on the Al foil. Non-volatile property makes RTILs more suitable for flexible supercapacitors than the volatile organic solvents. When temperature is elevated, the ionic conductance of RTILs will be improved more, which makes it perform better in higher-temperature regions where organic electrolyte cannot work. [SET_3][TFSI] has good solubility towards the lithium salt of LiTFSI and it has larger electrochemical window, higher ionic conductance and lower viscosity as electrolytes in EDLC. Supercapacitor based on this electrolyte has the highest specific capacitance among those using RTILs as well as conventional carbonate electrolytes (e.g. DMC) at room temperature. Addition of lithium salt can slightly improve the performance and it also gives the possibility to use such electrolyte in lithium ion batteries and make future flexible hybrid supercapacitor-battery device. The hybrid supercapacitor-battery device can enhance both power density and energy density for many applications including multifunctional electronics.

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