

# Application of 1-ethyl-3-methylimidazolium thiocyanate to the electrolyte of electrochemical double layer capacitors

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## Abstract

The performance of an electrochemical double layer capacitor composed of activated carbon electrodes and 1-ethyl-3-methylimidazolium thiocyanate ([EMIm]SCN) as the electrolyte possessing extremely high conductivity and low viscosity, was investigated by cyclic voltammetry and galvanostatic charging/discharging. The effect of various factors governing the extraordinary performance of this capacitor in terms of its specific capacitance, current density, voltage and cycle-life, was examined in detail.

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**Keywords:** Activated carbon; Electrochemical double layer capacitor; Cyclic voltammetry; Galvanostatic charging and discharging

## 1. Introduction

Electrochemical double layer capacitors (EDLCs) are the intermediate systems between electrochemical batteries that can store higher energy density and dielectric capacitors, which can deliver very high power during few milliseconds. So it is widely used in the fields of mobile communication, aviation and spaceflight, and information technology, etc. Since the electric energy stored in EDLCs are given rise by the separation of charged species in the electrochemical double layer across the electrode/electrolyte interface, the performance of the EDLCs depend strongly on the electrolyte and the specific surface area of the electrode materials. Most EDLCs use aqueous solution electrolytes for good conductivity, however, an obvious demerit for these devices is their inherently narrow electrochemical window (less than 1.23 V), which largely restrict both power and energy capability of these EDLCs.

Room temperature ionic liquids (RTILs) [1–9], as the electrolyte of electrochemical devices, have received increasing attention for the last few years, because of their greater

electrochemical stability window and relatively high ionic conductivity. Some ionic liquids have been synthesized and used in such electrochemical devices as lithium rechargeable batteries [10], electric double layer capacitors [11–14], and titanium oxide dye-sensitized solar cells [15]. However, their practical application has often been limited by their high viscosity at ambient temperature. For example, the viscosity of ionic liquid such as [EMIm]BF<sub>4</sub> [16], [BMIm]PF<sub>6</sub> [17] and [BMIm]BF<sub>4</sub> [18] which are frequently used to the electrolytes of EDLCs are 37.7cP, 312cP and 233cP, respectively, much higher than that of aqueous electrolytes. As we all know, viscosity increase can result in internal resistance (*R*) increase which is one of the most important impact factors of EDLCs, the smaller *R* is, the higher power output capability is, so reducing *R* is very important for EDLCs.

1-Ethyl-3-methylimidazolium thiocyanate [EMIm]SCN has high conductivity and low viscosity at room temperature compared to other ionic liquids, e.g. [EMIm]BF<sub>4</sub>, [BMIm]BF<sub>4</sub> and organic electrolytes [19], so it can be expected to be used as an EDLC electrolyte to reduce *R* of EDLCs. This paper presents our latest investigation into the application of ionic liquid [EMIm]SCN as the direct electrolyte for electrochemical double layer capacitors, based on activated carbon as an electrode material, without using any other solvent as diluent.

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## 2. Experimental

### 2.1. Reagents

1-Methylimidazolium (Michael Kors), ethylbromide, acetonitrile and ammonium thiocyanate acid (Chemistry Reagent Co. Ltd. of Shanghai, China), all chemicals were dried at room temperature and distilled under reduced pressure before use.

### 2.2. Preparation of activated carbon

Activated carbon powders with a specific area of  $3250 \text{ m}^2 \text{ g}^{-1}$  were prepared from petroleum coke (Jin Zhou, Liaoning, China), via reactions with KOH ( $m_{\text{petroleum coke}}:m_{\text{KOH}} = 1:6$ ) for 1.5 h at  $800^\circ\text{C}$ .

### 2.3. Preparation of 1-ethyl-3-methylimidazolium thiocyanate ([EMIm]SCN)

To prepare 1-ethyl-3-methylimidazolium bromide ([EMIm]Br), the precursor for [EMIm]SCN, 90 ml ethylbromide was first slowly added to  $35 \text{ cm}^3$  1-methylimidazole under stirring conditions. The mixture was further stirred for 3 h at ambient temperature before reflux at  $70^\circ\text{C}$  for 24 h. The mixture was then allowed to cool completely and age for about 12 h, thus giving rise to the formation of a two-phase system. After separation from the mixture using a separatory funnel, the viscous ionic liquid phase, i.e. (EMIm)Br, was washed twice with 100 ml of 1,1,1-trichloroethane and then dried at  $70^\circ\text{C}$  under reduced pressure. The yield of (EMIm)Br from this preparation was 69.3 g (57.6 wt%).

Next, 7.6 g of  $\text{NH}_4\text{SCN}$  was added into 250 ml acetonitrile containing 19.2 g [EMIm]Br, and the mixture stirred for 8 h. After the removal of the white  $\text{NH}_4\text{Br}$  precipitate by filtration and the solvent by evaporation at  $60^\circ\text{C}$  under reduced pressure, the liquid salt, (EMIm)SCN was obtained and further dried at  $80^\circ\text{C}$  in vacuum. The yield of the final product was 12.5 g (73.9 wt%).

### 2.4. Preparation of electrodes and capacitors

Activated carbon powder (ACP) (85 wt%), carbon black (CB) (5 wt%) and polyvinylidene fluoride (PVDF) (10 wt%) were mixed and stirred adequately, and the paste thus formed pressed onto a foam nickel. The electrodes formed in this way were 10 mm in diameter and 0.2–0.4 mm in thickness. Capacitors were then assembled by sandwiching the ionic liquid between the electrodes.

### 2.5. Measurement of electrochemistry performance

Electrochemistry performance was measured by using Arbin BT-4+ (America). Based on galvanostatic charging–discharging experiments, the specific capacitance was calculated from Eq.

Table 1  
Pore texture of activated carbon

$S_{\text{BET}}$ ( $\text{m}^2 \text{ g}^{-1}$ )	$V_{\text{total}}$ ( $\text{cm}^3 \text{ g}^{-1}$ )	$V_{<0.8 \text{ nm}}$ ( $\text{cm}^3 \text{ g}^{-1}$ )	$V_{(0.8-2 \text{ nm})}$ ( $\text{cm}^3 \text{ g}^{-1}$ )	$V_{(2-50 \text{ nm})}$ ( $\text{cm}^3 \text{ g}^{-1}$ )	$V_{>50 \text{ nm}}$ ( $\text{cm}^3 \text{ g}^{-1}$ )
3250	1.935	0.997	0.772	0.159	0.008

(1) in the voltage range of 0.1–0.4 V:

$$C = \frac{i \times \Delta t}{\Delta v} \quad (1)$$

where  $i$  is the discharge current (A) and  $\Delta t$  is the time duration (s) corresponding to voltage change in the discharge cycle. The specific capacitance of ACP ( $C'$ ) was obtained from the following Eq. (2):

$$C' = \frac{C}{2m} \quad (2)$$

where  $C$  is the capacitance in F of EDLC, and  $m$  is the mass of ACP (in grams) used in a single electrode.

### 2.6. Performance measurement of activated carbon

Specific surface area and pore structure of activated carbon were determined with  $\text{N}_2$  adsorption isotherms at 77 K (Sorptionomatic 1990, Italy). The main parameters of activated carbon were shown in Table 1. The surface morphology of active substances at the electrodes was observed through scanning electron microscopy (SEM) performed on a JEOL-JSM6360 (Japan) at an accelerating voltage of 20 kV.

## 3. Results and discussion

### 3.1. Physical properties of ionic liquid

Table 2 presents some physical properties of [EMIm]SCN, and other electrolytes such as aqueous  $\text{H}_2\text{SO}_4$  [20] and the organic electrolyte of  $(\text{CF}_3\text{SO}_2)_2\text{NLi}$  (0.1 M in PC:DME(1:2, v/v)) [21] for comparison. It can be seen that the conductivity of [EMIm]SCN was  $2.1 \text{ S m}^{-1}$ , being about 1/40 of that for 35 wt%  $\text{H}_2\text{SO}_4$  and about 5 times that for 0.1 M  $(\text{CF}_3\text{SO}_2)_2\text{NLi}$  in PC:DME(1:2, v/v). The electrochemical window of [EMIm]SCN was higher than that of 35 wt%  $\text{H}_2\text{SO}_4$  but lower than 0.1 M  $(\text{CF}_3\text{SO}_2)_2\text{NLi}$  in PC:DME(1:2, v/v), indicating that the electrochemical performance of [EMIm]SCN might lie between the two electrolytes.

Table 2  
Properties of various kinds of electrolytes

	Viscosity at RT (mPa s)	Conductivity ( $\text{S m}^{-1}$ )	Electrochemical window (V)
35 wt% $\text{H}_2\text{SO}_4$ [20]	2.5	84.8	1.23
0.1 M $(\text{CF}_3\text{SO}_2)_2\text{NLi}$ in PC:DME(1:2, v/v) [21]	–	0.4	5.2
[EMIm]SCN [22]	21	2.1	2.60

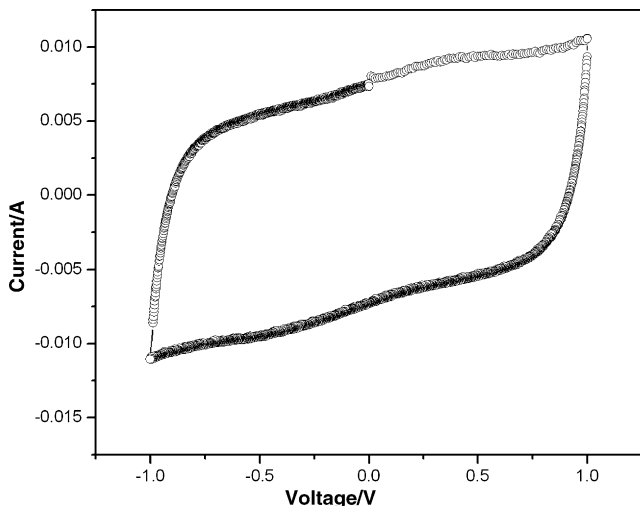


Fig. 1. Cyclic voltammogram of EDLC composed of activated carbon and [EMIm]SCN. Sweep rate:  $5 \text{ mV s}^{-1}$ ; room temperature.

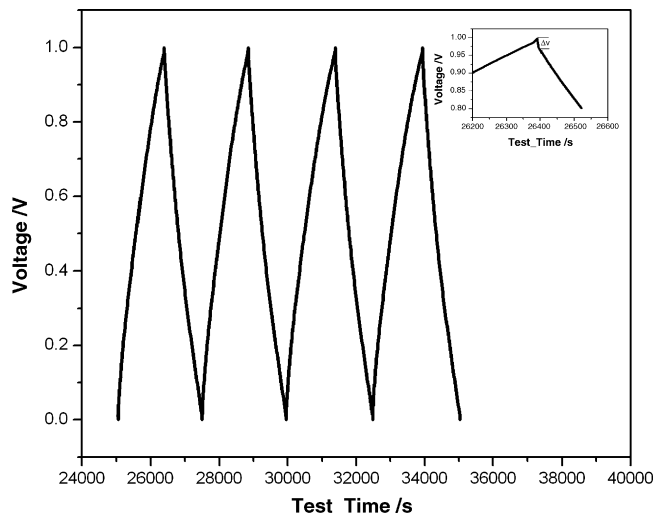


Fig. 2. Charging–discharging characteristic of EDLC composed of activated carbon and [EMIm]SCN. Current density:  $2 \text{ mA}$ ; room temperature.

### 3.2. Electrochemical performance of ionic liquid as electrolyte

Barisci et al. [23] investigated the electrochemical performance of 1-ethyl-3-methylimidazolium bis(trifluoromethanesulphony)amide ([EMIm](CF<sub>3</sub>SO<sub>2</sub>)<sub>2</sub>N), and obtained an irregular rectangular cyclic voltammogram at a scan rate of  $50 \text{ mV s}^{-1}$ . At the same time, a peak at about  $1.0 \text{ V}$  was observed, indicating large internal resistance. However, for ideal double layer electrodes, their cyclic voltammograms should be normally occurred as symmetrical rectangles, because of the double layers being rapidly formed at the interface of electrode/electrolyte and quickly reaching a steady state of current upon the changing of voltage sweep direction. Fig. 1 shows a cyclic voltammogram of [EMIm]SCN as electrolyte of EDLC. It can be seen that the curve produced was of a rectangular shape, being consistent with the capacitive behaviour expected. Obviously, [EMIm]SCN enabled a better rectangular characteristic, almost constant current and a symmetrical cathode/anode process in the voltage range from  $-1.0 \text{ V}$  to  $1.0 \text{ V}$ , all indicating that the charge–discharge process for the EDLC occurred at a constant rate with capacitance hardly changing with voltage. Fig. 1 also shows that the internal resistance of the EDLC was very small, because the rapid current reversion upon the changing of voltage sweep direction was considered. Therefore, all these results suggest that [EMIm]SCN might be a more suitable electrolyte for EDLC, compared with [EMIm](CF<sub>3</sub>SO<sub>2</sub>)<sub>2</sub>N.

Fig. 2 presents the results from four consecutive charging–discharging cycles conducted for the EDLC with [EMIm]SCN as the electrolyte. The well reproduced charge/discharge cycles, in terms of both the charge/discharge time and the shape of each individual cyclic voltammogram strongly suggests the excellent electrochemical stability of this capacitor. However, it is noteworthy that a slight voltage change was observed at the beginning of the charge and discharge stage [see insertion figure], which are considered to be usually associated with ohmic loss [24] of EDLC. In addition, a variation in the voltage, which

showed an increase for the charge and a decrease for the discharge stage, was observed.

The  $I$ – $V$  curves obtained at different voltage scan rates were compared in Fig. 3. It appears that the contribution of equivalent series resistance (ESR) [25] increased as voltage scan rate increased, as indicated by the gradual distortion of the  $I$ – $V$  curves, which normally display a nearly rectangular shape for a capacitor. However, this became significant only when the scan rate was increased to  $10 \text{ mV s}^{-1}$ . Using the same scan rate of  $5 \text{ mV s}^{-1}$ , the cyclic voltammograms were obtained for different voltage spans (Fig. 4). It can be seen that for the voltage ranges tested, the curves all showed a box-like shape, as expected for capacitors but with some variations being evident. At  $2.5 \text{ V}$ , a clear peak was observed, whilst at  $1.5 \text{ V}$  this peak was hardly detectable. However, no faradaic process actually arose in the system, although the electrochemical stability window was within the range of  $2.6 \text{ V}$ . This might be due to the

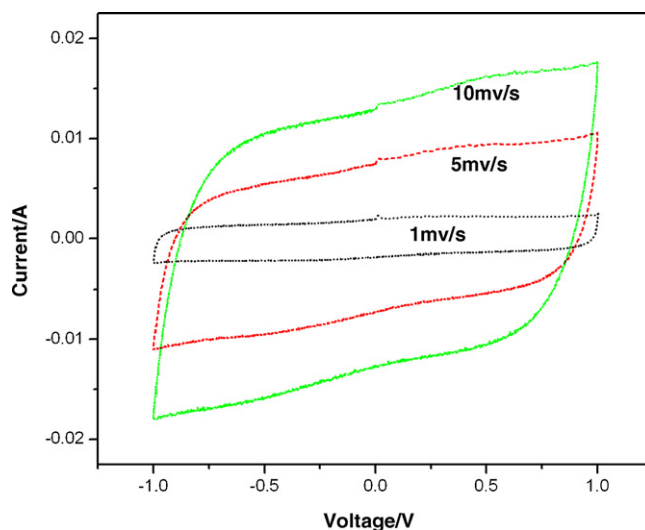


Fig. 3. Cycle voltammetry of EDLC composed of activated carbon and [EMIm]SCN at different sweep rate range. Room temperature.

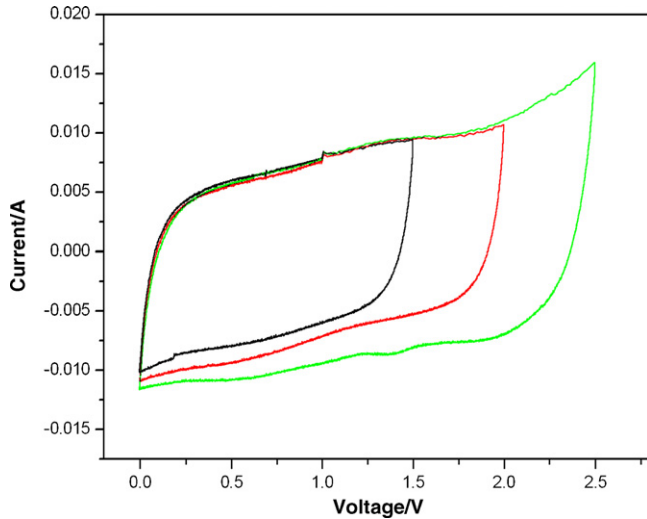


Fig. 4. Cycle voltammetry of EDLC composed of activated carbon and [EMIm]SCN at different potential range. Room temperature.

use of activated carbon powders as the EDLC electrode material, as opposed to the glassy carbon which was usually applied for the measurement of the stability electrochemical window of electrolytes. Consequently, the properties of the ACP, such as variable degrees of graphitization, pore size distributions and surface functionalities might all contribute to the properties of a given electrochemical process. For instance, the functional groups at the carbon surface could undergo redox pseudofaradaic processes, which can lead to variable deviations, increasing with rising potential, of cyclic voltammograms from their regular form [26].

### 3.3. Influence of current density on specific capacitance

The discharge curves and their associated capacitance were compared in Figs. 5 and 6, respectively, for different constant current densities, and it was indicated that the specific

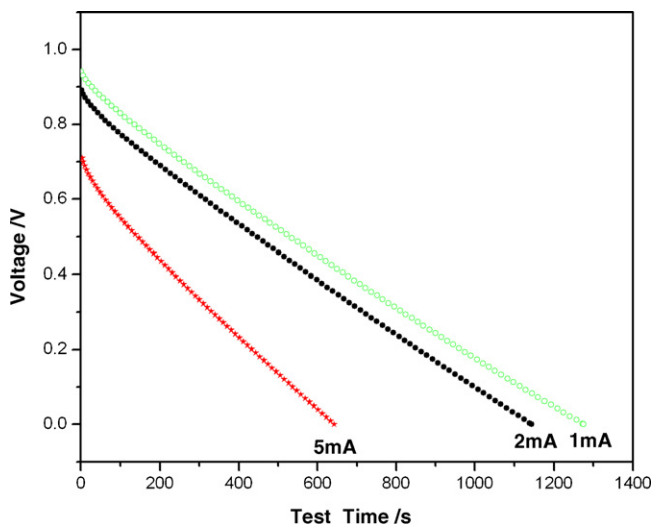


Fig. 5. Constant current discharge profiles of EDLC composed of activated carbon and [EMIm]SCN at different constant current densities. Room temperature.

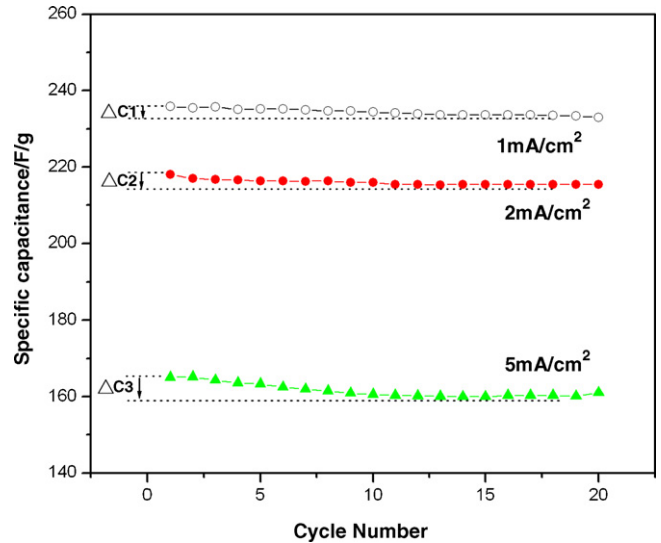


Fig. 6. Discharge capacitance vs. current density plots of EDLC composed of activated carbon and [EMIm]SCN. Room temperature.

capacitance decreased with increasing current intensity, from  $233 \text{ F g}^{-1}$  obtained at  $1 \text{ mA}$  to  $215$  and  $160 \text{ F g}^{-1}$  at  $2$  and  $5 \text{ mA}$ , respectively, which corresponds well to increasingly shorter durations of discharge. In addition, a sharp voltage drop was observed when current density was increased to  $5 \text{ mA}$ , indicating that the internal resistance of the EDLC increased dramatically at high current densities. The similar phenomenon is also observed by other investigators [27].

As shown in Fig. 6, the  $\Delta C$ , which was defined as the difference between the specific capacitance, relating to the first cycle, and the steady state, respectively, also showed an increase with current density. This might be associated with the mass transfer at the interface between the ACP and ionic liquid. Indeed, when the EDLC was charged at a lower current density, the charge-carrying ionic liquid was actually allowed more time to access the deeper pore structures of the ACP and, accordingly, the formation of double layer structures occurred at finer and more pronounced scales, and this is opposed to what might arise from using a higher charging current density where the mass transfer, and therefore the formation of double layers, most probably ended at macro- and/or meso-pore scales. Consequently, the discharge time, specific capacitance and stability of an EDLC often decline with increasing density of charging current employed [28].

The relation between specific capacitance and current density is presented in Fig. 7 for the EDLC capacitors examined, which can be expressed using the following equation:

$$y = kx + b \quad (3)$$

where  $y$  is the specific capacitance,  $x$  the current density, and the constant  $k$  and  $b$  represents the slope and intercept, respectively. Using linear regression analysis, the constants were obtained as  $-18.3$  for the slope ( $k$ ) and  $251.3$  for the intercept ( $b$ ).

Generally, the relationship between specific capacitance and current density is non-linear. The surprising linear relation observed under the conditions employed in this investigation

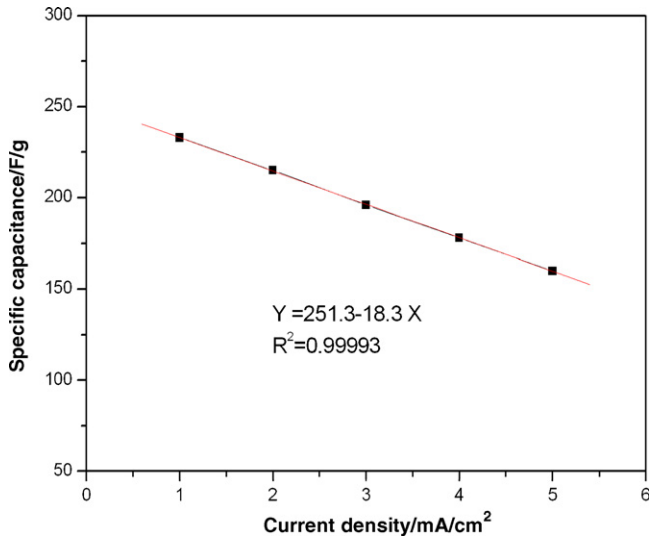


Fig. 7. Variations in the specific capacitance of ACP (specific area 3250 m<sup>2</sup> g<sup>-1</sup>) with current density of EDLC with [EMIm]SCN. Room temperature.

might indicate a current leakage during the charge/discharge processes, which could be accounted for by concentration gradients of electrolytes at the electrolyte/electrode interface. During the charging process, ion concentrations build up at the interface whereas, during discharging process, they start to decline and eventually disappear upon the finish of discharging. This process would lead to a leakage current being generated, and its intensity rises higher with increasing density of charging current, which obviously determines the gradient of ion concentration at the electrolyte/electrode interface. In addition, the extremely high surface area of the activated carbon powders used (3250 m<sup>2</sup> g<sup>-1</sup>) may also contribute to the generation of leakage current at such a level that proves high enough to change the relationship between specific capacitance and current density.

### 3.4. Influence of voltage on specific capacitance

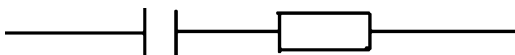
The capacity of the charge storage of an EDLC with [EMIm]SCN was found highly dependent on the voltage applied. Assuming that the electrochemical process of an EDLC could be treated as a series combination of resistors (*R*) and capacitors (*C*) (see Scheme 1) and according to the Ohm's law:

$$V(t) = I(t) \times Z(t) \tag{4}$$

where *Z*(*t*) is internal resistance and time-dependent for a simple RC circuit.

The volume of charge stored in an EDLC (*Q*) can be calculated using the following the equation:

$$Q(t) = C[V_c(t) - V_0] \tag{5}$$



Scheme 1. Equivalent circuit for an EDLC.

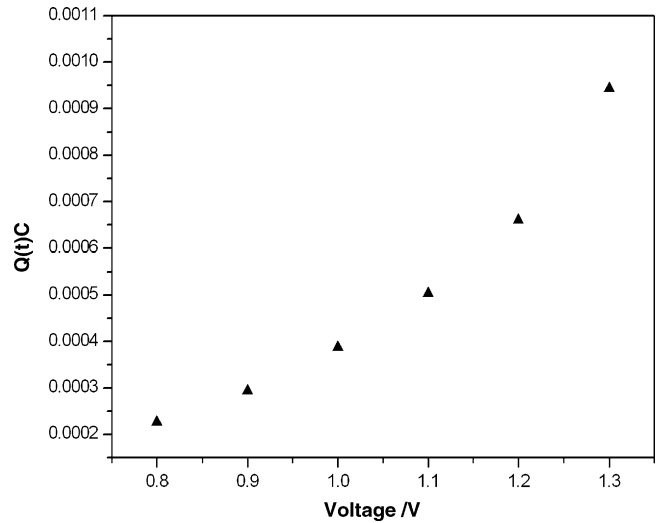


Fig. 8. Relationship between charges stored and applied voltage at room temperature.

where *V*<sub>0</sub> is the initial voltage and *V*<sub>*c*</sub>(*t*) is the voltage at the time of *t* and is a fraction of the voltage *V*<sub>*p*</sub>(*t*) applied to an EDLC:

$$V_c(t) = V_p(t) - I(t) \times Z(t) \tag{6}$$

From Eq. (5) into Eq. (6), the following equation can be obtained:

$$Q(t) = C[V_p(t) - V_0] - I(t) \times Z(t) \times C \tag{7}$$

*V*<sub>0</sub> can be given zero here, so Eq. (7) can further be simplified as follows:

$$Q(t) = C \times V_p(t) - I(t) \times Z(t) \times C \tag{8}$$

Based on Eq. (8), the charge stored in the EDLC, *Q*(*t*), was calculated and plotted against applied voltage (*V*<sub>*p*</sub>(*t*)) (Fig. 8), and the specific capacitance obtained for each individual voltage compared in Fig. 9. It is evident that the volume of charge stored *Q*(*t*), and hence the specific capacitance, increased

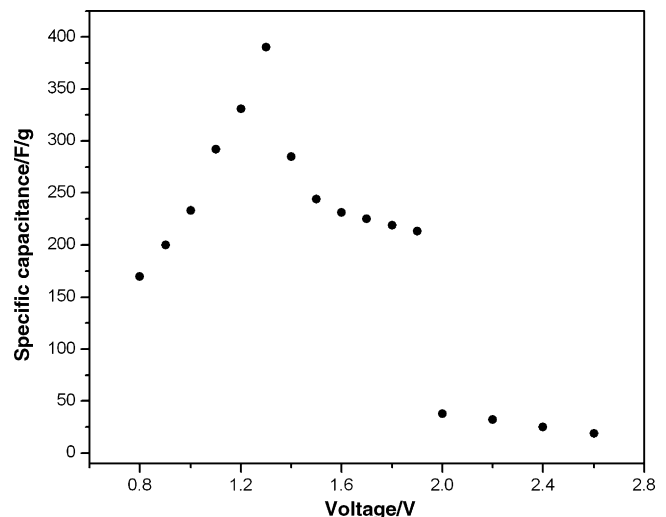


Fig. 9. Relationship between voltages and specific capacitance at room temperature.



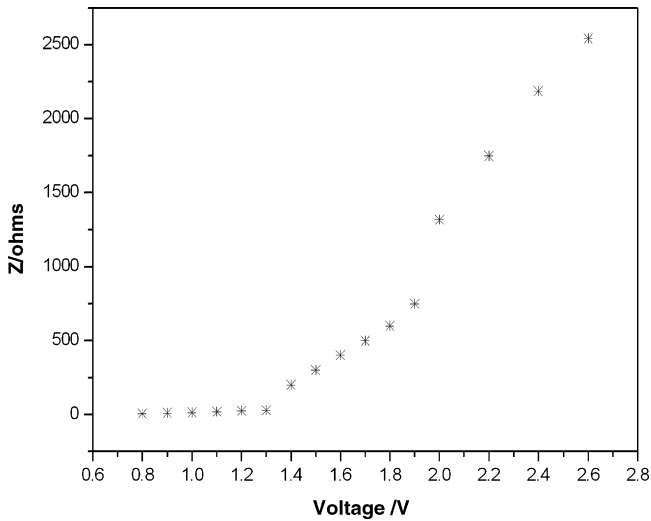


Fig. 10. Relationship between voltages and internal resistance at room temperature.

dramatically with the voltage applied to the EDLC examined with [EMIm]SCN as the electrolyte. However, as indicated in Fig. 9, when the applied voltage reached 1.3 V, a further increase in the voltage resulted in a sharp decrease in the specific capacitance, and this is in accordance with the simultaneous sharp increase in the internal resistance of the EDLC as shown in Fig. 10. This is especially noticeable when the voltage was higher than 2.0 V. Therefore, it seems that at high voltages (e.g. >2 V), the increase in the charge stored, and therefore the capacitance of the EDLC, can be largely compromised by an induced sharp rise in the internal resistance. Indeed, as revealed in Fig. 11, the variation of specific capacitance with charge stored in the EDLC does not follow the same trend for different voltages applied. At high-applied voltages, the variation in the specific capacitance with voltage was actually significantly less than that in the charge stored, because of the sharp rise in the internal resistance induced at such voltages. It is also noteworthy

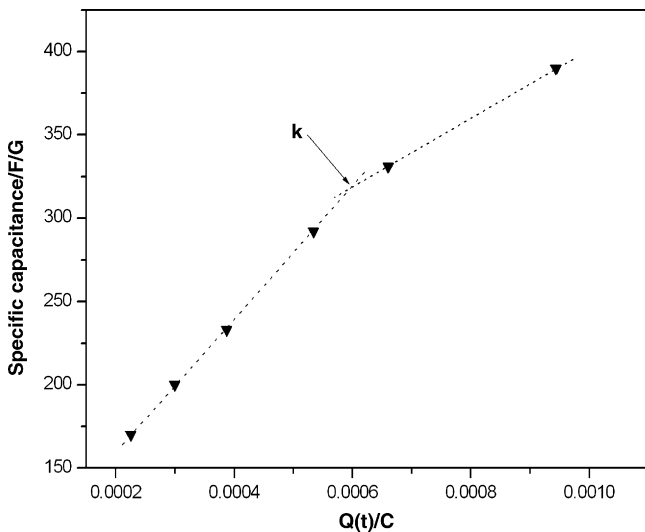


Fig. 11. Relationship between charge stored and specific capacitance at room temperature.

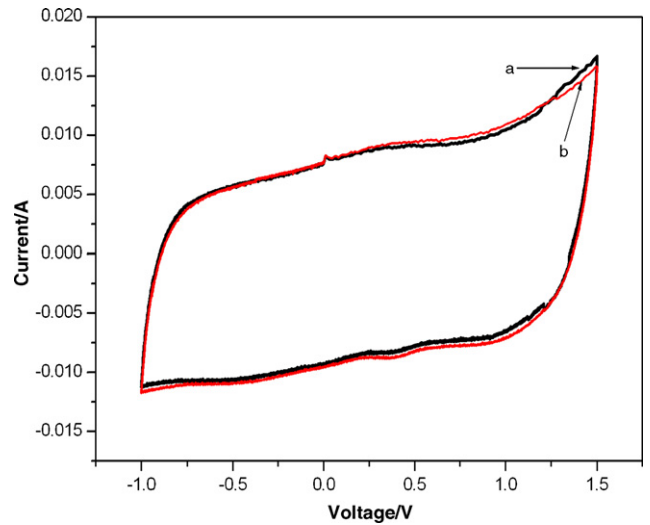


Fig. 12. Cyclic voltammograms of the EDLC before and after 300 cyclic operations (a, the initial and b, the 300th charge/discharge cycle).

thy that the sharp rise of internal resistance may also indicate a possible decomposition of the electrolyte arising from the high voltages.

### 3.5. Stability test of the EDLC performance with operation time

Long cycle-life is desired for EDLCs. Fig. 12 compares the cyclic voltammograms of the EDLC before and after it was subjected to 300 cyclic operations. Obviously, the voltammogram of the EDLC for the 300th cyclic operation were virtually unchanged, and this highlights the extraordinary performance of [EMIm]SCN as the electrolyte. However, as indicated by Fig. 12, a larger degree of polarization was observed after the EDLC was subjected to 300 cycles, indicating that a possible

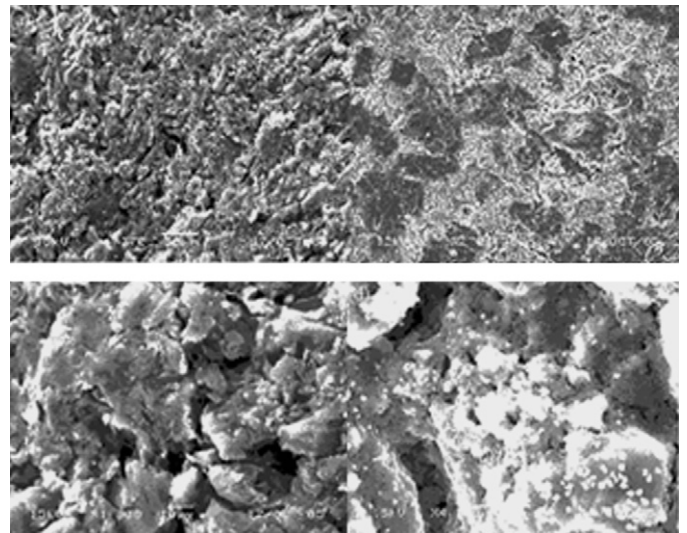


Fig. 13. Surface morphologies of ac electrodes before (a) and after (b) a 300 charge/discharge cycle measurement, and surface characteristic of ac electrodes before (c) and after (d) an increase voltage charge/discharge cycle measurement.

blockage of some pore structures might have occurred and resulted in an increase in internal resistance. To examine the possible changes of the ac electrodes after being subjected to these cyclic tests, the surface morphologies of the electrodes were analyzed using scanning electron microscope and presented in Fig. 13. It seems that the surface particles of the ac electrodes, after the repeated charge/discharge cycles, became noticeably finer and thus obtained a more uniform size distribution, giving rise to the higher surface uniformity of the electrodes that could potentially improve the charge-storage and charge-delivering capability of the electrodes. A further examination of the electrode surface achieved by increasing the SEM resolution to 4000 (Fig. 13d) revealed that there were some crystal structures formed on the ac electrode surface, which could be attributable to decomposition product(s), most likely imidazole derivative(s), of [EMIm]SCN when charged/discharged at elevated voltages.

#### 4. Conclusions

The preparation and use of ionic liquid [EMIm]SCN as an EDLC electrolyte has been investigated with great success, and the factors governing its electrochemical properties and specific capacitance have been examined. The extremely high specific capacitance, uncompromised performance and stability of the AC/[EMIm]SCN EDLC against repeated cyclic charge/discharge operations demonstrate that [EMIm]SCN can be an extraordinary EDLC electrolyte and possesses some unique characteristics when compared with other ionic liquids reported so far. However, as with other ionic liquids, the use of elevated voltage during charge/discharge cycles can potentially cause, though not significantly, the composition of this electrolyte at the cost of a possible increase in the EDLC internal resistance.

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