

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 (EDLC) 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.

Keywords: activated carbon; Electrochemical Double Layer Capacitor; Cyclic voltammetry; Galvanostatic charging and discharging

1. Introduction

Room temperature ionic liquids (RTIL) ^[1-2], 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, electric double layer capacitors (EDLC) ^[3-4], and titanium oxide dye-sensitized solar cells. However, their practical application has often been limited by their high viscosity at ambient temperature. For example, it is much lower viscous at room temperature than 1-ethyl-3-methylimidazolium tetrafluoroborate ([EMIm]BF₄)^[5] was used more frequently than [BMIm]PF₆ and [BMIm]BF₄.

1-ethyl-3-methylimidazolium thiocyanate [EMIm]SCN has extremely high conductivity and low viscosity at room temperature compared with other ionic liquids e.g. [EMIm]BF₄, [BMIm]BF₄ and organic electrolytes, so it can be expected to be used as an EDLC electrolyte. 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.

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 3250m²/g were prepared from petroleum coke (Jin Zhou, Liao ning, China), via reactions with KOH (m_{petroleum coke}:m_{KOH}=1: 6) for 1.5h at 800°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, 90cm³ ethylbromide was first slowly added to 35cm³ 1-methylimidazole under stirring conditions. The mixture was further stirred for 3 h at ambient temperature before reflux at 70°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 100ml portions of 1,1,1-trichloroethane and then dried at 70°C under reduced pressure. The yield of (EMIm)Br from this preparation was 69.3g (57.6 wt%).

Next, 7.6 g of NH₄SCN 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 NH₄Br precipitate by filtration and the solvent by evaporation at 60°C under reduced pressure, the liquid salt, (EMIm)SCN was obtained and further dried at 80°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) (85wt%), carbon black (5wt%) (CB) and Polyvinilidene fluoride (PVDF) (10wt%) 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. 1 in the voltage range of 0.1v~0.4v:

$$C = (i \times \Delta t) / \Delta v \quad \text{Eq. 1}$$

where *i* is the discharge current (A) and Δt is the time duration (s) corresponding to voltage change in the discharge cycle. The specific capacitance of ACP (*C'*) was obtained from the following equation (2):

$$C' = C / 2m \quad \text{Eq. 2}$$

Where *C* is the specific 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 N₂ adsorption isotherms at 77K (Sorptomatic1990, Italy). 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 20kv.

3. Results and discussion

3.1 Physical properties of ionic liquid

Table 1 presents some physical properties of [EMIm]SCN, and other electrolytes such as aqueous H₂SO₄^[6] and the organic electrolyte of (CF₃SO₂)₂NLi (0.1M in PC:DME(1:2v/v))^[7] for comparison. It can be seen that the conductivity of [EMIm]SCN was 2.1 S • m⁻¹, being about 1/40 of that for 35 wt% H₂SO₄ and about 5 times that for 0.1M (CF₃SO₂)₂NLi in PC:DME(1:2v/v). The electrochemical window of [EMIm]SCN was higher than that of 35wt%H₂SO₄ but lower than 0.1M (CF₃SO₂)₂NLi in PC:DME(1:2v/v), indicating that the electrochemical performance of [EMIm]SCN might lie between the two electrolytes.

Table 1. Properties of various kinds of electrolyte

	Viscosity at RT /mPa s	Conductivity /S • m ⁻¹	Electrochemical window /V
35wt%H ₂ SO ₄ ^[6]	2.5	84.8	1.23

0.1M (CF ₃ SO ₂) ₂ NLi in PC:DME(1:2v/v) ^[7]	—	0.4	5.2
[EMIm]SCN	21	2.1	2.60

3.2 Electrochemical performance of ionic liquid as electrolyte

Barisci and co-workers^[8] investigated the electrochemical performance of 1-ethyl-3-methylimidazolium bis(trifluoromethanesulphonyl)amide ([EMIm](CF₃SO₂)₂N), and obtained an irregular rectangular cyclic voltammogram at a scan rate of 50 mV/s. At the same time, a peak at about 1.0V was observed, indicating large internal resistance. However, for ideal double layer electrodes, their cyclic voltammograms should normally occur 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 -1.0V to 1.0V, 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](CF₃SO₂)₂N.

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^[9] 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.

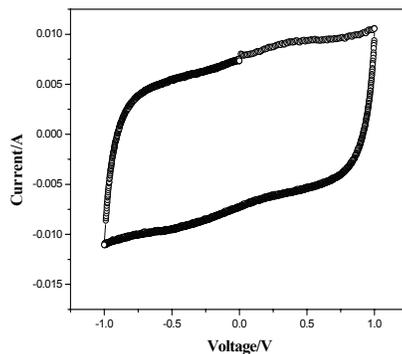


Figure 1. Cyclic voltammogram of EDLC composed of activated carbon and [EMIm]SCN. Sweep rate: 5mV/s; Room temperature

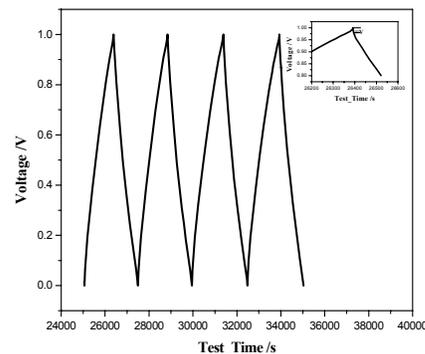


Figure 2. Charging-discharging characteristic of EDLC composed of activated carbon and [EMIm]SCN. Current density: 2mA; Room temperature

contribution of equivalent series resistance (ESR)^[1] 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 mv/s.

Using the same scan rate of 5 mV/s, the cyclic voltammetric curves 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 2.5V, a clear peak was observed, whilst at 1.5V this peak was hardly detectable. However, no faradaic process actually arose in the system, although the electrochemical stability window was within the range of 2.6V. This might be due to the use of activated carbon powders (ACP) 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 ^[11].

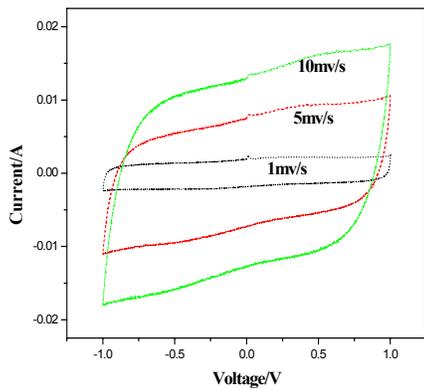


Figure 3. Cycle voltammetry of EDLC composed of activated carbon and [EMIm]SCN at different sweep rate range. Room temperature.

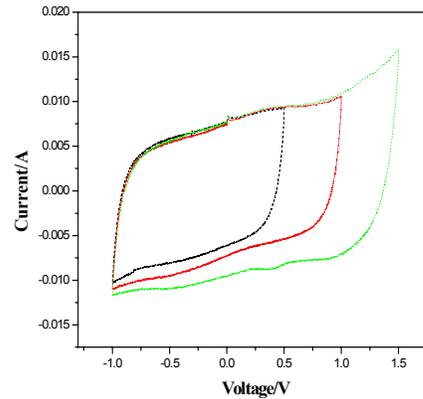


Figure 4. Cycle voltammetry of EDLC composed of activated carbon and [EMIm]SCN at different potential range. Room temperature.

for different constant current densities, and it was indicated that the specific capacitance decreased with increasing current intensity, from 233 F/g obtained at 1mA to 215 and 160F/g at 2 mA and 5 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 mA, indicating that the internal resistance of the EDLC increased dramatically at high current densities. The similar phenomenon is also observed by other investigators ^[12].

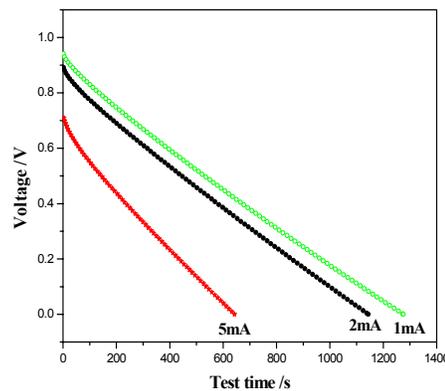


Figure 5. Constant current discharge profiles of EDLC composed of activated carbon and [EMIm]SCN at different constant current densities. Room temperature.

As shown in Fig. 6, the ΔC , 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 [13].

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:

$$y=kx+b \quad \text{Eq. 3}$$

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 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 ($3250 \text{ m}^2/\text{g}$) 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.

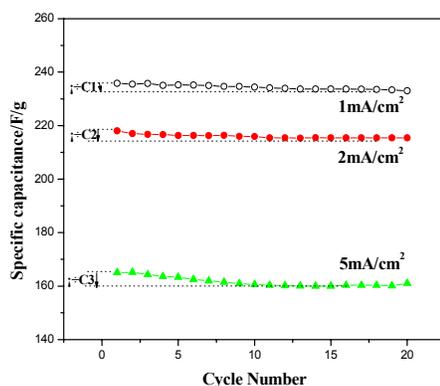


Figure 6. Discharge capacitance vs. Current density plots of EDLC composed of activated carbon and [EMIm]SCN. Room temperature.

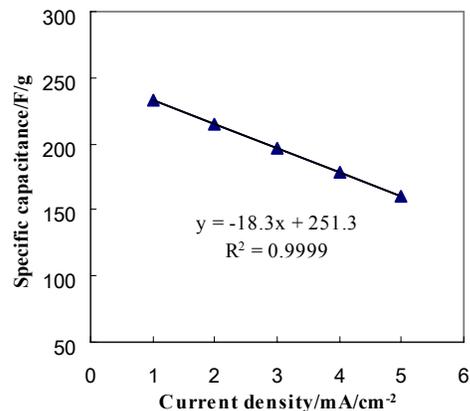


Figure 7. Variations in the specific capacitance of ACP (specific area $3250 \text{ m}^2/\text{g}$) with current density of EDLC with [EMIm]SCN. Room temperature.

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) and according to the Ohm's law:

$$V(t)=I(t)*Z(t) \quad \text{Eq. 4}$$

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,;

$$Q(t)=C[V_c(t)-V_0] \quad \text{Eq. 5}$$

Where V_0 is the initial voltage and $V_c(t)$ the voltage at the time of t and is a fraction of the voltage $V_p(t)$ applied to an EDLC:

$$V_c(t)=V_p(t)-I(t)*Z(t) \quad \text{Eq. 6}$$

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

$$Q(t)=C[V_p(t)-V_0]-I(t)*Z(t)*C \quad \text{Eq. 7}$$

V_0 can be given zero here, so Eq.7 can further be simplified as follows:

$$Q(t)= C*V_p(t)-I(t)*Z(t)*C \quad \text{Eq. 8}$$

Based on Eq. 8, the charge stored in the EDLC, $Q(t)$, was calculated and plotted against applied voltage $V_p(t)$ (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 the specific capacitance increased 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 1.3V, 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 2.0v. 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 that the sharp rise of internal resistance may also indicate a possible decomposition of the electrolyte or the functional groups at the carbon surface arising from the high voltages.

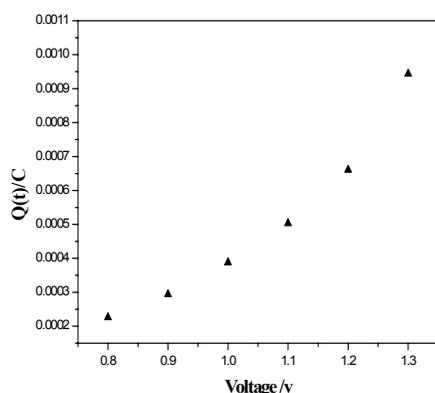


Figure 8. The relationship between charge stored and applied voltage at room temperature.

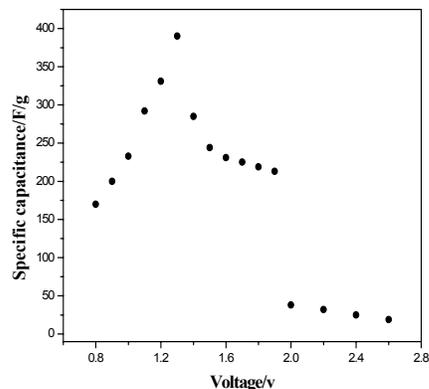


Figure 9. The relationship between voltages and specific capacitance at room temperature.

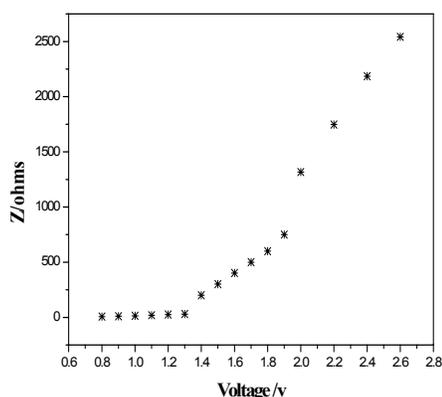


Figure 10. The relationship between voltages and internal resistance at room temperature.

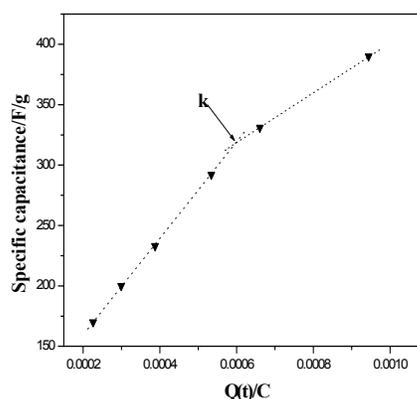


Figure 11. The relationship between charge stored and specific capacitance at room temperature.

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 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 (SEM) 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.

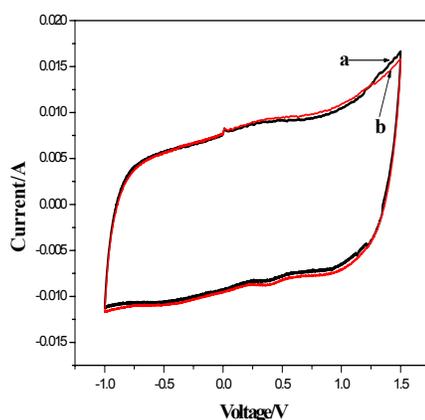


Figure 12. The cyclic voltammograms of the EDLC before and after 300 cyclic operations (a, the initial and b, the 300th charge/discharge cycle).

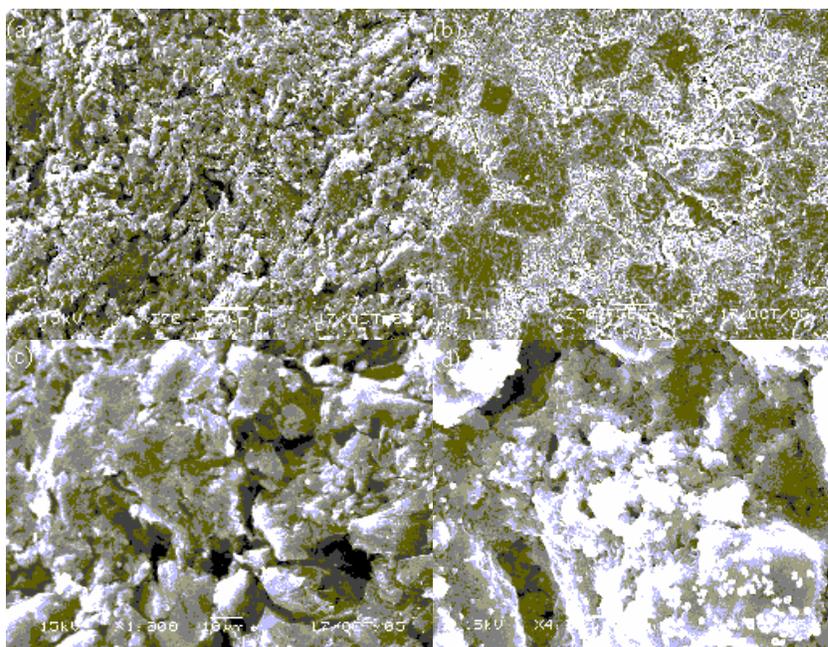


Figure 13. Surface morphologies of AC electrodes before (a) and after (b) an 300 charge/discharge cycle measurement, and surface characteristic of AC electrodes before (c) and after (d) an increase voltage charge/discharge cycle measurement

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 of EDLC against repeated cyclic charge/discharge cyclic 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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