



## A strategy for immobilisation of carbon nanotubes homogenised in room temperature ionic liquids on carbon electrodes

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### ABSTRACT

Functionalised multi-walled carbon nanotubes (MWCNT) were homogenised in the room temperature ionic liquids (RTILs) 1-butyl-3-methylimidazolium bis(trifluoromethane)sulfonimide (BmimNTF<sub>2</sub>), 1-butyl-1-methylpyrrolidinium bis(trifluoromethane)sulfonimide (BmpyNTF<sub>2</sub>) and 1-butyl-3-methylimidazolium nitrate, and the composite obtained was applied on the top of glassy carbon or carbon film electrode substrates. The modified electrodes were characterised electrochemically in aqueous electrolytes and ionic liquids using cyclic voltammetry and electrochemical impedance spectroscopy and the model redox couples potassium hexacyanoferrate and ferrocene were used for electrode characterisation in aqueous and RTIL media, respectively. It was found that the combination of MWCNT with BmimNTF<sub>2</sub> gave the best composite which augurs well for application in sensors and biosensors.

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### 1. Introduction

In recent years, room temperature ionic liquids (RTILs), have been explored with a view to identifying their advantages when used in conjunction with electrocatalytic and bioelectrocatalytic processes. RTILs are organic or mixed organic–inorganic salts that have melting points less than 100 °C, and they are usually liquid at room temperature [1–3]. Because of their low vapour pressure and resulting ease of containment, RTILs are often considered to be green solvents. Moreover, these solvents do not deactivate labile biologically active molecules as do other non-aqueous solvents [4], and their ability to dissolve a wide range of dissimilar substrates facilitates the reaction of polar substrates such as sugars [2]. RTILs are also frequently used as clean reaction media for organic synthesis [1–3]. In the last few years they have become more attractive in other fields such as in fundamental electrochemical studies of organic compounds and inorganic compounds [5–15], formation of metal nanostructures [16], analytical chemistry [17] including sensors [3,18–21], bioanalytical chemistry [2,3,22–28], and for electrochemical biosensors [3,29–31].

Carbon nanotubes (CNTs) have found wide application in different fields of electrochemistry and analytical science due to their unique electronic and mechanical properties [32,33]. As is well known, CNTs are formed by one or multiple cylindrical layers of

graphene sheets: single-walled (SWCNT) and multi-walled (MWCNT) carbon nanotubes. There are two models of MWCNT: (1) Russian Doll model, sheets of graphene are arranged in concentric cylinders, e.g. a smaller SWCNT within a larger SWCNT; (2) parchment model, a single sheet of graphene rolled in around itself, resembling a scroll of parchment or a rolled-up newspaper. The interlayer distance in MWCNT is close to the distance between graphene layers in graphite, approximately 3.3 Å (330 pm) [34]. Some properties of CNTs can be adjusted by their chemical modification, mainly by the following strategies: (1) functionalisation of the defects located on the sidewall and the rims; (2) non-covalent interactions; (3) sidewall covalent functionalisation; and (4) endohedral inclusion [33,34]. Unmodified and modified CNTs have been also employed in important applications in electronics, medicine, aerospace industry, etc., which has prompted the need for analytical methodologies to characterise and control the quality of these nanomaterials. The properties of CNTs depend on the methodology of their synthesis [32].

CNTs have also been successfully used in electroanalytical applications, in particular electrochemical sensors and biosensors, due to their ability to promote electron transfer in electrochemical reactions [32–37]. The electrocatalytic effect has been attributed to the activity of edge-plane-like graphite sites at the CNT ends [32,35]. MWCNTs have a sidewall structure similar to the graphite basal plane of highly oriented pyrolytic graphite (HOPG), and the open end is similar to the edge plane of HOPG. Moreover, it has been also demonstrated that the electrocatalytic activity of MWCNTs strongly

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depends on the CNT fabrication method and on the dispersing agent used to immobilise CNTs on the electrode surface [34,36].

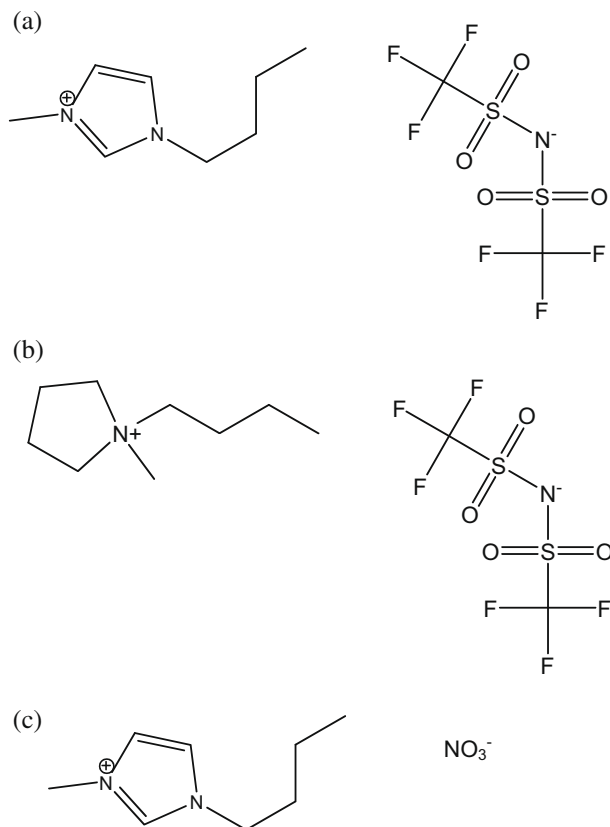
CNTs are used in electrochemistry as electrode modifiers and as separate composites. In both cases the binding material of CNTs, as well as the solvent for their solubilisation and homogenisation, is extremely important. There are several methods used to solubilise CNTs [38]; however, investigation of newer and simpler methods still continues. Recently, it has been observed that functionalised CNTs can be individually separated from each other as a suspension in RTILs due to interactions with the cationic part of the RTIL and a CNT-RTIL gel can easily be prepared using RTIL as binder [3,39–41]. A number of publications in the last few years concern the development of sensors and biosensors using CNT-RTIL gel [3,42–60]. Various RTILs were used for this purpose, but most of them possess the imidazolium cation [42–60] with either hexafluorophosphate ( $\text{PF}_6^-$ ) [42–49,51,53–59] or bis(trifluoromethane)sulfonimide ( $\text{NTF}_2^-$ ) [41,51] as anions.

In this work, a MWCNT-RTIL composite strategy was used for electrode modification. The modified electrodes were characterised electrochemically by cyclic voltammetry and electrochemical impedance spectroscopy in aqueous and RTIL solutions employing the model electroactive compounds potassium hexacyanoferrate and ferrocene for aqueous and non-aqueous media, respectively.

## 2. Experimental

### 2.1. Chemicals and solutions

The three room temperature ionic liquids 1-butyl-3-methylimidazolium bis(trifluoromethane)sulfonimide ( $\text{BmimNTF}_2$ ), 1-butyl-1-methylpyrrolidinium bis(trifluoromethane)sulfonimide



**Fig. 1.** Structure of ionic liquids used: (a) 1-butyl-3-methylimidazolium bistriflimide ( $\text{BmimNTF}_2$ ); (b) 1-butyl-1-methylpyrrolidinium bistriflimide ( $\text{BmpyNTF}_2$ ); (c) 1-butyl-3-methylimidazolium nitrate ( $\text{BmimNO}_3$ ).

( $\text{BmpyNTF}_2$ ) and 1-butyl-3-methylimidazolium nitrate ( $\text{BmimNO}_3$ ), structure presented in Fig. 1, were synthesised by ion metathesis of the corresponding chloride salts with  $\text{LiNTF}_2$  in acetonitrile. The ionic liquids were then dissolved in acetonitrile and impurities removed with activated carbon, as described elsewhere [60].

Ferrocene and  $\text{K}_3\text{Fe}(\text{CN})_6$  were obtained from Merck (Germany); KCl was purchased from Fluka (Switzerland). Multi-walled carbon nanotubes: purity 95%, diameter 30 nm, and length 1.5  $\mu\text{m}$ , were from NanoLab (USA). Milli-Q nanopure deionised water (resistivity  $\geq 18 \text{ M}\Omega \text{ cm}$ ) was used for the preparation of aqueous solutions. Electrolyte solutions were deoxygenated by bubbling ultrapure  $\text{N}_2$  gas through the solution.

### 2.2. Pretreatment of carbon nanotubes

MWCNT were purified and functionalised by stirring in 2 M nitric acid solution for 20 h. The solid product was collected on a filter paper and washed several times with nanopure water until the filtrate pH became nearly neutral. The functionalised MWCNT obtained were then dried in an oven at  $\sim 80^\circ\text{C}$  for 24 h. This procedure was performed to ensure complete removal of transition metal ion catalyst, used in the production of nanotubes, as well as of amorphous carbon. Nitric acid treatment of carbon nanotubes introduces  $-\text{COOH}$  groups at their ends, or at the sidewall defects in the nanotube structure [37,61].

### 2.3. Preparation of the CNT-RTIL composite

Functionalised CNT, MWCNT-COOH, were mixed in an agate mortar with RTIL in different proportions in order to optimise the mixing conditions for stable composite formation in terms of gelation time, its hardening and mechanical stability. The components were thoroughly mixed for 30 min and then left for 30 min to stabilise. In the best composite, which contained MWCNT-COOH and  $\text{BmimNTF}_2$ , the mixture prepared contained 0.3 mg of MWCNT-COOH and 6  $\mu\text{L}$  of  $\text{BmimNTF}_2$ .

### 2.4. Electrode preparation

Electrodes were made from either glassy carbon (GC) disc (2.5 mm diameter) or carbon film resistor ( $2.0 \pm 0.1 \Omega$  resistance) electrodes.

The GC disc electrode was polished with diamond slurry of particle size of 3 and 1  $\mu\text{m}$  (Kemet, UK), with sonication in water for 3 min after each polishing step.

The carbon film resistors were fabricated from ceramic cylinders of external diameter 1.5 mm and length 6.0 mm by pyrolytic deposition of a thin carbon film. One of the tight-fitting metal caps, joined to a thin conducting wire, was removed from one end of the resistor and the second one was sheathed in plastic tubing, adhered with epoxy resin as described previously [62,63], covering also the sides of the cylinder in order to have a disc electrode. In this way, the exposed electrode geometric area was  $\sim 0.020 \text{ cm}^2$ .

Electrodes were modified with carbon nanotubes by gently applying the CNT-RTIL mixture with a spatula on the top of the electrode and smoothing the surface. The electrodes were left to cure for 24 h at room temperature in order to be more stable mechanically.

### 2.5. Methods and instruments

The three-electrode electrochemical cell of volume 10 ml (aqueous solutions) or 300  $\mu\text{L}$  (RTIL solutions) contained a carbon film or glassy carbon working electrode modified with carbon nanotubes, a platinum wire as counter electrode and a saturated calomel electrode (SCE) (in aqueous solutions) reference electrode or a silver

wire covered with silver chloride (in ionic liquid) as solid-state pseudo-reference electrode (Ag/AgCl<sub>ss</sub>).

Cyclic voltammetry (CV) measurements were performed using a computer-controlled  $\mu$ -Autolab Type II potentiostat/galvanostat with GPES 4.9 software (Eco Chemie, Netherlands). All solutions were deoxygenated by nitrogen bubbling for 10 min.

Electrochemical impedance spectroscopy (EIS) measurements were carried out in the same cell with a PC-controlled Solartron 1250 Frequency Response Analyser coupled to a Solartron 1286 Electrochemical Interface (Solartron Analytical, UK). A sinusoidal voltage perturbation of 10 mV amplitude was applied over the frequency range 65 kHz to 0.1 Hz with 10 measurement points per frequency decade; integration time was 60 s using short integration mode. Fitting to electrical equivalent circuits was performed with ZView 2.4 software (Solartron Analytical, UK).

### 3. Results and discussion

#### 3.1. Optimisation of composition of CNT-RTIL composite

BmimNTF<sub>2</sub>, BmpyNTF<sub>2</sub>, and BmimNO<sub>3</sub> were used to produce a composite with MWCNT by mixing them in various ratios. The mixture formed was applied on the top of a glassy carbon and/or carbon film electrode and the chemical and mechanical stability of the CNT-composite was evaluated, tests being conducted with cyclic voltammetry in KCl solution.

Evaluation of the CNT-BmimNO<sub>3</sub> composite showed that it was unstable, which can be attributed to its hydrophilicity, with partial dissolution in aqueous electrolyte solution, so that it could not be used for CNT-RTIL modified electrode preparation. The identity of the ions has a large influence on film stability – in ionic liquid media more hydrophobic ions will tend to exchange with the ionic liquid, leading to a less stable film, whereas more hydrophilic ones will tend to exchange with aqueous media.

CNT-BmpyNTF<sub>2</sub> composites made with various ratios also exhibited no satisfactory result due to mechanical instability – the composite had rather poor adhesion to the electrode, and the film was cracked and became detached over time. In this case, it probably happened due to the hydrophobicity of BmpyNTF<sub>2</sub>, evidenced by the greater difficulty in wetting the carbon surface. Although a stable MWCNT-BmpyNTF<sub>2</sub> paste was obtained previously [41], it was in the form of a bulk paste and not as a thin film electrode modification.

CNT-BmimNTF<sub>2</sub> composites exhibited the best properties, in terms of both mechanical stability and curing time for MWCNT homogenisation. Thus, this RTIL was used for further composition optimisation. The best gelation time and stability of the CNT-RTIL film was found to be MWCNT:BmimNTF<sub>2</sub> 1:20 mass/volume fraction ratio. Films formed in such a way on glassy carbon were stable for a few weeks in aqueous solution, as well as under dry conditions in air. It should be noted that on carbon film electrodes the mechanical stability was only one week in aqueous solution, although it was stable for several weeks under dry conditions, showing the weaker adhesion of the composite to the carbon film caused by the different roughness of these electrode surfaces [64].

In this context it should be noted that stable bulk pastes were prepared from graphite powder and 1-butyl-3-methyl-imidazolium hexafluorophosphate and other imidazolium based RTILs without hydrophilic characteristics [59], which is in agreement with our observations.

#### 3.2. Electrochemical characterisation of MWCNT-modified electrodes

##### 3.2.1. Aqueous medium

MWCNT-BmimNTF<sub>2</sub> modified glassy carbon and carbon film electrodes were characterised in aqueous 0.1 M KCl solution. As

seen from Fig. 2, the capacitive current is rather large, as was already reported by several authors at CNT-modified electrodes [41,65,66]. This was more easily visible at CFEs and was probably related to a higher CNT loading at this electrode substrate. The potential window was found to be broader at GCE (from –1.4 to +1.2 V) than at CFE (from –1.2 to +1.0 V vs. SCE). Moreover, CNT-modified electrodes were more sensitive to oxygen reduction than at carbon electrodes without CNT, and the oxygen reduction peak was observed at –0.44 V vs. SCE (not shown), which disappeared after solution deoxygenation.

Both types of modified electrode were characterised in aqueous solutions of 3 mM K<sub>3</sub>Fe(CN)<sub>6</sub> with 0.1 M KCl as electrolyte by CV and EIS. Fig. 3 presents CVs at both GCE and CFE modified with MWCNT-BmimNTF<sub>2</sub> at different scan rates. The electrochemical kinetics of the redox process of K<sub>3</sub>Fe(CN)<sub>6</sub> was different at both electrodes: at GCE/MWCNT-BmimNTF<sub>2</sub>, the potential difference between the redox peaks increasing much faster with increase in potential scan rate than at CFE/MWCNT-BmimNTF<sub>2</sub>. This might be related to the different thickness of the modifying layer at the two electrode substrates. Furthermore, the oxidation to reduction current ratio was close to 1 at GCE/MWCNT-BmimNTF<sub>2</sub> electrode and this ratio was much lower at the CFE/MWCNT-BmimNTF<sub>2</sub> electrode; again indicating poorer reversibility of the redox process at CFE (Fig. 3b). From the peak current density (after background subtraction) in Fig. 3 it is seen that the response at GC modified with MWCNT-BmimNTF<sub>2</sub> is similar to that at carbon film electrodes, although the background current (Fig. 2) was higher at CFE.

When measurements are performed at the electrode modified with CNT-RTIL in aqueous solution a liquid/liquid interface appears and there are three possible mechanisms of action: (i) direct electron transfer at CNTs reaching into the aqueous phase, (ii) ion exchange into the RTIL phase followed by electron transfer and escape by diffusion, and (iii) ion exchange into the RTIL phase followed by electron transfer without escape. Since rather high capacitive currents were obtained after background subtraction (i.e. subtracting the CV without hexacyanoferrate), the conclusion might be drawn from the shape of the voltammograms in Fig. 3, representing the more hydrophobic IL, that the electron transfer mechanism proceeds by ion exchange into the RTIL phase. Detailed studies of the electron transfer mechanism will be undertaken in the future.

Plots of peak current,  $I_p$ , vs. square root of scan rate, were linear. The electrochemical parameters, calculated from the CVs shown in

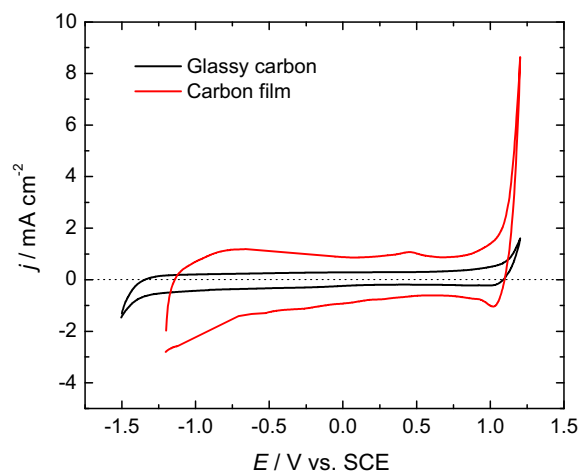
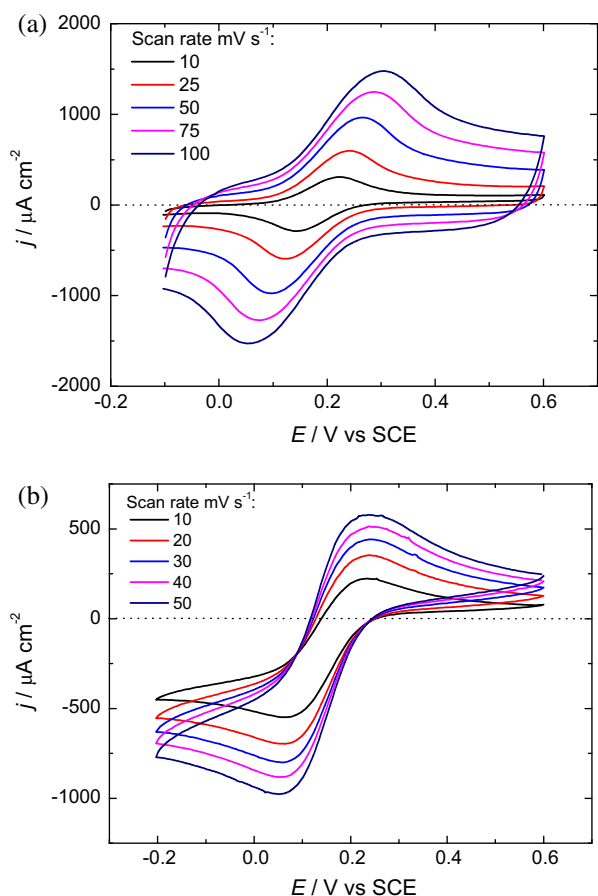


Fig. 2. CVs at glassy carbon (black line) and carbon film (red line) electrodes modified with MWCNT-BmimNTF<sub>2</sub> film in 0.1 M KCl deoxygenated solution. Scan rate 50 mV s<sup>-1</sup>. (For interpretation of the references to colour in this figure legend, the reader is referred to the web version of this article.)



**Fig. 3.** CVs, after background subtraction, at MWCNT-BmimNTF<sub>2</sub> modified (a) GC and (b) CF electrodes in 3 mM K<sub>3</sub>Fe(CN)<sub>6</sub> in 0.1 M KCl electrolyte solution.

Fig. 3, are presented in Table 1. The electroactive area was calculated from the Randles–Sevcik equation [67]:

$$I_p = 2.69 \times 10^5 n^{3/2} A_{EA} c D^{1/2} \nu^{1/2} \quad (1)$$

where  $n$  is the number of electrons,  $A_{EA}$  is the electroactive area in cm<sup>2</sup>,  $c$  is the concentration in mol cm<sup>-3</sup>,  $D$  is the diffusion coefficient in cm<sup>2</sup> s<sup>-1</sup> (in this case  $D = 6.2 \times 10^{-5}$  cm<sup>2</sup> s<sup>-1</sup> [68] was used), and  $\nu$  is the scan rate in V s<sup>-1</sup>. The values of  $A_{EA}$  increased after modification with CNTs, as expected, being 1.6 and 1.5 times larger than the geometric area of GCE and CFE, respectively. At both GCE and CFE the electrochemical redox process of hexacyanoferrate(III) was quasi-reversible and reversibility was even worse at CFE as seen from the peak potential difference ( $\Delta E$ ) and the reduction to oxidation current ratio ( $j_{red}/j_{ox}$ ) in Table 1.

Electrochemical impedance spectra recorded at different potentials in 0.1 M KCl solution in the presence of 3 mM K<sub>3</sub>Fe(CN)<sub>6</sub> at GCE/MWCNT-BmimNTF<sub>2</sub> are presented in Fig. 4a. CFE/MWCNT-BmimNTF<sub>2</sub> also exhibited very similar spectra except that the impedance values were slightly lower (not shown). The spectra obtained at GC modified electrodes exhibit typical spectra for CNT having two regions: a  $R_{ct}/C_{dl}$  time constant at high frequency range and a straight line at lower frequency (Fig. 4a).

The spectra at MWCNT-BmimNTF<sub>2</sub> modified electrodes were analysed using the Randles' equivalent circuit, often employed for CNT-modified electrodes [52,66,69], see Fig. 4b. The values of the parameters calculated from this fitting and normalised by geometric area are presented in Table 2. The solution resistance was  $24.0 \pm 0.2$  and  $20.5 \pm 0.3$   $\Omega$  cm<sup>2</sup> at GCE/MWCNT-BmimNTF<sub>2</sub> and CFE/MWCNT-BmimNTF<sub>2</sub>, respectively, at all potentials studied. The charge transfer resistance was also almost constant over the whole potential range at  $20 \pm 2$   $\Omega$  cm<sup>2</sup> at GCE/MWCNT-BmimNTF<sub>2</sub> electrode. Nevertheless, the double layer capacitance decreased with increase in electrode potential as seen from Table 2. These parameters depend on the film thickness. In this case the film was few micrometers thick but the exact thickness is difficult to determine. Nevertheless, these measurements were all performed with the same film, so that the thickness was the same and variations resulting from this dependence do not need to be considered.

### 3.2.2. Room temperature ionic liquid media

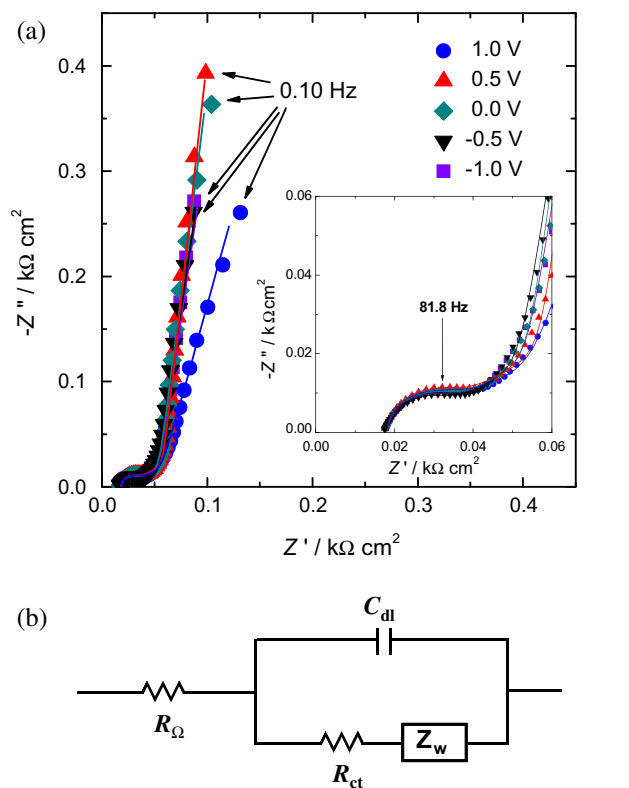
The electrochemical characterisation of MWCNT-BmimNTF<sub>2</sub> modified electrodes was also performed in the RTIL media of BmimNTF<sub>2</sub> and BmpyNTF<sub>2</sub>, which were chosen having in mind possible further application of this type of electrode for the development of the biosensors in non-aqueous media for the determination of water insoluble analytes. Surprisingly, the GC/MWCNT-BmimNTF<sub>2</sub> electrode performed well in BmimNTF<sub>2</sub> showing that the CNT layer formed on the top of glassy carbon was a stable composite despite this RTIL being a good binder for CNTs. Unfortunately, CF/MWCNT-BmimNTF<sub>2</sub> electrodes were not sufficiently mechanically stable in RTILs to be useable.

Fig. 5 shows CVs in 3 mM ferrocene in BmimNTF<sub>2</sub> and BmpyNTF<sub>2</sub> at a GC/MWCNT-BmimNTF<sub>2</sub> electrode. Two overlapping quasi-reversible redox couples were found in BmimNTF<sub>2</sub> (Fig. 5a). The peak separation was about 120 mV for the first redox couple and did not depend on the potential scan rate, and the second was even more separated, the peak separation significantly increasing with scan rate, thus showing slow kinetics. Since the first redox couple overlapped with the second one, it was difficult to determine the exact peak position as well as height. The peak height of the second redox couple depended linearly on the square root of the scan rate with slopes of 100 and  $-98$   $\mu$ A V<sup>-1/2</sup> s<sup>1/2</sup> for oxidation and reduction, respectively, and the ratio of the reduction and oxidation peak heights was  $0.98 \pm 0.08$ . The nature of

**Table 1**

Parameters of electrochemical K<sub>3</sub>Fe(CN)<sub>6</sub> redox reaction in 0.1 M KCl, calculated from the voltammograms in Fig. 3.

Electrode	$j_{red}$ vs. $\nu^{1/2}$ ( $\mu$ A cm <sup>-2</sup> V <sup>-1/2</sup> s <sup>1/2</sup> )	$j_{ox}$ vs. $\nu^{1/2}$ ( $\mu$ A cm <sup>-2</sup> V <sup>-1/2</sup> s <sup>1/2</sup> )	$A_{EA}$ (cm <sup>2</sup> )	$\nu$ (mV s <sup>-1</sup> )	$\Delta E$ (mV)	$ j_{ox}/j_{red} $
GC/MWCNT-BmimNTF <sub>2</sub>	$-2322 \pm 50$	$1929 \pm 35$	0.0801	10	78	1.00
				25	115	0.99
				50	161	0.92
				75	198	0.91
				100	227	0.94
CF/MWCNT-BmimNTF <sub>2</sub>	$-2200 \pm 40$	$1967 \pm 20$	0.0298	10	154	0.71
				20	160	0.77
				30	169	0.83
				40	175	0.78
				50	184	0.77



**Fig. 4.** (a) Complex plane electrochemical impedance spectra at GC/MWCNT-BmimNTF<sub>2</sub> electrode in 3 mM K<sub>3</sub>Fe(CN)<sub>6</sub> in 0.1 M KCl solution, at different potentials; line shows fitting to equivalent circuit. (b) Equivalent circuit:  $R_{\Omega}$ , solution resistance,  $R_{ct}$  charge transfer resistance,  $Z_w$  Warburg impedance, and  $C_{dl}$  double layer capacitance.

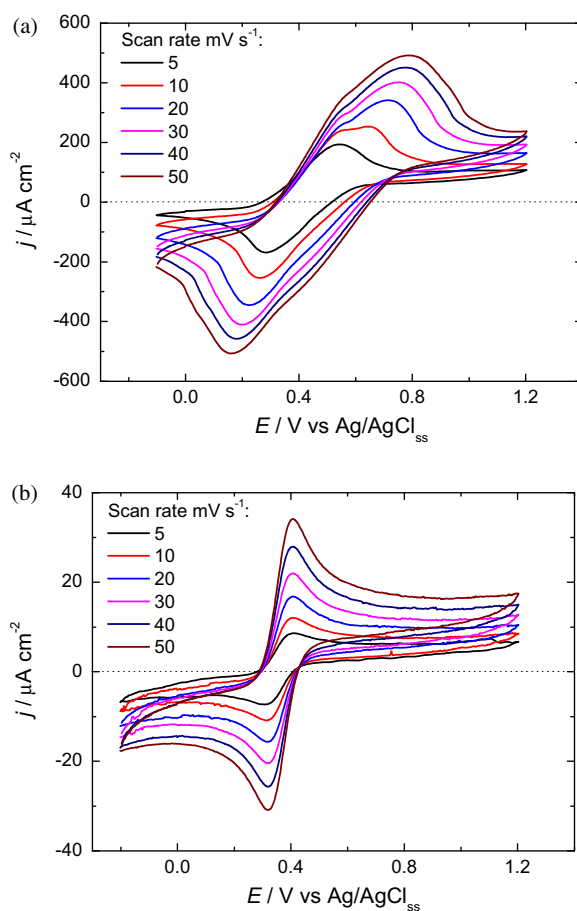
**Table 2**  
Impedance parameters obtained from the spectra in Fig. 4.

$E$ (V) vs. SCE	$R_{ct}$ ( $\Omega$ cm <sup>2</sup> )	$C_{dl}$ ( $\mu$ F cm <sup>-2</sup> )
-1.0	19.6 ± 0.5	43.0 ± 1.3
-0.5	18.7 ± 0.5	41.7 ± 1.3
0.0	20.5 ± 0.5	36.0 ± 1.0
0.5	22.5 ± 0.5	34.0 ± 0.9
1.0	20.0 ± 0.6	32.8 ± 1.0

the second electrochemical process is unknown, since ferrocene is a one-electron electrochemical redox compound.

A single redox couple of ferrocene was found in BmpyNTF<sub>2</sub> (Fig. 5b), with one apparently quasi-reversible peak and significantly lower peak current. The peaks did not shift with increase in scan rate and peak separation was 89 mV; this fact demonstrates fast electron transfer kinetics, and the peak separation could be caused by RTIL viscosity. The process is also limited by diffusion because the peak current depends linearly on the square root of scan rate with slopes of 7.2 and  $-7.0 \mu\text{A V}^{-1/2} \text{s}^{1/2}$  for oxidation and reduction, respectively. The ratio between reduction and oxidation peak height is almost one, i.e.  $0.97 \pm 0.03$ , usual for reversible systems.

Impedance spectra were different from those in aqueous solution; however, they were similar in both RTILs, Fig. 6. There is no clear separation between the diffusion and capacitive region as happens in aqueous solutions. A different equivalent circuit was employed in this case which consisted of a cell resistance in series with a parallel combination of  $R_{ct}$  and a constant phase element (CPE<sub>dl</sub>). The CPE describes a non-ideal capacitance, expressed by [70]:



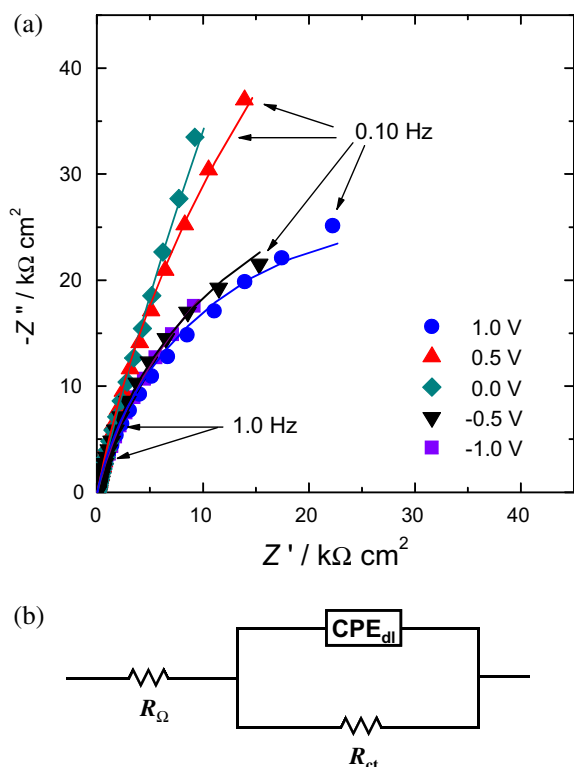
**Fig. 5.** CVs, after background subtraction, in 3 mM ferrocene in (a) BmimNTF<sub>2</sub> and (b) BmpyNTF<sub>2</sub> at GC/MWCNT-BmimNTF<sub>2</sub> electrode at different scan rates.

$$Z = \frac{1}{C(i\omega)^n} \quad (2)$$

where  $C$  is a CPE parameter – non-ideal capacitance,  $i$  is  $(-1)^{1/2}$ ,  $\omega$  is the angular frequency and  $n$  is the CPE exponent. The impedance values differ in both RTILs and the results obtained by equivalent circuit fitting are presented in Table 3; the double layer capacitance values were recalculated from the CPE parameter  $C$ , applying Eq. (2). The cell resistance was  $\sim 30 \pm 3$  and  $\sim 10 \pm 3 \Omega \text{ cm}^2$  in BmimNTF<sub>2</sub> and in BmpyNTF<sub>2</sub>, respectively. The charge transfer resistance was highest at 0.0 V and the lowest at  $-1.0$  and  $+1.0$  V vs. Ag/AgCl<sub>ss</sub> in both RTILs, but in general the resistance was lower in BmpyNTF<sub>2</sub>. The  $C_{dl}$  value decreased with increase in applied potential over the whole potential range from  $-1.0$  to  $+1.0$  V vs. Ag/AgCl<sub>ss</sub> in the case of BmimNTF<sub>2</sub> and from  $-1.0$  to  $+0.5$  V in BmpyNTF<sub>2</sub>, however, BmpyNTF<sub>2</sub> gave higher capacitance values. The roughness exponents were between 0.85 and 0.90 in both RTILs without any clear dependence on applied potential. The differences in the shape of spectra and impedance values between aqueous and RTIL solutions were probably due to the different viscosity of the media. The charge transfer resistance of the electrode in the RTILs is higher, compared to that in aqueous solutions, especially in the potential region where no redox process occurs. Both EIS and cyclic voltammetry show that the better RTIL electrolyte was BmpyNTF<sub>2</sub>.

### 3.2.3. Comparison of sensitivity and electrocatalytic effects with and without MWCNT

The sensitivity and electrocatalytic effects can be compared at both types of electrode with and without MWCNT. As expected, without MWCNT the electroactive area at the GC and CF electrodes



**Fig. 6.** (a) Complex plane electrochemical impedance spectra at GC/MWCNT-BmimNTF<sub>2</sub> electrode in BmimNTF<sub>2</sub> at different potentials; line shows fitting to equivalent circuit. (b) Equivalent circuit:  $R_{\Omega}$ , solution resistance,  $R_{ct}$ , charge transfer resistance, and  $CPE_{dl}$  as a CPE representing interfacial capacitance.

**Table 3**

Impedance parameters obtained from the spectra in Fig. 6. The last two parameters ( $C_{dl}$  and  $n$ ) are calculated or taken from CPE parameters.

RTIL	$E$ (V) vs. SCE	$R_{ct}$ ( $k\Omega\text{ cm}^2$ )	$C_{dl}$ ( $\mu\text{F cm}^{-2}$ )	$n$
BmimNTF <sub>2</sub>	-1.0	92 ± 2	73.2 ± 0.3	0.833 ± 0.001
	-0.5	71 ± 2	51.2 ± 0.5	0.858 ± 0.002
	0.0	860 ± 7	44.5 ± 0.2	0.847 ± 0.001
	0.5	226 ± 4	38.8 ± 0.4	0.870 ± 0.001
	1.0	60 ± 1	36.1 ± 0.5	0.873 ± 0.002
BmpyNTF <sub>2</sub>	-1.0	34 ± 1	194.6 ± 0.9	0.842 ± 0.001
	-0.5	28 ± 1	146.0 ± 0.6	0.844 ± 0.001
	0.0	167 ± 24	113.3 ± 0.6	0.898 ± 0.001
	0.5	43 ± 2	98.8 ± 0.6	0.886 ± 0.001
	1.0	51 ± 2	117.3 ± 0.5	0.872 ± 0.001

was almost the same as the geometric area. In KCl aqueous solution, although the peak separation increased much faster with scan rate at GC/MWCNT-BmimNTF<sub>2</sub> than at bare GCE due to diffusion limitations, the current response and sensitivity were higher at: 1412 vs. 130 and 1173 vs. 127  $\mu\text{A V}^{-1/2} \text{s}^{1/2}$  for reduction and oxidation, a factor of nearly 10. Similar results with MWCNT-RTIL-modified and bare GC electrodes were obtained in [71]. In the case of CFE, reversibility was improved after modification as well as the sensitivity: 66 vs. 35 and 59 vs. 31  $\mu\text{A V}^{-1/2} \text{s}^{1/2}$  for reduction and oxidation, respectively, a factor of nearly 2, which is less, however, than using GC electrode substrates. For both types of electrode substrate, background currents were higher at MWCNT-modified electrodes, since more functional groups (most carboxylic ones) were present at the electrode surface and the available surface area is higher.

In RTIL media, the current density for ferrocene oxidation was approximately 100 times higher at the GCE with CNT in BmimNTF<sub>2</sub>

than without, and at the bare GCE there was a linear dependence of the peak current on the potential scan rate, with the slopes of 5.1 and  $-5.0 \mu\text{A V}^{-1} \text{s}$  for oxidation and reduction, respectively, which is of a similar order of magnitude to with MWCNT (in this case the peak current varied linearly with the square root of scan rate). The oxidation and reduction peaks were at 0.470 V and 0.398 V vs. Ag/AgCl<sub>ss</sub>, respectively, and almost did not shift with the scan rate. This shows that in the RTIL, the presence of MWCNT increases the currents but makes the kinetics worse (see Fig. 5a). The reason for this is not clear.

The cyclic voltammetric behaviour of ferrocene in BmpyNTF<sub>2</sub> at unmodified and modified glassy carbon was similar with well-defined redox peaks, the peak current density being higher at the CNT-modified electrode by a factor of approximately 8. As for BmimNTF<sub>2</sub>, at the bare glassy carbon electrode the peak current depended linearly on the potential scan rate and the slopes were 5.8 and  $-5.7 \mu\text{A V}^{-1} \text{s}$  for oxidation and reduction, respectively, becoming a function of a square root of scan rate after immobilising CNT. In this RTIL medium, the mid-point potential of the oxidation and reduction peaks shifted negatively by 70 mV at the GC/MWCNT-BmimNTF<sub>2</sub> electrode compared with the bare electrode, which could be due to diffusion effects influencing the mechanism. The peak potential separation became smaller by approximately 6 mV, that can be attributed to a small electrocatalytic effect.

#### 4. Conclusions

Multi-walled carbon nanotubes (MWCNT) were homogenised using room temperature ionic liquids (RTILs) and the resulting mixture was applied on the top of glassy carbon or carbon film electrodes to form a composite. Three ionic liquids were used for carbon nanotube homogenisation: BmimNTF<sub>2</sub> and BmpyNTF<sub>2</sub> and BmimNO<sub>3</sub>, the last of which did not form a stable composite. The modified electrodes were characterised electrochemically in aqueous and ionic liquid electrolytes using cyclic voltammetry and electrochemical impedance spectroscopy. The results obtained showed that the best RTIL for CNT homogenisation was BmimNTF<sub>2</sub>, and the film of CNTs applied on the electrode substrate was stable mechanically and chemically. Potassium hexacyanoferrate and ferrocene redox couples were used to characterise the electrochemical behaviour of the assemblies in aqueous and RTIL media, respectively. BmpyNTF<sub>2</sub> exhibited better properties than BmimNTF<sub>2</sub> as RTIL electrolyte. The composite film was stable at least for one month.

Thus, it is suggested that MWCNT-BmimNTF<sub>2</sub> modified glassy carbon electrodes in BmpyNTF<sub>2</sub> be used in the preparation of sensors or biosensors for analytes insoluble in water, for which they represent promising electrode substrates.

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