

Short communication

# Polyaniline and polyaniline–carbon nanotube composite fibres as battery materials in ionic liquid electrolyte

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## Abstract

New battery materials are presented that consist of either a solid polyaniline (PANi) fibre or the same fibre containing carbon nanotubes (CNTs). An ionic liquid ethylmethyl imidazolium bis(trifluoromethanesulfonyl) amide (EMI.TFSA) is used as electrolyte. The electrochemical properties of PANi and PANi/CNT fibres are investigated by means of cyclic voltammetry, a.c. impedance and galvanostatic charge–discharge techniques. A PANi fibre with a CNT content of 0.25 wt.% exhibits a discharge capacity of  $12.1 \text{ mAh g}^{-1}$ .

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## 1. Introduction

Electronically conducting polymers exhibit a wide range of electrochemical properties and have been applied in areas such as sensors [1], electrochromic devices [2] and energy-storage devices including supercapacitors and batteries [3–5]. Polyaniline (PANi) has been studied extensively for use as a battery material. This organic conductor has good redox reversibility and high environmental stability. Polyaniline was usually been employed as a positive-electrode (cathode) material in batteries with zinc or lithium as the negative electrode (anode) [6]. The favoured electrolytes contain inorganic acids such as HCl, HClO<sub>4</sub> or H<sub>2</sub>SO<sub>4</sub> [7–9]. A battery voltage of 1.2 V and discharge capacities of up to  $121 \text{ mAh g}^{-1}$  have been demonstrated [8]. There have also been some reports concerning the application of polyaniline in all-polymer batteries. For example, the use of a polyaniline anode and a poly-L-naphthol cathode with methyl cyanide containing lithium perchlorate and perchloric acid as electrolyte has been described [10] and a discharge capacity of  $150 \text{ mAh g}^{-1}$  was obtained. In other work [11], a discharge capacity of  $79 \text{ mAh g}^{-1}$  was found for a cell composed of a polyaniline cathode and a polyindole anode with

sulfuric acid electrolyte. There is, therefore, great interest in developing batteries without such corrosive electrolytes and with alternative configurations to those in a conventional cell.

The aim of this study is to develop a wearable power source for wearable diagnostic systems. The integration of electronic components into conventional garments to introduce novel fashion effects, visual displays, or audio and computing systems has generated interest in recent years [12,13]. Such systems are also proving useful in the development of wearable diagnostic systems for monitoring of vital data (heart, pulse rate, etc.) in medical and military applications. Some promising results for a highly flexible fibre battery have been obtained in our group [14,15]. In those studies, polypyrrole–hexafluorophosphate (PPy/PF<sub>6</sub>) was electrodeposited on expensive platinum wire to be used as cathode, whereas a stand-alone polyaniline fibre was employed as an electrode. The latter was prepared by a wet-spinning method with a diameter of about 70–100 μm. This process has the advantage of easy processability and lower cost. Carbon nanotubes have also been added into the polyaniline to improve the electrical and mechanical properties of polymer fibres [16].

In the work presented here, an ionic liquid – ethylmethyl bis(trifluoromethane sulfonyl) amide (EMI.TFSA) – is used as an electrolyte as opposed to lithium hexafluorophosphate (LiPF<sub>6</sub>) in 1:1 (ethylene carbonate:dimethyl carbonate). High ionic conductivity, large electrochemical windows, excellent thermal

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and electrochemical stability and negligible evaporation make ionic liquids ideal electrolytes for such wearable diagnostics systems [17]. To our knowledge, no similar work has been reported.

## 2. Experimental

### 2.1. Fabrication of polyaniline fibres

The PANi, doped with 2-acrylamido-2-methyl-1-propane-sulfonic acid (AMPSA), spinning solution containing CNTs was prepared and fibres spun according to the method reported previously [18]. The surface morphologies of the polyaniline fibres were investigated with a scanning electron microscope (SEM, Leica Model Stereoscan 440) that was equipped with a secondary electron detector. To obtain clear cross-section images, the fibres were frozen in liquid nitrogen and then snapped.

### 2.2. Fabrication of polymer electrode

Polyaniline fibres or polyaniline fibres containing carbon nanotubes were cut into small segments of 3 cm length. Three such segments were bound together with platinum wire ( $\phi=0.125$  mm), which served as an electrical lead. The electrodes were soaked in the ionic liquid for 2 h to allow the latter to penetrate into the inner parts of the fibres before commencing experiments.

### 2.3. Electrochemical characterization

Electrochemical characterization of PANi or PANi/CNT fibres was performed in a standard one-compartment, three-electrode cell with a stainless-steel mesh counter electrode, a Ag/Ag<sup>+</sup> (EMI.TFSA) reference electrode and an ionic liquid EMI.TFSA electrolyte. Charge–discharge and cyclic voltammetry (CV) investigations were made with an EG&G PAR 363 Potentiostat/Galvanostat, a MacLab 400 system and EChem v 1.3.2 software (AD Instruments). The a.c. impedance spectrum was measured using CH Instruments Electrochemical Workstation Model 660B (CHI company, USA) in the range of  $0.1\text{--}1 \times 10^5$  Hz with 5 mV amplitude.

For charge–discharge tests, the cells were charged galvanostatically at a current density of  $0.1 \text{ mA cm}^{-2}$  to a cell voltage of 2.0 V, and then discharged at the same current density to a cut-off voltage of  $-1.2$  V. In CV tests, the scan rate was  $10 \text{ mV s}^{-1}$ .

## 3. Results and discussions

### 3.1. Surface morphology

The content of carbon nanotubes in the PANi fibre is given as a weight fraction with respect to the weight of PANi-AMPSA in the solid fibre, and is 0.25 wt.% in this work. The cross-section images of PANi or PANi/CNT fibres at low or high magnification are shown in Fig. 1. Some differences can be clearly observed between these two types of solid fibre. Pure PANi fibre shows

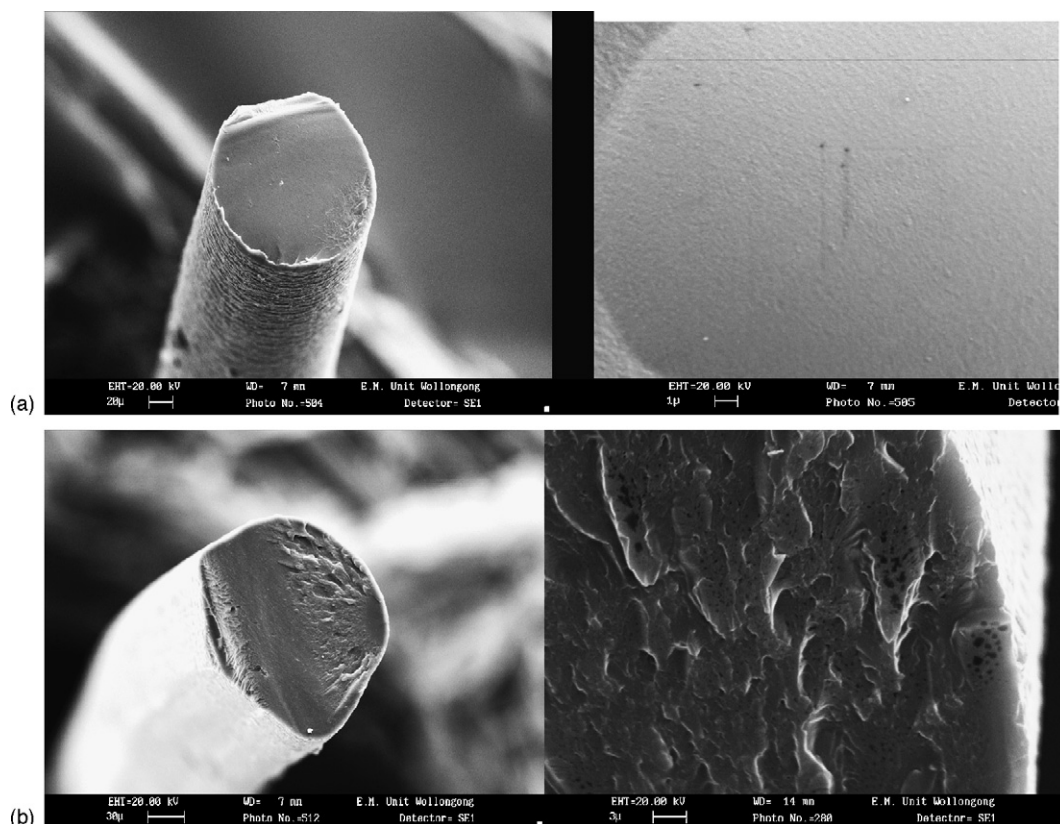


Fig. 1. Scanning electron micrographs of cross-section of (a) PANi and (b) PANi/CNT fibres at low and high magnification.

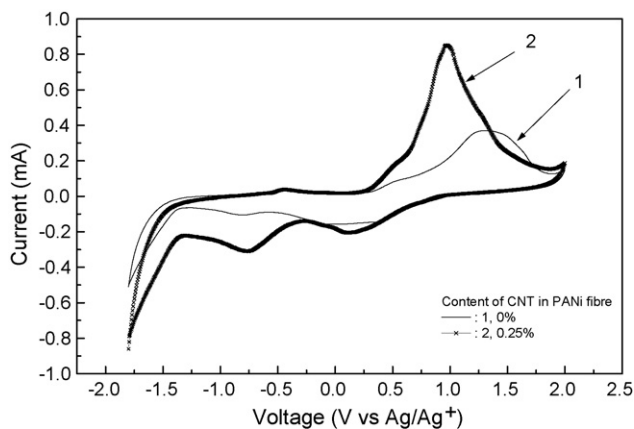


Fig. 2. Cyclic voltammograms of (1) PANi fibre and (2) PANi and PANi/CNT fibre in EMI.TFSA.

an even and featureless cross-section surface, (Fig. 1a), which is consistent with a fully-dense structure. By contrast, the PANi fibre containing CNTs displays fracture marks on its cross-section, and there is also evidence of some porosity in these fibres (Fig. 1b). Nevertheless, the whole volume is electrochemically active.

### 3.2. Cyclic voltammetry

To identify the oxidation and reduction potentials and electrochemical reactions of the fibre electrodes, cyclic voltammetry was performed in EMI.TFSA. The resulting cyclic voltammograms are shown in Fig. 2. Two pairs of redox peaks are present for both PANi and PANi/CNT fibre electrodes. The potentials at which these redox peaks appear are listed in Table 1. The differences between the oxidation and reduction peaks,  $\Delta E_{O,R}$ , have been calculated and are also listed in Table 1. The  $\Delta E_{O,R}$  is taken as an estimate of the reversibility of the redox reaction [16]. Values of 0.31 and 0.85 V are obtained for the redox reactions of PANi with carbon nanotube incorporation. They are smaller than the corresponding  $\Delta E_{O,R}$  values of 0.41 and 0.92 V for pure PANi fibre. These results suggest that the redox reactions appear to occur more reversibly after the addition of carbon nanotubes.

PANi emeraldine salt (ES) is electrochemically reduced to the PANi leucoemeraldine base (LEB) structure by gaining two electrons and two EMI cations per tetrameric repeat unit at low potential, meanwhile, PANi (LEB) loses two electrons and two EMI cations to form the ES structure when it is cycled to higher positive potentials. The mechanism of maintaining electron neutrality in a solid fibre during a charge–discharge process has

Table 1  
Data obtained from cyclic voltammograms

Sample	Potential					
	$E_{OX}$ (V)		$E_{RD}$ (V)		$\Delta E_{O,R}$ (V)	
	$E_{OX1}$	$E_{OX2}$	$E_{RD1}$	$E_{RD2}$	$\Delta E_{O,R1}$	$\Delta E_{O,R2}$
PANi/CNT (0.25%, w/w)	−0.46	0.98	−0.77	0.13	0.31	0.85
PANi	−0.39	1.30	−0.8	0.38	0.41	0.92

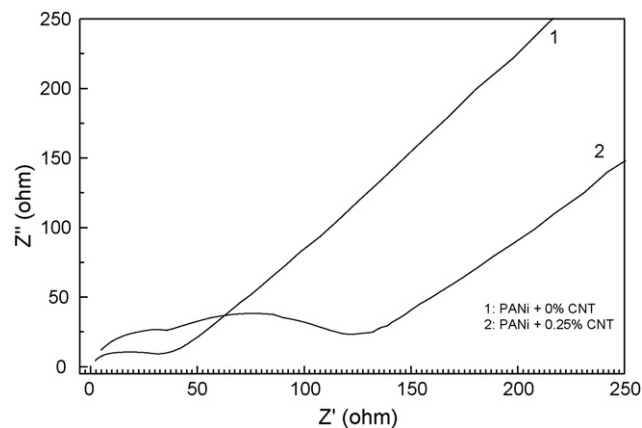


Fig. 3. Impedance spectroscopy of (1) PANi fibre and (2) PANi/CNT fibre in EMI.TFSA.

been explained by intercalation–de-intercalation of the cations between the fibre and the electrolyte. It has also been claimed that the transfer of protons is not probable to achieve electron neutrality during the redox process. Therefore, the pernigraniline base oxidation state is unlikely to be formed in an ionic liquid [12]. After the incorporation of CNTs, the redox peaks for PANi/CNT fibre become sharper and the voltammogram area increases, as shown in Fig. 2. All these results indicate that the oxidation and reduction reaction becomes more facile with CNTs addition and higher charge and discharge capacities are expected.

### 3.3. Impedance studies

To investigate the electrochemical behaviour of PANi fibre electrodes at the electrode|electrolyte interface, a.c. impedance measurements were carried out. The results are presented in Fig. 3. A semicircle is found at high frequency and Warburg diffusion ( $45^\circ$  line) occurs where the resistance of the circle diminishes in the Nyquist plot for PANi without CNT. These features indicate that the electrode process is limited by both charge-transfer kinetics and diffusion processes. By contrast, two semicircles are present at high frequency after the addition of CNT into PANi fibre. This implies that the cell is kinetically controlled by more complicated processes rather than by simple charge transfer. The additional features may be caused by the interaction between the polyaniline and carbon nanotubes. At low frequency, a typical Warburg diffusion process is again observed.

### 3.4. Charge–discharge characteristics

The charge–discharge characteristics of the PANi fibres were evaluated galvanostatically; the data are shown in Fig. 4. The charge–discharge capacity was calculated with respect to the weight of the PANi fibre electrodes. The charging potential increases and the discharging potential decreases as the depth of the charge–discharge process is increased. This behaviour is characteristic of electrode materials used in rechargeable batteries and demonstrates that polyaniline fibres can be used

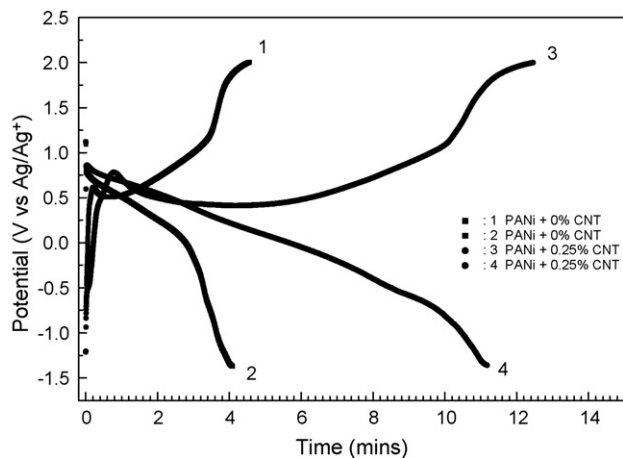


Fig. 4. Charge–discharge curves of PANi fibre (1 and 2) and PANi/CNT fibre (3 and 4) in EMI.TFSA.

as electrode materials in an ionic liquid. A discharge capacity of  $11.2 \text{ mAh g}^{-1}$  and charge capacity of  $12.1 \text{ mAh g}^{-1}$  are obtained for a polyaniline fibre with 0.25 wt.% CNT. These values are much higher than those obtained for pure polyaniline fibre, namely,  $4.1$  and  $4.5 \text{ mAh g}^{-1}$  for discharge and charge, respectively. It has also been noted that the charge voltage becomes lower and the discharge voltage becomes higher after carbon nanotubes are incorporated in the PANi fibre. This indicates that the energy consumed by the internal resistance is reduced and, therefore, the effective energy storage is improved. This improvement is perhaps due to the fact that the inner resistance of the electrode is reduced when carbon nanotubes are present. The charge and discharge capacity obtained in this work is, however, much lower than that for PANi in an electrolyte containing an inorganic acid, e.g.,  $121 \text{ mAh g}^{-1}$  as reported by Mirmohseni and Solhjo [8]. The main reason is perhaps because the fibre prepared in our work is very dense and solid and therefore results in the electrochemically accessible surface area becoming smaller and leading to a reduction in the number of electrochemically active sites. This problem can be solved if the electrochemically active area is increased for PANi fibre. The ionic liquid, electrolyte may also have contributed to the low capacity. The significance of this study is that stand-alone PANi fibre can be used as an electrode material in the EMI.TFSA ionic liquid and is a promising electrode for wearable diagnostics systems.

### 3.5. Cycle life

Discharge capacity as a function of the cycle number is shown in Fig. 5. The discharge capacity of undoped PANi fibre increases with the cycle number, and reaches  $9.7 \text{ mAh g}^{-1}$  after 10 cycles from an initial capacity of  $3.9 \text{ mAh g}^{-1}$ . This suggests that a slow activation process occurs during the charge–discharge process. For PANi/CNT fibre, however, an initial discharge capacity of  $10.9 \text{ mAh g}^{-1}$  is obtained that increases to  $12.1 \text{ mAh g}^{-1}$  after 10 cycles. No obvious activation process is found for PANi/CNT fibre. Thus, it can be concluded that the incorporation of carbon

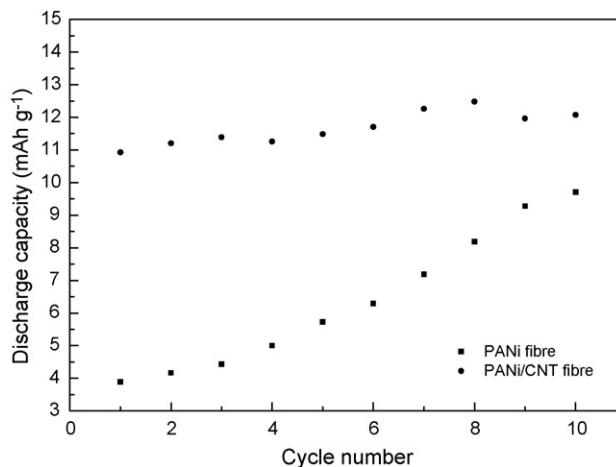


Fig. 5. Cycle-life of PANi fibre and PANi/CNT fibre in EMI.TFSA.

nanotubes into PANi fibre improves the discharge capability and shortens the activation process.

## 4. Conclusions

Solid polyaniline fibres have been prepared by a wet-spinning method. The neat PANi fibres are observed by SEM to be fully dense, while the polyaniline/CNT composite fibres have some porosity. Polyaniline fibre with 0.25 wt.% CNT exhibits a smaller  $\Delta E_{O,R}$  than untreated fibre, which indicates that the redox processes occur more reversibly. A higher charge–discharge capacity, lower charge voltage and higher discharge voltage are reported for PANi/CNT fibre. All these results show that solid polyaniline fibre can be used directly as an electrode in ionic liquid EMI.TFSA, and that the electrochemical properties of the fibre as an electrode material are improved by the incorporation of carbon nanotubes. Therefore, PANi/CNT fibre is a promising electrode material for wearable diagnostics systems.

## Acknowledgement

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