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

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Abstract

New battery materials are presented here that consist of either a solid polyaniline (PANi) fibre or a similar fibre but containing carbon nanotubes (CNTs). An ionic liquid ethylmethyl imidazolium bis(trifluoromethanesulfonyl) amide (EMI.TFSA) was chosen as electrolyte. The electrochemical properties of PANi or PANi/CNT fibres were investigated using cyclic voltammetry, AC impedance and galvanostatic charge/discharge techniques. The PANi fibre with a CNT content of 0.25% (w/w) exhibited a discharge capacity of 12.1 mAh g^{-1}.

Keywords: Fibre electrode, polyaniline, carbon nanotubes, wet-spinning, conducting polymer, ionic liquid.

1 Introduction

Electronically conducting polymers exhibit a wide range of electrochemical properties, and they have been applied in areas such as sensors [1], electrochromic devices [2], charge-storage devices including supercapacitors and batteries [3, 4, 5]. Polyaniline (PANi) has been extensively studied for use as a battery material. This organic conductor has good redox reversibility and high environmental stability. Polyaniline has usually been employed as a cathode material in batteries with Zn or Li as the anode [6]. The electrolytes used usually contain inorganic acids such as HCl, $HClO_4$ or H_2SO_4 [7, 8, 9]. A battery voltage of 1.2 V and discharge capacities of up to 121 mAh g^{-1} have been reported [8]. There have also been a few reports about the application of polyaniline in all-polymer batteries. The use of a polyaniline anode and poly-1-naphthol cathode with methyl cyanide containing lithium perchlorate and perchloric acid as electrolyte has been described [10] and a discharge capacity of 150 mAh g^{-1} was reported. In other work, a discharge capacity of 79 mAh g^{-1} was reported for a cell composed of polyaniline cathode and polyindole anode with sulfuric acid electrolyte [11]. There is, therefore, a need to develop batteries without these corrosive electrolytes as well as in alternative configurations rather than as a conventional cell.

The aim of this work 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) 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_6) was electrodeposited on expensive platinum wire to be used as cathode whereas a stand-alone polyaniline fibre was employed as an electrode directly in this work. This very thin fibre 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 were also added into the polyaniline to improve the electrical and mechanical properties of polymer fibres [16].

Moreover, ionic liquid was chosen as electrolyte in this work other than lithium hexafluorophosphate ($LiPF_6$) in 1:1 (ethylene carbonate : dimethyl carbonate). High ionic conductivity, large electrochemical windows, excellent thermal and electrochemical stability and negligible evaporation make ionic liquids an ideal electrolyte for such wearable diagnostics systems [17]. No similar work has been reported so far to our knowledge.

Polyaniline fibres and its CNT nanocomposite were investigated in ionic liquid EMITFSA in this work, and their electrochemical characteristics were investigated by cyclic voltammetry, AC impedance and galvanostatic charging/discharging techniques.

2 Experimental

2.1 Fabrication of polyaniline fibres

The PANi-AMPSA spinning solution containing CNTs was prepared based on the method reported previously [18]. The fibres were then spun according to previously reported procedures [18].

The surface morphologies of the polyaniline fibres were investigated with a scanning electron microscope (SEM, Leica Model Stereoscan 440) with a secondary electron detector. To obtain clear cross-section images, the fibres were frozen in liquid nitrogen before snapping them.

2.2 Fabrication of polymer electrode

Polyaniline fibres or polyaniline fibres containing carbon nanotubes were cut into small segments of 3 cm lengths. Three such segments were bound together with platinum wire

(ϕ = 0.125 mm), and the Pt wire was also used as a lead. The electrodes were soaked in ionic liquid for 2 hours to allow the ionic liquid to penetrate into the inner part of the fibres before electrochemical measurements.

2.3 Electrochemical characterisation

All the electrochemical characterisation of PANi or PANi/CNT fibres were performed in a standard one compartment three-electrode cell with a stainless steel mesh counter electrode, Ag/Ag^{+} (EMITFSA) reference electrode, and ionic liquid EMITFSA electrolyte. The charge/discharge and cyclic voltammetry (CV) investigations were carried out using an EG&G PAR 363 Potentiostat/Galvanostat, a MacLab 400, and EChem v 1.3.2 software (AD Instruments). The AC impedance spectrum was measured using CH instruments electrochemical workstation 660B (CHI company, USA) in the range of 0.1 to 1 X 10^5 Hz with 5 mV amplitude.

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

3 Results and Discussions

3.1 Surface morphology

The content of carbon nanotubes in PANi fibre is given as a weight fraction with respect to the weight of Pani-AMPSA in the solid fibre, and it is 0.25 %w/w 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. In Fig. 1a pure PANi fibre shows an even and featureless cross-section surface, consistent with a fully dense structure. The PANi fibre containing CNTs showed fracture marks on its cross-section, but there was also evidence of some porosity in these fibres (Fig. 1b). In any case, the whole volume was 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. Cyclic voltammograms are shown in Fig. 2. Two pairs of redox peaks are shown for both PANi and PANi/CNT fibre electrodes, and the potential for redox peaks obtained from the cyclic voltammograms is listed in Table 1. The difference between the oxidation and reduction peaks, $\Delta E_{O,R}$, is calculated and also listed in Table 1. $\Delta E_{O,R}$ is taken as an estimate of the reversibility of the redox reaction [16]. $\Delta E_{O,R}$ values of 0.31 and 0.85 V are obtained for the redox reactions of PANi with carbon nanotube incorporation. They are smaller than those $\Delta E_{O,R}$ values of 0.41 and 0.92 V for pure PANi fibre, respectively. 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 charging/discharging process has been explained by intercalation/ de-intercalation of the cations between the fibre and the electrolyte and it has 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 ionic liquid [12].

It has also been noted that the redox peaks for PANi/CNT fibre became sharper and the voltammogram area became larger as shown in Figure 2. All these results indicate that the oxidation and reduction reactions became more facile after carbon nanotubes incorporation, and higher charge and discharge capacity are expected.

3.3 AC Impedance

To investigate the electrochemical behavior of PANi fibre electrodes at the electrode/electrolyte interface, AC impedance measurements were carried out, with the results shown in Fig. 3. A semicircle was found at high frequency and a Warburg diffusion (45°line) occurred where the resistance of the circle diminished in the Nyquist plot for PANi without CNT. These features indicate that the electrode process was limited by both charge-transfer kinetics and diffusion processes. However, two semicircles were shown at high frequency after the addition of CNT into PANi fibre, which implies that the cell was kinetically controlled by more complicated processes rather than simple charge transfer. Perhaps the additional features were caused by the interaction between the polyaniline and carbon nanotubes. At low frequency a typical Warburg diffusion process was again observed.

3.4 Charge/discharge characteristics

The charge/discharge characteristics of the PANi fibres were evaluated galvanostatically, and the charge/discharge curves are shown in Fig. 4. The charge/discharge capacity was calculated based on the weight of the PANi fibre electrodes. It can be seen that the charging potential increases and discharging potential decreases as the depth of the charging/discharging process is increased; which is characteristic of electrode materials used in rechargeable batteries and proves that polyaniline fibres can be used as electrode materials in ionic liquid. A discharge capacity of 11.2 mAh g^{-1} and charge capacity of 12.4 mAh g^{-1} were obtained for polyaniline fibre with 0.25% CNT. They are much higher than those obtained for pure polyaniline fibre. Polyaniline fibre with 0% CNT exhibited a discharge capacity of 4.1 mAh g^{-1} and charge capacity of 4.5 mAh g^{-1} . It has also been noted that the charge voltage became lower and discharge voltage became higher after carbon nanotubes were incorporated into PANi fibre; which indicates that energy consumed for (IR) was reduced and effective energy storage was improved. This improvement was perhaps because the inner resistance of the electrode was reduced after the carbon nanotubes were incorporated. However, the charge and discharge capacity

obtained in this work is much lower than that for PANi reported in electrolyte containing inorganic acid such as 121 mAh g^{-1} reported by Mirmohseni and Solhjo [8]. The main reason is perhaps because the fibre prepared in this work was very dense and solid, resulting 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 electrolyte, ionic liquid, may also have contributed to the low capacity. The significance of this work is that stand alone PANi fibre can be used as electrode materials in ionic liquid EMI.TFSA 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 PANi fibre with 0% CNT increased with the cycle number, and it reached 9.7 mAh g^{-1} after 10 cycles from an initial capacity of 3.9 mAh g^{-1}. This suggests that a slow activation process occurred during the charge/discharge process. For PANi/CNT fibre, however, an initial discharge capacity of 10.9 mAh g^{-1} was obtained that reached 12.1 mAh g^{-1} after 10 cycles. No obvious activation process was shown for PANi/CNT fibre. It can be concluded that the incorporation of carbon nanotubes into PANi fibre improves the discharge capability and shortens the activation process.

4. Conclusions

Solid polyaniline fibres were prepared by a wet-spinning method. The neat PANi fibres were observed by SEM to be fully dense, while polyaniline/CNT composite fibres had some porosity. Polyaniline fibre with 0.25% CNT exhibited a smaller $\Delta E_{O,R}$ than a fibre with 0% CNT; which indicates that the redox processes occur more reversibly. A higher charge/discharge capacity, lower charge voltage and higher discharge voltage were shown for PANi/CNT fibre. All the 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 have been improved by carbon nanotube

incorporation. Therefore, PANi/CNT fibre is a promising electrode material for wearable diagnostics systems.

Acknowledgement

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Figure captions

Fig. 1. SEM images of the cross-section of the PANi (a) and PANi/CNT (b) fibres at low and high magnification.

Fig. 2. Cyclic voltammograms of a PANi fibre and a PANi/CNT fibre in EMI.TFSA.

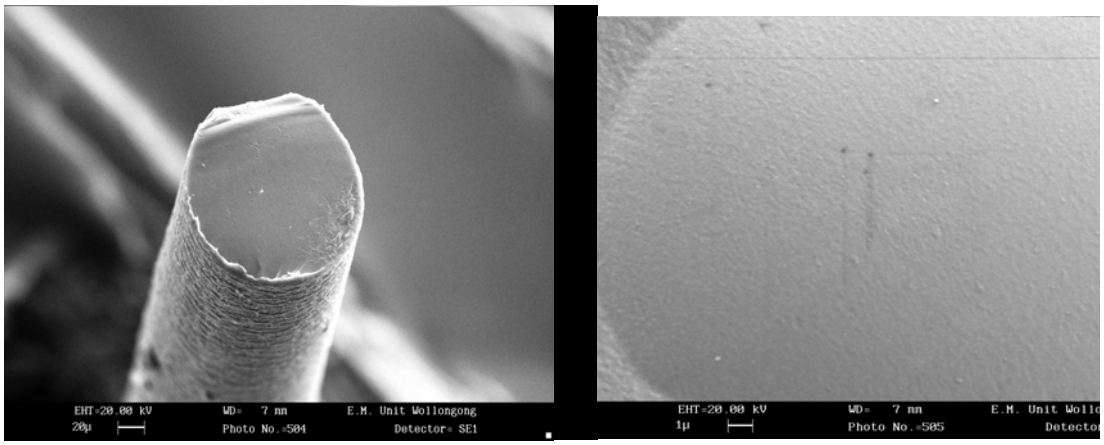
Fig. 3. Impedance spectroscopy of (1) a PANi fibre and (2) a PANi/CNT fibre in EMI.TFSA.

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

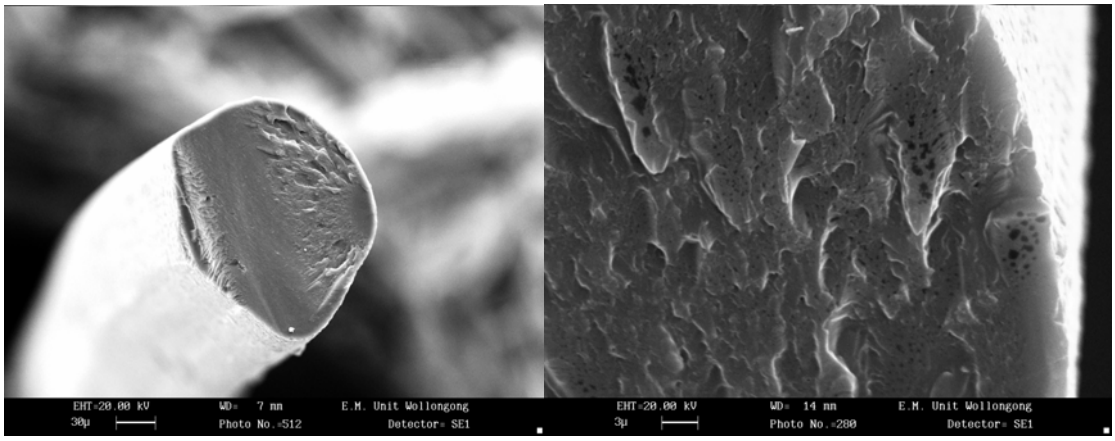
Fig. 5. Cycle life of a PANi fibre and a PANi/CNT fibre in EMI.TFSA.

Table 1 Data obtained from the cyclic voltammograms

Potential / Sample	E_{OX} (V)		E_{RD} (V)		$\Delta E_{O,R}$ (V)	
	$E_{OX\,1}$	$E_{OX\,2}$	$E_{RD\,1}$	$E_{RD\,2}$	$\Delta E_{O,R\ 1}$	$\Delta E_{O,R\,2}$
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


EHT=20.00 kV
WD= 7 mm
E.M. Unit Wollongong
20µ
Photo No.=504
Detector= SE1
EHT=20.00 kV
WD= 7 mm
E.M. Unit Wollo
1µ
Photo No.=505
Detecto

(a)


EHT=20.00 kV
WD= 7 mm
E.M. Unit Wollongong
30µ
Photo No.=512
Detector= SE1
EHT=20.00 kV
WD= 14 mm
E.M. Unit Wollongong
3µ
Photo No.=200
Detector= SE1

(b)

Fig. 1

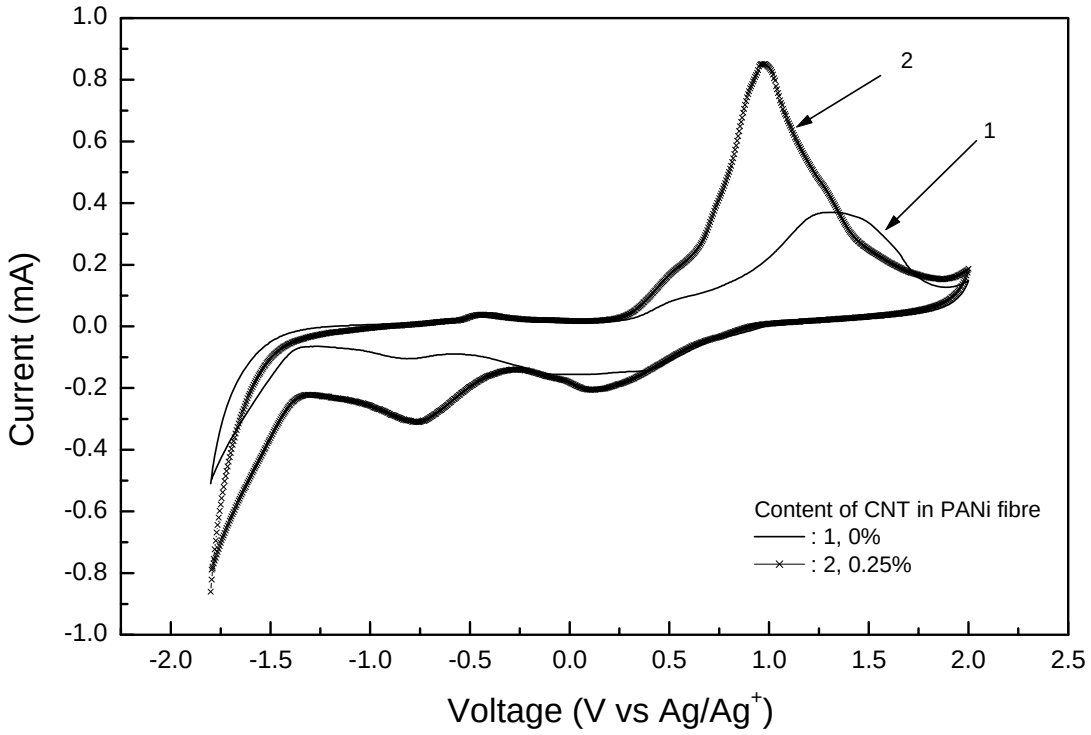

Current (mA)
Voltage (V vs Ag/Ag+)
1.0
0.8
0.6
0.4
0.2
0.0
-0.2
-0.4
-0.6
-0.8
-1.0
-2.0
-1.5
-1.0
-0.5
0.0
0.5
1.0
1.5
2.0
2.5
2
1
Content of CNT in PANi fibre
: 1, 0%
: 2, 0.25%

Fig. 2

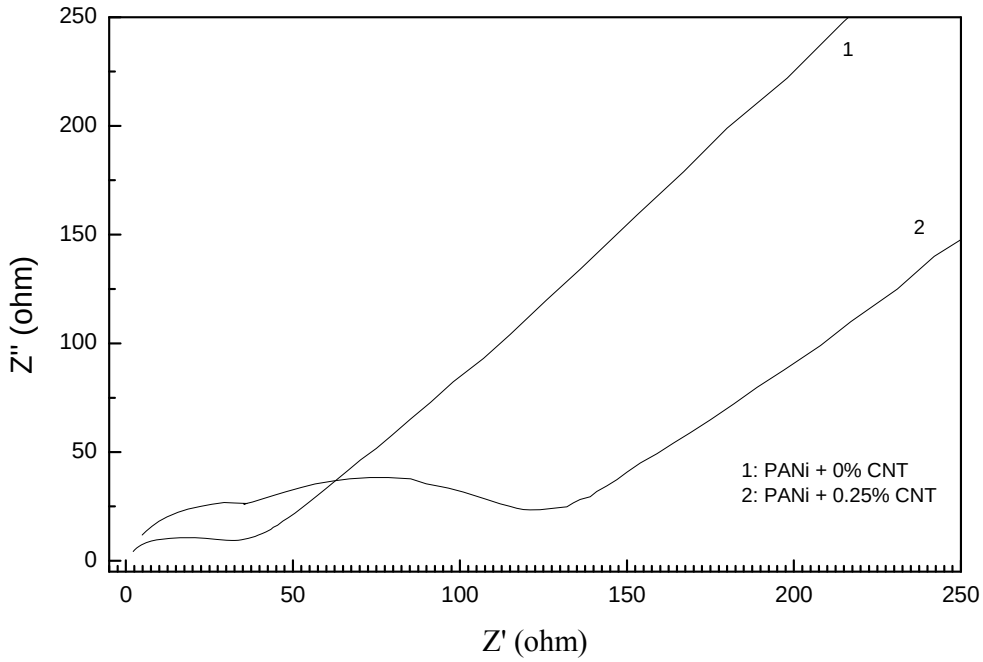

250
200
150
100
50
0
Z'' (ohm)
0
50
100
150
200
250
Z' (ohm)
1
2
1: PANi + 0% CNT
2: PANi + 0.25% CNT

Fig. 3

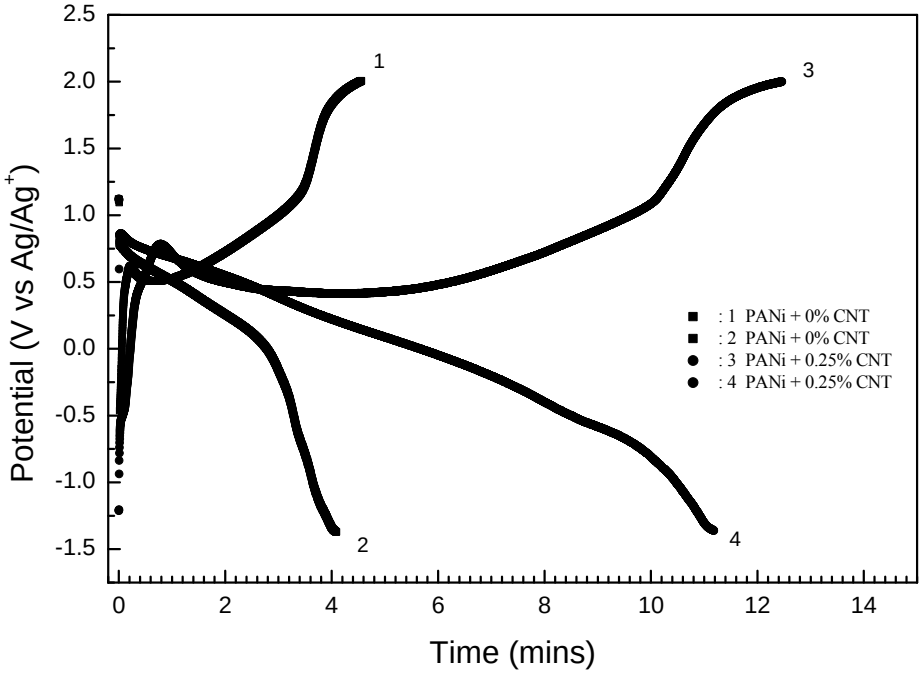

Potential (V vs Ag/Ag+)
Time (mins)
1
2
3
4
: 1 PANi + 0% CNT
: 2 PANi + 0% CNT
: 3 PANi + 0.25% CNT
: 4 PANi + 0.25% CNT

Fig. 4

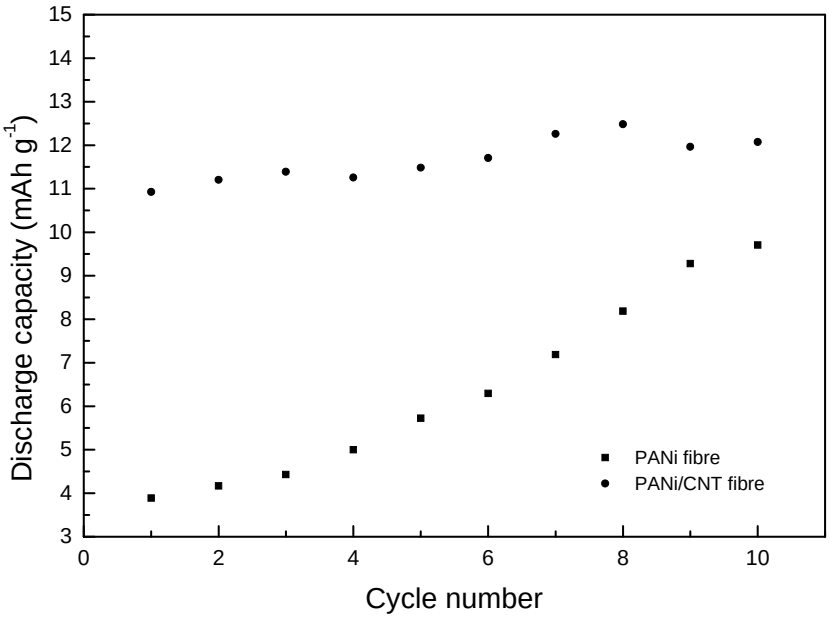

Discharge capacity (mAh g-1)
Cycle number
PANi fibre
PANi/CNT fibre
15
14
13
12
11
10
9
8
7
6
5
4
3
0
2
4
6
8
10

Fig. 5