Short communication

Highly-flexible fibre battery incorporating polypyrrole cathode and carbon nanotubes anode

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Abstract

The development of highly-flexible fibre batteries based on a conducting polymer and single-wall carbon nanotubes (SWNTs) is described. Initially, polypyrrole-hexafluorophosphate (PPy/PF$_6$) and SWNTs are tested in lithium cells to ascertain their performance. Based on the results, fibre batteries consisting of a PPy/PF$_6$ cathode and an anode based on SWNTs are fabricated and tested in both a "flooded cell" and 'dry cell', arrangement.

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1. Introduction

In recent years, conventional garments and electronic components have been integrated to produce novel fashion effects, visual displays, or audio and computing systems [1,2]. Similar systems are also being developed as wearable diagnostic systems for monitoring vital signs in medical and military applications. Another area of interest has been the integration of sensors and actuators into fibre textiles as the development of high efficiency conducting polymer actuator fibres [3] and conducting polymer fibres with chemical sensing [4,5] is realised. Sophisticated electronic textiles will, however, require wearable energy-storage capabilities. In the light of this, we have been interested in the advancement of conducting polymer based fibre batteries.

Numerous approaches have been adopted for the utilization of conducting polymers as rechargeable battery devices [6,7]. Such approaches have considered the potential of replacing either the negative (anode) or positive (cathode) electrode with a conducting polymer. More emphasis, however, has been placed on the cathode because traditional metal anodes have significantly higher specific energies than polymers [8]. Nevertheless, the possibility of developing 'all-polymer' batteries has also been

of interest. For example, Killian et al. [9] reported the development of an all-polymer battery structure using both p- and n-dopable polypyrrole. The battery had a specific charge capacity of 22 mAh g^{-1} at 0.4 V and showed no loss in capacity when cycled 100 times. Even though the charge capacity is much lower than that for a conventional lithium-ion battery, all-polymer batteries have an advantage in that they are flexible and can be configured in a wide variety of forms.

Our particular interest is in the integration of batteries into wearable or other textile-based structures. Consequently, we have reported a first step towards a flexible fibre battery construction based on a polypyrrole composite [10]. This battery yielded a capacity of about 10 mAh g^{-1} over 30 cycles. The work reported here, attempts to enhance the performance of this fibre battery through the use of single-wall carbon nanotubes (SWNTs) as the anode material. Other researchers [11] have disclosed the successful application of carbon nanotubes in lithium-ion batteries, but it is considered that this is the first report of the use of SWNTs in a flexible fibre battery.

2. Experimental

2.1. Fabrication of fibre electrodes

Fine polypyrrole (PPy) electrodes were fabricated by a single-step polymerization of polypyrrole on to platinum wire
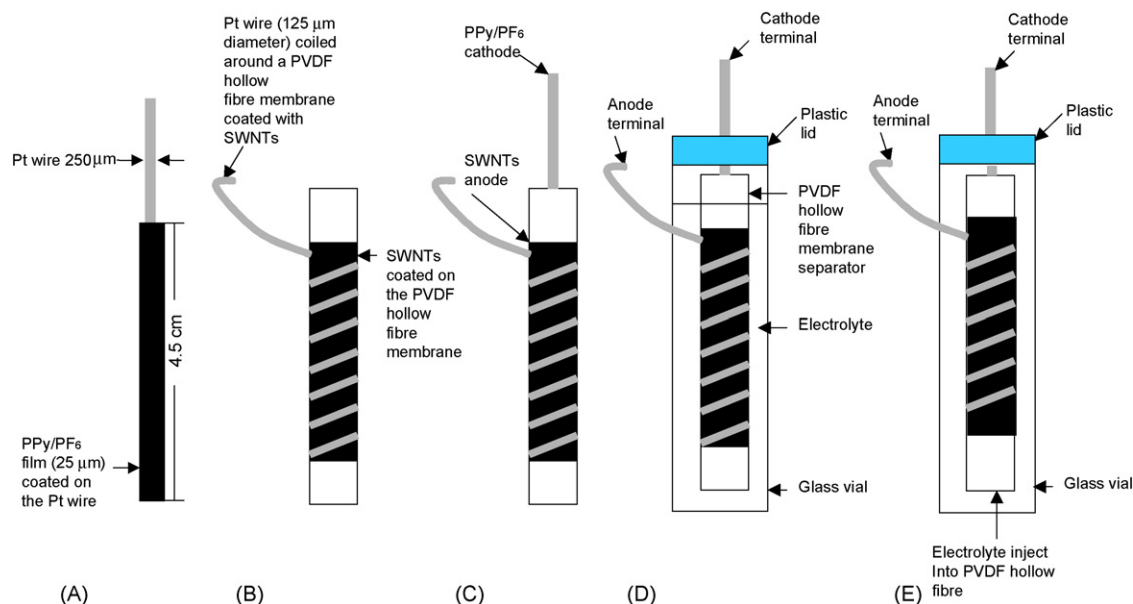

Fig. 1. Construction of fibre cell: (A) PPy/PF$_6$ cathode electrode, (B) SWNTs-coated PVDF hollow fibre membrane with Pt wire, (C) PPy/PF$_6$ cathode electrode inserted into the SWNTs anode, (D) schematic of 'flooded cell', and (E) schematic of 'dry cell'.

with diameter of 250 μm. Polymer samples were grown using an EG&G Princeton Applied Research Model 363 potentiostat/galvanostat. The electrodes were prepared by electropolymerization from a solution of 0.06 M pyrrole (Aldrich), 0.05 M TBAPF$_6$ (Aldrich) in propylene carbonate (PC) at 0.75 V (versus Ag/Ag$^+$) in 0.01 M AgNO$_3$ and 0.1 M tetrabutylammonium perchlorate (TBAP)/CH$_3$CN to a total deposition charge of 3 C cm^{-2}. Following electropolymerization, these electrodes were dried in a vacuum oven for 24 h at room temperature, and then stored in an argon-filled glove box. The dried electrodes were assembled into cells and tested. The length of the fine PPy/PF$_6$ electrodes was 4.5 cm.

A fibre electrode of single-wall carbon nanotubes (Carbon Nanotechnologies Inc., USA) was prepared by deposition of the carbon nanotubes on to a polyvinylidene fluoride (PVDF) hollow fibre membrane. A SWNT/Triton X-100 dispersion was prepared via addition of 50 mg of high purity (95%) single-walled carbon nanotubes and 0.5 g of a surfactant, Triton X-100, into 50 ml of Milli-Q water followed by ultrasonication for 2 h. A 5 cm long PVDF hollow fibre with a diameter of 0.4 cm was wetted in 50:50 (v/v) Milli-Q water to ethanol solution for 10 min. It was then immersed into the prepared SWNT suspension. The carbon nanotube dispersion was deposited on the PVDF hollow fibre membrane by suction with a syringe. A layer of SWNTs was formed by the vacuum filtration of the nanotube suspension on the PVDF hollow fibre membrane. Subsequently, the resultant SWNT fibre electrode was washed with 20 ml of Milli-Q water followed by 20 ml of methanol, where methanol was used to remove any residual surfactant. Finally, the SWNT fibre electrode was dried overnight in a vacuum oven before a platinum wire (125 μm diameter) was wound tightly around it.

2.2. Cell fabrication and testing

A fine PPy/PF$_6$ cathode and SWNT anode are shown in Fig. 1A and B, respectively. Initially, the individual components (cathode and anode) of the fibre battery were tested independently using lithium foil as a counter electrode and 1 M LiPF$_6$ in a mixture of ethylene carbonate (EC) and dimethyl carbonate (DMC) (1:1, v/v) as the electrolyte (Merck KgaA, Germany). The SWNT/PVDF hollow fibre electrode was charged in a cell with lithium foil as a counter electrode before the PPy/PF$_6$ cathode was inserted into it (Fig. 1C). Then, the electrodes were sealed in a "flooded cell" (Fig. 1D) and a 'dry cell' (Fig. 1E), respectively.

Charge–discharge testing was carried out by using a battery-testing device (Neware Electronic Co., China) interfaced to a computer with software. The system is capable of switching between charge and discharge automatically according to the pre-set cut-off potentials. The cells were tested at a constant current of 20 μA cm^{-2}.

3. Results and discussion

X-ray diffraction spectra were obtained for the SWNT powder and the SWNT electrodes prepared as described above (Fig. 2). The broad peak of the (0 0 2) diffraction of the carbon nanotubes indicates typical patterns for amorphous structures with a d_{002} of 0.38 nm, as calculated according to the Bragg equation. No peak shifts are observed when the SWNT powder and the SWNT electrodes are compared. A transmission electron micrographic (TEM) image of the single-wall carbon nanotube powder shows a web of hollow tubes with outer diameters 10–30 nm, Fig. 3. A scanning electron microscopy (SEM) image of a fibre SWNT electrode is shown
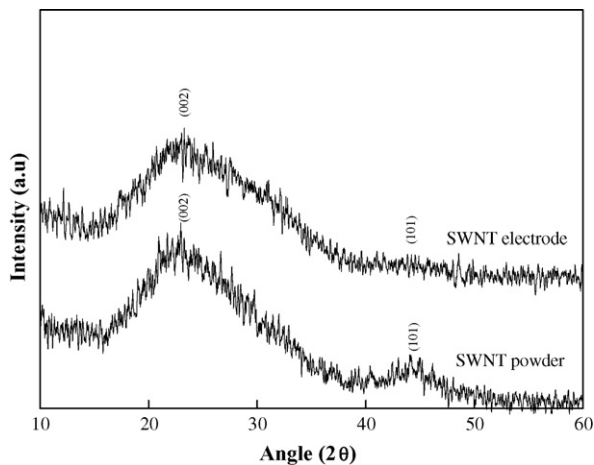
Fig. 2. X-ray diffraction pattern of single-wall carbon nanotube powder.
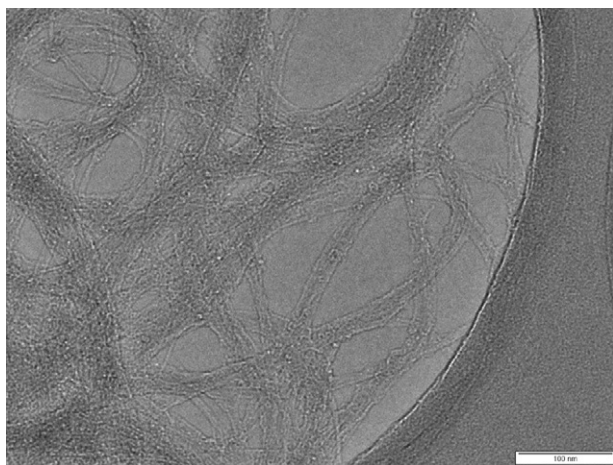

Fig. 3. TEM image of SWNTs powder.

in Fig. 4. The surface of the electrode is found to be smooth and dense.

The polypyrrole cathode was fabricated by electropolymerization of pyrrole on to platinum wire using a potentiostatic method. Polymerization of pyrrole (Py) produces the highly conductive and oxidized (doped) form of polypyrrole in which
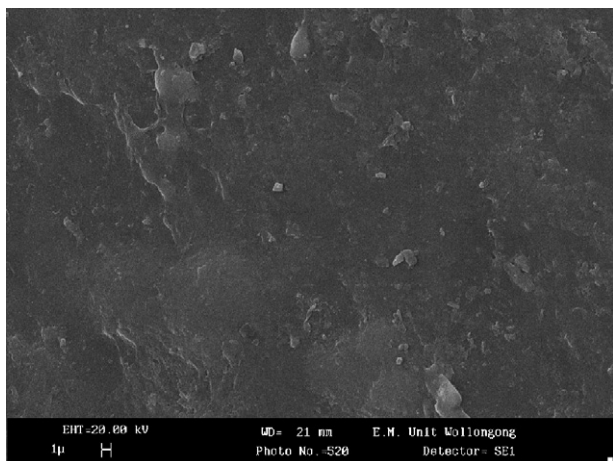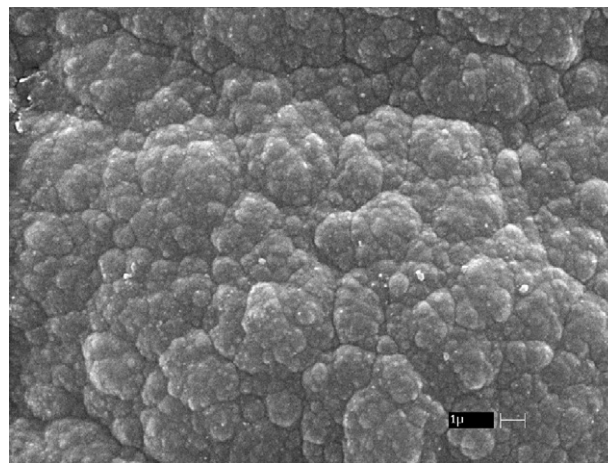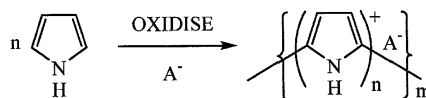

Fig. 4. SEM image of fibre SWNT electrode.


Fig. 5. SEM image of polypyrrole on platinum wire.

some electrons are removed from a delocalised π-system. The electro-neutrality of the oxidized polymer is retained by the incorporation of an adequate amount of anions from the electrolyte into the bulk of PPy according to:

$n \equiv$ indicates degree of doping, $m \equiv$ determines molecular weight.

$$(1)$$

During discharge, the polymer is reduced (undoped) to its neutral state by releasing the anion, namely:
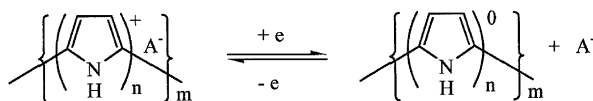
$$(2)$$

when charged again, anions migrate back into the polymer.

A scanning electron micrograph of a polypyrrole film on the platinum wire is presented in Fig. 5. A typical 'cauliflower' like nodular structure of electrochemically synthesized polypyrrole films is observed [12].

Initially, the PPy/PF$_6$-coated Pt wire electrode and the Pt-SWNT/PVDF hollow fibre membrane electrode were tested separately by using lithium foil as a counter electrode and an electrolyte of 1 M LiPF$_6$ dissolved in EC-DMC (1:1, w/w) to ascertain their performance. The discharge curves obtained for the PPy/PF$_6$ electrode (10th cycle) are shown in Fig. 6. As reported in previous investigation of a polypyrrole-based cathode in a lithium cell [13,14], no obvious discharge plateau is observed. The discharge capacity of the PPy/PF$_6$/Pt wire electrode cell is about 75 mAh g^{-1}, which is similar to the values obtained with a cell using a PPy/PF$_6$ film electrode [15]. Galvanostatic charge and discharge curves for the fibre SWNT electrode are given in Fig. 7. The first cycle of this electrode exhibits an enormous irreversible capacity, which can be attributed to reduction of oxygenated functional groups on the surface of the SWNT electrode [16], and the formation of a solid electrolyte interface (SEI) layer on the surface of the electrodes.
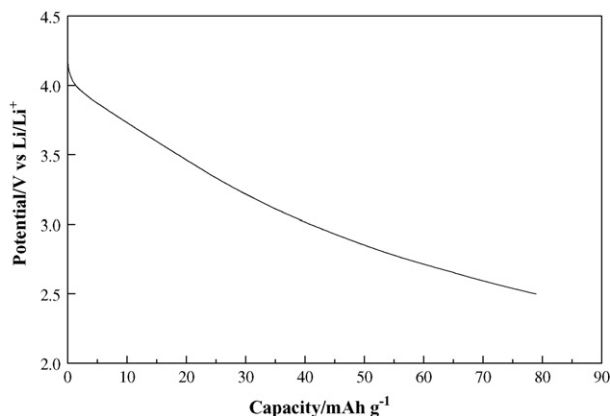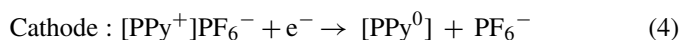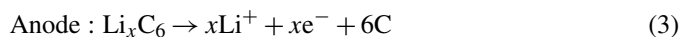
Fig. 6. Discharge curves of fibre electrode of PPy/PF$_6$ in a lithium cell. Current density = 0.1 mAh cm^{-2}.

Fig. 8. Discharge capacity vs. cycle number for cells of PPy/PF$_6$/LiPF$_6$–EC–DMC/SWNTs. Current density = 0.1 mAh cm^{-2}.

The galvanostatic charge–discharge curves are quite typical of this family of materials [17].

Batteries consisting of a PPy cathode and a SWNT-based anode in the fibre configuration were then constructed using 1 M LiPF$_6$ dissolved in EC-DMC (1:1, w/w) as electrolyte in a 'flooded cell' (Fig. 1D) or in a 'dry cell' (Fig. 1E). In the 'dry cell', the electrolyte was injected into the PVDF hollow fibre membrane anode with a syringe, and the PPy cathode was inserted into the PVDF tube. The assembly was immersed in the electrolyte for 1 h before it was sealed into a glass vial.

The reactions at the anode and cathode during discharge in a cell with LiPF$_6$ as the electrolyte can be represented as:

$$\text{Anode}: \text{Li}_x\text{C}_6 \rightarrow x\text{Li}^+ + x\text{e}^- + 6\text{C} \tag{3}$$

$$\text{Cathode}: [\text{PPy}^+]\text{PF}_6^- + \text{e}^- \rightarrow [\text{PPy}^0] + \text{PF}_6^- \tag{4}$$

The results are shown in Fig. 8. The initial reversible discharge capacity of the 'flooded cell' is quite high, i.e., about 28 mAh g^{-1}, then the capacity declines rapidly to about 20 mAh g^{-1} within 10 cycles. This capacity is maintained for more than 20 cycles by the 'flood cell'. Compared with our previous work on a flexible fibre battery construction based on a polypyrrole composite [10], the capacity has been improved significantly.
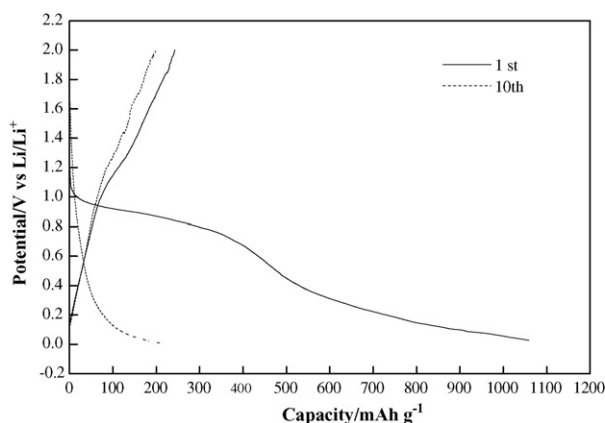
The fibre battery, 'dry cell' was then tested. An initial discharge capacity of about 10 mAh g^{-1} is obtained. This may be attributed to a lack of electrolyte that limits the movement of the anions and the cations in the dry cell. The results have demonstrated, however, that the unique design is practically feasible and that this type of cell can be cycled. The fibre cell needs to be optimized in further work.

4. Conclusions

A flexible fibre battery that uses polypyrrole-hexafluorophosphate (PPy/PF$_6$) as cathode, SWNTs as anode, and a PVDF hollow fibre membrane as a separator has been constructed and tested. Capacities of approximately 20 mAh g^{-1} are obtained and are twice those found in our previous work on the fibre batteries consisting of a PPy/PF$_6$ cathode, PPy/PSS anode in the 'flooded cells'. The capacity of the 'dry cell' is lower than that of the 'flooded cell' for the fibre battery with polypyrrole-hexafluorophosphate (PPy/PF$_6$) as cathode and SWNTs as anode.

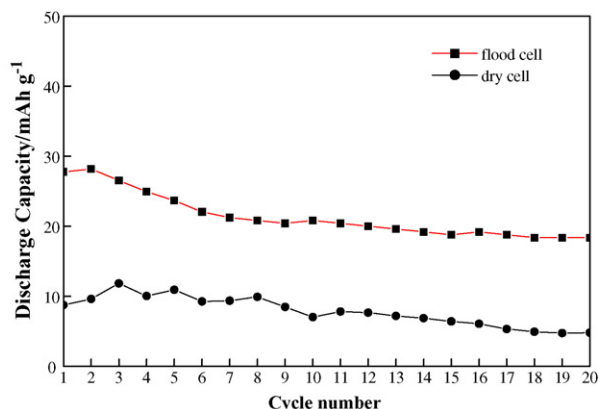Fig. 7. Charge–discharge curves of SWNTs fibre electrode in a lithium cell. Current density = 0.1 mAh cm^{-2}.

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