Electrochemistry Communications 61 (2015) 27–31

Contents lists available at ScienceDirect

Electrochemistry Communications

journal homepage: www.elsevier.com/locate/elecom

Short communication

3D braided yarns to create electrochemical cells

Chen Zhao [1], Syamak Farajikhah [1], Caiyun Wang, Javad Foroughi *, Xiaoteng Jia, Gordon G. Wallace **

Intelligent Polymer Research Institute, ARC Centre of Excellence for Electromaterials Science, University of Wollongong, NSW 2522, Australia

ARTICLE INFO

Article history:
Received 19 August 2015
Received in revised form 20 September 2015
Accepted 21 September 2015
Available online 30 September 2015

Keywords:
Wearable
Supercapacitor
Braiding
Polypyrrole

ABSTRACT

The demands for new configurations of electrochemical cells continue to grow and novel approaches are being enabled by the advent of new electromaterials and novel fabrication strategies. Wearable energy storage devices that can be seamlessly integrated into garments are a critical component of the wearable electronics genre. Recently, flexible yarn supercapacitors have attracted significant attention due to their ability to be integrated into fabrics, or stitched into existing textiles. Large-scale production of yarn supercapacitors using conventional manufacturing processes, however, is still a challenge. Here, we introduce the use of braiding technology to achieve a predetermined arrangement of fibre electrodes, the basis of a mass fabrication protocol to produce specific electrochemical cells: wearable supercapacitors. The resultant supercapacitors show a high capacitance of 1.71 mF cm^{-1}. The structure is highly flexible with a 25% capacitance loss recorded after 1000 bending cycles.

1. Introduction

The advent of new electromaterials, particularly in the form of fibres, has enabled creative approaches to the fabrication of novel electrochemical cell configuration. Smart garments are clothes with embedded functional electronic componentry including sensors and antennas [1,2]. They may be used for physiological measurement and monitoring [3], hazard detection [4], and/or wireless communication [5]. This approach has found widespread application in personalized wearable medical monitors, and even in the military field [6]. Wearable energy storage devices must be seamlessly integrated into such garments [7]. Supercapacitors have been extensively studied for energy storage due to their high power density, fast charge–discharge and extended life cycle [8]. Recently, flexible yarn supercapacitors have attracted significant attention due to the ability to integrate them into fabrics, or stitch into existing textiles [9].

Long lengths of fibre electrodes are necessary to fabricate yarn supercapacitors. Such fibre electrodes may be formed on thin metal wires [10–12], or metal coated plastic wires [13]. Alternatively carbon fibres [14], reduced graphene oxide (rGO) fibres [15], carbon nanotube (CNT) fibres [16], or composites containing them have been used [17–23]. Several device architectures have been developed for yarn supercapacitors. These include two parallel fibres, two-ply yarns and coaxial yarns [24]. In the first two types, two fibre electrodes and a separator or solid polymer electrolyte are fixed in parallel or twisted. And in the third type, the core electrode, separator or solid polymer electrolyte and outer electrode are assembled layer by layer. These yarn supercapacitors have yielded double-layer capacitance in the range of 0.01–6.30 mF cm^{-1}, and pseudo-capacitance values up to 263 mF cm^{-1} [23].

Yarns are generally made by twisting fibres together. For large-scale production of yarn supercapacitors, simply twisting or grouping two fibre electrodes will cause direct contact of the electrodes. Wrapping fibre electrodes with separator membranes [22] or winding with insulated wires [10] solves this short circuit problem, but limits large-scale manufacturing.

Braiding is a process that involves intertwining three or more sets of yarns over and under each other [25]. Two or more fibres can be braided into one yarn without contacting each other. Here, we introduce the use of braiding technology to enable production of yarn supercapacitors. Stainless steel (SS) wires and polyester fibres are braided into one yarn, and the SS wires play the role of current collectors and active material substrate. The SS wires in the yarn are fixed and separated by the insulated polyester fibres, so no additional separators are needed. Braiding is a fast continuous method of fabrication. To illustrate the use of this approach to create devices, polypyrrole (PPy) was electrodeposited onto the SS wires to produce active electrodes. The fabricated yarn supercapacitors showed good flexibility for application in wearable electronics. Other fine metal wires are commercially available including nickel, copper, titanium and platinum and would be amenable to this braiding method of fabrication. Apart from PPy, other conducting polymers or a variety of metal oxides/hydroxides such as γ-MnO_2 or $Ni(OH)_2$ can be simply electroplated onto such wires. Alternatively a

* Corresponding author. Tel.: +61 2 42981452; fax: +61 2 42981499.
** Corresponding author. Tel.: +61 2 42213127; fax: +61 2 42981499.
E-mail addresses: foroughi@uow.edu.au (J. Foroughi), gwallace@uow.edu.au (G.G. Wallace).
[1] These authors contributed equally in this paper.

http://dx.doi.org/10.1016/j.elecom.2015.09.021
1388-2481/

number of new organic conducting fibres have recently emerged [26]. All such materials would be suitable for use in these novel electrochemical devices.

2. Experimental

2.1. Reagents and materials

Polyester fibres (100D) and nylon/SS fibres were obtained from China (Shijiazhuang Yunchong Trading Co., Ltd.). Pyrrole was purchased from Merck, sodium *p*-toluenesulfonate and lithium sulphate monohydrate were obtained from Sigma-Aldrich. Pyrrole was freshly distilled, whereas other chemicals were used as supplied. All aqueous solutions were prepared using Milli-Q water (~18 MΩ).

2.2. Fabrication of yarn supercapacitor

3D yarns were braided from polyester and nylon/SS fibres using a Trenz-Export braiding machine. The nylon fibres were removed using formic acid after braiding. Electrodeposition of PPy was achieved at constant current (0.05 or 0.1 mA cm^{-1} for yarns with 2 or 4 SS wires, respectively) for 60 min from an aqueous solution containing 0.1 M pyrrole and 0.1 M sodium *p*-toluenesulfonate. During the deposition process, all the SS wires in the yarn were connected together. The samples were rinsed with water and dried in a fume hood overnight. Then the yarn samples were sealed in a transparent plastic tube injected with 1.0 M Li_2SO_4 aqueous solution to test capacitor performance. The quasi-solid state supercapacitor was fabricated using poly(vinyl alcohol) (PVA)/H_3PO_4 gel electrolyte prepared as described previously [27,28].

2.3. Characterization

Cyclic voltammetry (CV) was performed over the range of 0 to 0.8 V using a CHI 650D electrochemical workstation (CHI Instruments, USA). Electrochemical impedance spectra (EIS) were measured using a Gamry EIS 3000™ system over the frequency range of 100 kHz to 0.01 Hz with an AC perturbation of 10 mV at open circuit potential. Galvanostatic charge–discharge tests were performed using a battery test system (Neware electronic Co., China) between 0 and 0.8 V. The cyclic bending test of the yarn supercapacitor was carried out using Shimadzu EZ mechanical tester.

3. Results and discussion

The 3D braided yarns can be produced continuously without limitation in length. Two SS wires formed a double helix structure in the yarn (Fig. 1a). The SS wires in the yarn were fixed by the polyester fibres with a separation of ~2 mm to avoid direct contact. Electrodeposition of PPy on the SS wires was readily achieved using constant current.

The CV curves of the yarn supercapacitor retained a nearly rectangular shape at scan rates up to 50 mV s^{-1} (Fig. 2a). As the scan rate reached 100 mV s^{-1}, the CV curve became distorted. This can be explained by the slower inclusion/ejection and diffusion of counter ions compared to the electron transfer in PPy at high scan rates [27,28]. Consequently, the length specific capacitance of the yarn supercapacitor decreased with an increase in scan rate as presented in Fig. 2b. The length specific capacitances were calculated to be 0.78 to 1.71 mF cm^{-1}. This value exceeded that of the reported yarn supercapacitors based on pen ink/nickel wire (0.504 mF cm^{-1}) [10], Chinese ink/SS wire (0.1 mF cm^{-1}) [11], rGO/Au wire (0.01 mF cm^{-1}) [12], MnO_2/ZnO nanowire (0.2 mF cm^{-1}) [13], rGO fibre (0.02 mF cm^{-1}) [15], CNT/PEDOT fibre (0.47 mF cm^{-1}) [17], CNT fibre (0.018 mF cm^{-1}) [18], CNT/graphene fibre (0.027 mF cm^{-1}) [19], MnO_2/rGO fibre (0.143 mF cm^{-1}) [20], and CNT sheet (0.029 mF cm^{-1}) [29].

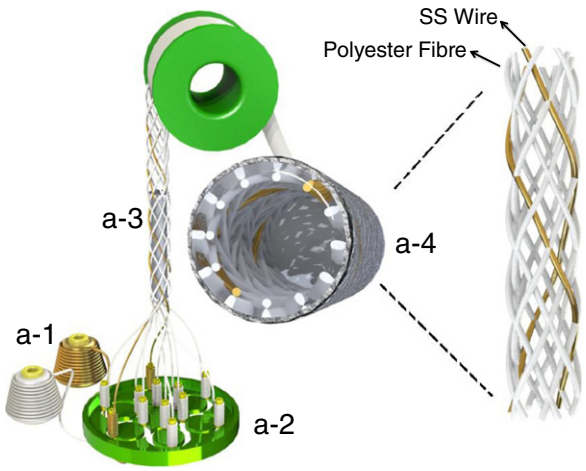

Fig.1. Schematic diagram to illustrate the 3D braiding process. (a-1) Polyester fibre and SS wire bobbins, (a-2) braiding head, (a-3) As-prepared braid structure, (a-4) braided supercapacitor.

The charge–discharge curves of the yarn supercapacitor at different current densities ranging from 5 to 50 μA cm^{-1} are presented in Fig. 2c. The curves showed a nearly symmetrical triangular shape, indicative of good capacitor behaviour. It delivered a length specific capacitance of 1.79 mF cm^{-1} at a current density of 5 μA cm^{-1}. Even at the current density of 50 μA cm^{-1}, the capacitance was still as high as 1.25 mF cm^{-1} (Fig. 2d).

The Nyquist plot of the yarn supercapacitor is shown in Fig. 2e. A semicircle in the high frequency region and a straight line in the low frequency region were obtained. The x-intercept of the Nyquist plot represents the equivalent series resistance (ESR) for the device [30]. The ESR of our yarn supercapacitor was measured to be ~11 Ω cm^{-1}. The straight line at low frequencies indicates capacitive behaviour [31].

The cycling stability of the yarn supercapacitor was tested at a current density of 20 μA cm^{-1}. After 1000 cycles, 30% of the initial capacitance was retained. PPy film swells and shrinks during the charge–discharge cycles, resulting in mechanical degradation [32].

For wearables, the yarn supercapacitor should possess excellent flexibility and maintain electrochemical performance under bending. CV tests were conducted at 5 mV s^{-1} while the yarn supercapacitor was held at different bending angles. The shapes of the CV curves only changed slightly up to 180° bending (Fig. 3a), reflecting that the yarn supercapacitor is highly flexible. The capacitance decreased by 13% as the device was bent from 0 to 180°. Furthermore, the yarn supercapacitor was subjected to repeated bending-relaxation to 90° for up to 1000 cycles and it suffered 25% loss (Fig. 3b).

Our single yarn supercapacitor shows good electrochemical performance, which makes it promising for integration with other microelectronic devices. However, the energy of a single yarn supercapacitor may not meet the requirement of those micro devices. The common approach is to connect two yarn supercapacitors or more in parallel. However, it will greatly increase the device dimension and also involve the package challenge. With the braiding technology, we can enhance the energy storage in the same yarn by simply incorporating more fibre electrodes. As a proof of concept, 4 SS wires were braided into the yarn. After PPy deposition, two SS wires were connected as positive electrode and the other two as negative electrode. This configuration equals to two single yarn supercapacitors connected in parallel. The output current doubled within the same voltage window as shown in the CV curves (Fig. 4a). The charge or discharge time was more than two times of the value of the 2-wire device at the same applied current density (Fig. 4b), since half of the total current is applied to each single device. According to the previous results of the capacitances at different current densities (Fig. 2d), the capacitance increased with the decreased current density.