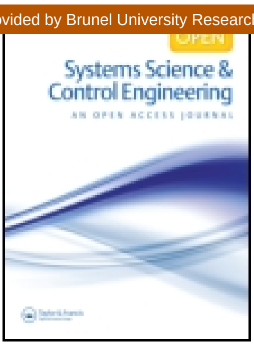

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Fabrication and characterization of smart fabric using energy storage fibres

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Fibre supercapacitors were designed and manufactured using a dip-coating method. Their electrochemical properties were characterized using a VersaSTAT 3 workstation. Chinese ink with a fine dispersion of carbon and binder was coated as the electrode material. The specific capacitance per unit length of a copper fibre supercapacitor with the length of 41 cm reached 34.5 mF/cm. When this fibre supercapacitor was bent on rods with a diameter of 10.5 cm, the specific capacitance per length was 93% of the original value (without bending). It showed that these fibre supercapacitors have good flexibility and energy storage capacity. Furthermore, the fibre supercapacitor in the fabric showed the same capacitance before and after weaving.

Keywords: supercapacitors; Chinese ink; energy storage fibre; gel electrolyte; flexible

1. Introduction

Recently, supercapacitors (also named electrochemical capacitors) have attracted much attention as energy storage devices. Because of their high power density, long cycle life and high reversibility (Kötz & Carlen, 2000), supercapacitors have a big potential to be used as high-power energy source in electrical vehicles, hybrid electric vehicles, portable electronic devices and emergency power supplies. Electrochemical energy can be stored in two ways in supercapacitors (Gómez et al., 2011; Kötz & Carlen, 2000; Seo, Yang, Kim, & Park, 2010; Shen et al., 2012). In electrical double-layer capacitors (EDLCs), there are no faradic reactions in the charge storage process; the capacitance arises from the charge separation at the electrode/electrolyte interface. Pseudocapacitors are another kind of supercapacitors, in which there is a faradic reaction in the energy storage process.

In recent years, there has been great interest in developing flexible, lightweight, low-cost and environmentally friendly energy storage devices. Supercapacitors can deliver higher power than batteries and store more energy than conventional capacitors (Seo et al., 2010). However, lots of existing supercapacitors are still too heavy and bulky for the intended applications. It is a challenge to develop highly efficient miniaturized flexible supercapacitors for future energy storage. Recently, some attempts have been made to manufacture flexible and weaveable supercapacitors (Bae et al., 2011; Cherenack, Zysset, Kinkeldei, Münzenrieder, & Tröster, 2010; Fu et al., 2012; Harrison et al., 2013; Jost et al., 2011; Le et al., 2013; Milczarek, Ciszewski, & Stepniak, 2011; Pushparaj et al., 2007; Qiu, Harrison, Fyson, & Southee, 2014; Wang et al., 2011; Zhang et al., 2014). Bae et al. (2011) developed a kind of novel fibre supercapacitor using ZnO nano-wires as electrodes, which showed a high specific capacitance of 2.4 mF/cm^2 and 0.2 mF/cm using polyvinyl alcohol (PVA)/H_3PO_4 as the gel electrolyte. Fu et al. (2012) developed a novel flexible fibre supercapacitor which consisted of two parallel fibre electrodes using Chinese ink as the active electrode materials, a helical spacer wire and an electrolyte that showed good capacitance. A low-cost and flexible mesh-based supercapacitor using commercial pen ink as active material has been developed by Shi, Zhao, Li, Liao, and Yu (2014). This device showed good electrochemical performance, with a specific capacitance of 47.4 mFcm^{-2} at the scan rate of 2 mVs^{-1}. Pen ink (Chinese ink) as the active material of the electrodes showed good adhesive and porous morphology. A coaxial fibre supercapacitor was designed (Harrison et al., 2013; Qiu et al., 2014; Zhang et al., 2014) and manufactured in this study. This coaxial fibre structure contains five layers of materials: two electrode layers, two current collector layers and a gel electrolyte layer. The structure of this coaxial fibre supercapacitor developed was different from that of others (Fu et al., 2012; Shi et al., 2014). The coaxial fibre was all-solid and had the useful potential of being able to be woven to produce different-shaped energy storage fabrics. Herein, coaxial fibre supercapacitors, using Chinese ink as active materials, were designed, manufactured and characterized.

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The results are discussed in this study. The particular novelty reported in this paper is the significant increase in specific capacitance (from 0.5 to 34.5 mF/cm), achieved by increasing the number of coatings on the carbon electrodes from 4 to 24 (Zhang et al., 2014).

2. Experiment

2.1. Materials

Phosphoric acid (H_3PO_4, dry) and PVA (MW 146,000–186,000, > 99% hydrolysed) were used without further purification. The gel electrolyte was made by dissolving 0.8 g H_3PO_4 and 1 g PVA in 10 mL deionized water. Copper wire (50 μm in diameter) was used as the core conductor material. Commercial carbon-based Chinese ink purchased from an art shop was used as the active coating material.

2.2. Design of the structure of the energy storage fibre

Based on the working mechanism (Harrison et al., 2013; Kötz & Carlen, 2000), fibre supercapacitors have been designed (Zhang et al., 2014). As shown in Figure 1(a), the typical EDLCs consist of five layers which are two current collectors, two active layers with electrolyte and a separator with electrolyte. Following this typical structure of an EDLC, the coaxial single fibre supercapacitor with five layers was designed and manufactured (see Figure 1(b)). The central metal wire and the outer layer of silver paint are current collectors. Two active layers made of Chinese ink are separated by a gel electrolyte layer and serve as electrodes. The energy is stored by the accumulation of electrical charges at the boundary layers between the two electrodes and the electrolyte.

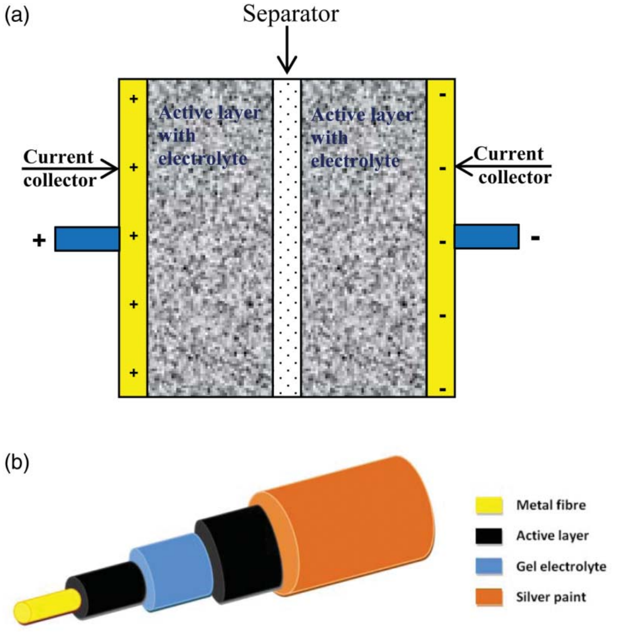

Figure 1. (a) Typical structure of an EDLC; (b) 3D schematic of four coating layers on the metal fibre.

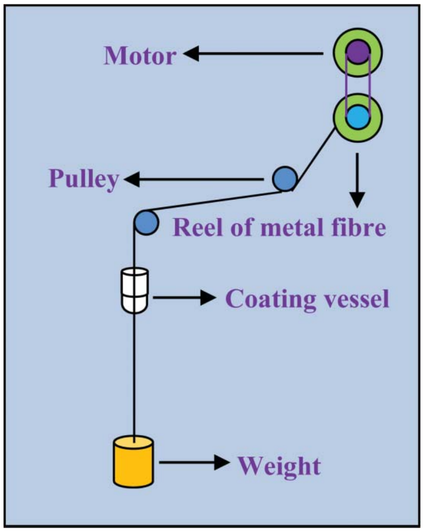

Figure 2. The schematic of coating method.

2.3. Manufacturing method

Figure 2 schematically shows the experimental set-up for coating the energy storage fibre. A reel of metal wire and two pulleys are fixed horizontally onto a plate. A weight is clamped to the bottom end of the core wire to keep the wire straight and in alignment with the coating vessel. A motor with a two-direction controller was used to drive the reel axle to control the coating speed. When the coating process is carried out, a coating liquid is filled in the coating vessel. During the movement of the core metal wire through the hole, the wire drags the coating liquid with it, the solvent is evaporated and the coating materials deposit on the wire.

2.4. Characterization of the electrochemical properties

The electrochemical performance of the energy storage fibre developed was studied by cyclic voltammetry (CV) and galvanostatic charge/discharge using a VersaSTAT 3 electrochemical workstation. The structure of a cross section of the supercapacitor was studied by optical microscopy, and the morphology of the active layer was characterized using a scanning electron microscope (SEM).

A CV test is carried out by applying a positive (charging) voltage sweeping at a rate of dV/dt (scan rate) in a specific voltage range and then reversing (discharging) the voltage sweep polarity immediately after the maximum voltage range is achieved. The electrochemical behaviour of a supercapacitor could be evaluated based on the corresponding current response against the applied voltage by the following equations:

$$C = \frac{Q_{\text{total}}/2}{\Delta V}, \tag{1}$$

$$C_L = \frac{C}{L}, \tag{2}$$

where C is the capacitance and C_L is the specific capacitance per unit length. Q_{total} is the supercapacitor's charge in coulombs. The charge is automatically calculated by the workstation software. L is the length of the fibre supercapacitor.

A galvanostatic charge/discharge test is the most preferred DC (direct current) test performed on supercapacitors for performance evaluation. The measurement consists of two steps: (1) charging a supercapacitor at a constant current and then (2) discharging at a specific voltage range or charge/discharge time. The capacitance C can be directly calculated by the following equation:

$$C = \frac{i \cdot \Delta t}{\Delta V}, \tag{3}$$

where i is the discharge current in amperes (A), Δt is the discharging time (s) and ΔV is the voltage of the discharge excluding *iR* drop (V).

3. Results and discussion

Following the schematic of fibre supercapacitors (as shown in Figure 1), the energy storage fibres were made using the commercial Chinese ink as the active material.

A hand-made fibre supercapacitor with a length of 5 cm was made by a dip-coating method, and was tested using the electrochemical workstation. The typical galvanostatic charge/discharge curve record (first five cycles at a charge current of 0.5 mA) is shown in Figure 3(a). The charge/discharge curve is well defined. All the charge/discharge curves showed that the iR drop happened at the early stage, and the size of the iR drop is similar in each charge/discharge curve. This suggests that the performance of this short fibre supercapacitor is stable. Figure 3(b) shows the cyclic charge/discharge curves run on this fibre supercapacitor at different currents. It can be seen that the charge and discharge time decreases as the charge current increases, and the iR drop increases as the charging current increases as one would expect. The capacitance can be calculated using Equation (3). When the charging current increased from 0.5 to 1.5 mA, the capacitance decreased from 1.32 to 1.04 mF; the specific capacitance per length unit decreased from 0.26 to 0.21 mF/cm (Figure 3(c)). This may be caused by the slow diffusion of electrolyte ions through the double layer on the electrode surface or the slower permeation of ions through the pores in the carbon particles at higher currents. The capacitance at the charging current 1.5 mA was still 79% of that measured at the charging current of 0.5 mA. This suggests that the Chinese ink used as the activated material has reasonably well-behaved electrical properties.

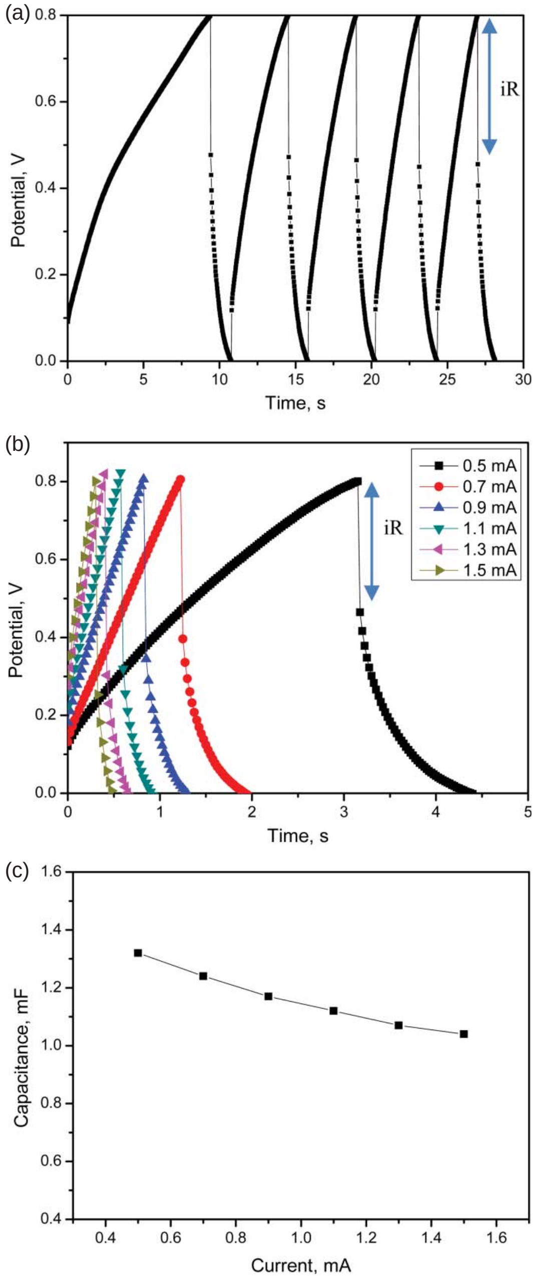

Figure 3. (a) Galvanostatic charge/discharge curve recorded at a charging current of 0.5 mA; (b) Galvanostatic charge/discharge curve at different charging currents (0.5, 0.7, 0.9, 1.1, 1.3 and 1.5 mA); (3) the corresponding capacitances calculated based on Figure 3(b).

A longer energy storage fibre was made using the dip-coating device as shown in Figure 2. The CV curve of the fibre supercapacitor sample with the length of 35 cm is illustrated in Figure 4. The CV curve is closed and regular; therefore, the capacitance and specific capacitance can be evaluated using Equations (1) and (2). The capacitance and specific capacitance per unit length were 18 mF

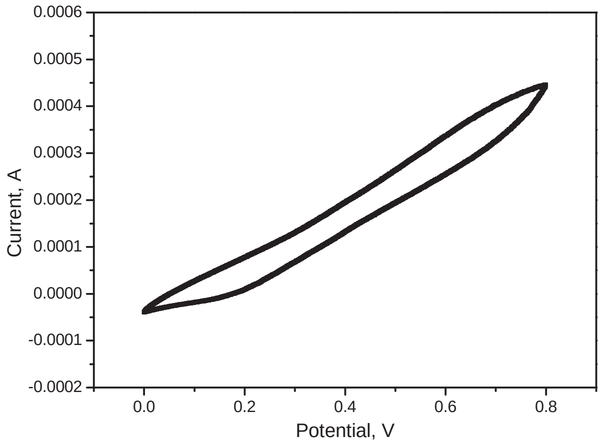

Figure 4. The cyclic voltammogram of the 35 cm long fibre supercapacitor sample.

and 0.5 mF/cm, respectively. This shows that this kind of energy storage fibre made by the dip-coating device is functional, although the capacitance was not as high as expected. This is probably because insufficient active material was coated on the fibre due to the manufacturing process.

A typical cross section of a copper fibre supercapacitor is shown in Figure 5(a). The five-layer structure can be seen clearly. The copper fibre core is easy to see. The second Chinese ink layer was not uniform. The gel electrolyte layer, the third layer, was complete but the thickness was not uniform. The fourth layer was also of Chinese ink and was also uneven. Figure 5(b) shows the typical porous structure of the Chinese ink layer surface. The diameter of the holes is about 200 nm. This micro structure will allow a good electrolyte accessibility to the inner surface of the active layer. This porous structure should also provide a large surface area for electrical charge storage.

A new fibre supercapacitor with the length of 41 cm was made based on the technical manufacturing skills gained from the experience of many laboratory trials (Figure 6). The first ink layer was deposited 24 times in this fibre supercapacitor, which was 6 times more than that of the initial 35 cm sample. The specific capacitance of the new sample was about 34.5 mF/cm, which is 69 times that of the trial 35 cm sample. Generally, when the number of coatings is increased substantially, the thickness of the ink layer increases dramatically as does the amount of the active materials in each of the electrodes. This should increase the electrical storage capacity of the fibre supercapacitor.

The flexibility of the fibre supercapacitors was also studied. The specific capacitance of the 41 cm long supercapacitor was examined when the fibre was bent on a glass rod with different curvatures. The diameters of the glass rods were 10.5, 3.0 and 1.5 cm. Figure 6 shows the CV curves of the fibre supercapacitor bent at different curvatures. It can be seen the CV curves were the same when

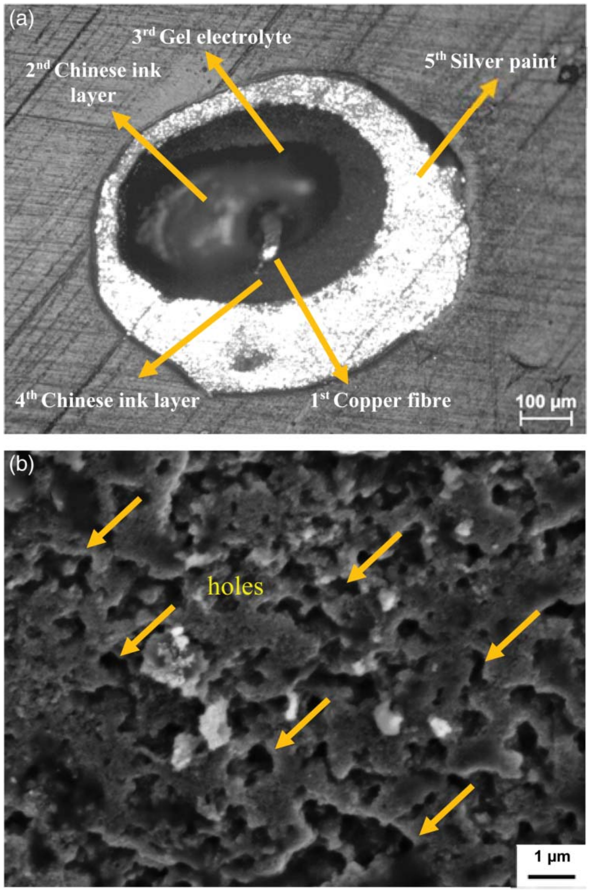

Figure 5. (a) Optical image of the cross section of a fibre supercapacitor; (b) SEM photo of the surface of the Chinese ink layer.

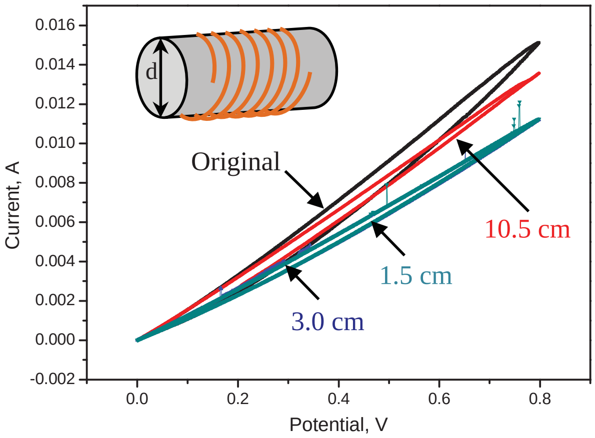

Figure 6. CV curves of the 41 cm long fibre supercapacitor at different testing conditions (straight and bent with different curvatures).

the fibre supercapacitor was bent using the glass rods with the diameters of 1.5 and 3.0 cm. When the fibre supercapacitor was bent on the glass rod with the diameter of 10.5 cm, the specific capacitance decreased slightly to 32.2 mF/cm, which was about 93% of the original straight

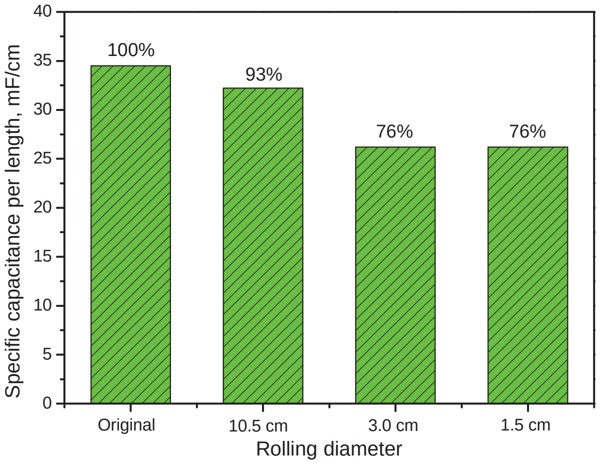

Figure 7. Comparison of the specific capacitance per length of the fibre supercapacitor being bent with different curvatures with the original straight sample.

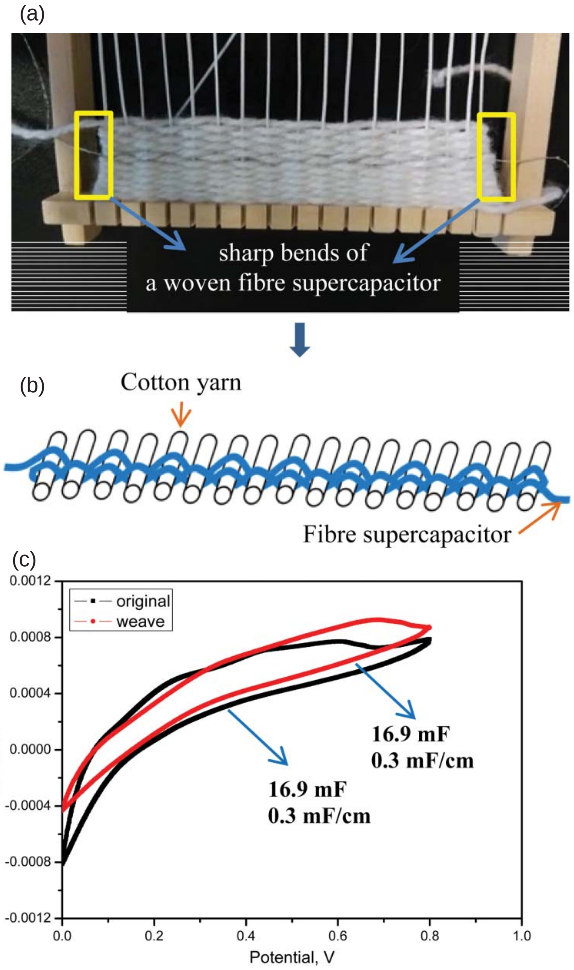

Figure 8. (a) Photo of the fibre supercapacitor woven into a fabric; (b) the schematic of the fibre supercapacitor in the fabric; (c) CV curves of the free fibre supercapacitor and that woven into fabric.

sample. When the diameter of rods decreased to 3.0 and 1.5 cm, the specific capacitance changed to 26.2 mF/cm for both cases, which was 76% of the straight sample.

The comparison of the specific capacitance of the fibre supercapacitor at different bending conditions with the original sample is shown in Figure 7. These results show that the fibre supercapacitors are able to work whilst being severely bent. As shown in Figure 8(a) and 8(b), a 50 cm long fire supercapacitor was woven with cotton yarn to produce a fabric using a simple loom. There are sharp bends along the two sides of the fabric. CV was employed to test the effect of weaving a fibre supercapacitor. Figure 8(c) shows the CV curves recorded at 30 mV/s of this fibre supercapacitor before and after being woven into the fabric. It demonstrates that even with a few sharp bends, the woven fibre supercapacitor can still work and its flexibility is more than sufficient for this use. There are a few differences between the features of these two CV curves. The CV curve of the fibre supercapacitor woven into the fabric showed a smaller slope, revealing its smaller resistance. The reason could be that the thickness of the PVA gel electrolyte layer decreases as it is being stretched in the weaving process. The capacitance of this woven supercapacitor calculated using Equation (1) is 16.9 mF, which was the same as the capacitance of the free fibre supercapacitor. This demonstrates that the charge storage capacity of this fibre supercapacitor is capable of being woven into fabric. It also shows that fibre supercapacitors are flexible enough to be woven into fabrics to make smart textiles.

4. Conclusions

Coaxial single fibre supercapacitors were successfully manufactured and characterized in this study. Chinese ink was used as the electrode material. A hand-made short sample proved that the fibre supercapacitor designed was functional. A dip-coating set-up was designed to produce longer fibre supercapacitors. When the coating number of carbon ink in each electrode layer increased substantially, the amount of active materials deposited on the electrodes increased dramatically. This improved the electrical storage of the fibre supercapacitor tens of times. The specific capacitance of the supercapacitors at various bending conditions was examined. The results showed that the supercapacitors manufactured using the present method kept a good electrochemical performance under severe bending conditions. The fibre supercapacitor kept the same capacitance as the original capacitance of the original free fibre when it was woven into a fabric. This indicated that the fibre supercapacitors designed and made in this study have very good flexibility. Based on these results, as the next step, the mechanical property will be tested and a new ink made with activated carbon, binder and an appropriate solvent will be used to optimize the energy storage performance. This could be used as a flexible energy storage and woven or perhaps embroidered into other fabrics to make smart textile materials.

Disclosure statement

No potential conflict of interest was reported by the authors.

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