Flexible solid-state fabric based supercapacitor

S Yong[1], J R Owen[2], M J Tudor[1], S P Beeby[1]

[1]Electronic &Electrical Engineering Group, Electronics and Computer Science, University of Southampton, Southampton, SO17 1BJ, UK
[2]Electrochemistry, Chemistry, University of Southampton, Southampton, SO17 1BJ, UK

E-mail: sy2g11@soton.ac.uk

Abstract. This paper reports details of the design, fabrication and characterisation of a solid-state fabric supercapacitor device. The proposed supercapacitors were based on fabric electrodes fabricated with low cost carbon materials via a spray coating technique. The two layer supercapacitors achieved a specific capacitances of 10.6 $F.g^{-1}$, area capacitance of 71.8 $mF.cm^{-2}$ and maintained 99% of the initial capacitance after cycling the device for more than 15000 times

1. Introduction

Wearable electronics can be defined as the integration of electrical system in clothing and accessories. Powering such system could benefit from a flexible solid-state energy storage device with high energy and power density. A supercapacitor also known as ultra-capacitor, is an electrochemical energy storage device that can provide both high energy density and power density, supercapacitor have been commonly used in smart sensor networks [1], energy harvesting powered systems [2] and power backup systems [3]. This paper presents a detailed fabrication process for a flexible solid-state supercapacitor device based on non-hazardous materials and polyester-cotton fabric substrates.

Previously carbon fabric (CF) [7] or carbon nanotube (CNT) [4] have been typically used in fabric supercapacitor electrodes. CF has the advantages of good mechanical stability, relative low cost in comparison with CNT, flexible, wearable and good electrical conductivity. Jin. H et.al [7] implemented a solid-state flexible supercapacitor using functionalized CF; this device achieved an aerial capacitance of 155.8 mF.cm-2 with an operating voltage up to 1.6 V. Cheng .H [4] reports of a supercapacitor electrode made by weaving CNT coated graphene woven fabric film, the scalable electrode achieves very high specific capacitance of 200.4 $F.g^{-1}$ (0.98 $mF.cm^{-2}$). Activated carbon, is another potential carbon material for supercapacitor electrode, it has large specific surface area, low electric resistivity and relatively low cost in comparison with other materials like CF and CNTs. Previously M. Cowell et.al [5] presented a flexible supercapacitor made with stencil casted polymer-carbon electrodes and gel- electrolyte. The symmetrical capacitive cells achieved 43 $mF.cm^{-2}$.

In comparison with conventional rigid supercapacitor, the supercapacitor used in wearable electronics needs to be lightweight, flexible, solid-state and made with non-hazardous gel-electrolyte and electrode. Previously, researchers have used hazardous substances in their solid-state supercapacitor, for example acid [6] in the gel electrolyte or corrosive oxide material [8] in the electrode. In wearable electronics application, supercapacitor made with hazardous materials requires extra care when packaging reduces the potential for skin irritation. Therefore although such supercapacitor may demonstrate electrochemical performance the use of hazardous materials mean they are not the best opinion for wearable electronics.

Supercapacitors store energy with two types of capacitive mechanisms: the electrical double layer capacitance (EDLC) and redox pseudocapacitance. The EDLC is based on the capture and release of electrostatic charge that occurs at the electrode and electrolyte solution interface. It is constructed using two electrical double layer interfaces, each having opposite polarity with respect to the electrolyte solution. Conventionally a charge separator containing an aqueous electrolyte will be placed in between the two supercapacitor electrodes to prevent the electrical short circuits. In solid-state supercapacitor, a gel electrolyte will replace the charge separator to prevent the short circuits, and provide free ions to forms the double layer interfaces. Therefore, in a solid-state supercapacitor it is not essential to place another layer of charge separator in between the two supercapacitor electrodes [9].

This work demonstrates an energy storage device for wearable electronics by fabricating a solid-state fabric electric double layer supercapacitor with non-hazardous materials. The fabric electrodes were achieved via the spray coating process with various inexpensive carbon powders and poly-cotton fabric substrates that are commonly used in the clothing industry. The supercapacitor was fully tested with a gel electrolyte in order to study their operation and stability as a function of cycle rate and cycle number.

2. Device fabrication

In order to create a permanently conductive carbon-coated fabric, carbon powders are mixed with a liquid binder that provides the adhesion between the carbon powders and fabrics to form a carbon ink. The carbon ink will be spray coated on selected area of the poly-cotton fabric substrate. In this work the carbon powder was mixed with binder Poly (vinyl alcohol-co-ethylene), dimethyl sulfoxide solvent and a surfactant. The carbon powders used in this work are activated carbon powder Kuraray Yp-80F and carbon black powder Shawinigan Black. Kuraray Yp-80F, has high purity, a particle size between 5-25 μm in diameter and an effective surface area of 2200 $m^2.g^{-1}$. Shawinigan Black has a mean particle size of 42 nm in diameter and an effective surface area of 75 $m^2.g^{-1}$.

In the next step the carbon ink was spray coated on both side of the fabric samples with a mask and spray gun connected to an air compressor. The fabric substrate in this work is polyester cotton material that has both the advantages of polyester and cotton material. During the spray coating process, carbon vapor penetrates into the selected part of the fabric substrate and adheres to the yarns of fabrics uniformly. After the sample is fully cured, the carbon powder bonds to the fabric substrate via the polymer binder; it introduces a large, conductive surface area that forms an electrical double layer on contact with the electrolyte. The photograph of the spray coated carbon fabric electrode on the poly-cotton fabrics can be seen in figure 1 (a)

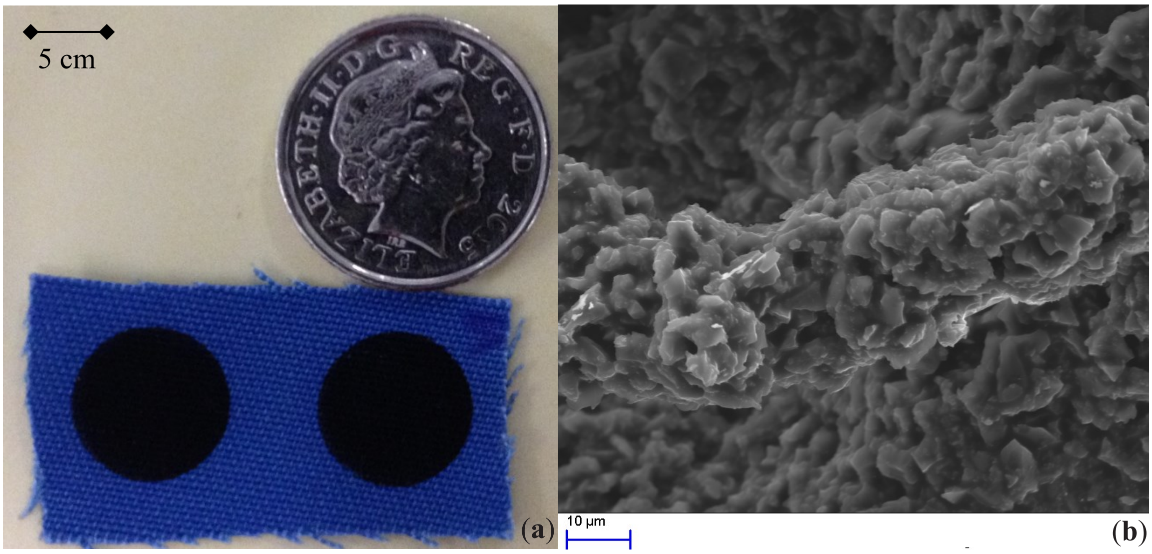

Figure 1. (a) Black carbon fabric electrode on original blue fabric substrate. **(b)** SEM photograph of carbon fabric electrode

Figure 1 (b) shows the SEM micrograph of the carbon particles adhered to the fibre to make a conductive network in the fabric substrate. The circular fabric electrode shown in figure 1 (a) will be cut out to assemble the supercapacitor cell. In this study the area of each poly-cotton fabric electrode is 0.785 cm^2 with thickness about 350 µm, each single piece of fabric electrode has a weight of 21.9 $mg.cm^{-2}$ before coating and carbon materials account for 13.4% of the final electrode weight.

The gel electrolyte was prepared by mixing ammonium salt, vinyl- alcohol polymer and water. The gel electrolyte solution was put under vacuum for 2 hours to reduce the amount of air bubbles inside the solution. In the next step, the two pieces of fabric electrodes were dipped into the gel electrolyte under vacuum for 20 minutes. This step enhances the wettability between the fabric electrodes and the polymer electrolyte. Finally, the two fabric electrodes containing the wet gel electrolyte were compressed together and cured in oven for 2 hours at 60 ^{o}C.

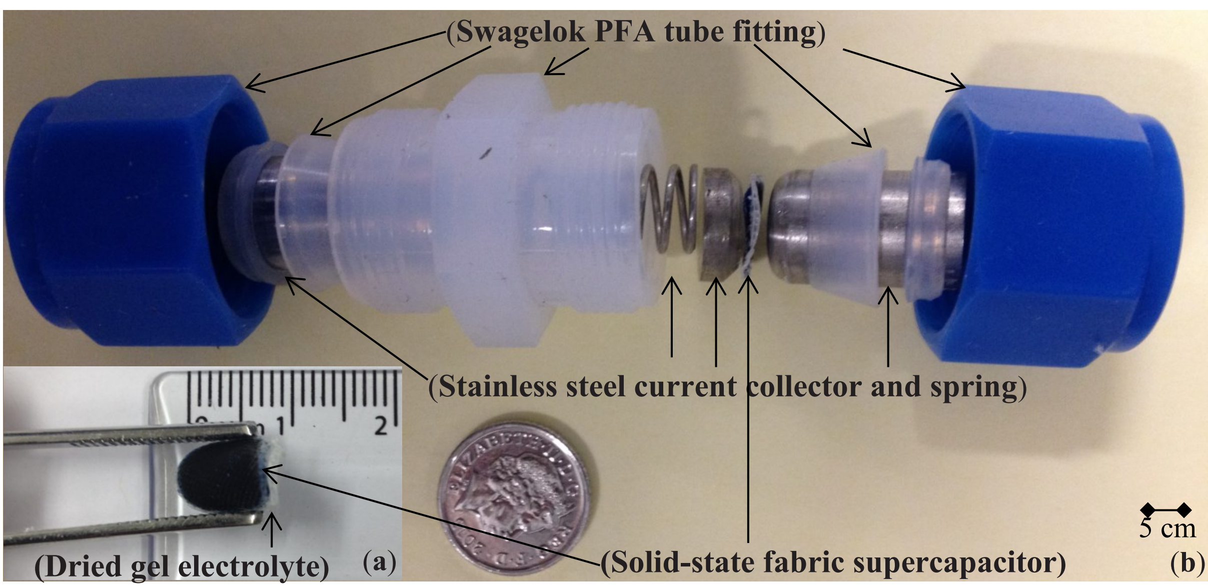

Figure 2. (a) Photograph of solid-state fabric supercapacitor before assembly. **(b)** Swagelok PFA tube fitting used to test the fabric supercapacitor before closing the two fitting caps

Figure 2 (a) shows the dried solid-state fabric supercapacitor is flexible after curing, The white layer in figure 2 (a) is the dried polymer electrolyte that had flowed out from the fabric electrodes. As shown in figure 2 (b) the assembled supercapacitor device is compressed from the top to bottom electrodes using spring loaded stainless steel current collectors and spring housed within a Swagelok PFA tube fitting for testing.

3. Results and discussion

The Solid-state fabric supercapacitor was tested using a VMP2 potentiostat/galvanostat (Biologic, France). The encapsulated supercapacitor was characterised by impedance spectroscopy (EIS), cyclic voltammetry (CV) at different scan rates and galvanostatic cycling (GC). and 4.

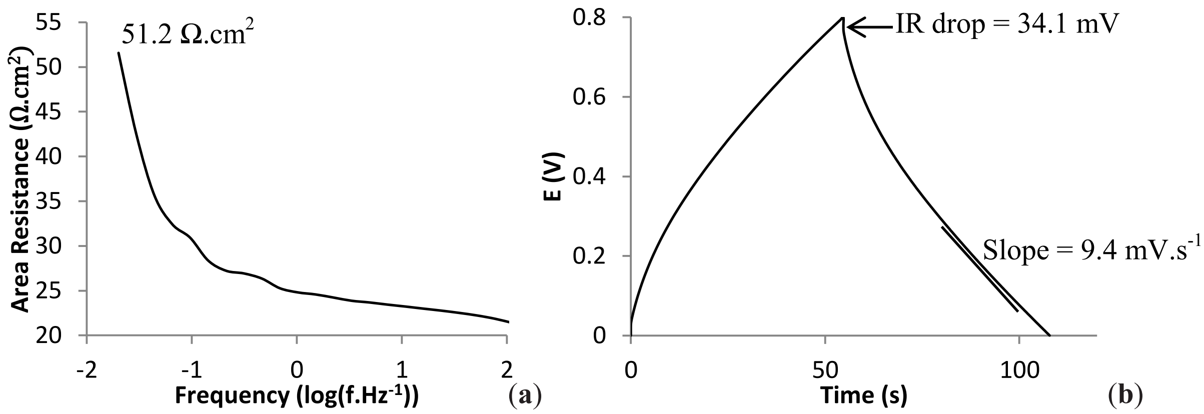

Figure 3. (a) Bode plot of device from 100 Hz to 20 mHz, extract from EIS test with equivalent series resistance (ESR) marked. **(b)** Galvanostatic cycling (GC) tests (0.675 $mA.cm^{-2}$)

The ESR of the supercapacitor was determined from the EIS test from the bode plots extracted from the EIS response at 20 mHz. In the GC test, the ESR of supercapacitor was calculated by measuring the ohmic drop or IR drop and the test current. Figure 3 (a) shows at low frequency (20 mHz) the ESR of the solid-state fabric supercapacitor is 51.2 $\Omega.cm^2$ This ESR is due to the electrolyte and electrode materials and the diffusion resistance. From figure 3 (b) The ESR result from the EIS test is very close to the ESR (50.5 $\Omega.cm^2$) calculate from the IR drop and test current in the GC test. According to figure 3 (b) the mass specific capacitance is found to be 10.6 $F.g^{-1}$, the area capacitance 71.8 $mF.cm^{-2}$.

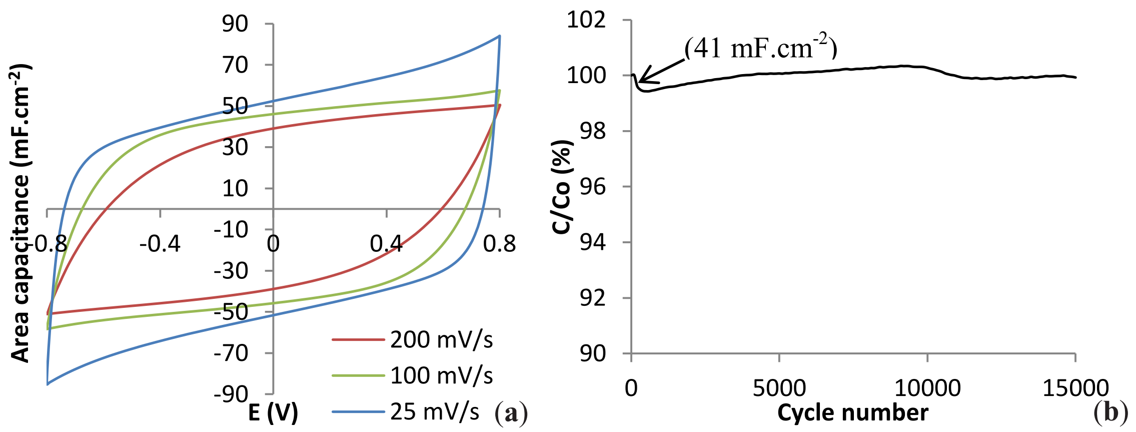

Figure 4. (a) CV test of the device between +/- 0.8 V at the scan rate of 200, 100, 25 $mV.s^{-1}$, **(b)** stability of device over 15000 cycles. C_o is the initial area capacitance (41 $mF.cm^{-2}$) of the device measured from cycle 1 of the CV test between +/- 0.8 V at the scan rate of 200 $mV.s^{-1}$.

As shown in figure 4 (a), the CV curves indicate that the device is electrochemically stable at the scan rates from 25 to 200 mV, and area capacitance values vary from about 40 to 80 mF.cm^{-2} depending on the different scan rate. Figure 4 (b) shows the device stability with a CV response. The overall variation of less than 1% correlates with the small temperature changes in the test lab. The high device stability indicates excellent adhesion of the carbon powders forming a continuous conducting network, which is due the use of the spray coating technique and vacuum impregnation process with poly ethylene vinyl alcohol binder and gel electrolyte. The spray coating process results in the blend of activated carbon and carbon black powder being spread uniformly over the fabric samples and infiltrate into the poly-cotton fabrics and fill up the fabric yarns to form a conductive network. The vacuum impregnation process ensures the gel electrolyte get in contract with maximum amount of the electrode materials to forms an effective double layer interface during characterisation.

4. Conclusion

This report presents a two layer supercapacitor on a fabric substrate. The non-hazardous solid-state fabric supercapacitor implemented in this work achieves a mass specific capacitance of 10.6 F.g^{-1}, area specific capacitance of 71.8 mF.cm^{-2}, a low normalized ESR of 50.5 Ω.cm^{-2} and achieves good cycling stability of less than 1% capacitance variation over 15000 cycles. In comparison with other works, These result are not as good as formal aqueous supercapacitor, however the individual carbon electrode can be sprayed on selected area of the fabrics, the proposed supercapacitor is non-hazardous, fully wearable, scalable, inexpensive and made without an individual charge separator. This work offer a practical approach for achieving a low cost and reliable energy storage supercapacitors in fabrics for wearable applications. Future work will include improving the formulation of the carbon and gel electrolyte ink so they can be spray painted into single piece of fabric to forms a solid-state fabric supercapacitor. The final device could see use applications in a wide range of wearable electronic systems like energy harvesters, medical sensors and a wide range of personal wearable electronics.

5. Acknowledgment

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