

# INTEGRATED FLEXIBLE SOLID-STATE SUPERCAPACITOR FABRICATED IN A SINGLE FABRIC LAYER

S Yong<sup>1</sup>, J R Owen<sup>2</sup>, M J Tudor<sup>1</sup>, S P Beeby<sup>1</sup>

<sup>1</sup>Electronic & Electrical Engineering Group, Electronics and Computer Science,  
University of Southampton, Southampton, SO17 1BJ, UK

<sup>2</sup>Electrochemistry, Chemistry, University of Southampton, Southampton, SO17 1BJ,  
UK

E-mail: sy2g11@soton.ac.uk

**Abstract.** This paper presents the design, fabrication and characterization of a flexible solid-state electrical double layer supercapacitor fabricated in a single fabric layer. The proposed supercapacitors were based on fabric electrodes fabricated with low cost carbon materials via a spray coating technique. The single layer solid state supercapacitors achieved a specific capacitances of  $40.5 \text{ F.g}^{-1}$ , area capacitance of  $40.5 \text{ mF.cm}^{-2}$ .

## 1. Introduction

Wearable electronics also known as electronic textile or e-textile is 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 is an electrochemical device used for storing electrical energy, it can act as a standard energy storage and buffer devices with high capacitance while having a fast cycling rate like a conventional capacitor. Traditional energy storage devices such as electrochemical secondary batteries are limited in several areas such as poor cycling stability, lack of flexibility and low power density that not always compatible with wearable application like electronic textile. Therefore, new lightweight and flexible energy storage devices like fabric supercapacitors are highly of great interests as energy reservoir for smart fabric applications and desirable for e-textile approaches [1], but these have not yet been fully developed [2].

To date there are many examples of multilayer solid-state supercapacitor implemented on different flexible substrate, most of them attempt used either expansive carbonized materials like carbon nanotube (CNT) [3] and reduced graphene oxide [4], or pseudo-capacitive material such as manganese oxide [3] and conductive polymer [5] that suffered relative short device life time. H Sun et.al [4] implemented a solid-state flexible supercapacitor with polyester textile electrodes and gel electrolyte, the textile substrate was coated by reduced graphene oxide and conductive polymer (polyaniline), this multilayer device achieved an aerial capacitance of  $781.8 \text{ mF.cm}^{-2}$ . D V Lam et al. [6] demonstrated a flexible and all solid state supercapacitor with calligraphic ink coated hybrid cotton textile electrode and lithium salt based gel electrolyte. This device achieved area capacitance of  $36 \text{ mF.cm}^{-2}$ .

An electrical double layer supercapacitor is constructed using two electrical double layer interfaces, each having opposite polarity with respect to the electrolyte solution. The supercapacitor used in wearable electronics needs to be lightweight, flexible, solid-state, easy to be integrated into the system and made with non-hazardous materials. Previously, researchers have used hazardous substances in their solid-state supercapacitor, for example acid [7] in the gel electrolyte or corrosive oxide material [8] in the electrode, also these devices are consisting of two layers of fabric electrode and possibly a paper separator. In wearable electronics application, these supercapacitor requires extra care when packaging reduces the potential for skin irritation and compress/seal the multilayer device. Therefore, although



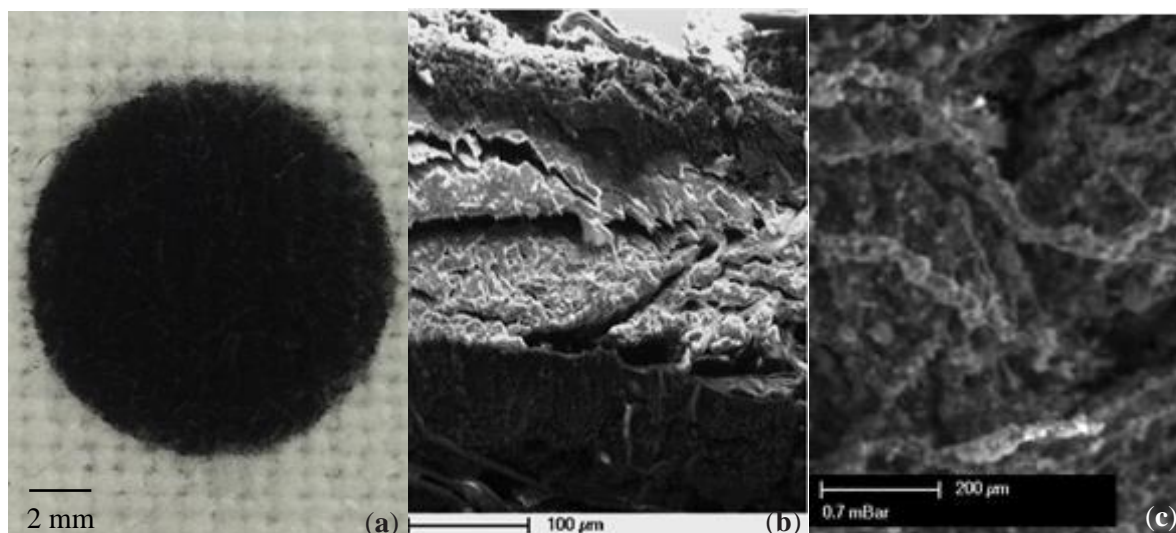
such supercapacitor may demonstrate electrochemical performance the use of hazardous materials and multilayer device structure mean they are not the best opinion for wearable electronics.

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

## 2. Device fabrication

Firstly, the conductive carbon ink for the coating process is prepared, the ink contains the commercial available inexpensive carbon powders, 1, 2, 4- Trichlorobenzene (1, 2, 4 TCB) solvent, a surfactant and polymer binder Ethylene-co vinyl acetate (EVA) that provides the adhesion between the carbon powders and fabrics. In this work the carbon powders used 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  $\mu\text{m}$  in diameter and an effective surface area of  $2200 \text{ m}^2.\text{g}^{-1}$ . Shawinigan Black has a mean particle size of 42 nm in diameter and an effective surface area of  $75 \text{ m}^2.\text{g}^{-1}$ .

In the next step the carbon ink was spray coated on both side of the cotton fabric substrates with a stainless steel mask and pneumatic spray system. During the spray coating process, carbon vapor coats the selected part of the fabric substrate and adheres to the yarns of fabrics uniformly, the penetration depth of the carbon vapor in the fabric substrate and was controlled by the pressure and the distance of the spray coating process, it allows carbon vapor get into the cotton substrate but did not penetrate all the way through the fabric substrate. After curing process, the carbon powder bonds to the fabric substrate via the polymer binder. The photograph of the spray coated carbon fabric electrode on the cotton fabrics can be seen in figure 1.a. As shown in figure 1.b, the SEM photograph of cross section view of cotton electrode indicates the top and bottom carbon coated cotton electrode yarns are physically separated by the cotton fibres.

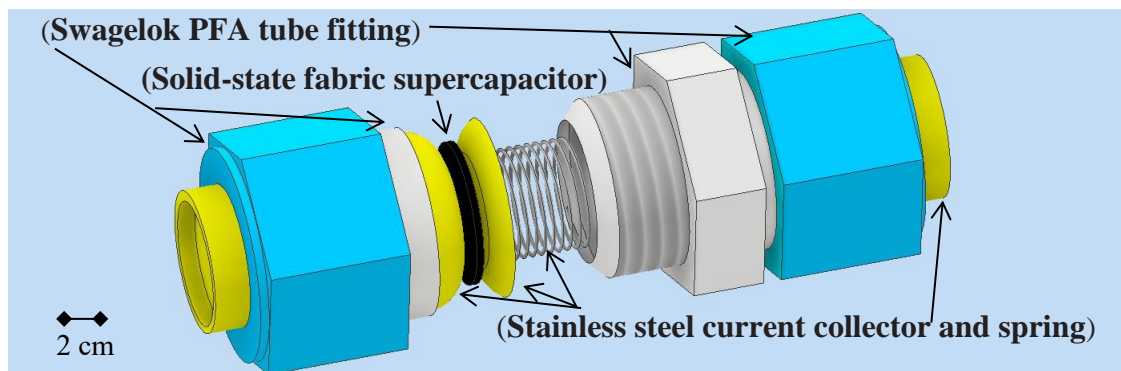


**Figure 1.** (a) Black carbon fabric electrode on original white cotton fabric substrate. (b) SEM photograph of cross section view of cotton electrode. (c) SEM photograph of carbon cotton electrode

Figure 1 (c) 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 cotton fabric electrode is 0.785

$\text{cm}^2$  with thickness about  $400\ \mu\text{m}$ , each single piece of fabric electrode has a weight of  $69.8\ \text{mg.cm}^{-2}$  before coating and carbon materials account for 1.8% of the final electrode weight.

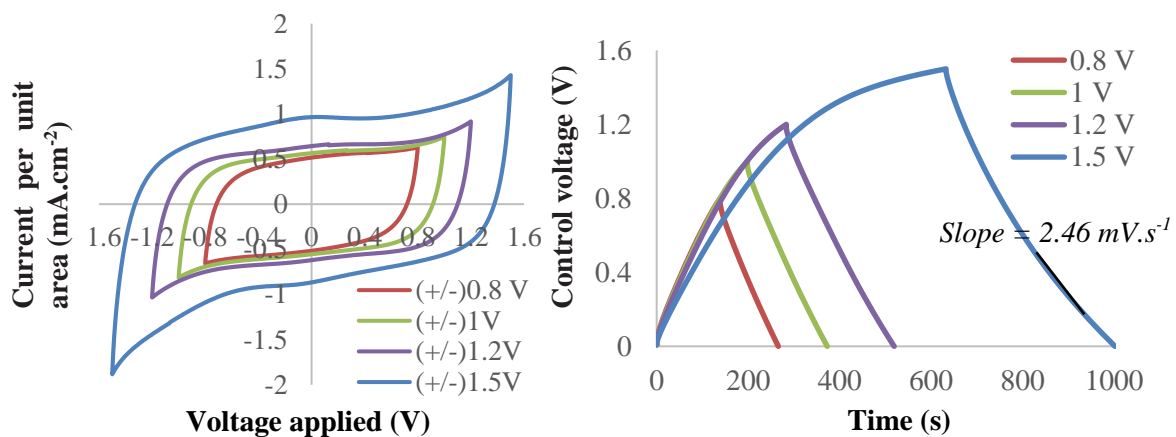
The gel electrolyte was prepared by mixing ammonium salt, vinyl- alcohol polymer and water. The gel electrolyte solution was put under vacuum for 2 hours to reduce the amount of air bubbles inside the solution. In the next step, the cotton electrode was dipped into the gel electrolyte under vacuum for 20 minutes. Finally, the cotton electrodes containing the wet gel electrolyte were compressed and cured in oven for 2 hours at  $60\ ^\circ\text{C}$ . As shown in figure 2 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.



**Figure 2.** Swagelok PFA tube fitting used to testing before closing the two fitting caps

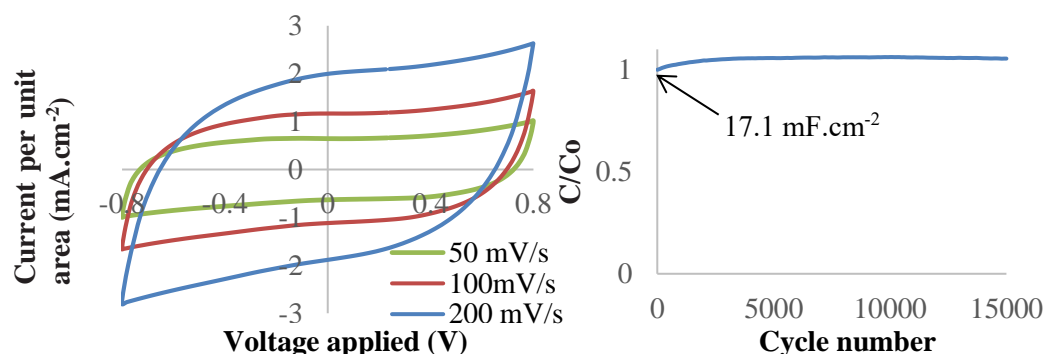
### 3. Results and discussion

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



**Figure 3.** (a) Cyclic voltammetry tests ( $25\ \text{mV.s}^{-1}$ ) between  $\pm 0.8\ \text{V}$  to  $\pm 1.5\ \text{V}$ . (b) Galvanostatic cycling tests ( $0.127\ \text{mA.cm}^{-2}$ ) between  $0.8\ \text{V}$  to  $1.5\ \text{V}$

As shown figure 3(a) The cyclic voltammetry curve (CV) shows the device did not exhibit any chemical reaction or instability on both positive and negative scan directions. Figure 3 (b) shows the Galvanostatic cycling (GC) test results ( $0.127\ \text{mA.cm}^{-2}$ ) with different test voltages. The encapsulated single layer fabric supercapacitor achieved an equivalent series resistance of  $54.1\ \Omega.\text{cm}^{-2}$  and an area capacitance of  $40.5\ \text{mF.cm}^{-2}$  at a test voltage of  $1.5\ \text{V}$ .



**Figure 4.** (a) CV test of the device between  $\pm 0.8$  V at the scan rate of 200, 100, 50  $\text{mV.s}^{-1}$ , (b) stability of device over 15000 cycles.  $C_0$  is the initial area capacitance ( $17.1 \text{ mF.cm}^{-2}$ ) of the device measured from cycle 1 of the CV test between  $\pm 0.8$  V at the scan rate of 200  $\text{mV.s}^{-1}$ .

According to figure 3 (a) and figure 4 (a), the CV curves show that the device is electrochemically stable at the scan rates from 25 to 200 mV, and area capacitance values vary from about 17.1 to 25.7  $\text{mF.cm}^{-2}$  depending on the different scan rate. Figure 4 (b) indicates the device stability with a CV response. The overall capacitance increased about 5% in the first 2500 test cycles, it is correlates with the devices were not fully immersed by the gel electrolyte solution. In the rest of 12500 test cycles the device demonstrates a good cycling stability of less than 1% capacitance variation, it is correlates with the small temperature changes in the test lab. However 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 EVA polymer binder and gel electrolyte. The spray coating process results in activated carbon and carbon black powder being spread uniformly over the fabric samples and infiltrate into but not penetrate the cotton fabrics. The vacuum impregnation process ensures the gel electrolyte get in contact with most of the electrode materials to forms an effective double layer interface during characterisation.

#### 4. Conclusion

This report presents a single layer supercapacitor on cotton fabrics. The non-hazardous solid-state fabric supercapacitor implemented in this work achieves a mass specific capacitance of  $40.5 \text{ F.g}^{-1}$ , area specific capacitance of  $40.5 \text{ mF.cm}^{-2}$ , a low normalized ESR of  $54.1 \text{ }\Omega.\text{cm}^{-2}$  and achieves good cycling stability of less than 1% capacitance variation over 12500 cycles. In comparison with other works, these result are not as good as formal multilayer supercapacitor, however in this work both spray coated carbon electrodes and gel-electrolyte reinforced charge separator are integrated into just a single layer of cotton fabrics, the proposed supercapacitor is non-hazardous, fully wearable, scalable, inexpensive. This work demonstrates a reliable approach for obtaining a low cost and appropriated energy storage supercapacitors in fabrics for wearable applications. Future work will include improving the formulation of the carbon and gel electrolyte ink so the single layer solid-state fabric supercapacitor can achieve better electrochemical performances. The final device could see use applications in a wide range of wearable electronic systems.

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