Fabric based supercapacitor

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Abstract: Flexible supercapacitors with electrodes coated on inexpensive fabrics by the dipping technique. This paper present details of the design, fabrication and characterisation of fabric supercapacitor. The sandwich structured supercapacitors can achieve specific capacitances of 11.1 F/g, area capacitance 105 mF.cm⁻² and maintain 95% of the initial capacitance after cycling the device for more than 15000 times.

1. Introduction

Wearable electronics require the implementation of electronic functions on a flexible, wearable substrate. The electronic functions require specific energy storage devices with minimal weight and size that can be integrated on to such a flexible substrate. Research and development of a flexible energy storage system is essential for the powering of wearable electronics devices. The supercapacitor is a commonly used storage devices for smart sensor node [1] and energy harvesting systems [2]. This paper present a detailed investigation in to supercapacitor fabricated on standard polyester-cotton fabrics.

Conventionally, carbon nanotube (CNT) and/or pseudo-capacitive materials are the most common materials used in the fabrication of flexible supercapacitor electrodes. Supercapacitor electrodes made with CNT benefit from the unique properties of CNT such as porous structure, excellent electrical conductivity, high specific surface area, and good thermal and mechanical stability. Previous reports on flexible supercapacitors using CNT and/or pseudo-capacitive materials achieve high specific capacitance, but it is essential to note that these materials are expansive. The use of CNT can also reduce the device stability, as found by K Wang et al [3] in flexible electrodes of PANI-CNT-Cotton whose specific capacitance of 410 F.g⁻¹ fell to 61% of its original value after 3000 cycles. Activated carbon, also known as engineered carbon, is another suitable material for flexible supercapacitor electrodes due to its large specific surface area, low electric resistivity and low cost in comparison with some specific treated materials like carbon nanotubes.

In comparison with a conventional rigid supercapacitor, a fabric based supercapacitor needs to be conducting, lightweight, and wearable and must not react with the electrolyte. Previously, researchers have focused on using substrates that are either lack of mechanical strength witch is not directly appropriate for device integration, such as non-woven fabric[3] or paper [4] to support a high mass loading of active conducting material, or have adopted complex procedures to make flexible conductive substrates, such as woven graphene fibres [5] or conductive polymers [6]. These methods
permit the fabrication of flexible supercapacitors with high storage capacities and power/energy efficiencies; however they also involve high materials cost and fabrication complexity which limits their commercialisation.

2. Theory

Supercapacitors store energy with two types of capacitive mechanisms: the electrical double layer capacitance (EDLC) and redox pseudocapacitance. The EDLC is based on the accumulation and release of electrostatic charge that occurs at the interfaces between the electrode and electrolyte solution. A supercapacitor is constructed using two electrical double layer interfaces, each having opposite polarity with respect to the charge separator that contains electrolyte solution.

The exchange of electrostatic charge occurs via the balance of ions and electrons at the interface between electrode and electrolyte and introduces an internal potential difference across the interface, which acts as a dielectric. Charge on the inner surface of electrodes will be balanced by the accumulation of counter-ions in the electrolyte. The ratio of charge to the voltage difference gives the capacitance between the electrodes [7]. The maximum potential difference between the top and bottom electrodes is restricted by the thermodynamic stability of the electrolyte material [7].

This work demonstrates energy storage in wearable devices by implementing a wearable electric double layer supercapacitor into a fabric substrate. The proposed fabric electrode is made via the dipping process using various inexpensive commercial carbon powders and poly-cotton fabric substrates that are used in the clothing industry. The supercapacitors will be fully tested in order to study their operation and stability as functions of cycle rate and cycle number.

3. Device fabrication

Firstly the liquid coating mixture containing the active material carbon is prepared. In order to create a permanently conductive carbon-coated fabric, a polymer binder is required to provide adhesion between carbon powders and the yarns of the fabric. In this work the carbon powder is mixed with a polystyrene, ethyl acetate solvent and a surfactant. The carbon powders used in this work are activated carbon powder SX ULTRA and carbon black powder Shawinigan Black. SX ULTRA, processed from peat by Cabot Norit, has high purity, a mean particle size of 100µm in diameter, a neutral pH balance and an effective surface area of 1200 m².g⁻¹. Shawinigan Black has a mean particle size of 42 nm in diameter and an effective surface area of 75 m².g⁻¹.

The next step of this process is to load the carbon powders into the fabric using a dipping process. The fabric substrate in this work is poly-cotton material that combines both the advantages of polyester and cotton material. During the dipping process, the fabric material absorbs the liquid and is quickly filled with the carbon mixture as the solvent evaporates at room temperature. After the sample is fully cured, carbon powder bonds to the substrate through the polymer binder to introduce a large, conductive surface area that forms an electrical double layer on contact with the electrolyte. The photograph of original fabric and carbon fabric electrode can be seen in figure 1 (a).

Figure 1. (a) Original blue fabric substrate and black carbon fabric electrode. (b) SEM photograph of carbon fabric electrode (b).
Figure 1(b) is the SEM micrograph of the carbon fabric electrode which shows that the carbon particles adhere to the fibre to make the fabric conductive. The assembled supercapacitor device shown in figure 3 is compressed from the top to bottom electrodes using spring loaded stainless steel current collectors housed within a Swagelok® PFA tube fitting shows in figure 2(b). In figure 2(a) the white circle is the filter paper layer that acts as the charge separator to prevent short circuit of device. In our design the electrolyte is 1M lithium sulphate solution is chosen as a chemically safe and inexpensive electrolyte compared with an organic electrolyte.

Figure 2. (a) Photograph of fabric supercapacitor before assembly Swagelok® PFA tube fitting. (b) Swagelok® PFA tube fitting test rig

4. Results and discussion
The performance of the textile based supercapacitor is assessed by several methods. First, the encapsulated device is using electrochemical impedance spectroscopy (EIS), and then the stability of the device is examined by cyclic voltammetry (CV) at different scan rates. These can be seen in figure 3.

Figure 3. (a)(b) Bode plot of device from 10 kHz to 20 mHz, extract from EIS test with equivalent series resistance (ESR) marked. (c) CV test of the device between +/- 0.8 V at the scan rate of 200, 100, 25 mV.s⁻¹
In each tested fabric supercapacitor, carbon materials account for 17% of the electrodes weight; each electrode has the area of 0.785 cm$^2$. As shown in figure 3 (a) and (b) the impedance result is expressed as a series combination of the frequency dependent capacitance and a series resistance. The high frequency resistance indicates a total resistance of 1.78 Ω.cm$^2$ due to the electrolyte and electrode materials. At the lowest frequency, the specific capacitance is found to be 11.1 F.g$^{-1}$, the area specific capacitance 105 mF.cm$^{-2}$ and a normalized ESR of 21.8 Ω.cm$^2$ that includes the diffusion resistance. As shown in figure 3, the CV curves indicate that the device is electrochemically stable at the scan rates from 25 to 200 mV, and capacitance values of about 10 F.g$^{-1}$ according to the ratio of the maximum current to the scan rate.

![Figure 4](image_url)

*Figure 4.* (a) CV test of the device for 15000 cycles between +/- 0.8V at the scan rate of 200 mV.s$^{-1}$, (b) stability of device over 15000 cycles. $C_0$ is the capacitance of device calculated at the beginning (cycle 1) of the CV test.

Figure 5(a) (b) shows the device stability with a CV response that is unchanged from its initial value after 15000 cycles. The overall variation of less than 5% in the low frequency capacitance is correlated with small temperature changes causing variation of the diffusion coefficients. The high device stability shows excellent adhesion of the carbon powders forming a continuous conducting network, which is due to an effective and stable polymer binder with a good chemical resistance both the electrolyte and carbon material.

5. Conclusion

This report presents a three layer supercapacitor on a fabric substrate. The supercapacitor fabricated in this work achieves a mass specific capacitance of 11.1 F.g$^{-1}$, area specific capacitance of 103 mF.cm$^{-2}$, a low normalized ESR of 1.78 Ω.cm$^2$ and achieves good cycling stability of less than 5% capacitance variation over 15000 cycles. In comparison with other supercapacitors, the electrode and separator materials of the device are potentially wearable, fully scalable, and inexpensive. Future work will include developing a encapsulation structure and materials that seal the device, retain the electrolyte and protecting it against damage. The final device could see use applications in a wide range of wearable electronic systems like energy harvesters, medical sensors and energy sources for all kinds of personal wearable electronics.

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