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Flexible Fabric-based Wearable Solid-State Supercapacitor

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***Abstract*—In this paper, we present a novel wearable flexible supercapacitor with the conductive carbon-nanotube (CNT)/fabric electrode and PVA/H_3PO_4 solid-state electrolyte, which is cost-effective and can be easily mass produced. Two kinds of fabric as the electrode substrates, cotton knitting fabric and polyester-fiber knitting fabric, are used for comparison respectively. The flexible fabric-based supercapacitors show good specific capacitance (11.51 mF/cm^2 for cotton fabric-based supercapacitor (CFSC), 15.67 mF/cm^2 for polyester-fiber fabric-cased supercapacitor (PFSC)) and high cycling stability (remaining more than 90% after 1000 cycles). This low cost and simple fabrication process makes this kind of supercapacitors feasible to be power supplies for wearable electronic devices.**

Keywords—supercapacitor; carbon nanotube; wearable; fabric electrode

I. Introduction

In recent years, wearable electronic devices[1,2] compose a new category of hardware with various functionalities[3]. Almost all these wearable devices are required to be stable, lightweight and high-performance, meanwhile they are called for low-power consumption, high efficiency, and rechargeable, energy storage technologies[4], such as batteries and supercapacitors (SCs). Compared with others, solid-state supercapacitors are more multifunctional[5], environmentally-friendly, small in size and easy to handle, especially. Flexible solid-state supercapacitors[6] with high stability, quick charge-discharge capability[7], negligible decay[8] after thousands of cycles and compatibility with environment. Normally, a solid-state supercapacitor is composed of electrodes, solid-state electrolyte and separator, here. The characters of electrodes, including conductivity, available surface area, amounts of active material, determine the capacitive performance mostly.

Nowadays, coating active carbon materials such as carbon nanotube (CNT)[9,10], graphene[11] and their composite sponge[12] on the flexible substrate, like fabric[13,14] and paper[15,16], is an ideal and appealing ways for electrode fabrication. Specifically, fabric, which acts as the cloth material for more than thousand years for its softness, flexibility and breathability, is a promising material for wearable devices. Moreover, the porous fabric that can absorb enough carbon nanotubes provides an apt substrate to build large-scale electronic network and system. The flexible supercapacitor based on fabric electrode can meet the requirements mentioned above, which can be simply fabricated and easily mass produced.

In previous work[17,18], fabric has been a kind of common substrate of electrode. However, most fabric has been used is original cotton mat, which is not the material of cloth in reality, as the cotton mat is not well stretchable and strong enough. In this work, we utilize an easy fabrication process for supercapacitors with CNT/fabric electrode. A smooth-face cotton fabric and a rough-face polyester-fiber fabric are selected because they have been weaved well in factory as a cloth material. These flexible and stretchable fabric are coated with carbon nanotube by dipping and drying. Both kinds of fabric-based supercapacitors have good capacitive characters and well flexibility and extremely promising as supercapacitor electrode for wearable devices in reality.

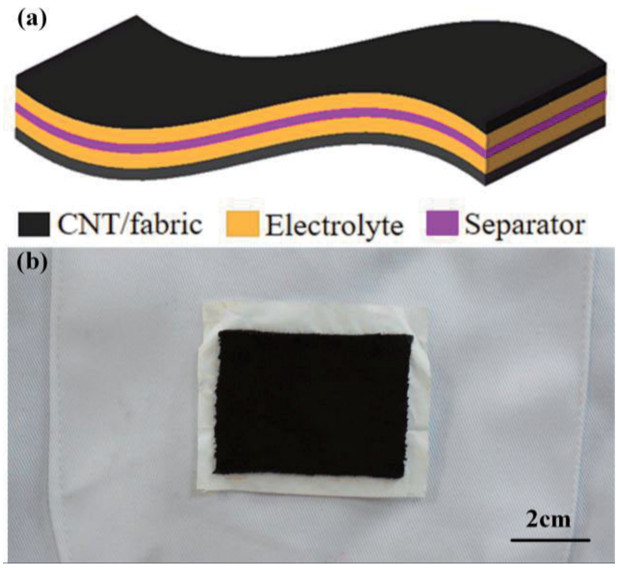

Figure 1: (a) Schematic diagram of solid-state super- capacitor based on sandwiched structure. (b) Optical image of flexible wearable supercapacitor.

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II. Experimental Procedures

2.1 Fabrication Process

The schematic diagram of proposed wearable flexible supercapacitors is shown in Figure 1a, which is composed by the flexible CNT/textile electrode, solid-state polyvinyl alcohol (PVA)/phosphoric acid (H_3PO_4) electrolyte and the separator membrane. Besides, optical image of wearable supercapacitor is also shown in Figure 1b, which is placed on the lab-gown as a part of cloth. The dimension of device is 4 cm × 5 cm × 2 mm.

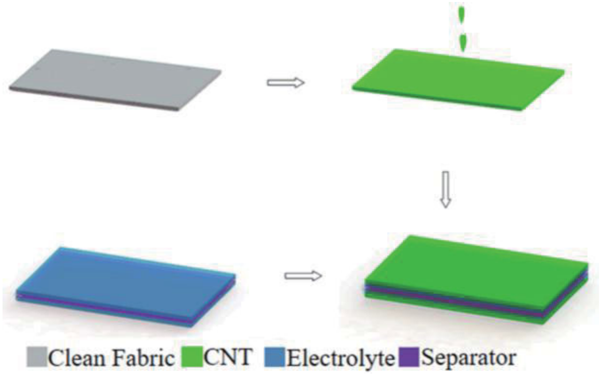

Figure 2: Fabrication flow process of fabric-based super- capacitor, consisting of CNT/fabric electrode, PVA/H3PO4 electrolyte and NKK TF44 separator.

As shown in Figure 2, the fabrication process is illustrated in four steps. First, two pieces of cotton fabric and polyester fiber fabric and two cellulose membranes (TF44, NKK, Japan) as separator films with an area of 20 cm^2 are prepared in advance. Four pieces of fabric are cleaned in deionized water. Second, 60 mg CNTs are dispersed in 60 ml deionized water containing 60 mg surfactants sodium dodecylbenzene sulfonate(SDBS). The mixture is bath-sonicated for 4 hours to disperse uniformly. Then, CNT solution is used to dye fabric pieces, and then all fabric pieces are dried on the hot plate at 90°C for 15 min. The same processes are repeated for 30 times. In this way, the conductive electrode is ready. Third, Then PVA/H_3PO_4 electrolyte is prepared by adding PVA powder (6g) into H_3PO_4 aqueous solution (6g H_3PO_4 into 60ml deionized water). The whole process of prepare electrolyte is at 85°C, under vigorous stirring until the solution become clear. The separator membrane submerged into the solid-state PVA/H_3PO_4 is sandwiched between two pieces of CNT/fabric electrodes. Lastly, supercapacitors based on CNT/fabric are dried in a regular oven at 40°C for 12 hours to absolutely vaporize the excess water.

As shown in Figure 3a, the CNT/fabric pieces are highly flexible. Besides, CNTs coated on fiber fabric can tolerant diverse deformation. In Figure 3b, sheet resistance of two different fabric-based electrodes decreases exponentially with dipping cycles increasing. When the resistance decreases to 1 kΩ/sq, the resistance changes slowly in several dip-drying recycles. Later, decrease rate of resistance is about 50 Ω ~ 100 Ω/cycle.

2.2 Measurement and Analysis

By using a scan electron microscope (SEM) (Quanta 600F, FEI Co.), the morphologies of the CNT/fabric electrodes are analyzed. In addition, all of the electrochemical tests of the fabric supercapacitors are carried out by a two-electrode system using CHI660C (CH instrument) electrochemical workstation at room temperature.

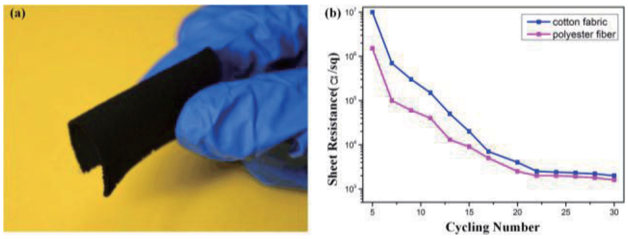

Figure 3: (a) flexible cotton fabric electrode. (b) Change of sheet resistance of electrodes of cotton fabric and polyester fiber fabric with dipping cycle increasing.

III. Results and Discussions

3.1 Optical and SEM analysis

In Figure 4a and 4b, it can be clearly seen from the SEM images that initial cotton fabric and polyester fiber fabric, their diameter and surface roughness are different, respectively. As shown in Figure 4c and 4d, two kinds of electrodes, CNT/cotton fabric and CNT/polyester-fiber fabric which are prepared by simple dip-drying as mentioned before, are covered by CNTs. SEM images suggest that CNTs are densely coated on the surface of fabric fibers, forming the conductive network. The thickness of the CNTs covering is enough for conductive and decreases the effect of some slight abrasion.

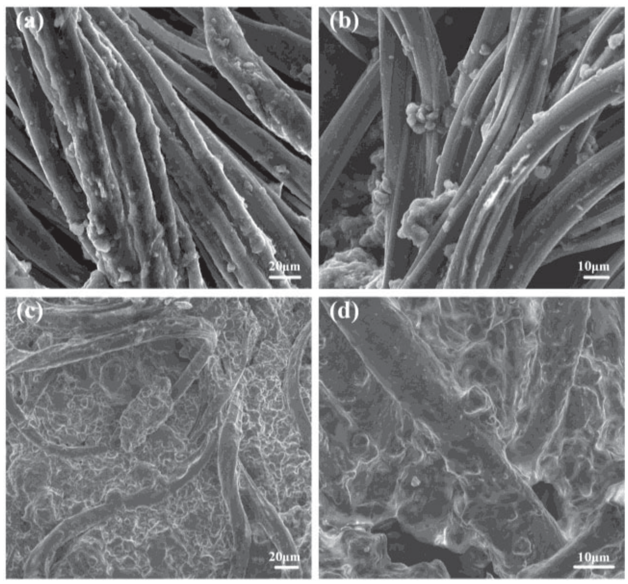

Figure 4: Images of knitting fabric. (a) SEM of clean cotton fabric. (b) SEM of clean polyester fiber fabric. (c) SEM of MWCNTs coated cotton fiber. (d) SEM of MWCNTs coated polyester fiber fabric.

3.2 Electrochemical analysis

The electrochemical performance of our fabric-based supercapacitors is measured at room temperature by electrochemical workstation. The fabric-based supercapacitors, fabricated for electrochemical analyzes, are both solid-state, with area being 20 cm^2. We choose two kinds of supercapacitors as the analyze samples, one cotton fabric-cased supercapacitors (CFSC), another polyester-fiber fabric-based supercapacitors (PFSC). For the former, the electrochemical properties of CFSC include cyclic voltammetry (CV), galvanostatic charge-discharge (GCD) and cycle life measurements. For the latter, the electrochemical properties of PFSC include CV and GCD. In detail, the CV analyses are measured with a potential window from 0 V to 1.0 V at scan rates varying from 10 mV/s to 200 mV/s. Besides, the GCD analyses are measured at different charging-discharging current densities ranging from 2 mA to 10 mA.

As shown in Figure 5a and 5b, the CV curves of CFSC and PFSC, both retain rectangular shapes, showing the ideal capacitive characters. The images in Figure 5c and 5d show the GCD curves of CFSC and PFSC, presenting nearly triangular shapes at different current densities. For comparison, it can be found that the capacitive characters of PFSC is better than the characters of CFSC, because of the more regular rectangle shapes and more regular triangle shapes in electrochemical analyses of PFSC. The main reason is that the fabric pieces have different roughness and thickness, and the PFSC has more CNTs as active material and more surface area between electrodes and electrolyte.

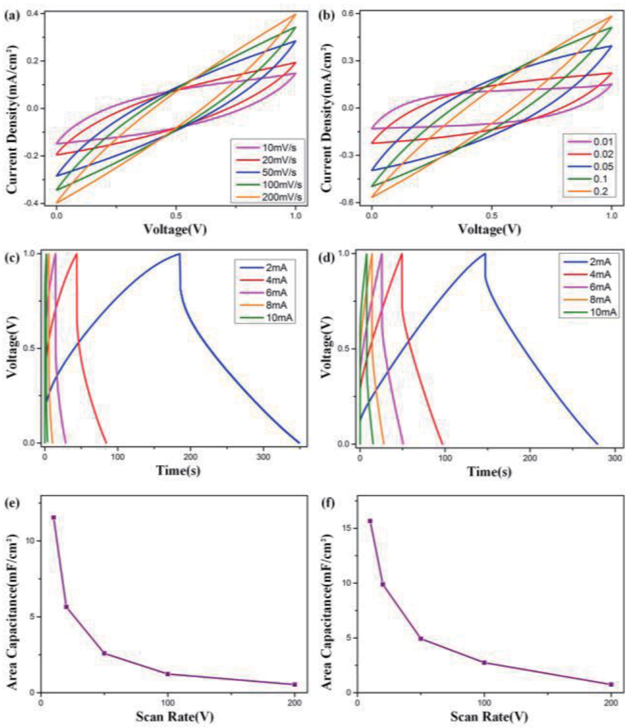

Figure 5: Electrochemical characterization of the super- capacitor. (a) CV curves of CFSC, (b) CV curves of PFSC, (c) GCD curves of CFSC, (d) GCD curves of PFSC, (e) calculated areal capacitance of CFSC, (f) calculated areal capacitance of PFSC.

Besides, we calculate the areal capacitance (C_A) using CV curves of these two kinds of supercapacitors as follows:

$$C = \frac{Q}{\Delta V} = \frac{1}{k \cdot \Delta V}\int_{V_1}^{V_2} I(V)dV \qquad (1)$$

$$C_A = \frac{C}{A} = \frac{1}{k \cdot A \cdot \Delta V}\int_{V_1}^{V_2} I(V)dV \qquad (2)$$

, where C is the total capacitance, k is the scan rate, ΔV is potential window during discharging process, $I(V)$ is the discharging current density function, A is the area of these supercapacitors. The areal capacitance of CFSC has the maximum value, 11.51 mF/cm^2 at 10 mV/s, and PFSC is 15.67 mF/cm^2 at 10 mV/s, respectively, as shown in Figure 5e and 5f. We can find out that the consequence is the same as the result discussed above.

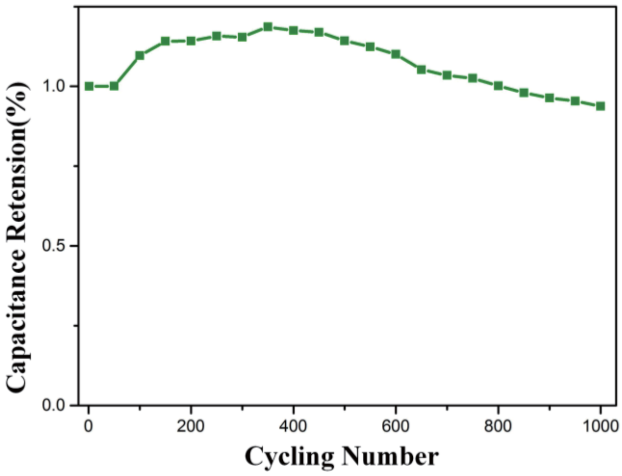

Figure 6: cycling tests of the supercapacitor with cotton fabric electrode during first 1000 cycles at 100 mV/s.

Furthermore, this wearable fabric-based solid-state supercapacitor has the excellent stability in cycling performance in Figure 6, in which the capacitance has a decrease of 7% after 1000 cycles. The variation of capacitance is rising before 350 cycles and then descending due to the fact of activation of active carbon material.

IV. CONCLUSIONS

In summary, the wearable fabric-based solid-state supercapacitors are fabricated using simple dip-drying method with high flexibility. The common fabric provides a cost-efficient material for wearable power supply, which can be easily bent and folded as cloth. The consequences of comparison between CFSC and PFSC is resulted from the surface roughness and thickness of surface. The polyester-fiber fabric has more grooved and fibrous surface, which can absorb more CNTs and has larger surface area to transport proton between electrode and electrolyte. Therefore, the capacitance of fabric-based supercapacitors can be enhanced by using high hydroscopic fabric material with larger surface area. This wearable supercapacitor based on CNT/fabric electrodes has the stable capability and wearable feasibility, which can be a better candidate for industrial fabric supercapacitors and energy devices in wearable applications.

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