Towards flexible and wearable supercapacitors: A hierarchical approach in material design

Anna Batlle[1], Llorenç Servera[1, 2], Aïda Varea[1], Albert Cirera[1*]

[1]*Department of Engineering: Electronics. IN2UB, Universitat de Barcelona, Martí i Franquès 1, Barcelona, 08028, Spain*
[2]*EUSS: Escola Universitaria Salesiana de Sarria, Passeig de Sant Joan Bosco, 74, Barcelona, 08017, Spain*

*Corresponding author: Tel: (+34) 934039167; E-mail: acirera@ub.edu

Received: 10 February 2017, Revised: 18 February 2017 and Accepted: 09 April 2017

DOI: 10.5185/amlett.2017.1680
www.vbripress.com/aml

Abstract

Wearable devices requires from macroscopic mechanical properties laying in macro-scale in comparison with chemical processes that requires from material design in the nanoscale. Besides, such reactions and phenomena involves charge transfer, and therefore a charge transducer in mean scale is required. In this paper we propose a flexible and wearable supercapacitor that takes advantage of a conductive fabric current collector that is coated by electrospray with MnO_2-decorated carbon nanofibers (CNF). The results point out that a high capacitance is obtained due to the pseudocapacitive reactions in MnO_2; moreover, the long and conductive structure of CNF allow transferring charge to conductive fabric, keeping a low equivalent serial resistance (ESR). The results indicate a specific capacitance on fabric collector of (226.40 ± 0.3) F/g, about 10 times higher than on aluminum foil collector, with a similar ESR which indicates a suitable way to wearable devices. The proposed technique is scalable, and can be easily applied in the industry.

Keywords: Supercapacitor, fabric, CNF, MnO_2, electrospray.

Introduction

Nowadays, there is a huge interest on wearable electronic devices [**1**] due to they can be applied in a widespread of advanced technological and social purposes. In this sense, high efforts to apply these devices in new technological areas, as energy harvesting, make researchers to improve the efficiency of such devices taking into account that flexibility and stretchability are both limiting requirements. For these reasons, develop an efficient device with wearable energy storage system, becomes a challenge. Batteries based on traditional technology, are not able to fulfill these mechanical requirements. Supercapacitors are promising devices for its long-life cycles, high power density and quick storage, and release electric energy through an adequate supercapacitors cell design towards covering wearable energy storage [**2**].

Supercapacitors are usually classified in three types: (i) electric double layer capacitor (EDLC), (ii) pseudo-capacitor and (iii) hybrids supercapacitors. EDLCs storage the energy in the double-layer formed between the surface of the electrode and the electrolytic solution (Helmholtz double layer) [**2**]. In the other hand, the pseudo-capacitor is not an electrostatic device; a faradic current is induced when a difference of potential is applied [**3**], and thereby a fast and reversible redox reaction takes place at the surface of the electrodes. In addition, hybrid supercapacitors are a combining system of EDLC and pseudo-capacitors. When both systems are sinergistically combined an increase of the cell voltage and capacitance is achieved improving the efficiency of the device (stored energy density and power charge/discharge rate).

Furthermore, the suitable selection of the cell conforming materials not only can increase the storage of the energy density and the working potential window, but also can decrease the equivalent serial resistance (ESR) to overcome the ohmic loses [**4**].

Carbon materials as graphene, carbon nanotubes (CNT), carbon nanofibers (CNF) and active carbon are often used as electrode materials in EDLCs due they good chemical and physical properties: high conductivity, high surface area range, good corrosion resistance, high temperature stability, controlled pore structure, processability and compatibility in composite materials and relatively low cost [**5**]. Among these, CNF [**6**] exhibits a suitable elongated graphitic structure thus providing to cell device a high specific capacitance with low ESR at very low cost [**7**].

In order to improve the specific capacitance of carbon materials, metal oxides are usually added to generate pseudocapacitance. Metal oxides, undergo fast reversible redox reactions at their surface, displaying strong pseudocapacitive behavior. Composites of carbon with redox active materials, introducing particles of transition metal oxide into the carbon material, have been evaluated

as electrode materials showing an improved performance [**8**]. The contribution between the double layer capacitor and pseudo-capacitance produce high capacitance devices. Among different metal oxides, MnO_2 is commonly used to dope carbon electrodes due to its physical and chemical properties, low cost respect other metal oxides and low toxicity described in some studies [**9**].

Carbon materials usually deposited on aluminum foil have been used as electrode and current collector respectively in previous studies [**10, 11**]. Aluminum is a cheap and good conductor appropriate to act as current collector with low contribution to ESR. However aluminum does not have the required the mechanical properties for wearable devices. To overcome this issue, flexible and stretchable conductive fabric can be used as substrate for carbon-based materials and also as current collector to develop a supercapacitor with the required properties. Textile, as cotton coated with carbon materials used as current collector and electrode respectively for supercapacitors, has been proved in previously studied [**12**]. Authors have demonstrated that textil-based capacitances can achieve higher capacitances than their counterparts based on aluminum supercapacitors. The main drawback of this structure is the low conductivity of cotton fabric, and high ESR. Besides such cell does not take advantage of pseudo-capacitive effect.

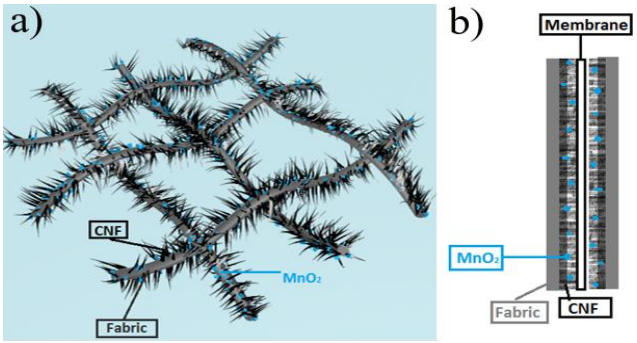

Fig 1. a) Scheme of the hierarchical structure composed by silver-coated polyamide fibers, CNF and MnO_2. b) Scheme of the hierarchical structure of the supercapacitor architecture.

In this work, we propose for the first time a hierarchical approach to flexible and wearable supercapacitors **(Fig. 1)**. In the range of the millimeters/centimeters we use conductive silver-coated semi-aromatic polyamide fabric, which collect charge and is stretchable. In the scale of micrometers (and hundreds of nanometers) we use CNFs, that work as high specific capacitance and can easily induce charges to collector (low ESR). Finally, MnO_2 is used to dope CNFs in the scale of nanometer to improve the pseudo-capacitance. In **Fig. 1** is shown a schematic of the hierarchical structure of the current collector and electrode with fabric.

A new cell design has been developed, using a conductive fabric made up of silver-coated polyamide fibers, because its high conductivity and porosity are benefits to use it simultaneously as electrode substrate and current collector. Its hierarchical structure promotes fluid flow-through the porous mesh. By other hand, an ionic conductor membrane has used as separator to fulfill the mechanical and functional requirements.

The hierarchical porous electrode material is created by depositing by electrospray on fabric fibers, which at the same time creates a weave structure. Using a hierarchical structure, higher specific capacitance is created, but keeping low ESR values.

Experimental

Materials

A high ionic silver release plated nylon elastic knit double direction fabric was used as current collector. CNF from Grupo Antolin, (GANF) has been used as electrode material, it has helical graphitic stacked cup structure, with 20-80 nm of diameter and length higher than 30 µm [**6**]. Particles of manganese (IV) oxide activated was purchased from Sigma Aldrich has been used as pseudo-capacitance doping, the particle size is less than 10 µm. 1M Na_2SO_4 was used as electrolyte, due to the good properties as electrolyte solutions for supercapacitors [**6, 13**]. Fumasep® FAP-450 membranes have been used as separators [**14**]. This porous polymeric membrane allows the ion conductivity though it and it is often used in flux batteries. Previous to set up the supercapacitor architecture, the membrane was submerged in a solution of 20 wt% sulfuric acid in Milli-Q deionized water to be activated and then dried.

Preparation of electrode and current collector

The new hybrid electrode-collector system has been developed through threefold coating process: (i) polyamide fibers coated with silver has used as substrate and then a hierarchical structure is created through the deposition of (ii) CNF deposition on fabric substrate by electrospray technique; and finally, (iii) the deposition of MnO_2 particles through the same electrospray process.

Yflow® Electrospinner 3.2.D-400® has been used to deposit the electrode material (CNF and MnO_2). Electrospray technique is used to produce thin film from liquid dispersion that contains the materials to be deposited. Due the potential difference, between the substrate and the needle, a Taylor cone is created in the needle to after broke on nanodroplets forming a spray. The electrode material is dispersed in isopropanol (IPA). The substrate is heated to evaporate the dispersion alcohol [**15**]. After CNF deposition by electrospray, a second deposition were done with MnO_2. Electrospray deposition was done at 3 ml/h, with a potential difference of 5 kV. Under these conditions, a first deposition was carried out for 4 h using a dispersion that contained 30 mg of CNF in 40 ml of IPA; afterwards, MnO_2 particles were deposited for 36 minutes using a new dispersion that containced 20 mg of MnO_2 particles dispersed in 40 ml of IPA.

Using this procedure four different systems were prepared, two on aluminum and the others on fabric. Among them, two containing only CNF and two with CNF decorated with MnO_2.

Morphology characterization

Morphology of fabric fibers before and after the CNF+MnO_2 coating processes have been examined by a field emissions scanning electron microscope (FE-SEM) JEOL J-7100 microscope at 20 kV.

Electrochemical studies

Electrochemical characterization was performed in a 600TM Gamry Instruments potentiostat/galvanostat/ZRA [**16**]. A two-electrode Stainless Swagelok type cell is used for electrochemical measurements, where the supercapacitor architecture is built inside and after closed. Both cyclic voltammetry (CV) and charge-discharge cycles (CCD) were carried out with a voltage ranging from 0 V to 1 V, and a CV scan rate of 100 mV/s. Previous studies made in our laboratory showed that this is the optimal working voltage range for this device. From the CCD curves capacitance (C_s) is obtained through:

$$C_s = \frac{2 \cdot I}{Slope \cdot m} \quad (1)$$

where, I is the 80% value of the maximum intensity, "*Slope*" refers to the discharge curve slope and m is the mass of the electrode (CNF+MnO_2 particles) [**17**]. Electrochemical impedance spectroscopy (EIS), between 100 kHz and 1 Hz, allows obtaining ESR values [**18**].

Results and discussion

Fig. 2(a) and **(b)** show FE-SEM images of the silver-coated fabric without CNF+MnO_2 particles. The uniform surface of the fabric fibers is changed when CNFs and MnO_2 particles are deposited **(Fig. 2(c)).** This morphological change indicates an increase of the effective surface area of the electrode. Therefore, we have a porous fabric fiber coated by the CNFs and the MnO_2. It is worth to note how MnO_2-decorated CNFs penetrates in the fiber fabrics, as shown in **Fig. 2(c).** This becomes important by to facts. First we are clearly increasing specific surface in comparison with aluminum foil, but keeping conductive collector. And second, fabric allow the penetration of the electrolyte in the structure.

In order to know the effect of the hierarchical distribution, we have proceeded in a bottom-up approach, first considering the simplest structure with no fabric neither metal oxide doping. Thus, a supercapacitor was built using as electrode CNFs deposited on aluminum foil.

With this sample we obtained an EDLC system with low specific capacitance of (9.2 ± 0.3) F/g and an ERS of (2.77 ± 0.01) Ω.

Higher hierarchical state was generated by doping with MnO_2. A hybrid supercapacitor was developed to improve its properties.

To optimize the amount of MnO_2, we analyze three different electrodes, each one with a different percentage of MnO_2. We start with 5 wt% of MnO_2 against the nanofibers weight, after with 10 wt%, and finally 15 wt%. The electrode with 10 wt% of MnO_2 exhibits the optimum percentage to increase the specific capacitance.

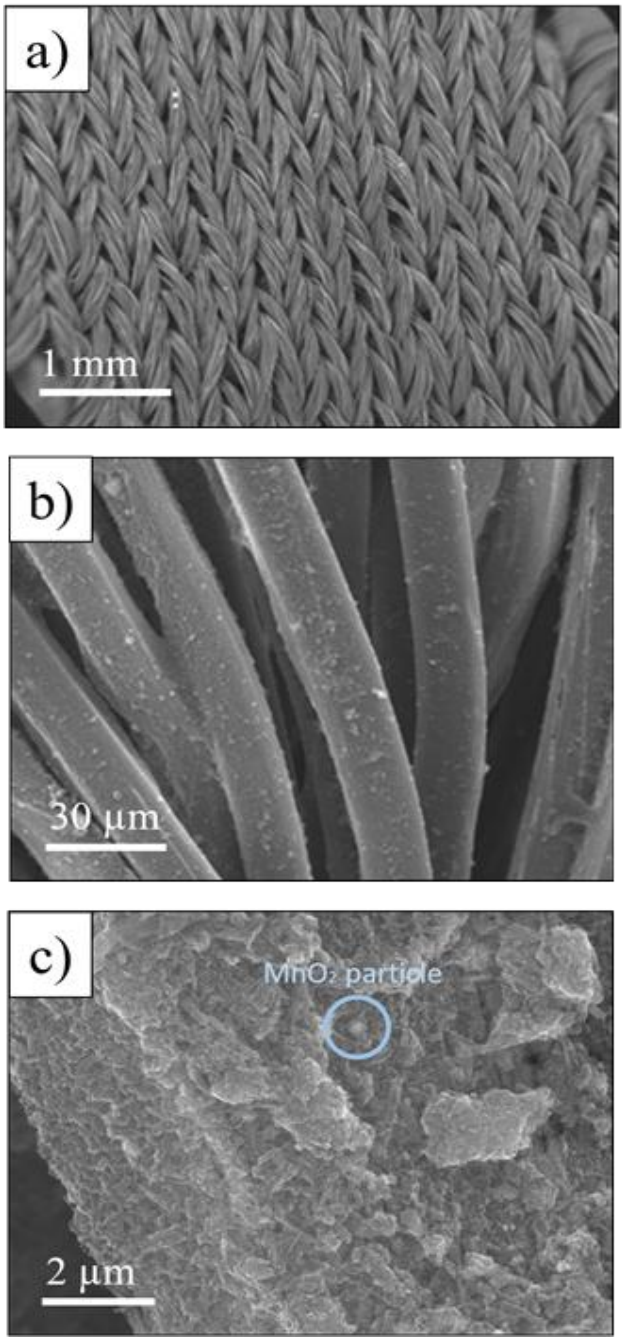

Fig. 2. FE-SEM images at different magnifications of a) and b) fabric without CNF+MnO_2 and c) with CNF+MnO_2 coating. The electrode with 5 wt% could be not enough doping, and 15 wt% of MnO_2 seems to block some fabric porous.

The pseudocapacity effect of MnO_2-decorated CNF in comparison with non-decorated is shown in **Fig. 2**. The CNF electrode shows a CV with a quasi-rectangular shape while for the electrode with the MnO_2 appears the pseudocapacity. The electrode with MnO_2 have a significant increases on the capacity, as can be seen in **Fig. 3(b)**. The specific capacity obtained is (17.6 ± 0.3) F/g and the ESR is (3.66 ± 0.02) Ω. However, the ERS is higher, which means that the supercapacitor will be less efficient.

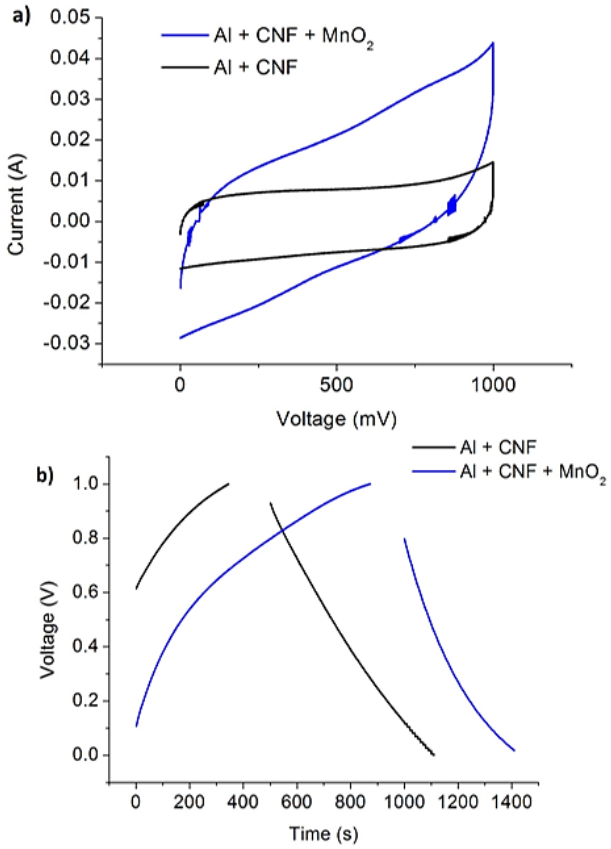

Fig. 3. Comparison between CNF electrode on aluminum foil with MnO_2 and without MnO_2 decoration (a) CV comparison at 100 mV/s (b) CCD comparison.

In general, the use of doping, such as MnO_2, lightly increases capacitance. There are several considerations to this fact. The first concerns the porosity of the whole system; do we arrive to proper porosity coating on aluminum foil? In fact aluminum is being use as current collector even in commercial supercapacitors, but its continuous nature does not optimize surface contribution. To overcome this problem we used a commercial conductive fabric as current collectors. To prove the benefits of conductive fabric as current collector, we coated with non-decorated CNFs and MnO_2-decorated CNFs. Un decorated CNF electrode on fabric exhibit a specific capacitance of (19.14 ± 0.3) F/g and an ESR of (2.90 ± 0.01) Ω. It is interesting to note that conductive fabric doubles specific capacitance with respect aluminum foilbut keeping similar ESR.

Electrochemical measurements of fabric electrode compared with aluminum electrode are depicted in **Fig. 4**. As seen in CV, the use of a whole hierarchical approach allows the storage of a larger amount of energy. The obtained specific capacitance is (226.40 ± 0.3) F/g, about 10 times higher than on aluminum foil, with an ESR of (2.55 ± 0.01) Ω.

Conclusion

A supercapacitor based on a conductive and stretachable fabric coated with MnO_2-CNF is presented. In comparison, with aluminum foil current collector, such approach increases 10 times the specific capacitance, but keeping a low ESR value.

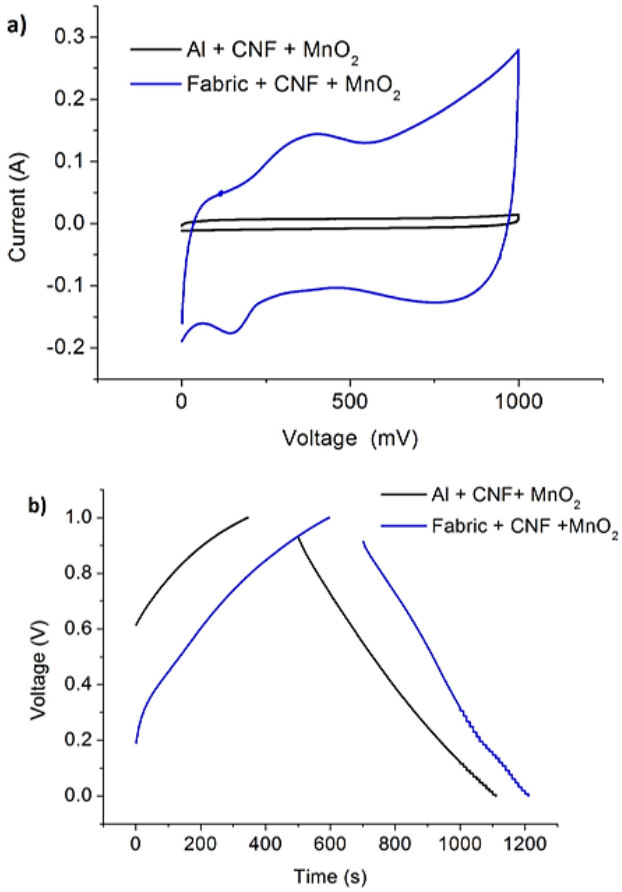

Fig. 4. Comparison between MnO_2 decorated CNF electrodres on aluminum foil collector and on fabric collector (a) CV comparison at 100 mV/s (b) CCD comparison

The results are discussed in terms of a proper hierarchical structure. The easy manufacturing conductive fabric and the ionic conductor membrane allows mechanical properties for wearable devices, and together with CNF a low ESR is achieved, moreover, the addition of MnO_2 increased the specific capacitance due to pseudocapative effects. This process is sustainable, environmental friendly and easy to upscale in future industrial applications.

Acknowledgements

A. Cirera acknowledges support from the 2015 edition of BBVA Foundation Grants for Researchers and Cultural Creators.

Author's contributions

Conceived the plan: AB, LS, AV, AC; Performed the experiments: AB, LlS; Data analysis: AB, LS, AV, AC; Wrote the paper: AB, LS, AV, AC.. Authors have no competing financial interests.

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