

Fabrication and characterization of solution-processed carbon nanotube supercapacitors

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ABSTRACT

We report the fabrication and characterization of supercapacitors prepared on a flexible substrate using a printable, high-viscosity carbon nanotube (CNT) ink. The CNT-hemicellulose composite ink was prepared using ultrasonication and applied on the substrate with a doctor blade. Aqueous sodium chloride was used as electrolyte. The capacitance of the supercapacitors was 16 mF for a device size of 2 cm². The measurements were carried out in accordance to an international standard for electric double layer capacitors.

INTRODUCTION

Supercapacitors have become an interesting alternative for batteries due to their long cycle lifetime and high output power [1]. In 2012, Keskinen et al. demonstrated that supercapacitors can be fabricated with printing methods, using environmentally friendly materials [2]. The use of printing methods provides new possibilities for the economic mass production of disposable, low cost devices, where the supercapacitor could be integrated with other printed electronics components. A potential application for the printed supercapacitors could be as an energy storage in an autonomous system which harvests energy from ambient light, vibrations or RF fields, powering for example sensor nodes [3, 4].

Graphitic nanomaterials such as carbon nanotubes (CNT) are interesting applicants for supercapacitor electrodes due to their high surface area and high conductivity [5]. Using carbon nanotubes as the sole electrode material facilitates very simple processing, because the material is conductive enough to act as the current collector in addition to being the active, high surface area electrode.

We present the fabrication of solution processable carbon nanotube supercapacitors on a flexible substrate. The conductive ink for the electrodes is a nanocomposite of multi-walled carbon nanotubes (MWNT) and a hemicellulose, xylan. Hemicelluloses are the second most abundant polymer in nature, constituting up to 50 % of annual and perennial plants [6]. The hemicellulose acts as a dispersing agent for the nanotubes in water, but it also increases the ink's viscosity and thereby improves its printability. The electrolyte used here is aqueous NaCl, which means the supercapacitors consist of only plastic, carbon, hemicellulose, water and regular table salt. This makes the devices environmentally friendly and safe to use in any application of ubiquitous electronics.

EXPERIMENT

Supercapacitor electrodes were prepared on a poly(ethylene terephthalate) (PET) film. To promote ink wetting, a polyurethane primer layer (Edolan GS from Tanatex Chemicals) was first applied on the surface. The aqueous primer dispersion was rod-coated and dried in an oven with a temperature ramp from 80 °C to 130 °C in 20 minutes.

The electrodes were fabricated from a MWNT-hemicellulose composite ink. First, 2 g of the MWNTs (NC7000, Nanocyl) were mixed with 195 mL of water and 5 mL of ethanol (ethanol is used to lower the surface tension of the water and help wet the nanotubes). The mixture was sonicated for 2 minutes with 100 W power and magnetic stirring. Next, 1 g of xylan powder was added to the mixture in four 250 mg portions every two minutes. Sonication and stirring was continued for 2 minutes after adding the last portion, resulting in a stable dispersion with 1 w-% CNTs.

The CNT dispersion ink was applied on the substrate using a manual doctor blade coating method. Prior to the coating, the substrate was masked to define an electrode area of 1.4 cm by 3.2 cm. Multiple (4–7) layers were coated and dried between deposition steps in a convection oven at 50 °C. The number of layers was determined with an approximate evaluation of the electrode resistance, to yield similar values for all electrodes. Sheet resistances were measured with a Zahner Zennium Electrochemical Workstation using a 4-point probe method [7]. Scanning electron microscopy (SEM) was used to image the electrode cross section.

Supercapacitors were assembled from the electrodes with a paper separator (TF4050 from NKK) and aqueous NaCl electrolyte (1.0 mol L⁻¹), and sealed with an adhesive film (UPM Raflatac). The structure is illustrated in Fig. 1b. Two gaskets of width 1 cm were cut from the adhesive film and placed on the substrates, around the active electrode area. The separator was placed on one electrode, an excess amount of the electrolyte was dropped on it, and the other electrode was placed on top, rolling the substrate carefully onto the other to avoid trapping air bubbles inside. A photo of a finished sample is presented in Fig. 1a. The device size was defined by the overlapping electrodes (2 cm²). For the electrical measurements, a conductive silver flake paste was added on the electrode ends to ensure a good electrical contact with the measurement probes.

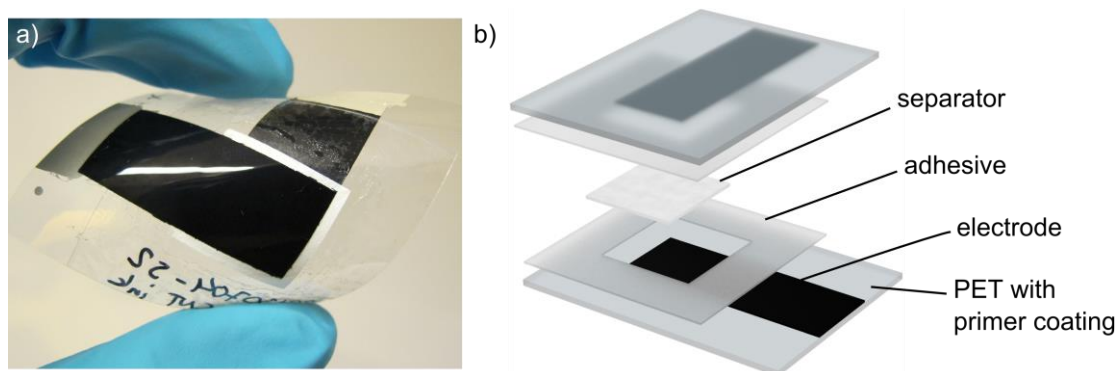


Figure 1. a) Photograph of a supercapacitor sample. b) Schematic of the sample assembly.

The electrical characterization was performed with the Zahner Zennium Electrochemical Workstation. The supercapacitors were characterized according to an international standard for electric double layer capacitors [8], which specifies a galvanostatic discharge method for capacitance and equivalent series resistance (ESR) determination. Device class 3 was selected from the standard.

First, cyclic voltammetry (CV) was performed to get a qualitative picture of the devices as well as an initial estimate of device properties. CV curves were recorded at 100, 50, 10 and 5 mV/s voltage sweep rates from 0 V to 0.9 V. The maximum voltage of 0.9 V was selected sufficiently below the theoretical maximum voltage of the water electrochemical window to avoid electrochemical reactions which can cause leakage and gas formation.

In the galvanostatic measurement, the supercapacitor was first charged to 0.9 V in one minute, held at this potential for 30 minutes, and discharged with a constant current. The current magnitude is defined in the standard with a linear dependence on capacitance. For this reason, the first measurement current was selected on the basis of an approximate capacitance determined in the CV measurement. The measurement was repeated iteratively until the obtained capacitance value was unchanged; typically two iteration rounds were made. The ESR was measured from a similar galvanostatic discharge, but with a current 10 times that of the capacitance measurement. [8]

DISCUSSION

A scanning electron microscope image of an electrode cross section is presented in Fig. 2. The electrode is approximately 9 μm thick, although it is quite uneven. There are large pores which extend all the way through the electrode. While this is beneficial for the total available surface area of the electrode, the electric conduction in the lateral direction may be decreased due to the porous structure of the material.

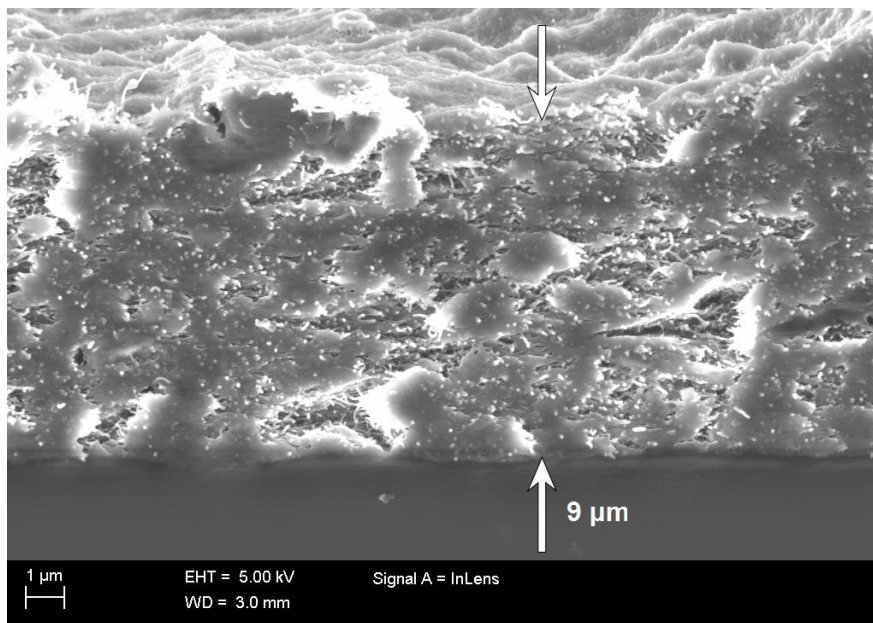


Figure 2. A SEM image of an electrode cross section. Scale bar 1 μm .

CV curves for a representative sample are presented in Fig. 3a, normalized to voltage sweep rate. For an ideal capacitor, the normalized curves would be identical. There is, however, a noticeable decrease in the normalized current with higher sweep rates. The decrease is caused by the limited mobility of the electrolyte ions inside the pores: with a high voltage sweep rate, not enough ions can move to the electrode surfaces to form the electric double layers. The shape of the curves is quite rectangular, indicating good capacitive behaviour.

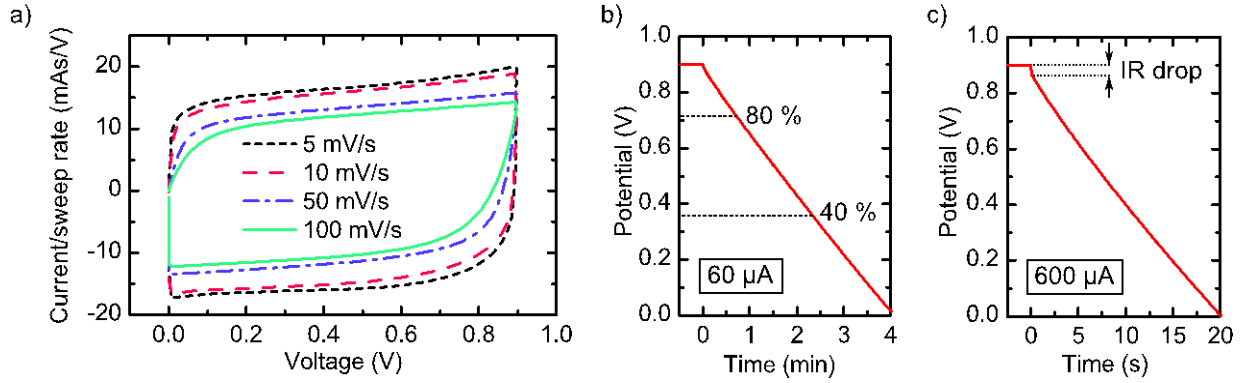


Figure 3. a) CV curves of supercapacitor sample 7, normalized to sweep rate. b) Galvanostatic discharge, where the capacitance is calculated from the slope between 80 % and 40 % discharge. c) ESR determination from the IR drop of the galvanostatic discharge.

The capacitance and ESR of the supercapacitors were determined from the galvanostatic discharge measurements (Fig. 3b and 3c). The capacitance was calculated from the slope of the voltage vs. time through Eq. 1:

$$C = I / \left(\frac{dV}{dt} \right), \quad (1)$$

where I is the discharge current and dV/dt the slope of the voltage decline, fitted to the data points between 80 % and 40 % of the maximum voltage [8]. The ESR was calculated from the voltage drop at the beginning of discharge by dividing the voltage drop by the discharge current. To get an accurate value for the voltage drop, a line was fitted to the beginning of the discharge curve. The voltage drop was determined by the value of the fitted line at the beginning of discharge.

A summary of the results is presented in Table 1. Due to the fabrication process of the electrodes, some variation in electrode thickness can be assumed, resulting in variation of capacitance and ESR. The capacitances ranged from 14 mF to nearly 18 mF with an average of 16.6 mF.

The ESR of the supercapacitors varied from 50 to 100 Ω . As there was no metallic current collector, the main source of ESR is the resistance of the electrode. The sheet resistance of the electrodes was 10 to 15 Ω/\square , which is two orders of magnitude larger than in conventional metallic current collectors. The ESR and sheet resistance values are similar to previously published results on CNT supercapacitors without current collectors [9, 10].

The leakage current of the supercapacitors was determined from the same measurement as the capacitance and ESR. While the sample was held at 0.9 V, the current to it declined from the

initial charging current to a steady leakage value, which was recorded at the end of the 30-minute charging time. The leakage currents are also presented in Table 1 for the individual samples. Samples with high ESR values have lower leakage currents, which is expected. The leakage current values are quite large. Possible reasons are impurities in the electrode material and electrolyte, as well as dissolved oxygen in the electrolyte. When the capacitor is used in an application, the leakage current of course decreases with decreasing supercapacitor voltage.

Table I. Supercapacitor sample properties.

sample	capacitance measurement current (μA)	capacitance (mF)	ESR (Ω)	average leakage current (μA)
1	50	14.3	100	6
2	62.5	17.4	87	2
3	62.5	17.0	58	8
4	55	15.5	71	6
5	65	17.9	66	6
6	60	17.1	100	5
7	60	16.5	66	6
8	57.5	15.8	65	5
9	62.5	17.8	57	11
average	59	16.6	74	6

The potential application in an autonomous energy harvesting system would probably require higher operating voltage than is available from a single supercapacitor, as this is limited by the aqueous electrolyte. To reach the higher voltage without losing the safety and disposability of the supercapacitor devices, two or three similar supercapacitors could be connected in series.

Powering for example a wireless temperature sensor would require approximately $8 \mu\text{A}$ current for 0.2 ms sampling time and a voltage of 3.3 V [11]. The capacitance of the supercapacitors presented here would be adequate for this kind of an application. Connecting supercapacitors in series would also result in the effective ESR of the stack to be in series, lowering the resulting leakage current to well below the output current of the supercapacitors.

CONCLUSIONS

Solution processable carbon nanotube supercapacitor electrodes were fabricated on a plastic substrate and used in a supercapacitor assembly with aqueous NaCl electrolyte. The capacitance of the 2 cm^2 devices was on average 16 mF and the ESR 74Ω . The low-cost and high-throughput compatible preparation of the supercapacitors facilitates their use in many ubiquitous electronics applications such as an ambient energy harvester for wireless sensors. Future goals are improving the conductivity of the electrode material to reduce the ESR of the supercapacitors, and improving the printability of the ink.

ACKNOWLEDGMENTS

The authors would like to thank Veijo Kangas of Morphona for the preparation of the ink and Mari Honkanen of Tampere University of Technology Dept. of Materials Science for SEM imaging. This work was funded by the Academy of Finland (Dec.No. 138145 and 139881) and the Finnish Funding Agency for Technology and Innovation (TEKES, Dec. no. 40049/12). S. Lehtimäki would like to thank Tekniikan Edistämmissäätiö for supporting the research.

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