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Hierarchical cellulose-derived carbon nanocomposites for electrostatic energy storage

V Kuzmenko[1,2], A M Saleem[1,3], A Bhaskar[1], H Staaf[1], V Desmaris[1,3] and P Enoksson[1,2,6]

[1] Department of Microtechnology and Nanoscience, Chalmers University of Technology, Kemivägen 9, Gothenburg, SE-41296, Sweden
[2] Wallenberg Wood Science Center, Chalmers University of Technology, Kemivägen 4, Gothenburg, SE-41296, Sweden
[3] Smoltek AB, Regnbågsgatan 3, Gothenburg, SE-41755, Sweden

E-mail: peter.enoksson@chalmers.se

Abstract. The problem of energy storage and its continuous delivery on demand needs new effective solutions. Supercapacitors are viewed as essential devices for solving this problem since they can quickly provide high power basically countless number of times. The performance of supercapacitors is mostly dependent on the properties of electrode materials used for electrostatic charge accumulation, i.e. energy storage. This study presents new sustainable cellulose-derived materials that can be used as electrodes for supercapacitors. Nanofibrous carbon nanofiber (CNF) mats were covered with vapor-grown carbon nanotubes (CNTs) in order to get composite CNF/CNT electrode material. The resulting composite material had significantly higher surface area and was much more conductive than pure CNF material. The performance of the CNF/CNT electrodes was evaluated by various analysis methods such as cyclic voltammetry, galvanostatic charge-discharge, electrochemical impedance spectroscopy and cyclic stability. The results showed that the cellulose-derived composite electrodes have fairly high values of specific capacitance and power density and can retain excellent performance over at least 2 000 cycles. Therefore it can be stated that sustainable cellulose-derived CNF/CNT composites are prospective materials for supercapacitor electrodes.

1. Introduction

The growing interest in long-lasting energy storage devices leads to the necessity of using more efficient carbon electrode materials [1]. Flexible sheets made of carbon nanofibers (CNFs) with their well-interconnected pores, high mechanical and electrochemical stability are prospective electrode materials for electrostatic energy storage devices such as supercapacitors. Their mesoporosity is of great importance, as it allows unrestricted ion diffusion into electrode cavities. Therefore, CNFs sustain a substantial uptake of electrolyte solution and enable high ion conductivity. In addition to that, the freestanding nature of CNF material allows using it without a polymeric binder [2, 3].

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[6] To whom any correspondence should be addressed.

However, the main drawbacks of the CNF material are its relatively low specific surface area and electrical conductivity, which leads to low values of specific capacitance. Functionalization with chemical vapor deposited carbon nanotubes (cvdCNTs) should improve the mentioned flawed properties of CNFs making CNT/CNF composites more suitable for supercapacitors [4].

Previous studies have shown beneficial impacts of cvdCNTs on the electrochemical performance of carbon nanocomposite electrodes in supercapacitors [5-7]. Yet, composites in the aforementioned studies consisted of unsustainable components, while efficient use of carbonaceous electrodes derived from sustainable renewable resources is still very limited for supercapacitors. As demand on carbon nanostructures continues to grow, renewable resources should be accounted as an alternative to the currently most used CNF precursors: coal tar pitch and synthetic polymers. The biopolymer cellulose is a vast source that could be used for the synthesis of CNFs [8]. In this study, new cellulose-derived freestanding hierarchical carbon nanocomposite materials with prospective properties for electrostatic energy storage were evaluated as electrodes that potentially can be used for novel on-chip supercapacitors [9].

2. Experimental

2.1. Fabrication of composite electrodes

The composite CNF/CNT electrodes were produced via chemical vapor deposition of CNTs on top of cellulose-derived CNFs. Initially, CNF sheets were made by three consecutive steps of cellulose acetate electrospinning (17 wt% solution of the polymer in 2:1 solvent ratio of acetone and dimethylacetamide), cellulose regeneration (in 0.1 M water solution of NaOH) and carbonization (in a quartz tube furnace with N_2 flow by heating up to 800 °C with the heating rate of 5 °C/min) according to [8]. Subsequently, CNTs were thermally deposited on CNF substrates at 700 °C for 10 min using acetylene as a carbon source, 2 nm thick iron layer as a catalyst and hydrogen as a carrier gas (in AIXTRON Nanoinstruments Black Magic 2-inch machine).

2.2. Material characterization

The morphology of the composite materials was observed using high resolution scanning electron microscopy (SEM, Leo Ultra 55 FEG SEM, Zeiss) in a secondary electron mode at an acceleration voltage of 3 kV. The surface area of the materials was measured using the Brunauer-Emmett-Teller (BET) nitrogen adsorption method, and mesopore size distribution was quantified by the Barett-Joyner-Halenda (BJH) method using an adsorption isotherm (TriStar 3000 V6.04 A surface area and pore analyzer). The samples were degassed under vacuum at 225 °C for 4 h prior to the measurements. The electrical conductivity of the materials was evaluated using a four-point probe system (Parameter Analyzer-Keithley 4200-SCS).

2.3. Electrochemical analysis

Electrochemical performance was measured in a supercapacitor cell consisting of a symmetrical two-electrode system with the nanocomposites as working electrodes, electrospun cellulose as a separator, and 6 M aqueous solution of KOH as an electrolyte. The working electrodes and separators were cut to circular area of 0.5 cm^2 to fit the current collectors. Before starting the measurements the electrodes were immersed into the electrolyte solution for 24 h. Electrochemical measurements were performed with Gamry Reference 3000 potentiostat/galvanostat/ZRA and data were analyzed with Gamry Echem Analyst. A voltage range between □-0.5 V and 0.5 V was used for CV (cyclic voltammetry) measurements at five different scan rates (5, 10, 20, 100 and 200 mV s^{-1}). GCD (galvanostatic charge-discharge) tests were performed at four different current densities (0.75, 1, 1.5 and 2 A g^{-1}). EIS (electrochemical impedance spectroscopy) was done at open circuit potential with amplitude of 5 mV over a frequency range from 100 kHz to 10 mHz. An electrochemical stability tests were performed by cyclic charge-discharge (CCD) for 2 000 cycles with a current density of 1 A g^{-1}.

3. Results and discussion

3.1. Morphology and surface properties

CNF mats with a thickness of 25-40 mm were obtained via carbonization of electrospun cellulosic precursors. The mats consist of fibers with 50-250 nm diameters. The continuous fibers are randomly oriented and have smooth topography (figure 1a, bottom). The morphology of the composite material is rather different (figure 1a, top). After chemical vapor deposition the bigger CNFs were densely covered with much smaller CNTs (1-20 nm tube diameters) thus forming a hierarchical nanocomposite material.

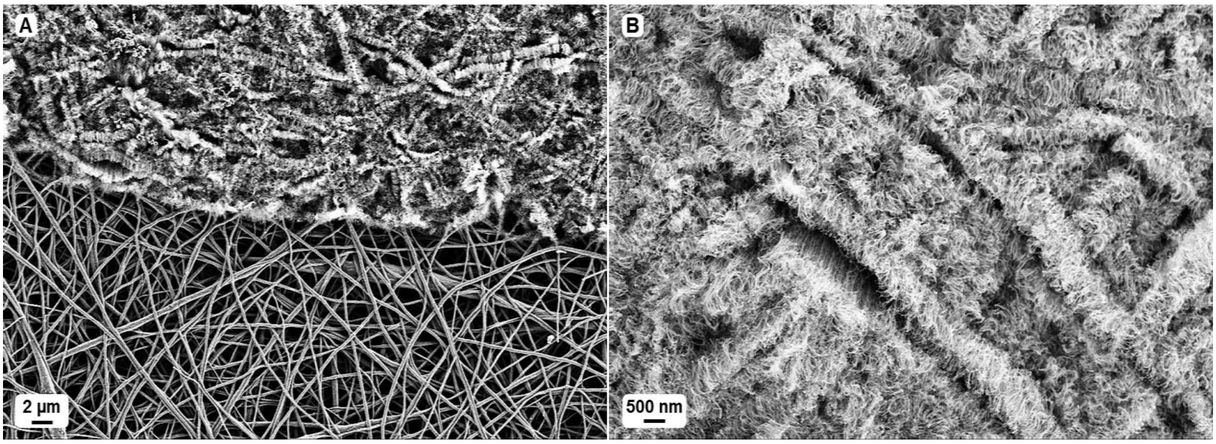

Figure 1. SEM images of the electrode material: A. The interface between pristine CNF region (bottom) and CNF region after deposition of CNTs (top); B. Deposited CNTs on top of CNFs.

Cellulose-derived CNF sheets have great mechanical and electrochemical stability along with valuable mesoporosity. On the one hand, mesoporous CNFs uptake the substantial amount of electrolyte ions and enable these ions to diffuse quickly in and out of electrode cavities [2], while on the other hand, much smaller CNTs increase surface area of the material, i.e. introduce microporosity (figure 2), and improve its electrical conductivity (table 1). These contributions from both components of the resulting composite material are favorable for supercapacitor high power and energy performance [4].

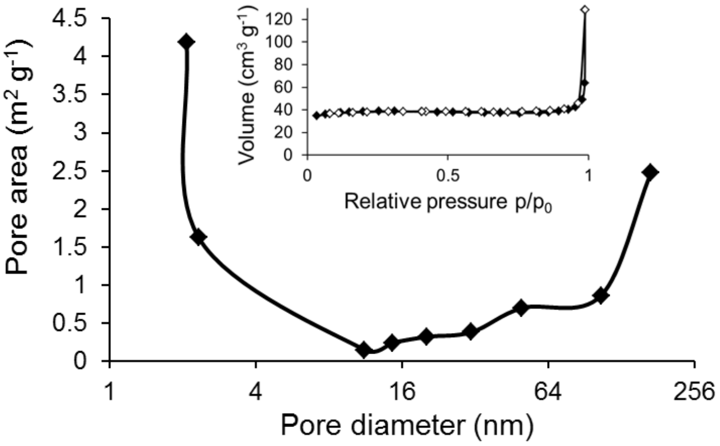

Figure 2. Nitrogen adsorption/desorption isotherms (inset) and pore size distribution (main image) of the electrode material.

Table 1. Properties of cellulose-derived carbon electrode materials.

Sample	Surface area (m^2 g^{-1})	Micropore area (m^2 g^{-1})	Electrical conductivity (S cm^{-1})	Capacitance (F g^{-1})	Energy density (W h kg^{-1})	Power density (W kg^{-1})	Capacitance retention (%)
CNF	45	32	4.2	12.8	0.31	432	88.7
CNF/CNT	131	103	69.4	22.9	0.99	2470	96.6

3.2. Electrochemical performance

Various electrochemical measurements were used to evaluate the performance and behavior of the electrode materials.

Figure 3A shows dependence of capacitance on a scan rate for the composite CNF/CNT electrode. CV curves have moderately rectangular shape, which indicates an electrical double layer (EDL) capacitive behavior [10]. Distortion of the rectangular shape at higher scan rates happens because of the lack of time for electrolyte ions to penetrate completely inside the electrode, whereas for lower scan rate the ions get to the inner surface of electrode providing higher accumulative charge [2]. The comparison of the CV curves of two different CNF-based nanostructured materials is presented in figure 3B. It is clear seen that the CNF/CNT composite electrodes show higher values of specific capacitance in comparison to the pure CNF electrodes.

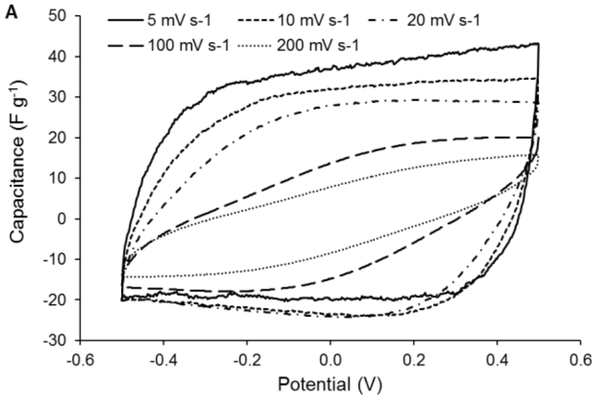

Figure 3. A. CV curves of the CNF/CNT composite electrode at different scan rates. B. CV curves of the composite and pure CNF electrodes at 10 mV s^{-1} scan rate.

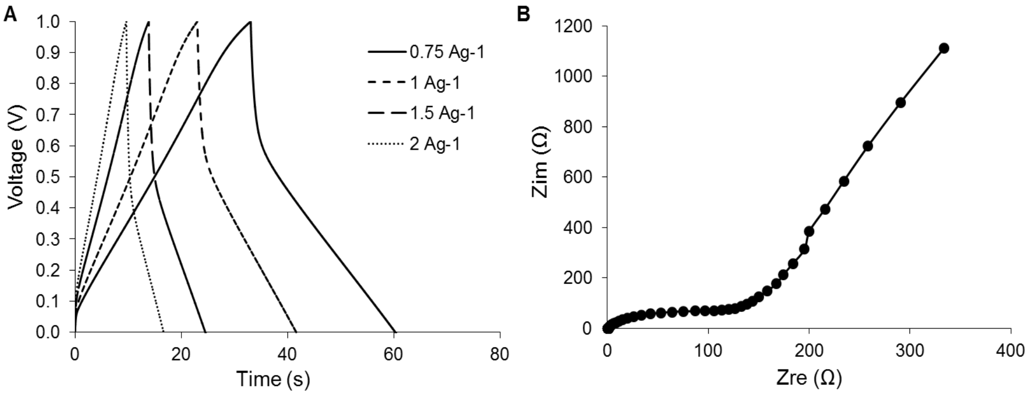

Figure 4. A. GCD curves of the electrode material at different current densities. B. Nyquist impedance plot of the electrode material.

GCD curves show almost symmetrical shape specifying EDL behavior as well (figure 4A). From GCD test power and energy density values were found to be reasonably higher for the composite electrode materials. Fast current-voltage response proves that electrode material have high power density [11].

According to EIS equivalent series resistance of the system is defined as an initial intercept of the plot with the X-axis in the high frequency region (figure 4B). Resistance value is only 0.57 Ohm, which is beneficial for effective performance of a supercapacitor. The verticality of the Warburg line at medium frequency validates sufficient pore accessibility for electrolyte ion diffusion [6].

Moreover, the electrodes retained 96.6% of the initial capacity after 2 000 charge-discharge cycles, which is a very good stability for an energy storage device such as supercapacitor as it has to deliver the harvested energy through quick charging and discharging many times [12].

4. Conclusions

Overall, functionalization of CNF led to the composite materials with higher capacitance values. This positive effect can be explained by few factors. First of all, the deposition of CNTs on top of the CNF substrate improved electrical conductivity (electrode's ability to transfer charges), while CNTs also increased surface area (electrode's ability to uptake electrolyte and accumulate charges). Hence, the hierarchical cellulose-derived CNF/CNT nanocomposites showed their great potential as electrode materials for electrostatic energy storage.

Acknowledgments

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