Materials Chemistry and Physics 160 (2015) 59–65

Contents lists available at ScienceDirect

Materials Chemistry and Physics

journal homepage: www.elsevier.com/locate/matchemphys

Capacitive effects of nitrogen doping on cellulose-derived carbon nanofibers

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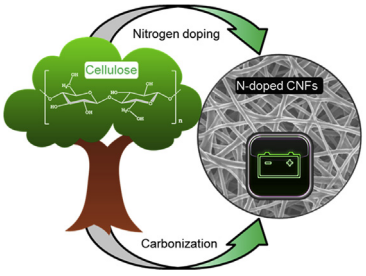
HIGHLIGHTS

- The sustainable carbon nanofibrous materials are derived from cellulose.
- The convenient method is used to dope the materials with nitrogen.
- The nitrogen doping makes specific capacitance of the CNFs 2.5 times higher.
- The nitrogen content of 4–4.6 at.% is an optimal doping concentration.

GRAPHICAL ABSTRACT



ARTICLE INFO

Article history:
Received 28 November 2014
Received in revised form
25 March 2015
Accepted 6 April 2015
Available online 15 April 2015

Keywords:
Nanostructures
Surfaces
Electrochemical properties

ABSTRACT

Carbons with valuable electrochemical characteristics are among the most convenient electrode materials used for energy storage. At the moment, their production is mostly reliant on unsustainable fossil fuels. A preferential sustainable production of enhanced carbonaceous electrodes can be achieved with more extensive utilization of abundant renewable resources instead of fossils. In this study, nitrogen-doped carbon nanofibers (CNFs) were synthesized from cellulose, the most abundant renewable resource, via consecutive steps of cellulose acetate electrospinning, subsequent deacetylation to cellulose, impregnation with nitrogen-containing additive (ammonium chloride), and carbonization. Results of material characterization showed that the carbonization of functionalized cellulose samples led to formation of CNFs doped with 4–5.6 at.% of nitrogen. In comparison with pristine CNFs N-doped samples had a slightly lower specific surface area, but higher conductivity and hydrophilicity. Moreover, electrochemical measurements indicated that the enhanced N-doped materials had about 2.5 times higher

Abbreviations: CNFs, carbon nanofibers; EDL, electric double-layer; CA, cellulose acetate; CV, cyclic voltammetry; GCD, galvanostatic charge–discharge; EIS, electrochemical impedance spectroscopy; ESR, equivalent series resistance.

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http://dx.doi.org/10.1016/j.matchemphys.2015.04.006
0254-0584/

specific capacitance which was increasing throughout 1000 charge–discharge cycles. These results suggest that nitrogen doping method used in this study has a positive pseudocapacitive effect on the electrochemical performance of carbonized cellulose materials.

1. Introduction

During the last decades a lot of attention has been attracted to electric double-layer (EDL) capacitors as efficient storage devices for sustainable use [1]. These devices store energy electrostatically at the interface between an electrode and an electrolyte and are characterized by high power density and much longer lifetime [2,3] than modern batteries [4,5]. At present, the most commonly used electrodes in EDL capacitors are prepared from various carbonaceous materials with have high surface area and conductivity [6]. Carbon electrodes can achieve high values of specific capacitance and power density through a sufficient number of charge and discharge cycles without significant deterioration [7]. However, pure carbon electrodes with EDL principle of energy storage are characterized by a low energy density. This limits their use to applications where fast and relatively small amounts of energy are needed, such as electric vehicles, phone chargers, uninterruptible energy supplies for computers, wireless sensors [8–11].

Pseudocapacitive effects from faradaic reactions can bring the performance of storage systems to a next level [12]. Pseudocapacitance implies transfer of charges across a double layer at an electrode surface and can be reached by addition of an n-type dopant such as nitrogen [13]. This phenomenon substantially increases the total amount of accumulated charges and thus the energy density of a supercapacitor [14].

Taking into account increasing demand on the production of sustainable energy storage devices, the search of innovative carbon materials is motivated equally by the outlook of consistent performance and by low cost, easy preparation, and minimal detrimental impact on the environment. From the performance point of view, lightweight materials made of carbon nanofibers (CNFs) with high mechanical strength and electrochemical stability, with well interconnected pores of controlled size and distribution, and with enhanced pseudocapacitance, can fulfill the requirements of a supercapacitor electrode material [15]. From the cost and sustainability point of view, utilization of renewable resources should be considered as a future alternative to coal tar pitch and synthetic polymers which are usually used as CNF precursors [16]. For the above mentioned reason, such an abundant biopolymer as plant cellulose [17] is obviously an attractive candidate for the synthesis of CNFs.

Recently plant cellulose has been effectively used as a suitable precursor for the production of sustainable low cost carbon materials for energy storage applications [18,19], however the electrochemical results shown by those materials are fairly inferior to industrial standards [20]. In this study, we analyze potential capacitive effects of N-doping on cellulose-derived electrode materials. Our convenient method of doping provides efficient incorporation of nitrogen atoms into free-standing carbon nanomaterials via carbonization of NH_4Cl-treated electrospun cellulosic precursors. As a result, capacitive performance of such carbons is enhanced by doping with an intention to combine two different principles of energy storage: electrostatic from EDL and electrochemical from pseudocapacitance.

2. Experimental

2.1. Electrodes synthesis

The sheets of carbonaceous electrode materials were produced by three consecutive steps of cellulose acetate (CA) electrospinning, cellulose regeneration and carbonization. For electrospinning 17 wt % CA solution in mixture of acetone and dimethylacetamide (volume ratio 2:1) was used as described previously [21]. Resulting CA fibrous mats with the dimensions of 5 × 5 cm^2 were placed in beakers filled with 50 ml of 0.1 M water solution of NaOH to hydrolyze CA and obtain regenerated cellulose. After the regeneration process, cellulose mats were immersed into 0.3 M and 0.5 M solutions of NH_4Cl for 1 and 4 days to obtain cellulosic precursors for N-doped CNFs. Afterward the samples were transferred to polystyrene Petri dishes for drying at ambient conditions in air. The carbonization of all the cellulosic precursors was carried out in a quartz tube furnace in N_2 flow by heating up to 800 °C with the heating rate of 5 °C/min and holding the samples at 800 °C for 2 h. The resulting N-doped CNFs were named NCNF031, NCNF034, NCNF051 and NCNF054, where the first two digits represent the molar concentration of NH_4Cl solution and the last one represents the days of immersion.

2.2. Characterization

The morphology of the samples was investigated with 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 electrode materials was measured using the Brunauer–Emmett–Teller (BET) nitrogen adsorption method at a TriStar 3000 V6.04 A surface area and pore analyzer. Mesopore size distribution was quantified by the Barett–Joyner–Halenda (BJH) method using an adsorption isotherm. Prior to measurements the samples were degassed under vacuum at 150 °C for 3 h.

Electron Spectroscopy for Chemical Analysis (ESCA) was performed with the Quantum 2000 scanning ESCA microprobe from Physical Electronics to evaluate the level of nitrogen doping of the samples. An Al Kα (1486.6 eV) X-ray source was used and a beam size was 100 μm.

Raman spectroscopy was carried out to evaluate the microstructure of CNF materials. Raman spectra were collected using a 638 nm laser source on a Horiba XploRA spectrometer equipped with an Olympus BX41 microscope. Spectra analyses were performed with LabSpec software.

X-ray Diffraction (XRD) Analysis was carried out with a Philips X'Pert Materials Research Diffractometer. Radiation was generated with an X-ray tube with Cu anode (Kα radiation, λ = 1.54184 Å) at 45 kV and 40 mA. An X-ray lens (glass polycapillary optics) with a Ni filter was used as incident optics and a thin film collimator was used as diffracted optics. A 2θ range was 10–50°, and resolution was 0.05° with 10 s averaging time per step. Phase analysis was performed with X'Pert HighScore 3.0 (PANalytical BV).

Water contact angle measurements were carried out by a sessile droplet technique (4 μm droplet volume) with VCA 2500 (Video Contact Angle System), AST Inc. (Advanced Surface Technology Inc.).