Electrochimica Acta 196 (2016) 189–196

Contents lists available at ScienceDirect

Electrochimica Acta

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

Hierarchical porous carbon nanofibers as binder-free electrode for high-performance supercapacitor

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ARTICLE INFO

Article history:
Received 28 December 2015
Received in revised form 20 January 2016
Accepted 9 February 2016
Available online 6 March 2016

Keywords:
Electrospinning
THF
hierarchical porous
carbon nanofiber
supercapacitor

ABSTRACT

1D hierarchical porous carbon nanofibers (HPCNFs) are prepared via electrospinning ternary PAN/N, N'-dimethylformamide (DMF)/tetrahydrofurar (THF) and using commercially available nano-$CaCO_3$ as template. In the process of carbonization, nano-$CaCO_3$ template decomposes and releases CO_2 to form micropores and mesopores. Macropores are generated by removing the CaO nanoparticles using acid subsequently. The hierarchical pores are fairly well distributed because the nano-$CaCO_3$ particles are highly dispersed in the fiber due to the better wettability in binary solvent. The obtained HPCNFs attain high specific surface area without physical and chemical activation. The HPCNF mats, possessing free-standing architecture, are used as binder-free electrodes for supercapacitor. Because of high specific surface area, rational pore diameter distribution and binder-free characterization of electrodes, the HPCNFs display a high capacitance of 251 $F g^{-1}$ at a current density of 0.5 $A g^{-1}$ as well as excellent rate capability and outstanding cycling stability (over 88% capacitance retention after 5000 cycles at the current density of 1 $A g^{-1}$). These results demonstrate that the binary solvent method is effective to achieve high-performance electrode materials and it has a promising prospect on applications of energy storages.

1. Introduction

Supercapacitors (SCs) are one of important energy storage devices due to their higher power density and charge/discharge rates as well as long lifespan [1–5]. The performance of supercapacitors depends intimately on the physical and chemical properties of their electrode materials [6–8]. In the recent years, carbon electrode materials for supercapacitors have been widely investigated, because of its high conductivity, lower resistance and good stability [9–12].

Among numerous carbon electrode materials, porous carbon nanofibers (PCNFs) have been actively developed as an indispensable candidate for electrode materials of supercapacitors [13–16]. One dimensional (1D) structure of PCNFs can be designed into free-standing material for binder-free electrode which not only simplifies operating steps but also avoids using any binder. So it has attracted significant attention [17–19]. Moreover, carbon nanofibers, as free-standing electrode, are easy relatively to prepare by electrospinning technique [20–23]. It is well-known that electrospinning has growing increasingly versatile as a promising method to fabricate 1D porous nanofibers. Therefore, most of the PCNFs electrode materials are prepared by electrospun precursor solutions of incorporating porogen. The porogens mainly contain hard template, soluble salt and sacrifice polymer [24–30]. Among these, hard template mothed is facile and easy controlled. In particular, nano-$CaCO_3$ as typical hard template has double pore-forming function in carbonation process of fibers, and finally removal of template is simple. The relative literatures suggest that the dispersion of nano-$CaCO_3$ particulars in nanofiber is a crucial factor for the specific surface area and pore diameter distribution of PCNFs material which are important influences to capacitance performance [26,31,32].

In this work, HPCNFs electrode materials are synthesized via electrospinning technology using PAN as carbon precursor and nano-$CaCO_3$ as double purpose template. Meanwhile, in order that nano-$CaCO_3$ template has better dispersion in as-spun composite nanofiber, DMF/THF mixed solvent as a delicate design is applied in electrospinning solution. The incorporation of THF in electrospinning solution reduces the agglomeration of nano-$CaCO_3$ as well as ensures its homogeneous dispersion in composite nanofibers, because the nano-$CaCO_3$ particles have better wettability in THF than that in DMF. In addition, the decomposition of nano-

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http://dx.doi.org/10.1016/j.electacta.2016.02.050
0013-4686/

$CaCO_3$ particles and removal of the as formed CaO nanoparticles generate micropores, mesopores and macropores. The electrode material combines the advantages of hierarchical pore and high specific surface area, and has exhibited excellent capacitance performance. In addition, the method presented in this work which the hard template was well dispersed in the mixed solvent can be employed to synthesize more porous electrode materials.

2. Experimental

2.1. Materials

Polyacrylonitrile (PAN, Mw = 80000) was purchased from Kunshan plastic Co., Ltd. Nano-$CaCO_3$ was purchased from Huayu nano technology Co., Ltd. N, N-Dimethylfirmamide (DMF) and tetrahydrofuran (THF) were purchased from Aladdin. Regents and materials were analytical grade and used without any further purification.

2.2. Fabrication of nano-$CaCO_3$/PAN composite nanofibers by electrospinning

The nano-$CaCO_3$/PAN composite nanofibers were prepared by a facile electrospinning method. In a typical procedure, 0.3 g of nano-$CaCO_3$ was dispersed in DMF by sonication for 30 min, then 0.8 g of PAN was added and the mixture was vigorous stirring. After 12 h, the THF was drop into the milky suspension and kept stirring to form a homogeneous suspension. The suspension was set into a glass syringe to yield a stable Taylor cone on tip of needle under 15 kV high-voltages. The collector to needle distance was maintained at 18 cm to collect a white nonwoven composite nanofiber mat. In this procedure, the mixed solvent of DMF and THF was 9.2 g in total, which was used in different weight ratio for 3:1, 4:1, and 1:0, respectively. The obtained composite nanofibers were denoted as NFs-3-1, NFs-4-1, NFs-1-0.

2.3. Preparation hierarchical porous carbon nanofiber

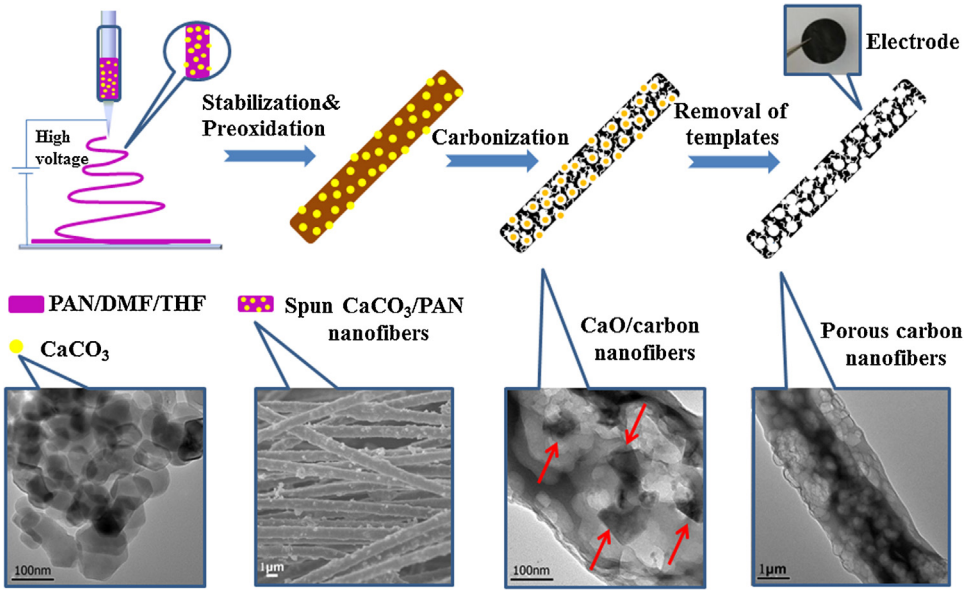
These as-electrospun composite nanofibers were peeled off from the collector and put into a horizontal tube furnace for annealing treatment. The nonwoven white mat was heated to 250 °C in air at a rate of 5 °C per min and maintained for 2 h for stabilization, then the sample was heated up to 800 °C at a rate of 2 °C per min and kept for 2 h in N_2 gas atmosphere for carbonization of PAN and pyrolysis of $CaCO_3$ to CaO. After cooled to room temperature under N_2 atmosphere, the carbon nanofibers embedded with nano-CaO were obtained. In order to remove the CaO nanoparticles, the obtained CaO/carbon nanofibers were immersed in 1.5 M HCl acid for 1 h and then rinsed with deionized water and ethanol thoroughly. The hierarchical porous carbon nanofiber were prepared and named HPCNFs-3-1, HPCNFs-4-1 and HPCNFs-1-0.

2.4. Characterization

The microstructure and morphology were characterized by transmission electron microscopy (TEM Tecnai-F20 system) and field emission scanning electron microscopy (FESEM JSM-7500F). Pore structures of these samples were characterized by nitrogen adsorption/desorption experiments at 77 K (Quantachrome ASIQM0001-3). The surface areas were calculated using the Brunauer-Emmett-Teller (BET) equation. Pore size distributions were calculated by the Barrett-Joyner-Halenda (BJH) method using the desorption branch of the isotherm. X-ray diffraction (XRD) pattern was obtained from ground-up samples of HPCNFs using a Bruker D8 FOCUS diffractormeter and Cu Kα (λ=0.15418). Raman spectrum was recorded by Renishaw inVia with a wavelength of 514 nm to calculate the degree of crystallinity. The surface chemical composition was examined by X-ray photoelectron spectroscopy (XPS Axis Ultra DLD). The wettability was evaluated by contact angle measuring device (Data-physics OCA15). The $CaCO_3$ powder was press to become a wafer under 8 MPa. Then, the contact angles were tested by dropping solvent of pure DMF and THF, 4:1 of DMF:THF, and 3:1 of DMF:THF on wafer of $CaCO_3$ powder.

2.5. Electrochemical measurements

Electrochemical performance was detected on a CHI 660D electrochemical workstation with the typical symmetrical two-electrode. The electrodes were obtained by cutting the HPCNFs mat into disk shapes (diameter: 12 mm; thickness: 200 μm; weight:



Scheme 1. Schematic illustration of the synthesis process for HPCNFs.