Carbon 116 (2017) 518–527

Contents lists available at ScienceDirect

Carbon

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

Free-standing activated flax fabrics with tunable meso/micropore ratio for high-rate capacitance

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ARTICLE INFO

Article history:
Received 15 November 2016
Received in revised form
24 January 2017
Accepted 10 February 2017
Available online 12 February 2017

Keywords:
Flax
Activated carbon fiber
Hierarchical structure
Meso/micropore

ABSTRACT

Free-standing and flexible activated flax fabrics (AFFs) with hierarchical meso/microporous structures have been prepared through a novel one-step synthetic strategy of rapid carbonization/activation of flax fabrics in CO_2. The fast heating and the high partial pressure of CO_2 inhibit the decomposition of flax fabrics during heating up, and thus keep more char materials for gasification at high temperature. It is found that such a process retains a considerable amount of oxygen groups and creates relatively large pores, bringing a one-step process to carbonize and activate flax fabrics at the same time and offering the freedom of tuning the mesopore volume/total pore volume (V_{meso}/V_{total}) ratio. Notably, the V_{meso}/V_{total} ratio is significantly increased from 27.6% to 67.0%. As a result, the flexible electrodes show excellent electrochemical performance in aqueous electrolyte, exhibiting a large specific capacitance (205 F g^{-1} or 140 F cm^{-3} at current density of 0.1 A g^{-1}), a good rate capability (139 F g^{-1} or 95 F cm^{-3} at 35 A g^{-1}), and an excellent cycling stability (~96.6% retention after 3000 cycles). The excellent rate performance can be attributed to the improved ion transport (due to large pore size) and the good wettability (due to the oxygen group) of electrolyte.

1. Introduction

Electric double-layer capacitor (EDLC), which is also called as supercapacitor, has been regarded as one of the most promising energy storage devices due to its high power density and long cycle life [1], and has been successfully applied in a variety of equipment including portable consumer electronics, uninterruptable power sources, memory back-up systems, electric vehicles, and emergency systems [2–4]. Given the fact that an EDLC stores charges on the surface of the electrodes, carbon materials such as activated carbons (ACs) [5,6], ordered mesoporous carbons [7], carbide-derived carbons (CDCs) [8,9], carbon nanotubes (CNTs) [10–12], and graphene [13–15] have always been employed as EDLC electrode materials because of their high specific surface area (SSA) and high electric conductivity.

Among various carbon materials, AC is so far the most successful commercial electrode material due to its high SSA, low cost, high chemical stability, and good electric conductivity [16,17]. Unfortunately, the SSA of most ACs is mainly contributed by the micropores that have small pore size (<2 nm) and high diffusion resistance [18,19]. Consequently, it is difficult for electrolyte ions to be fully absorbed onto the huge surface of ACs, resulting in a limited specific capacitance (SC) [20,21]. Moreover, the massive micropores with disordered texture would lead to a poor rate capability for AC-based EDLCs, giving rise to a significantly decreased SC at high current densities or scan rates [22,23]. In order to solve the stated problems, researchers now focus more on developing hierarchical porous ACs with high meso/micropore ratios to guarantee both large pore size for rapid ion diffusion and high effective SSA for charge accumulation [24–27]. Recently, novel ACs with ultrahigh SSA (1500–3100 m^2 g^{-1}) and tunable volume fraction of the mesoporosity have been prepared, through KOH activation of different precursors especially of various biomasses (such as gelatin [28], pollen [19], corn stalk core [26], bacterial cellulose [29], hemp [30], *etc.*). These biomasses are sustainable, low-cost, and environmental friendly, and have exhibited enhanced SC and rate capability.

However, in order to assemble these powdered ACs into

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http://dx.doi.org/10.1016/j.carbon.2017.02.029
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electrodes with certain geometric shapes, they have to be composited with some organic binders such as polyvinylidenefluoride (PVDF) and poly-tetrafluoroethylene (PTFE). These binders usually possess poor electrical conductivity and have no contribution to the capacitance [16,31]. As a result, the electrochemical performance of the as-prepared electrodes is usually poorer than the theoretical prediction. Compared with AC powders, AC fibers/fabrics (ACFs) are continuous, self-supporting, and flexible [32]. Without using any additives, ACFs can be directly employed as EDLC electrodes and are thus expected to exhibit better electrochemical properties [33]. Previous studies mainly focused on the fabrication of polyacrylonitrile (PAN)-based ACFs, which typically showed relatively low SC and poor rate capability, because their moderate SSA were largely contributed from micropores [31–33]. In addition, due to the use of unsustainable and toxic raw materials in manufacturing, the application of PAN-based ACFs in EDLCs is limited [31]. Therefore, it is highly desired to develop novel ACFs with both high SSA and high mesoporosity from nontoxic materials. On account of their high yield, low cost, renewability, and environmental friendliness, natural fibers have been regarded as promising precursors for ACFs [34]. Among various natural fibers, flax has attracted wide attention owing to its high tensile strength, large aspect ratio, relatively high SSA, regular shape, and smooth surface [35]. Nevertheless, to the best of our knowledge, most related research simply employed carbonized natural fibers with poor SSA as conductive substrates to support other electro-active materials such as CNTs, MnO_2 and PPY for supercapacitor electrodes, in which the potential of flax was not fully achieved [35–37].

Herein, for the first time, we report the fabrication of free-standing and flexible activated flax fabrics (AFFs) with tunable meso/micropore ratio through a novel one-step synthetic strategy, which combines rapid heating and direct carbonization/activation in CO_2. The effects of the heating rate and the carbonization/activation temperature on the SSA, porous structure, morphology, graphitization degree, and surface chemical structure of the as-prepared AFFs were studied in detail. The results showed that the mesopore volume/total pore volume (V_{meso}/V_{total}) ratio could be significantly enhanced by increasing the heating rate. The resultant sample was directly employed as an EDLC electrode without using any binders, and exhibited excellent electrochemical performance including a high SC of 205 F g^{-1} (140 F cm^{-3}) at current density of 0.1 A g^{-1}, a superior rate capability, and an excellent cycling stability. To the best of our knowledge, this is the first report of fabricating self-supporting ACFs with tunable meso/micropore ratios for high-rate capacitance from natural fibers. This facile process is generic, and is thus expected to be applied to other natural fibers such as cotton, jute, ramie, etc., enabling new applications of these old materials.

2. Experimental section

2.1. Materials

Commercially available unbleached flax fabrics were provided by ZHEJIANG JINYUAN FLAX Corp. (China). The fabrics were washed thoroughly with deionized water before use. Potassium hydroxide (KOH, AR, 90%) was purchased from Aladdin Corporation. Carbon dioxide (CO_2, 99.99%) was purchased from Xi'an Tiantai Gas Corporation. Both KOH and CO_2 were used as received without further purification.

2.2. Fabrication of activated carbon fabrics

AFFs were fabricated from flax fabrics through a simple one-step process of direct carbonization/activation. Detailed procedures are as follows: 2.0 g of flax fabric was placed in an infrared-heating rapid thermal processing furnace (BTF-1200C-RTP-S90B, 10 kW, AnHui BEQ Equipment Technology Co., Ltd). The sample was then heated to the desired temperatures (700, 800 °C) for 1 h with different heating rates (5, 30, 60, and 300 °C min^{-1}) in a flowing CO_2 atmosphere (with flow rate of 0.15 L min^{-1}). The as-prepared products were denoted as AFF-r-t, where r is the heating rate (°C min^{-1}), and t represents the final carbonization/activation temperature (°C). For comparison, normally carbonized flax fabric, denoted as CF-300-700, was prepared in the same furnace at 700 °C for 1 h with a rapid heating rate of 300 °C min^{-1} in argon.

2.3. Physical characterization

The TGA/DSC curves of the flax fabric in CO_2 and argon atmosphere were respectively investigated by a NETZSCH STA 449 F3 thermal analysis system with a heating rate of 10 °C min^{-1} and a gas flow rate of 80 mL min^{-1}. The temperature range was changed from room temperature to 1000 °C, and the initial weight of the sample was 10–15 mg. The morphology and microstructure of the samples were characterized using field emission scanning electron microscopy (FESEM, Hitachi S-4700 operated at 15 kV) and field emission transmission electron microscopy (FETEM, FEI-Tecnai F-30 operated at 300 kV). Nitrogen adsorption/desorption analysis was carried out at 77 K using an Autosorb-iQ (Quantachrome) automatic analyzer. The S_{BET} was calculated by the Brunauer-Emmett-Teller (BET) method based on the adsorption data in the relative pressure (P/P_0) ranging from 0.05 to 0.3. The total pore volume was obtained from the amount of nitrogen adsorbed at a relative pressure (P/P_0) of 0.99. Pore size distribution as well as micropore and mesopore volumes were calculated from the nitrogen adsorption/desorption data, using the Non-Local Density Functional Theory (NL-DFT) software (SAIEUS, Micromeritics Instrument) with the standard slit pore model. The X-ray diffraction (XRD) patterns of the samples were recorded on a Bruker D8 Advance system using Cu Ka radiation (k = 0.1542 nm, 40 kV, 40 mA). The X-ray photoelectron spectroscopy (XPS) studies were performed on a Thermo Scientific X-ray photoelectron (K-Alpha). The Raman spectra were collected on a Renishaw-inVia Confocal Raman Microscope with an excitation wavelength of 514.5 nm. The mass density (ρ, g cm^{-3}) of the AFFs was calculated according to $\rho = m_{AFF}/V_{AFF}$, where m_{AFF} (g) is the mass of one bundle of AFFs, and V_{AFF} (cm^3) is the volume (cm^3). Each fiber was approximated as a cylindrical fiber to calculate its volume. The number and the diameter of the AFFs were measured with an optical microscope, and at least 20 fibers were tested to get an average diameter value. The tensile strength of the AFFs was tested using an Instron 3345 universal tensile testing instrument. The loading velocity and gauge length is 0.2 mm min^{-1} and 50 mm, respectively. 10 bundles of AFFs were tested to get an average value.

2.4. Electrochemical measurements

All electrochemical tests were carried out in a conventional three-electrode system with 6 M aqueous KOH solution as the electrolyte, Hg/HgO as the reference electrode, and a platinum plate as the counter electrode. Without using any organic binder or conductive carbon black, AFFs were directly employed as working electrodes. The cyclic voltammetry (CV) curves, galvanostatic charge-discharge studies, and electrochemical impedance spectroscopy (EIS) measurements were performed using an electrochemical workstation (CHI660E, Shanghai Chen Hua Co., Ltd, China). The CV and galvanostatic charge-discharge tests were performed in a voltage window from −1.0 to 0 V vs. Hg/HgO electrode