



# Electrochemical performance of fulvic acid-based electrospun hard carbon nanofibers as promising anodes for sodium-ion batteries



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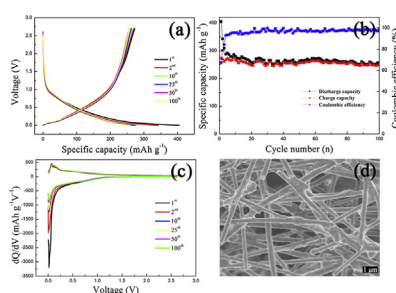
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## HIGHLIGHTS

- Biomass fulvic acid is characterized before preparation for carbon nanofibers.
- PF-CNFs are applied as high-performance anode materials in sodium-ion batteries.
- Intrinsic oxygenic functionalities contribute to good electrochemical performances.

## GRAPHICAL ABSTRACT



## ARTICLE INFO

### Article history:

Received 25 May 2016  
Received in revised form  
5 September 2016  
Accepted 8 October 2016

### Keywords:

Sodium ion batteries  
Fulvic acids  
Carbon nanofibers  
Electrospinning

## ABSTRACT

The electrochemical performance of fulvic acid-based electrospun hard carbon nanofibers (PF-CNFs) as anodes for sodium-ion batteries is reported. PF-CNFs were prepared, stabilization in air at 280 °C and then carbonized in N<sub>2</sub> at 800, 1000, 1300 or 1500 °C. The PF-CNFs prepared at 1300 °C had abundant oxygen functional groups, large interlayer spaces and stable morphologies and when used as anodes in sodium-ion batteries, a reversible sodium intercalation capacity of 248 mAh g<sup>-1</sup> was obtained with capacity retention ratio of 91% after 100 cycles at a current density of 100 mA g<sup>-1</sup>. This large capacity combined with the superior cycling performance indicates that fulvic acid-based carbon nanofibers are promising electrode materials for use in rechargeable sodium-ion batteries.

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## 1. Introduction

Rechargeable lithium-ion batteries (LIBs) play important roles in portable electronic devices due to their long cycle lifetimes and high energy densities [1]. However, the abundance of lithium in the

Earth's crust is only 20 ppm [2]. This coupled with the uneven distribution of lithium minerals has led to increasing concerns about the scarcity of lithium resources [2]. Sodium, on the other hand is the most abundant alkali metal in the oceans, and it can be easily extracted from sea salt. The redox potential of Na<sup>+</sup>/Na is -2.71 V vs the standard hydrogen electrode compared to -3.04 V for Li<sup>+</sup>/Li. Because of the abundance of sodium resources and its large negative redox potential, sodium-ion batteries (SIBs) have gained increasing attention over the past few years [3–6].

However, the size difference between the two ions (68 p.m. for

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$\text{Li}^+$  and 95 p.m. for  $\text{Na}^+$ ) means that the anode materials of LIB and SIB cannot be interchanged [7]. Further, unlike LIBs,  $\text{Na}^+$  ions can hardly intercalate in graphite [7,8]. For LIBs, the graphitic anode has the chemical formula  $\text{LiC}_6$  after intercalation, whereas in the SIBs counterpart, the anode formula is  $\text{NaC}_{70}$  [9]. Thus there has been much effort devoted to fabricating appropriate SIBs anodes in other fields as disordered graphitic carbons also known as hard carbons [10]. Many of the proposed solutions, have used inexpensive, non-toxic, and easily attainable, hard carbon materials, such as hierarchically porous carbon [10], carbon microspheres [11], carbon black [12], carbon nanostructures [13,14], graphene nanocomposites [15] and nitrogen doped carbons [16,17]. After these effects, there are still many unexplored aspects of hard carbons.

Nanotechnology has equipped scientists' with increasing viable methods modifying the structure and properties of electrode materials [18–22]. In particular, one dimensional carbon nanofibers have shown promise for improving SIBs capacities and cyclic characteristics due to their good conductivities, short ion diffusion distances and excellent stress tolerances [13,14]. The fabrication of flexible freestanding electrodes from carbon nanofibers where all materials are involved in charge storage is being investigated in order to further enhance the power densities of SIBs [23]. This drastically simplifies the preparation process by eliminating inert current collectors and binders which enhances electrochemical performances. There have been extensive investigations on LIBs nanomaterial electrodes [23–28], but little research has been done on SIBs [29].

Due to their low costs and environmentally friendly features, biomass materials, such as sucrose [30,31], peanut shells [32], rice husks [33], green tea [34] and coconut shells [35] have been studied as anode materials. As the major biomass components of soil, humic substances are high molecular weight organics with various structures, and can be categorized into three types based on their acid/base solubilities: humin, humic acids (HAs), and fulvic acids (FAs) [36].

FAs are abundant natural organic substance which is important in ecological systems. During past decades, FAs have been extensively studied due to their biological characteristics [36]. As the final decomposition product of lignin after black humic acids and humic acids [36], they are often used to evaluate natural organic matters [37–39]. Methods of preparing FAs are well established [37]. The precise chemical formula of FAs is still unknown but FAs are believed to be a complicated hybrid of organic species and polymers with high molecular weights from 1000 to 10000 g/mol, and can be depicted as a series of phenol rings connected by alkyl chains with carbohydrate, residues of fat and protein including different ionic groups like non-ionic polar alcohol or carboxylic acids, ketone, aldehyde.

HAs have been used in high-rate performance electrodes in supercapacitors [40], but little attention has been given to FAs as a potential electrode material for sodium-ion batteries. In this study, mechanically flexible fulvic acid-based electrospun hard carbon nanofibers (PF-CNFs) were fabricated by electrospinning and thermal annealing. The PF-CNFs were then directly applied as electrodes in SIBs and their electrochemical performances were investigated. The influence of the treatment temperature on the structure of the PF-CNFs is explained by analyzing the sodium insertion mechanisms in the PF-CNFs.

## 2. Experimental

### 2.1. Preparation of PF-CNFs electrodes

First the salts and ash in the fulvic acid (Beijing Zimingyuan Co., Ltd) were removed by alkali dissolution and acid precipitation

[40] to give refined fulvic acid (RF). Next the RF was blended with polyacrylonitrile (PAN, Aldrich Co., Mw = 80000). The RF (30% of the weight of the PAN) was added to a 12 wt % PAN solution in *N,N*-Dimethylformamide and the mixture was stirred at 50 °C for 12 h. Finally, fibers were prepared from this solution by electrospinning. The polymer solution was transferred to a syringe pump (10-mL syringe). Voltages of –5.00 and + 20 kV were applied to the plate and needle, respectively. The distance between the plate and needle was 20 cm. The flow rate during the process was 1 mL h<sup>-1</sup>. This process is shown in Fig. 1a.

The prepared fibers were then placed in a vacuum drying oven at 60 °C for 12 h. After that they were stabilization in air (500 cm<sup>3</sup>/min) for 1 h at 280 °C and then carbonization in a tube furnace at 800, 1000, 1300 or 1500 °C for 0.5 h under N<sub>2</sub> (300 cm<sup>3</sup>/min). These samples are denoted as PF-800, PF-1000, PF-1300 and PF-1500, respectively. PAN fibers from 12 wt % PAN solution in *N,N*-Dimethylformamide without fulvic acids was also fabricated and denoted as PAN-1300 for comparison.

### 2.2. Material characterization

Elemental analysis was conducted on Galbraith Laboratories, including combustion of C, H, N, and S. FTIR spectroscopy was processed from 600 to 4000 cm<sup>-1</sup> with a Nicolet Magna-IR 560 FTIR spectrometer. Scanning electron microscopy (SEM) was conducted with a Nano 430 spectrometer. A Philips Tecna G2 F20 spectrometer was utilized for high resolution transmission electron microscopy (HRTEM) measurements. X-ray diffraction (XRD) (Rigaku D/Max 2500) was performed at 40 kV and 90 mA with Cu K $\alpha$  radiation ( $\lambda = 0.154056$  nm) from 5° to 90° at the rate of 5°/min. The inter-layer distance  $d_{002}$ , the a-axis length ( $L_a$ ), and the crystallite size of the c-axis length ( $L_c$ ) were obtained using Bragg and Scherrer equations [41]. Raman spectra were performed with a Renishaw MKI-2000 Raman microscope with an Ar ion laser as the excitation source. The sample surface was characterized by X-ray photoelectron spectroscopy (XPS) by a PHI-1600ESCA equipment (America PE Company) with Al K (1486.6 eV) radiation. N<sub>2</sub> adsorption measurements were done on a TriStar 3000, GA instrument at 77 K and the surface areas of the samples were calculated using the Brunauer Emmette Teller (BET) equation.

### 2.3. Electrochemical characterizations

The carbonized fibers were cut into electrodes and then directly assembled into SIBs. No metal current collectors or additives were used. Before preparing the cells, the electrodes were kept in a vacuum drying oven for 12 h at 120 °C. The loading weights were ~2 mg/cm<sup>2</sup>.

The SIBs were assembled with a sodium plate as the counter electrode and 1.0 M NaClO<sub>4</sub> in a 1:1 volume of ethylene carbonate and dimethyl carbonate was used as the electrolyte. Cyclic voltammetry measurement were made between 0 and 2.7 V at a scan rate of 0.1 mV s<sup>-1</sup>. Electrochemical impedance spectroscopy (EIS) measurements were conducted from 100 kHz to 0.01 Hz. Both the EIS and CV measurement were performed on an electrochemical workstation (Chenhua Company, China). The above electrochemical measurements were conducted at around 25 °C.

## 3. Results and discussion

Fig. 1b shows an approximate chemical structure of fulvic acids. FAs contains many highly reactive oxygen groups, such as carboxyls, alcohols and phenolic hydroxyls groups. The presence of these groups was confirmed using FTIR and the results are shown in Fig. 1c. The bands in the FTIR spectrum can be assigned as follows:

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