



Effect of surface modification on high-surface-area carbon nanosheets anode in sodium ion battery



Huanlei Wang, Wenhua Yu, Nan Mao, Jing Shi*, Wei Liu*

Institute of Materials Science and Engineering, Ocean University of China, Qingdao 266100, China

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ABSTRACT

This paper reports a case study of the effect of nitrogen and oxygen functional groups of high-surface-area carbon nanosheets anode on electrochemical performance in sodium ion batteries. Hemp bast fiber is chosen to fabricate high-surface-area carbon nanosheets ($2190 \text{ m}^2 \text{ g}^{-1}$). After being treated with urea under hydrothermal condition, the as-prepared carbon nanosheets are functionalized with nitrogen- and oxygen-containing groups on the surface. Both the as-obtained and functionalized carbon nanosheets are used as anodes for sodium ion batteries, and the effect of nitrogen and oxygen functional groups on the electrochemical performance is investigated. The results indicate that the surface area of functionalized carbon nanosheets is significantly reduced to $840 \text{ m}^2 \text{ g}^{-1}$. However, both the carbon nanosheets display similar high capacity, rate capability and good cyclability. The electrodes deliver a capacity of $162/173 \text{ mAh g}^{-1}$ at 1 A g^{-1} after 2000 cycles and retain a capacity of $49/62 \text{ mAh g}^{-1}$ at 10 A g^{-1} . Besides the ultrahigh surface area and dilated graphitic layer of porous carbon nanosheets, chemisorption through functional groups are also found to be responsible for the high capacity. Moreover, the functionalized carbon nanosheets exhibit elevated Coulombic efficiency. These results confirm that modifying the surface of carbons is a promising strategy to improve the electrochemical performance.

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1. Introduction

In the field of electric energy storage, lithium ion batteries have been successfully utilized as a power source in portable devices and hybrid electric vehicles for several decades [1,2]. Concerning the cost and limitation of lithium terrestrial reserves [3], it is necessary to explore low-cost new rechargeable battery systems to meet the growing demands for energy storage. Owing to the wide availability and low cost of sodium, sodium ion batteries turn to be the promising candidate for the large-scale energy storage systems. It is worth to note that sodium ions are approximately 55% larger in radius than lithium ions, which can lead to the difficult insertion/extraction of sodium ions into graphitic layers [4,5]. Until now, compared to lithium ion batteries, sodium ion batteries still shows the disadvantages associated with low energy density and poor cycle life. However, recent study demonstrates that certain sodium ion battery electrode materials are approaching the efficiencies of lithium ion battery electrodes [6]. Thus, developing high-

performance electrode materials with high capacity and long-term stability is essential for further development of sodium ion batteries.

Carbonaceous material is a dominant candidate as electrode material for electric energy storage devices [7–10]. The commercial graphite anode for lithium ion batteries is not suitable for sodium ion batteries [11], which is ascribed to the difficult insertion of sodium ions into graphitic layers. An efficient strategy to facilitate the sodium insertion and extraction is to expand the graphitic interlayer spacing [12], which helps to improve the electrochemical performance of the carbon electrodes. Alternative carbon anodes, including disordered carbon [13,14], partially graphitic carbon [15–17], graphene [18,19], and graphene hybrids [20,21], all show improved electrochemical performance for sodium ion batteries. These materials with dilated graphitic layer either possess high surface area with abundant micro- and mesoporosity, or have “openness” sheet-like morphologies, which allows for fast solid-state diffusion kinetics.

Another popular approach to improve the electrochemical performance of carbon anode for sodium ion batteries is to introduce heteroatoms in carbon structure [22]. The heteroatom doping can

* Corresponding authors. Tel.: +86 532 66781906.

E-mail addresses: shijing@ouc.edu.cn (J. Shi), weiliu@ouc.edu.cn (W. Liu).

create a significant amount of defects, which may serve as additional active sites for sodium storage. Recent reported nitrogen doped carbons, including hollow carbon nanowires [12], porous nitrogen doped nanosheets [9], N-doped carbon nanofiber [23], nitrogen-doped carbon nanotubes [24], nitrogen-doped ordered mesoporous carbon [25] and nitrogen doped graphene foams [18], exhibited promising electrochemical properties. Besides, the oxygen-containing groups can also be functionalized for providing high electrochemical performance, which is related with the surface redox reaction between carbon-oxygen functional groups and alkali metal ions [26,27]. This strategy is firstly utilized in lithium ion batteries, and can also be employed to develop high-performance sodium ion batteries.

In this paper, we aim to study the synergistic effect of nitrogen- and oxygen-containing surface functional groups of high-surface-area carbon nanosheets anode on its performance in sodium ion battery. The carbon nanosheets were derived from the biomass-hemp bast fiber [28], and biomass derived carbons receive extensive attention due to the low-cost character [29–33]. Hydrothermal treatment with urea resulted in an incorporation of a significant amount of nitrogen and oxygen in the surface of carbon nanosheets. This mild hydrothermal treatment was different from the conventional high temperature hydrolysis process performed in excess of 600 °C, and it was unique in introducing sufficient nitrogen and oxygen functional groups but not destroying the macroscopic morphology of carbon nanosheets. The surface modification by functional groups can reduce the surface area and improve the Coulombic efficiency without sacrificing the excellent electrochemical performance, suggesting the functional groups play a positive effect on enhancing the electrochemical property. The post-treatment method provides us a promising way to achieve high-performance carbon anode for sodium ion batteries.

2. Experimental

2.1. Synthesis of high-surface-area carbon nanosheets

The carbon nanosheets (denoted as CNS) were prepared according to previously reported procedure [28,34]. An aqueous dispersion (60 g L⁻¹) of hemp bast fiber was placed in a stainless steel autoclave. The autoclave was heated up to 180 °C and maintained at the target temperature for 12 h. The resultant solid, denoted as hydrochar, was recovered by filtration, washed with distilled water and dried at 100 °C. The hydrochar material was thoroughly mixed with KOH at a weight ratio of 1:1 in an agate mortar. Then, the mixture was heated to 850 °C under argon atmosphere (5 °C min⁻¹), and followed by a “heat soak” time of 30 min at this temperature. The resulting carbon nanosheets were then thoroughly washed with 10 wt% HCl and distilled water. Finally, the carbons were dried in an oven at 100 °C.

2.2. Synthesis of N,O-codoped carbon nanosheets

Before the treatment with urea, the pretreatment of carbon nanosheets with nitric acid is to enhance the dispersivity of carbon nanosheets in aqueous solution. The carbon nanosheets were firstly refluxed in 50 wt% nitric acid at 60 °C for 4 h. Nitric acid treated carbon nanosheets and urea (the mass ratio of urea and carbon nanosheets is 300:1) were added to 30 mL of distilled water. After stirring for 1 h, the solution was sealed in the autoclave and maintained at 180 °C for 15 h. After that, the N,O-codoped carbon nanosheets were washed thoroughly with distilled water to remove the residual inorganic species and dried at 100 °C. The obtained sample was labeled as CNS-U, where U represents the urea treatment.

2.3. Material characterization

Powder X-ray diffraction (XRD) pattern was performed on a Bruker D8 Advance X-ray diffractometer using K α radiation. The chemical composition of the carbon samples was determined by X-ray photoelectron spectroscopy (XPS, Kratos Analytical) equipped with a monochromatic Al-K α radiation. Nitrogen adsorption and desorption isothermal at 77 K was conducted with an Autosorb-1 (Quantachrome) surface area-pore size analyzer. The morphologies and structures of carbons were examined using transmission electron microscopy (TEM, JEOL JEM-2100). Raman spectra were collected with a 532 nm laser under ambient conditions with a confocal micro-Raman system (LabRAM HR800) at room temperature.

2.4. Electrochemical measurements

Electrochemical evaluations were performed using CR2032-type coin cells assembled in an argon-filled glove box with sodium metal as the counter electrode. As prepared sample, super P and poly(vinyl difluoride) dissolved in *N*-methyl-pyrrolidone were mixed at a weight ratio of 80:10:10 to form a slurry, which was then spread on the stain steel spacer and dried at 120 °C under vacuum to obtain working electrodes. The working electrode and counter electrode were separated by a polyethylene separator. An electrolyte consisting of a solution of 1 M NaClO₄ in a 1:1 volume ratio of ethylene carbonate and diethyl carbonate was used. Cyclic voltammetry (CV) experiments were carried out using a CHI 660 workstation at a scan rate of 0.1 mV s⁻¹. The discharge-charge measurements were conducted in the voltage range of 0.01–3 V using a Land CT2001A battery test system.

3. Results and discussion

The chemical bonding state of all types of surface groups was characterized by using XPS analysis. From the XPS survey (Fig. S1), it can be concluded that the surface of CNS and CNS-U mainly contains oxygen (B.E. ~530 eV) and nitrogen (B.E. ~400 eV) besides carbon (B.E. ~285 eV) with no other heteroatoms being observable. The total nitrogen and oxygen contents reached up to 4.18 at% and 15.06 at% for CNS-U, as shown in Table 1. The high-resolution O1s and N1s XPS spectra of CNS and CNS-U are shown in Fig. 1. For oxygen, there are generally three types of oxygen functionalities: C=O quinone groups (O-I, ~531 eV), C–OH phenol groups and/or C–O–C ether groups (O-II, ~532 eV), and COOH carboxylic groups (O-III, ~535 eV) [35,36]. In CNS, the O 1s spectrum reveals the presence of two main peaks (Fig. 1a), which can be assigned to O-I (2.22 at%) and O-II (4.48 at%) functionalities. However, for CNS-U (Fig. 1b), the contents of O-I (4.51 at%) and O-II (5.40 at%) groups are significantly increased, whereas the hydrothermal process also introduces the O-III group (5.15 at%) into the carbon surface. It is generally accepted that these oxygen-containing functional groups can result in the surface redox reaction between carbon-oxygen functional groups and sodium ions, especially through –C=O/–C–O–Na redox pair [16]. Besides, more nitrogen-containing functional groups can be observed on the surface after urea treatment (Fig. 1c and d), and it appears that urea treatment favors the formation of pyridinic nitrogen (N-6, ~398.4 eV, 1.03 at%), whereas the content of pyrrolic/pyridine nitrogen (N-5, ~400 eV, 3.15 at%) is significantly increased. It can be assumed that nitrogen doping can induce a large number of defects and add sodium insertion sites, thus enhancing the sodium storage capacity.

The functional groups on the surface of carbon nanosheets, although important, can enhance the wettability of electrolyte if the surface is accessible for the electrolyte ions. This accessibility is

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