Materials Research Bulletin 83 (2016) 590–596

Contents lists available at ScienceDirect

Materials Research Bulletin

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

Facile synthesis of three-dimensional porous carbon sheets from a water-soluble biomass source sodium alginate for lithium ion batteries

Zhongyi Wang, Feng Zhang*, Yonggang Lu, Bin Zhai, Shangru Zhai, Zuoyi Xiao, Qingda An*, Changshun Yu, Shiping Gao

School of Light Industry and Chemical Engineering, Dalian Polytechnic University, #1 Qinggongyuan, Dalian 116034, PR China

ARTICLE INFO

Article history:
Received 28 March 2016
Received in revised form 29 June 2016
Accepted 10 July 2016
Available online 11 July 2016

Keywords:
A. Nanostructures
A. Thin films
C. Transmission electron microscopy
D. Electrochemical properties
D. Energy storage

ABSTRACT

Three-dimensional porous carbon sheets are successfully prepared from a readily available water-soluble biomasses sodium alginate via a simple method without using chemically activated agents. By adjusting the thickness of wet films, we can produce carbon samples and target the surface area and pore volume. The results show that the porous carbon sheets possess superior electrochemical performance when they are used as anode materials for lithium-ion batteries. The porous nanostructure could provide the pathways for easy accessibility of electrolyte and fast transportation of lithium ions and electrons. The existence of micropores can also ensure high reversible capacity.

1. Introduction

Lithium-ion batteries (LIBs), which possess high energy and high power densities, are attracting increased attention because of the increasing demand to power electric vehicles and portable electronic devices [1–3]. Graphite is currently the most popular anode material for LIBs. However, the lithium-storage capacity (theoretical value = 372 mAh g^{-1}) of graphite is not high enough to meet the demands of electric devices.

Many studies have indicated that materials with nanostructures could significantly improve their electrochemical performance [4–7]. Thus, nanostructured carbon materials have been extensively studied to increase lithium-storage capacity. So far, a series of nanostructured carbon materials have been studied as anode materials for LIBs, such as carbon nanotube, carbon fibers, and so on [8–14]. Graphene is attracting considerable attention since its discovery in 2004 by Geim et al. [15] because of its novel, fascinating physicochemical properties, such as superior electron mobility, flexibility, and high surface area. Graphene, which has a theoretical capacity of approximately 764 mAh g^{-1} (significantly larger than that of graphite), is also a good candidate material for energy storage and conversion [16–18]. Although these carbon-based materials possess relatively superior electrochemical performance, some drawbacks such as complex synthesis processes, high cost, low yields, and environment pollution still limit their practical use. Several studies focusing on nanostructured anode materials indicate that the existence of hierarchical porous nanostructures exert significant effects on their electrochemical performance [4,12,13,19]. The micropores and/or mesopores provide an easily accessible pore system that facilitates electrolyte transportation and lithium-ion diffusion, and the micropores could ensure high reversible capacity. To date, a series of porous carbons have been successfully prepared through templating methods using mesoporous silica, zeolites, and closely packed poly(methyl methacrylate) spheres as hard templates, and/or amphiphilic copolymer surfactants as soft templates [20–26]. However, such templating approaches usually involved tedious and costly preparation procedures, which limit their practical applications. As a renewable source, biomasses have been recently paid much attention for their promising applications in the preparation of porous carbons, such as wood, coconut, cornstalk, rice straw, and so on [27–33]. The surface area of the porous carbon could be controlled by varying the amount of activated agents. However, most biomasses are water-insoluble and the preparation processes for porous carbons usually need chemically activated agents, including KOH, NaOH, H_3PO_4, and so on [29–36]. Subsequently, it is still a great challenge to obtain the porous carbon materials by using a water-insoluble biomass source as raw materials via a simple approach without using chemically activated agents.

---

* Corresponding authors.
E-mail addresses: zhang_feng@dlpu.edu.cn (F. Zhang), anqingda@dlpu.edu.cn (Q. An).

http://dx.doi.org/10.1016/j.materresbull.2016.07.009
0025-5408/

Herein, we report a simple, cheap, and high-yield strategy for the preparation of three-dimensional porous carbon sheets with a controlled surface area and microporous volume from sodium alginate, which is one of the most popular and readily available water-soluble biomasses. The carbon materials obtained in the present study exhibit a porous nanostructure that provides the pathways to ensure easy accessibility of electrolytes and fast transportation of lithium ions. These three-dimensional porous carbon sheets were tested as anode materials for high-rate and high-capacity LIBs.

2. Experimental section

2.1. Synthesis of three-dimensional porous carbon sheets

All chemicals were used as received. A four-step method was used in the preparation of three-dimensional porous carbon nanosheets as shown in Scheme 1. At first, 5 g of sodium alginate was dissolved in 160 mL of deionized water to form a thick solution. The solution was spread onto a self-made mould with controlled thickness from 50 to 500 μm to form a wet film. Then, the wet film with the mould was dried at 80 °C in air to form a thin film. Afterward, the thin films were separated by using a knife and carbonized at 750 °C in the presence of N_2 for 4 h to obtain the porous carbon materials. The obtained carbon materials were further treated with dilute HCl solution with a concentration of around 1.0 M at 100 °C for 4 h under hydrothermal treatment. Finally, the carbon materials were washed with distilled water until the pH value of the system reached about 7.0, and dried at 80 °C. The products were denoted as C-*n*-T, where n and T are the thickness of wet film and carbonization temperature.

2.2. Characterization

The powder X-ray diffraction (XRD) patterns were performed on a Rigaku XRD spectrometer with Cu Kα radiation (λ = 0.15418 nm). Raman spectra were measured using a Leica Micros-ystems Raman spectrometer with a laser of 532 nm. The transmission electron microscopy (TEM) was carried out on a JEOL 2100 electron microscope at 200 kV, whereas the scanning electron microscopy (SEM) was performed on a JEOL 6610 scanning electron microscope operating at 10.0 kV. The N_2 adsorption/desorption isotherms were recorded at 77 K with a JW-BK222 surface area and pore size distribution analyzer. Prior to analysis the samples were degassed at 150 °C under vacuum for 2 h. The surface area data was calculated on the basis of the Brunauer–Emmett–Teller (BET) model whereas the pore size distribution (PSD) was obtained through the Barrett–Joyner–Halenda (BJH) method. Fourier-transform infrared spectra (IR) were performed on a Perkin–Elmer.

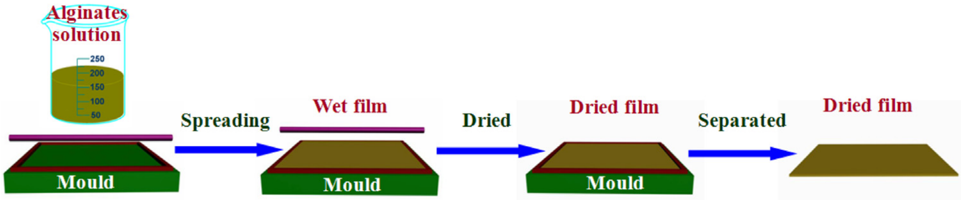
2.3. Electrochemical test

The working electrode was prepared by mixing the carbon materials (80 wt%), acetylene black (10 wt%), and polyvinylidene fluoride (10 wt% PVDF) in N-methylpyrrolidone (NMP) to form a homogenous slurry. The obtained slurry was then spread onto a copper foil and dried at 100 °C for 24 h in a vacuum oven. 1 M $LiPF_6$ in a mixture of ethylene carbonate (EC), dimethyl carbonate (DMC) and ethyl methyl carbonate (EMC) (1:1:1 by weight) was used as the electrolyte. The assembly of the test cells was carried out in an argon-filled glove box. The batteries were charged and discharged at the various rates (1C = 372 mAh g^{-1}) in the voltage range of 0.01–3.0 V on a LAND CT2001A cell test apparatus.

3. Results and discussion

To investigate the morphology and texture of the obtained carbon materials, C-200-750 derived from a wet film with a thickness of 200 μm is characterized by SEM and TEM images. The SEM image shown in Fig. 1A and B reveals that the products are mainly composed of numerous large 3.5 μm-thick carbon sheets. Furthermore, the large sheets contain a loose structure and consist of a number of curved carbon nanosheets less than 50 nm. These curved nanosheets are cross-linked with one another and are assembled in an irregular manner, leaving plenty of large porous channels with a diameter of approximately 1 μm between the carbon nanosheets. The texture of the as-synthesized products was further investigated by TEM. As shown in Fig. 1C and D, the carbon material contains thin nanosheets. A considerable amount of larger mesopores with the diameter of approximately 20 nm and smaller mesopores of 3–5 nm in diameter are observed in the carbon nanosheets. Some micropores smaller than 2 nm also exist in C-200-750. Based on the SEM and TEM observations, the obtained carbon materials are considered to be porous nanostructures. To study the crystallinity of the carbon materials, the XRD pattern of the final samples is also performed (Fig. 2A). A broad peak at around $2\theta = 23.0°$, as previously reported for several non-graphitized carbon materials, exists in the pattern, indicating that the as-synthesized materials is mainly composed of single graphene sheets and that both flat and curved graphene sheets may exist. In other words, the carbon material obtained in the present study is essentially low in graphitization degree. Nearly no ordered stacking of graphene sheets is present in the structure, although the material has been synthesized at a temperature as high as 750 °C.

To further study the porous feature of the carbon materials, the N_2 adsorption/desorption isotherm with corresponding pore size distribution for C-200-750, as illustrated in Fig. 2B, is carried out. The adsorption isotherms with an obvious hysteresis loop are seen to belong to type IV curves according to the classification from the International Union of Pure and Applied Chemistry [37], implying the existence of mesopores in the obtained materials. Furthermore, C-200-750 shows a very significant degree of N_2 adsorption at 77 K, especially at a low relative pressure, which is related to the presence of micropores. Fig. 2B also gives the pore size distribution curves for the carbon materials. the majority of the mesopores in the carbon materials are approximately 3.5 nm in diameter, which is consistent with the pore sizes observed via TEM analysis.



Scheme 1. Schematic illustration for the preparation of dried films.