



Sulfur-enriched, hierarchically nanoporous carbonaceous materials for sodium-ion storage



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ABSTRACT

Na-ion batteries (NIBs) have had much attention as post Li-ion batteries (LIBs) due to abundant Na resources and a similar chemistry to LIBs; however NIBs have suffered from a lack of proper anode materials. In this study, sulfur-enriched, hierarchically nanoporous carbonaceous materials (SH-NCMs) were fabricated by an inclusion complex of cellulose hosted by urea hydrate through simple pyrolysis and heating with elemental sulfur. SH-NCMs had unique materials characteristics, such as a large amount of heteroatoms, containing 21.7 at.% sulfur, 12.6 at.% oxygen and 5.7 at.% nitrogen, and a 3D-interconnected mesostructure with a high surface area of $201 \text{ m}^2 \text{ g}^{-1}$. Interestingly, SH-NCMs showed a high specific capacity of 456 mAh g^{-1} at a current density of 1 A g^{-1} , and even after 50 cycles at 10 A g^{-1} , a specific capacity of 170 mAh g^{-1} was achieved. In addition, stability over more than 500 repetitive cycles with nearly 100% Coulombic efficiency was maintained.

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1. Introduction

Li-ion batteries (LIBs) are one of the most reliable energy storage systems [1,2]. However, Li resources are insufficient and their reserves are located in remote or politically sensitive areas [3,4]. As an alternative to LIBs, a feasible post-LIB are Na-ion batteries (NIBs), due to abundant supplies and widespread terrestrial reserves of Na resources as well as a similar chemistry to LIBs [3,4]. In the chemistry of NIBs, the primary hurdle of a proper anode material for Na-ion storage is absent because Na-ions cannot be intercalated in graphite, one of the best anode materials which led to the commercial success of LIBs [5]. Therefore, various alternative anode materials have been studied for NIBs, such as hard carbons, [6,7] metal oxides, [8,9] phosphides [10] and phosphorous [11,12]. However, these anode materials have limitations in terms of poor rate performance, cyclic stability, high-cost and/or complex synthetic processes. In contrast, nanostructured carbonaceous materials (NCMs) have shown great rate performances and cyclic stabilities by pseudocapacitive Na-ion storage behavior [13–19]. Tang et al. reported hollow carbon nanospheres with superior rate capabilities in which a specific capacity of approximately 50 mAh g^{-1} was achieved at a current rate of 10 A g^{-1} [13]. Wang et al. showed that carbon nanofibers

have a reversible capacity of 73 mAh g^{-1} at a current density of 20 A g^{-1} and good cyclic stabilities over 200 cycles [14]. Additionally, various types of carbon nanofibers [15,16], and carbon nanosheets [17,18] have been designed as anode materials for NIBs. The Na-ion storage performance on NCMs is highly dependent on their nanostructure and surface properties because the pseudocapacitive charge storage primarily happens on the surface and/or near the surface of the electrode materials. Therefore, a more advanced design, such as numerous redox active heteroatoms, could result in a dramatic enhancement of the electrochemical performances for sodium-ion storage.

In this study, hierarchically nanoporous carbonaceous materials containing numerous sulfur atoms (SH-NCMs) were fabricated from an inclusion complex (IC) of cellulose hosted by urea hydrate using pyrolysis and heating with elemental sulfur. The SH-NCMs exhibited unique material properties, leading to notable electrochemical performances as an electrode material for Na-ion storage. This study provides effects of sulfur atoms on nanostructured carbonaceous electrodes for Na-ion storage.

2. Methods

2.1. Preparation of SH-NCMs

Hierarchically nanoporous carbonaceous materials (H-NCMs) were prepared using a previously reported procedure [20,21]. A mixture of a 7 wt.% NaOH/12 wt.% urea/81 wt.% water solution pre-

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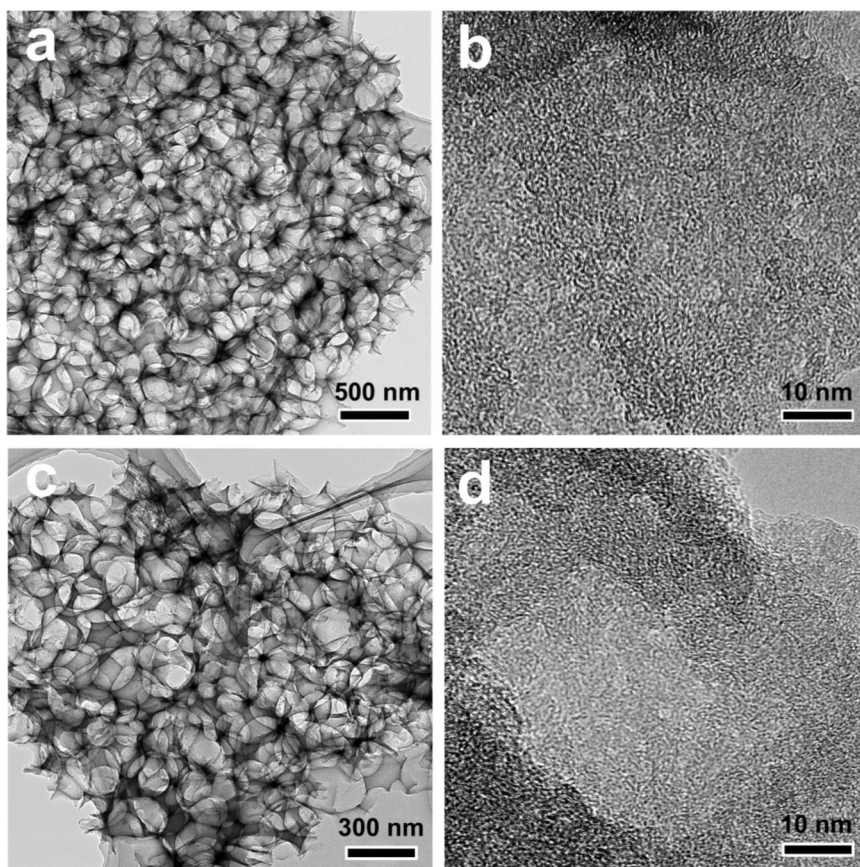


Fig. 1. FE-TEM images of (a), (b) SH-NCMs and (c), (d) H-NCMs.

cooled to -12°C for 2 h was prepared, and 5 wt.% cotton cellulose (Aldrich) was immersed in the mixture solution, which was then intensely stirred for approximately 5 min at ambient temperature (IC solution). The IC solutions were then frozen at -196°C and then freeze-dried for three days. The IC cryogel was carbonized starting at room temperature to 600°C for 1 h. A heating rate of $10^{\circ}\text{C min}^{-1}$ and an Ar flow of 200 mL min^{-1} were applied. After the cryogel was carbonized, it was washed using distilled water and ethanol and then dried in a vacuum oven at 30°C for 24 h. Next, the product materials (H-NCMs) were heated with elemental sulfur at a weight ratio of 1:1 starting at room temperature to 600°C for 1 h. A heating rate of $10^{\circ}\text{C min}^{-1}$ and an Ar flow of 200 mL min^{-1} were applied. After the heat treatment, the resulting products (SH-NCMs) were washed using distilled water and ethanol, and then stored in a vacuum oven at 30°C .

2.2. Characterization

The morphologies of the samples were observed by field emission transmission electron microscopy (FE-TEM; JEM2100F, JEOL, Japan). XRD (Rigaku DMAX 2500) analysis was performed using Cu K α radiation (wavelength $\lambda = 0.154\text{ nm}$) operated at 40 kV and 100 mA. The porous properties of the samples were characterized using nitrogen adsorption and desorption isotherms, which were obtained using a surface area and porosimetry analyzer (ASAP 2020, Micromeritics, USA) at -196°C . X-ray photoelectron spectroscopic analysis (XPS, PHI 5700 ESCA) was performed using monochromated Al K α radiation ($h\nu = 1486.6\text{ eV}$). A four-probe method with an electrical conductivity meter

(Loresta GP, Mitsubishi Chemical, Japan) was used to measure the electrical conductivity of the samples.

2.3. Electrochemical characterization

The electrochemical properties of the SH-NCMs were characterized using a Wonatec automatic battery cycler and CR2032-type coin cells. The coin cells were assembled in a glove box filled with argon using SH-NCMs as the working electrode and metallic Na

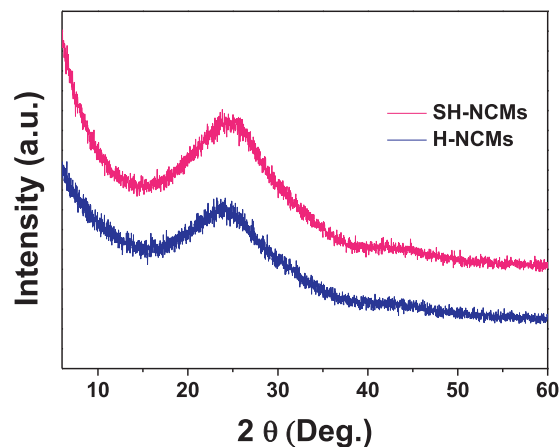


Fig. 2. XRD patterns of SH-NCMs and H-NCMs.

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