



# Rod-like Ordered Mesoporous Carbons with Various Lengths as Anode Materials for Sodium Ion Battery



Lvqiang Yu<sup>a</sup>, Huaihe Song<sup>a,\*</sup>, Yutong Li<sup>a</sup>, Yaxin Chen<sup>a</sup>, Xiaohong Chen<sup>a</sup>, Jisheng Zhou<sup>a</sup>, Zhaokun Ma<sup>a</sup>, Xingyun Wan<sup>b</sup>, Ping Tian<sup>b</sup>, Jiao Wu<sup>b</sup>

<sup>a</sup> State Key Laboratory of Chemical Resource Engineering, Beijing Key Laboratory of Electrochemical Process and Technology for Materials, Beijing University of Chemical Technology, Beijing, 100029, PR China

<sup>b</sup> Infinitus (China) Company Ltd., Guangzhou, PR China

## ARTICLE INFO

### Article history:

Received 30 July 2016

Received in revised form 21 September 2016

Accepted 25 September 2016

Available online 26 September 2016

### Keywords:

ordered mesoporous carbon  
length  
pore size  
anode  
sodium ion battery

## ABSTRACT

To investigate the pore structural effects on the electrochemical performance of ordered mesoporous carbons (OMCs) as anode materials for sodium ion battery (SIB), we prepared OMCs with various rod lengths from 350 nm to 1300 nm, and different pore sizes from 4.7 nm to 6.5 nm by changing the hydrochloric acid concentration in the P123/silica/glycerol composite system. The reversible capacities of OMCs with the average length of 350 nm, 700 nm, 900 nm and 1300 nm were 214 mA h g<sup>-1</sup>, 217.4 mA h g<sup>-1</sup>, 232.6 mA h g<sup>-1</sup>, and 228.9 mA h g<sup>-1</sup> at 50 mA g<sup>-1</sup>, respectively. Furthermore, the OMC with largest pore size (6.5 nm) presented the highest capacity and even remained 100 mA h g<sup>-1</sup> after 1000 cycles at 500 mA g<sup>-1</sup> with the coulombic efficiency of nearly 100%. We confirmed that the carbon with ordered mesostructure, bigger pore size and shorter length of pore channel exhibited higher capacity. The results propose an effective direction and strategy for designing mesoporous materials to enhance the electrochemical performance of SIB.

© 2016 Elsevier Ltd. All rights reserved.

## 1. Introduction

As one of the promising electrochemical energy storage devices, lithium ion batteries (LIBs) have been widely developed all over the world to meet the demands of portable electric devices and electric vehicles [1–3]. However, large scale application of LIBs has been restricted because of the limitation and high cost of lithium resources. As an alternative, sodium ion batteries (SIBs) have many advantages including natural abundance and low cost [4]. However, it is more difficult for sodium ion intercalation and deintercalation in the rigid lattice since the sodium ion is much larger and heavier than lithium ion [5]. Up to now, it still has a large challenge to design electrode materials to enhance the electrochemical performance of SIBs [6]. Various carbon materials, such as graphene and hard carbon, have been applied in the anode materials for SIBs. Wang et al. [7] synthesized reduced graphene oxide by modified Hummer's way, and found that this material presented a reversible capacity of 174 mA h g<sup>-1</sup> at 40 mA g<sup>-1</sup> and 93.3 mA h g<sup>-1</sup> at 200 mA g<sup>-1</sup>. Zhou et al. [8] reported that the highly disordered carbon (HDC) showed a reversible capacity of 225 mA

h g<sup>-1</sup> at 100 mA g<sup>-1</sup>. The mesoporous carbon with large pore size synthesized by Liu et al. [9] exhibited 125 mA h g<sup>-1</sup> at 100 mA g<sup>-1</sup>. Cao et al. [10] prepared mesoporous soft carbon from mesophase pitch, showing a reversible capacity of 331 mA h g<sup>-1</sup> at 30 mA g<sup>-1</sup>.

Ordered mesoporous carbons (OMCs), one of non-graphitic and mesoporous carbons as electrodes for SIB, have attracted much attention owing to its high electrical conductivity, large surface area and uniform mesoporous channels, which can facilitate the migration of electrolyte and diffusion of ion. As to the cathode, Jiang et al. [11] compared the Na<sub>3</sub>V<sub>2</sub>(PO<sub>4</sub>)<sub>3</sub>@ mesoporous carbon with the Na<sub>3</sub>V<sub>2</sub>(PO<sub>4</sub>)<sub>3</sub>@ordered mesoporous carbon in SIB, and found that the later showed better performance because of the uniform pore size and interconnected pore structure. To the best of our knowledge, a little report on OMC as anode materials for SIBs has been published. Kim et al. [12] reported that the Nb<sub>2</sub>O<sub>5</sub>/OMC electrode showed the reversible capacity of 175 mA h g<sup>-1</sup> at 50 mA g<sup>-1</sup>. Jo et al. [13] prepared ordered porous carbons with different pore sizes through evaporation induced self-assembly, and found that the initial irreversible capacity was more than 500 mA h g<sup>-1</sup> with a low first coulombic efficiency. Furthermore they confirmed that carbon electrode with medium size exhibited a higher reversible capacity of 134 mA h g<sup>-1</sup> at the current density of 25 mA g<sup>-1</sup>, and that the electrode performance of mesoporous

\* Corresponding author.

E-mail address: [songhh@mail.buct.edu.cn](mailto:songhh@mail.buct.edu.cn) (H. Song).

materials could be enhanced by increasing pore size and decreasing wall thickness.

Aimed at inspecting the effects of different structures of OMCs on the performance of OMCs electrodes for SIBs and improving the electrochemical performance of SIBs, herein, we synthesize OMCs (without using the SBA-15 [14] as a hard template) with various lengths from 350 nm to 1300 nm and different pore sizes from 4.7 nm to 6.5 nm by changing the concentration of hydrochloric acid in triblock copolymer/silica/glycerol system. Then we investigate the electrochemical performance of various structural carbons electrodes for SIBs to correlate the relationship between OMC rod lengths/pore sizes with the sodium-storage performance.

## 2. Experimental

### 2.1. Preparation of OMC materials

OMCs were synthesized by one-step carbonization from triblock copolymer/silica/glycerol [15,16], as shown in Fig. 1.

First of all, the micelle of triblock copolymer and glycerol was formed via a solvent self-assembly. Then, triblock copolymer/silica/glycerol composites were generated in the existence of inorganic precursor. In detail, OMC was synthesized by cross-linking, solidification, carbonization and etching processes. The steps are shown as following: 3.6 g triblock copolymer (EO<sub>20</sub>-PO<sub>70</sub>-EO<sub>20</sub>, P123,  $M = 5800 \text{ g mol}^{-1}$ ) was dissolved in 138 ml hydrochloric acid at 40 °C under stirring. After the P123 was dissolved completely, 2.9 mL glycerol and 8.3 ml tetraethyl orthosilicate (TEOS,  $M = 208.33 \text{ g mol}^{-1}$ ) were added into the solutions. The liquid was kept static for 24 h after stirring for 5 minutes. Then the solution was transferred into a teflon container and heat treated under 100 °C for another 24 h. In one way, 1 g products would be mixed with 1 ml sulfuric acid and 10 ml deionized water and then solidified at 160 °C for 6 h. The resulting powders were carbonized under N<sub>2</sub> atmosphere. At last 15 wt% hydrofluoric acid was used to remove the silica to obtain the last OMCs. In another way, we can obtain the silicas by calcining the composites at 550 °C for 2 h after the thermal treatment. Ordered mesoporous silicas and carbons were prepared by changing the concentration of hydrochloric acid, 2.5 mol L<sup>-1</sup>, 2.0 mol L<sup>-1</sup>, 1.5 mol L<sup>-1</sup> and 1.0 mol L<sup>-1</sup>. The obtained carbons and the silicas were remarked C1, C2, C3, C4 and Si1, Si2, Si3 and Si4 respectively.

### 2.2. Materials structure characterization

The OMCs and silicas were measured by X-ray diffraction (XRD) on a Rigaku D/max-2500B2+PCX system at 40 kV and 20 mA by Cu

K $\alpha$  radiation ( $\lambda = 1.5406 \text{ \AA}$ ). Scanning electron microscopy (SEM) was characterized through Zeiss Supra 55 electron microscope at 20 kV. Transmission electron microscopy (TEM) was conducted by a Hitachi H-800 at 200 kV. Nitrogen sorption experiments were performed with an ASAP 2020 Micromeritics Instrument at 77 K. The specific surface area was calculated from the adsorption data by the Brunauer-Emmett-Teller (BET) method. The pore size distribution was derived from desorption branch isotherms through the Barrett-Joyner-Halenda (BJH) method. Fourier transform infrared spectroscopy (FTIR) was measured by Nicolet IS50 infrared spectroscopy instrument. Raman was taken out on an Aramis system (Jobin Yvon) with 532 nm wave length incident laser light.

### 2.3. Electrochemical measurements

Electrochemical tests were conducted using CR2025 coin cells with Na foil as the counter electrode. The cells were assembled in an argon-filled glove box ( $\text{H}_2\text{O} < 1 \text{ ppm}$ ,  $\text{O}_2 < 1 \text{ ppm}$ ). The working electrodes were manufactured by casting a paste consisted of active materials, acetylene black and carboxyl methyl cellulose at the weight ratio of 8:1:1. Distilled water was used as the solvent to make a slurry paste. The electrolyte was 1.0 M NaSO<sub>3</sub>CF<sub>3</sub> in diglyme. The prepared electrodes were dried at 80 °C for 4 h and 120 °C for overnight in a vacuum. The galvanostatic charge/discharge capacitance of each electrode with about 2 mg active material was measured using a Program Testing System (Wuhan LAND Co. Ltd., China). The discharge and charge voltage was ranged from 0.01 to 2.5 V. The cyclic voltammetry (CV) and the electrochemical impedance spectral measurements were carried out on a Zahner-Zennium (Germany) electrochemical working station.

## 3. Results and discussions

The structures of as-prepared silicas and carbons were determined by XRD and Raman tests. As shown in Fig. 2(a), all of the silicas present three peaks implying the highly ordered structures. The peaks appeared in the XRD pattern are indexed as (100), (110) and (200) lattices, which are characteristics of two-dimensional space group (p6mm) [17]. In Fig. 2(b), the ordered structures of C1, C2 and C3 are still reserved after carbonization. However, the ordered structures of carbons become weak with decrease of hydrochloric acid concentration from 2.5 mol L<sup>-1</sup> to 1.0 mol L<sup>-1</sup>, and the very small-angle diffraction peaks of C4 indicate the structure is destroyed in a certain extent after carbonization. The self-assembly behavior of P123 micelle, glycerol

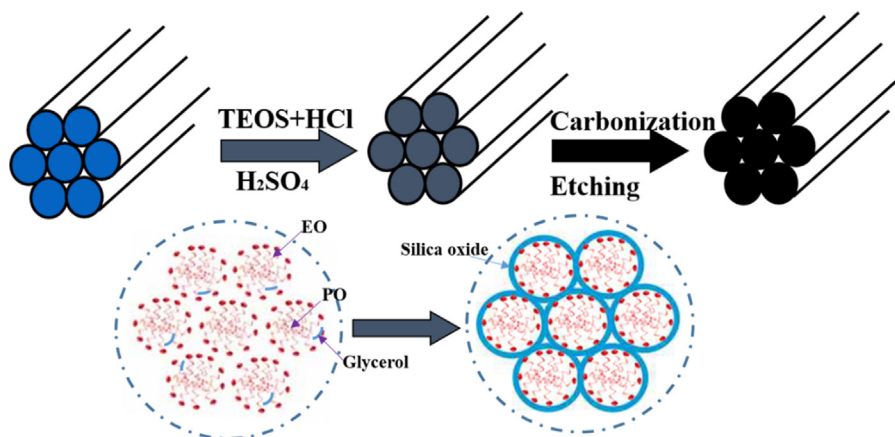


Fig. 1. Synthesis procedure of OMCs by carbonizing the triblock copolymer/silica/glycerol composite directly.

Download English Version:

<https://daneshyari.com/en/article/4767669>

Download Persian Version:

<https://daneshyari.com/article/4767669>

[Daneshyari.com](https://daneshyari.com)