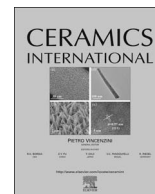




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# Porous carbon spheres as anode materials for sodium-ion batteries with high capacity and long cycling life

Hongmei Tang, Miao Wang, Ting Lu, Likun Pan\*

Shanghai Key Laboratory of Magnetic Resonance, School of Physics and Materials Science, East China Normal University, 3663 N. Zhongshan Rd., Shanghai 200062, China

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## ABSTRACT

Porous carbon spheres (PCSs) with high surface area were fabricated by the reaction of D-Glucose monohydrate precursor with sodium molybdate dihydrate ( $\text{Na}_2\text{MoO}_4 \cdot 2\text{H}_2\text{O}$ ) via a facile hydrothermal method followed by carbonization and aqueous ammonia solution ( $\text{NH}_3 \cdot \text{H}_2\text{O}$ ) treatment. The as-prepared PCSs exhibit a highly developed porous structure with a large specific surface area and show an excellent electrochemical performance as anode material of sodium-ion batteries (SIBs). A reversible capacity of  $249.9 \text{ mA h g}^{-1}$  after 50 cycles at a current density of  $50 \text{ mA g}^{-1}$  and a long cycling life at a high current density of  $500 \text{ mA g}^{-1}$  are achieved. The excellent cycling performance and high capacity make the PCSs a promising candidate for long cycling SIBs.

## 1. Introduction

Sodium-ion batteries (SIBs) have recently been considered as an alternative to lithium-ion batteries (LIBs) for the large-scale stationary energy storage applications due to the wide abundance of sodium resource and the similar chemistry between lithium and sodium [1–7]. Similar to their LIBs partner, the capacity of SIBs strongly depends upon the properties of electrode materials. Nevertheless, sodium ion is about 55% larger in radius than lithium ion [8–13], and it is more difficult to find a suitable host material to accommodate sodium ions that allows reversible and rapid ion insertion and extraction. Therefore, the electrode materials are regarded as the most important component in SIBs.

Carbonaceous materials are considered to be excellent anode materials for both LIBs and SIBs due to their relatively high capacity, chemical stability, nontoxicity, low cost and abundance [14–16]. Doeff et al. [17] first reported sodium-ion insertion into hard carbon derived from petroleum-coke, but only a reversible capacity of  $85 \text{ mA h g}^{-1}$  was deserved. Alcantara and co-workers [18] studied the behavior of SIBs using amorphous and non-porous carbon black as anode material that delivered a reversible capacity of about  $200 \text{ mA h g}^{-1}$ . Recently, many studies have been conducted to improve the electrochemical performance of carbon materials in SIBs by tuning the microstructure or introducing the heteroatoms. Tang et al. [19] demonstrated that hollow carbon nanospheres possessed excellent cycling stability, which displayed a high reversible capacity of  $223 \text{ mA h g}^{-1}$  at a current density of  $50 \text{ mA g}^{-1}$ . Soon later, Fu and co-workers [20] synthesized the nitro-

gen-doped carbon fibers by the pyrolysis of polypyrrole, and a reversible capacity of  $243 \text{ mA h g}^{-1}$  at a current density of  $50 \text{ mA g}^{-1}$  was achieved after 50 cycles due to the combination of fiber-like morphology and high content of pyridinic and quaternary N. Li et al. [21] reported that coating soft carbon on the surface of hard carbon spherules through the pyrolysis of toluene could improve the initial coulombic efficiency to a high value of 83%. These studies demonstrate that hard carbon is a promising anode material for SIBs.

As known, designing the porous structure is an efficient method to shorten the transport length of sodium ion, provide abundant active sites and space for chemical reactions, and buffer the volume change during the ion insertion and extraction [22–24]. Recently, many porous carbon materials have been synthesized through activating treatment or templating technique. Hong et al. [25] reported that the porous hard carbon materials fabricated through the pyrolysis of  $\text{H}_3\text{PO}_4$ -activated pomelo peel delivered a reversible capacity of  $181 \text{ mA h g}^{-1}$  after 220 cycles at a current density of  $200 \text{ mA g}^{-1}$ . Wang and co-workers [26] demonstrated that the nitrogen-doped porous carbon sheets via chemically activating treatment with KOH showed an enhanced cycling performance compared to their counterpart without KOH activating. Li et al. [27] prepared the porous carbon nanofibers through the soft template treatment with F127, which delivered a reversible capacity of  $\sim 140 \text{ mA h g}^{-1}$  after 1000 cycles at a current density of  $500 \text{ mA g}^{-1}$ . These studies demonstrate that porosity is an important factor on influencing the performance of carbon anode materials for SIBs. However, the above-mentioned synthetic strategies suffer from more or less-severe drawbacks, such

\* Corresponding author.

E-mail address: [lkpan@phy.ecnu.edu.cn](mailto:lkpan@phy.ecnu.edu.cn) (L. Pan).

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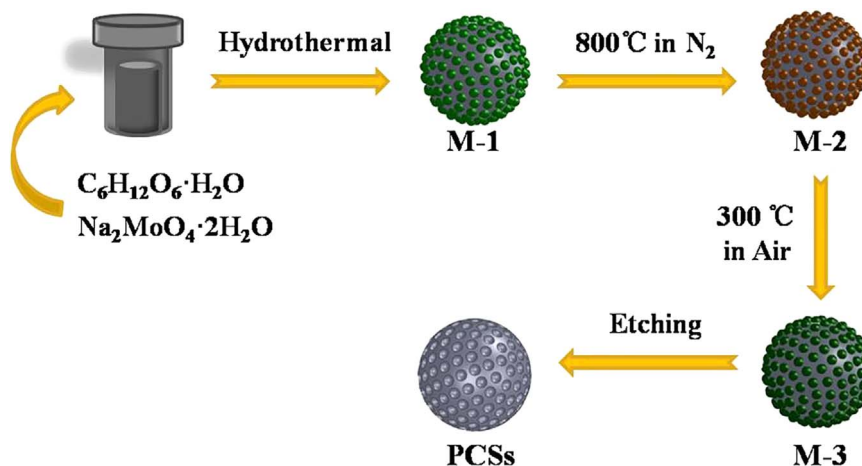


Fig. 1. Schematic illustration of the synthetic process of PCSs.

as the side reaction of heteroatom or the requirement of toxic reagent. Furthermore, further improvement of the performance of porous carbon anode materials is necessary for practical applications.

In this work, porous carbon spheres (PCSs) with large specific surface area and adjustable pore structure were synthesized through a facile hydrothermal treatment of D-Glucose monohydrate precursor via the reaction with  $\text{Na}_2\text{MoO}_4 \cdot 2\text{H}_2\text{O}$ . The as-prepared PCSs exhibit a high reversible capacity and excellent cycling stability as anode material for SIBs.

## 2. Experimental section

### 2.1. Synthesis of PCSs

All the chemicals were used as purchased without further purification. In a typical procedure, a certain amount of  $\text{Na}_2\text{MoO}_4 \cdot 2\text{H}_2\text{O}$  and 1.08g D-Glucose monohydrate were dissolved in 10 mL 0.5 M HCl solution and stirred for 1 h at room temperature. Afterwards, the solution was put into a Teflon-lined stainless steel autoclave and hydrothermally treated at 180 °C for 6 h. After cooled down naturally, the dark product precipitate was centrifuged, washed with deionized water and ethanol, dried at 60 °C for 12 h. The as-prepared intermediate product, named as M-1, was thermally treated at 800 °C for 4 h under a  $\text{N}_2$  atmosphere. The obtained product was named as M-2. After that, the as-collected product M-2 was oxidized at 300 °C for 3 h in air with a heating rate of 1 °C  $\text{min}^{-1}$ . The black powder was obtained and denoted as M-3. Finally, M-3 was immersed in aqueous ammonia solution and stirred to remove the oxides. The final product PCSs were obtained. When the amount of  $\text{Na}_2\text{MoO}_4 \cdot 2\text{H}_2\text{O}$  was 90, 120 and 150 mg, the obtained PCSs were labelled as PCS-90, PCS-120 and PCS-150, respectively. For comparison, the carbon sphere (denoted as CS) was prepared according to the similar procedure to PCSs without the addition of  $\text{Na}_2\text{MoO}_4 \cdot 2\text{H}_2\text{O}$ .

### 2.2. Material characterization

Field-emission scanning electron microscopy (FESEM) (Hitachi S-4800) was used to characterize the morphology of the samples and their structures were examined by Raman spectroscopy (Horiba Jobin Yvon T64000) with an excitation wavelength of 532 nm and X-ray diffraction (XRD, Holland PANalytical PRO PW3040/60) with Cu-K $\alpha$  radiation ( $V=30$  kV,  $I=25$  mA, and  $\lambda=1.5418$  Å). The interlayer spacing ( $d$ ) was calculated from Bragg's equation ( $d=\lambda/2\sin\theta$ ). Nitrogen adsorption-desorption isotherms were measured at 77 K with an ASAP 2020 Accelerated Surface Area and Porosimetry System (Micrometitics, Norcross, GA).

### 2.3. Electrochemical Measurement

The as-prepared samples were used as anode materials of SIBs for electrochemical testing. To prepare the working electrode, the PCSs, Super-P carbon black and CMC were mixed in deionized water with a weight ratio of 80:10:10 to produce a homogenous slurry that was then coated on a copper foil current collector by an automatic coating drying machine (MSK-AFA-III) with a typical thickness of 50–60  $\mu\text{m}$  and further dried at 120 °C in a vacuum for 12 h. The active material loading in the resultant working electrode (the diameter is 14 mm) was  $\sim 1.0$   $\text{mg cm}^{-2}$ . Coin-type cells (CR2032) were assembled with sodium metal foil as counter electrode, Whatman glass fiber membrane as separator, and 1 M  $\text{NaClO}_4$  electrolyte solution dissolved in a mixture of ethylene carbonate and propylene carbonate (1:1 w/w) as electrolyte, which was carried out in a glove box (MB-10-compact, MBRAUN) under argon atmosphere with oxygen and water of less than 0.5 ppm. The galvanostatic charge-discharge data was collected by a LAND2001A battery test system in a voltage range of 0.005–3 V. Cyclic voltammetry (CV) was performed in a voltage range of 0.005–3 V at a scan rate of 0.2  $\text{mV s}^{-1}$  with an electrochemical workstation (AUTOLAB PGSTAT302N). And the electrochemical impedance spectroscopy (EIS) measurement was carried out on the same electrochemical workstation in a frequency range of 0.1–100 kHz after 50 galvanostatic charge-discharge cycles at a specific current of 50  $\text{mA g}^{-1}$ . The applied bias voltage and ac amplitude were set at the open-circuit voltage of the cells and 5 mV, respectively.

## 3. Result and discussion

Fig. 1 illustrates the synthetic process of the PCSs. Firstly,  $\text{Na}_2\text{MoO}_4 \cdot 2\text{H}_2\text{O}$  was reduced to molybdenum dioxide ( $\text{MoO}_2$ ) by the D-Glucose monohydrate during the hydrothermal reaction under the acidic condition and the product M-1 was obtained. The added acid plays a role in controlling the precipitation kinetics of both molybdenum oxide and porous carbonaceous matrix in the hydrothermal conditions, which is crucial to form uniform carbon encapsulated spheres [28]. Subsequently, after carbonization in  $\text{N}_2$  at 800 °C, molybdenum carbide ( $\text{Mo}_2\text{C}$ ) and carbon composite (product M-2) was obtained due to the reduction reaction of  $\text{MoO}_2$  by the carbon as the reducing reagent. When exposed in air and thermally treated at 300 °C,  $\text{Mo}_2\text{C}$  was oxidized to be molybdenite ( $\text{MoO}_3$ ) and product M-3 was obtained. After immersed in aqueous ammonia solution,  $\text{MoO}_3$  was removed completely, resulting in lots of pores in the final product PCSs.

The morphologies of M-120-1, M-120-2, M-120-3 and PCS-120 investigated by FESEM are shown in Fig. 2a-d. M-120-1, M-120-2 and M-120-3 represent the products M-1, M-2 and M-3 during the

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