



# Properties and sodium insertion behavior of Phenolic Resin-based hard carbon microspheres obtained by a hydrothermal method



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## ARTICLE INFO

### Article history:

Received 21 March 2015

Received in revised form 10 July 2015

Accepted 21 July 2015

Available online 26 July 2015

### Keywords:

Thermosetting Phenolic Resin

Carbon microspheres

Hydrothermal

Sodium-ion batteries

## ABSTRACT

Phenolic Resin-based hard carbon microspheres (PF-HCSs) were successfully synthesized by a simple hydrothermal route in a stainless steel autoclave and followed carbonization at different temperatures. The materials possess perfect spherule shape and interlayer spacing above that of equilibrium graphite, facilitating Na intercalation and favoring efficient ion storage. A high reversible capacity of 311 mAh g<sup>-1</sup> and good long-term electrochemical stability are achieved in the PF-HCS-1250 anode obtained at 1250 °C. Carbonizing the samples at higher carbonization temperature than 1250 °C results in such a decrease of the reversible capacity down to 270 mAh g<sup>-1</sup>. That can be related to the appearing closed pore structure and the decreasing interlayer space which exceeds the limited value sodium ion can insert. Hence the most suitable hard carbon anode material for sodium ion batteries should possess a large interlayer space and a suitable pore structure.

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## 1. Introduction

Due to abundance of the sodium resources, and the similar chemistry of sodium and lithium, sodium ion batteries (SIBs) constitute a major contender for large-scale energy storage applications [1–5]. Disordered carbon electrodes have been investigated as the anode in SIBs, such as carbon black [6], hard carbon from pyrolyzed glucose [7], PAN-based carbon fibers [8], and carbon microspheres prepared from resorcinol–formaldehyde (RF) resin [9]. They have exhibited considerable reversible capacities due to their large interlayer distance and disordered structure and developed with adequate capacity and cycle stability in recent years [10–13]. Especially, disordered carbon with a spherical structure has proven to be an excellent anode material owing to their high packing density, low surface-to-volume ratio and maximal structural stability [1,2,14–16]. However, there have been few reports about the properties and sodium insertion behavior of Phenolic Resin (PF)-based hard carbon microspheres. It has been known that Phenolic Resin is one kind of flexible precursors leading to high purity carbons and allowing the production of carbon materials with a wide range of pore structures [17,18]. Furthermore, PF-derived carbon materials are much cheaper than those based on resorcinol–formaldehyde (RF) resin [17].

In this work, we have synthesized hard carbon microspheres (PF-HCSs) by a hydrothermal method with PF as the precursor. The synthesis proved to be an easy and low-cost approach to obtain carbon microspheres. After carbonization treatment at different temperatures, the electrochemical performance of the PF-HCS was investigated for use as anode materials for SIBs.

## 2. Experimental

### 2.1. Synthesis of PF-HCS

In the two step syntheses of thermosetting Phenolic Resin, a certain quality of phenol (P) and formaldehyde (F) were added in a three flask, respectively. Then, an aqueous solution of sodium hydroxide was added and an excess F was again added. The mixed solution was reacted at 90 °C for 1 h. After that, the obtained aquagel was added into a stainless steel auto. The reaction furnace was maintained at 500 °C for 12 h, and then cooled to room temperature naturally. The pure resins were obtained by treatment of high speed centrifugation and then dried in a vacuum at 80 °C for 12 h. Then they were carbonized in a programmable tube furnace at 800, 1000, 1250, and 1500 °C for 3 h under N<sub>2</sub> atmosphere to obtain the PF-HCS-800, PF-HCS-1000, PF-HCS-1250 and PF-HCS-1500 electrode materials, respectively.

### 2.2. Material characterization

The morphologies of the samples were performed using a field emission scanning electron microscopy (FESEM, Nano430). Crystallographic

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structure was characterized by X-ray diffraction (XRD, a Rigaku D/Max 2500 X-ray diffractometer) with Cu K $\alpha$  radiation (40 kV, 150 mA,  $\lambda = 1.54056 \text{ \AA}$ ) and Raman spectrum on a Renishaw via reflex Raman microscope with 523 nm line of Ar-ion laser as excitation source. The interlayer distance  $d_{002}$  was calculated by XRD spectra using the Bragg equations. Brunauer–Emmett–Teller (BET) specific surface area and total pore volume were examined by nitrogen adsorption measurements at 77 K on Micromeritics Analytical Services (TriStar 3000, GA).

### 2.3. Electrochemical measurements

The as-synthesized PF-HCS (80 wt.%), acetylene black (10 wt.%) and polyvinylidene fluoride (PVDF, 10 wt.%) were dispersed in N-methyl-2-pyrrolidone (NMP) to form a slurry. The slurry was uniformly spread on a copper foil and then dried at 120 °C under vacuum for 12 h, followed by rolling. Coin-type cells (CR2430) were assembled in an argon-filled glove box, using lithium sheets as the counter electrodes and 1 M NaClO<sub>4</sub> dissolved in a mixture of ethylene carbonate and dimethyl carbonate (1:1 by volume) as the electrolyte. Galvanostatic charge–discharge experiments were tested using a multichannel Land Battery Test System over the range of 0.01 ~ 2.7 V.

## 3. Results and discussion

### 3.1. Characterizations of morphology and structure

Fig. 1 shows the scanning electron microscopy (SEM) images of PF-HCS carbonized at different temperatures. It is noticed that the carbonization temperature does not show an obvious effect on the shape of the PF-HCS, they all show perfect spherule shape with widely dispersed particle size varying from 1 to 8  $\mu\text{m}$ . However, the higher carbonization temperature leads to the fabrication of more and smaller spheres and the appearance of a faint adhesion. PF-HCS-800 and PF-HCS-

1000 possess relatively smooth surfaces, but the surface of PF-HCS-1250 and PF-HCS-1500 becomes coarser. This may be attributed to that more chemical bonds thermally break at higher temperature in an inert nitrogen atmosphere.

Characterization of PF-HCS was performed by means of XRD, Raman spectroscopy and BET surface area measurements. The results are shown in Table 1. Fig. 2a and b gives the XRD patterns and Raman spectra of the samples under heat-treated temperatures from 800 to 1500 °C. Two broad and weak diffraction peaks in Fig. 2a at around 23° and 43° correspond to the (002) and (100) diffraction modes, indicating non-graphitic carbon materials with a highly disordered nanocrystalline structure. The calculated interlayer spacing of “ $d_{002}$ ” increased gradually with the carbonized temperature increasing from 800 to 1250 °C, as shown in Table 1. However, when carbonized temperature further increased to 1500 °C, the “ $d_{002}$ ” decreased slightly compared to 1250 °C. In all cases the spacing is significantly above that of equilibrium graphite (0.3354 nm), which is favorable for sodium ion storage and transport. In Raman spectra shown in Fig. 2b, all of them display two broad bands located at 1350 and 1590  $\text{cm}^{-1}$  corresponding to the defect-induced D band and the crystalline graphite G band of carbon. The comparative intensity ratio of the D band and G band ( $I_D/I_G$ ) used to quantify the disorder degree of carbon is 1.1 [19,20]. With increasing heat-treated temperatures, the full width at half-maximum values of the D band and G band gradually decrease, showing a change from amorphous carbon structure to a planar graphite structure. This is also in agreement with the results of XRD.

The N<sub>2</sub> adsorption–desorption isotherms for PF-HCS are shown in Fig. 3, which show type-I/IV behavior. Increasing the carbonization temperature promotes a shift from microporosity to mesoporosity, even produces “embedded fullerenes” formed by the closure of micropores [21], resulting in a decrease in surface area and total pore volume (cf. Table 1). However, all the resultant materials have relatively low surface area, ranging from 350.2 to 101.3  $\text{m}^2 \text{g}^{-1}$ , indicating a poor structure of the PF-HCS material itself.

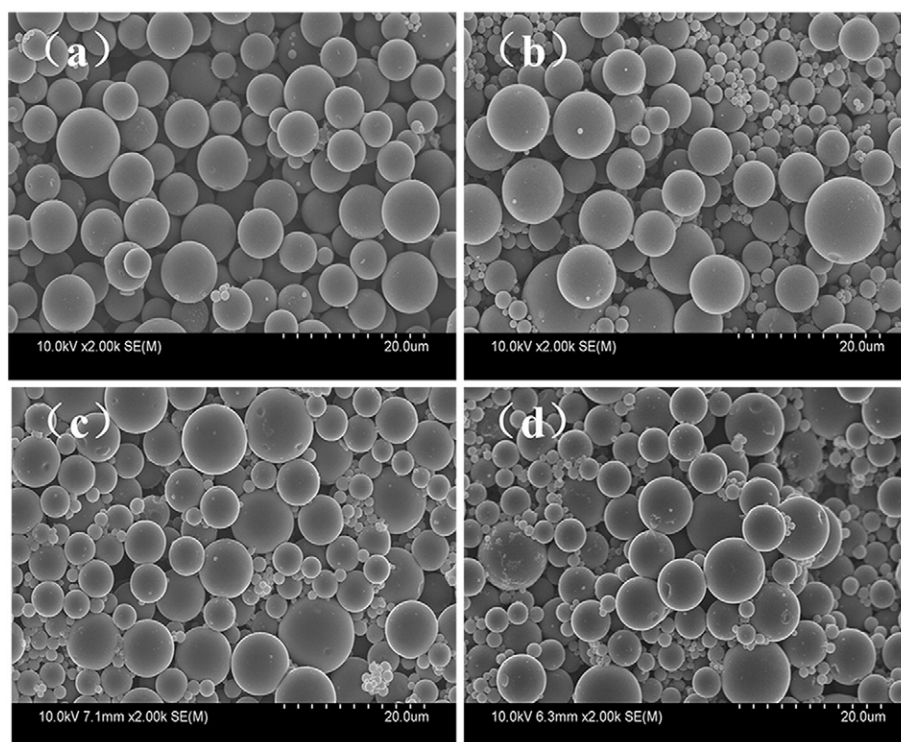


Fig. 1. SEM images of (a) PF-HCS-800; (b) PF-HCS-1000; (c) PF-HCS-1250; and (d) PF-HCS-1500.

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