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

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ABSTRACT:

Phenolic Resin-based hard carbon microspheres (PF-HCS) were successfully synthesized by a simple hydrothermal route in a stainless steel autoclave and followed carbonization at different temperature. The materials possess perfect spherule shape and interlayer spacing above that of equilibrium graphite, facilitating Na intercalation and favoring the efficient ion storage. A high reversible capacity of 311 mAh g⁻¹ 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⁻¹. 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], carbon microspheres prepared from resorcinol–formaldehyde (RF) resin [9], etc. 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 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-HCS) 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 steps synthesis 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, 1500 °C for 3 h under N₂ atmosphere to obtain the PF-HCS-800, PF-HCS-1000, PF-HCS-1250 and PF-HCS-1500 electrode materials, respectively.

2.2. Materials characterization

The morphologies of the samples were performed using a field emission scanning electron microscope (FESEM, Nano430). Crystallographic structure was characterized by X-ray diffraction (XRD, a Rigaku D/Max 2500 X-ray diffractometer) with Cu K α radiation (40 KV, 150 mA, $\lambda = 1.54056$ Å) and Raman spectrum on a Renishaw in Via reflex Raman microscope with 523 nm line of Ar-ion laser as excitation source. The interlayer distance d_{002} were 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 (TriStar3000, 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 NaClO₄ 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 temperature. It is noticed that the carbonization temperature does not show obvious effect on the shape the PF-HCS, they all show perfect spherule shape with widely dispersed particle size varying from 1 to 8 μm . However, the higher carbonization temperature leads to the fabrication of more and smaller spheres and the appearing 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 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° corresponds to the (002) and (100) diffraction modes, indicating an non-graphitic carbon materials with a highly disordered nanocrystalline structure. The calculated interlayer spacing of “ d_{002} ” increased gradually with the carbonized temperature increased 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 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 the 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_2 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.

3.2. Electrochemical characterization

The galvanostatic charge/discharge profiles of the PF-HCS electrodes measured at a constant current density of 20 mA g^{-1} between 0 and 2.7 V are presented in Fig. 4. The charge/discharge capacities and coulombic efficiencies of the samples are shown in Table 1. The pyrolyzing temperature has an insignificant influence on charge-discharge characteristics of the resin carbon anodes. As presented in Fig.4, during the first cycle, the voltage profiles of all the PAN-CNFs electrodes show an irreversible slope from 1.1 to 0.2 V caused by solid electrolyte interphase (SEI) formation and irreversible trapping of Na at the highly defective graphene sites, resulting in irreversible capacities.

The subsequent profiles show good reversibility and repeatability, displaying a sloping-voltage region and a nearly flat plateau at potentials lower than 0.2 V, which can be ascribed to intercalation of sodium ions between graphene layers [7, 9, 22]. There are subtle differences in initial efficiency and some changes in reversible capacities. As carbonization temperature is increased from 800 to 1500 °C, the initial coulombic efficiencies increase from 57.9% to 62.5%, a progressively decreasing surface area and lower heteroatom content (less SEI formation) play an important role in this trend. The Na reversible capacity of PF-HCS increases with increased carbonization temperature, between 800 and 1250 °C, which be caused by that the larger interlay spacing at higher HTTs are more suitable for sodium ion with a large size reversible insertion and extraction [11]. Further increasing carbonization temperature to 1500 °C, when graphitization starts, the Na capacity decreases. This phenomenon can be explained by that some ordered domains appearance, where with a narrow interlayer spacing close to graphite, resulting in the interlay spacing of “ d_{002} ” decrease, as shown in Table 1. However, these domains are inactive with sodium ions because of the interlayer spacing is too narrow to accommodate the relatively bigger sodium ions [22]. So PF-HCS-1250 exhibites the highest reversible specific capacity of 311 mAh g⁻¹.

The rate performances of the PF-HCS anodes at various current densities in SIBs are plotted in Fig.5. When charged at altering rates ranging from 20 to 100 mA g⁻¹, PF-HCS-1250 electrode achieves the highest capacity. However, at higher charge rates, the PF-HCS-1000 shows higher reversible capacity than other samples. These rate trends indicate that the rate performances of PF-HCS are closely related to heat treatment process and the microstructure of material itself. With carbonization temperature increasing, on the one hand, the increasing electric conductivity is conducive to sustain a large current, but on the other hand, the decreasing interlayer spacing of the relatively ordered domains

is not favorable for the capacity retention of electrodes during large current operation [22-24]. The rate capabilities of all PF-CNFs electrodes are not so good. It is closely related with the undeveloped pore structure of this PF-CNFs material itself, leading the slow diffusion kinetics of sodium ion [25]. But it should be noted its rate capacity could be improved in the future by introducing nanoporosity and a hierarchical pore system into the anode to reduce solid-state Na diffusion distances within the carbons [25-27] or optimizing carbonization process (such as heating temperature, heating rate and holding time) to balance the relationship between intergraphene spacing and electric conductivity [8,11].

Fig. 6 displays the cycle performances of the PF-HCS electrodes, tested at 50 mA g^{-1} for the first 5 cycles and at 100 mA g^{-1} for the next 100 cycles. All of them have more than 80% capacity retention after 100 cycles, exhibiting stable cycling performances. The coulombic efficiency increases dramatically upon cycling, reaching over 98% after 5 cycles and stabilizes at $\sim 100\%$ after 10 cycles. Thus the PF-HCS electrodes possess good reaction reversible and structural stability, which is a critical property for practical application.

4. Conclusions

We created a unique low surface area hard carbon sphere (PF-HCS) that was derived from Phenolic Resin by a facile, sustainable hydrothermal method. The effect of carbonization temperature on the structural evolution and sodium insertion behavior of PF-HCS is meticulously studied. The best electrochemical performances with a high reversible capacity of 311 mAh g^{-1} and good cycling stability are obtained for the sample heat treated at 1250°C . We believe that PF-HCS can be a promising candidate for low-cost sodium ion battery systems by further modification of material parameters such as morphology, size and pore structure, which is an effective strategy to improve the rate capacity by boosting ion transport and storage.

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Figure Captions

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

Fig. 2 (a) XRD patterns and (b) Raman spectra of PF-HCS

Fig. 3 N₂ adsorption-desorption isotherms of PF-HCS

Fig. 4 Galvanostatic charge/discharge profiles of (a) PF-HCS-800 (b) PF-HCS-1000 (c) PF-HCS-1250
(d) PF-HCS-1500 in SIBs

Fig. 5 Rate performances of the PF-HCS electrodes

Fig. 6 Cycle performances of the PF-HCS electrodes at 100 mA g⁻¹

Table 1 Physical Parameters and Electrochemical Properties for different PF-HCS

Sample	d_{002} (nm)	$S_{\text{BET}}^{\text{a}}$ ($\text{m}^2 \text{g}^{-1}$)	$V_{\text{total}}^{\text{b}}$ ($\text{cm}^3 \text{g}^{-1}$)	Q_{D}^{c} (mAh g^{-1})	Q_{C}^{d} (mAh g^{-1})	CE^{e} (%)
PF-HCS-800	0.378	350.2	0.148	225.5	389.5	57.9
PF-HCS-1000	0.386	286.5	0.121	299.9	506.7	59.2
PF-HCS-1250	0.389	219.5	0.087	311.2	517.2	60.2
PF-HCS-1500	0.380	101.3	0.049	270.0	432.0	62.5

^a Surface area was calculated with Brunauer-Emmett-Teller (BET) method.

^b The total pore volume was determined at a relative pressure of 0.98.

^c The discharge capacity in the first cycle.

^d The charge capacity in the first cycle.

^e The initial coulombic efficiency.

figure 1

figure 2

figure 3

figure 4

figure 5

figure 6