Preparation And Electrochemical Performance of Nano Si@Short Hard Carbon Fiber Composites as Anodes for Lithium Batteries

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Abstract. The bamboo paper was soaked by the silica sol. After drying, the nano-silicon@short hard carbon fiber was prepared by vacuum high-temperature carbonization treatment followed by grind, which was one-dimensional composite. The structure and morphology of the composite material were characterized by X-ray diffraction and Scanning electron microscopy (SEM). The results show that the diameter of the short hard carbon fiber is about 2~8 μm and the length is about several tens of microns. The nano-silicon particles are sparsely distributed on the outer wall of the short bamboo charcoal fiber. The adhesion between nano silicon and short hard carbon fiber is strong due to the effect of thermal diffusion and Van der Waals’ force. The prepared nano-silicon@short hard carbon fiber composite was used as a negative electrode material for lithium battery for charge and discharge test. When the current density was 100 mA.g⁻¹, the capacity was only attenuated by 6.54% after 50 cycles. Meanwhile, the composite also exhibits well rate performance.

Keywords. one dimensional composites; short hard charcoal fiber; anode material; lithium ion batteries

1. Introduction

The lithium-ion battery has many advantages, such as small size, high energy density, high power, long term using and good safety, which is ideal for energy storage [1-3]. Cathode materials play an important role in the performance of lithium-ion batteries [4-6]. The cathode material should have as low as possible electrode potential, high Li⁺ mobility, high reversibility of Li⁺ embedding and de-embedding, good conductivity and thermodynamic stability. At present, graphite is the commercialized cathode material for lithium-ion batteries [7-9]. Compared with graphite, hard carbon cathode has higher theoretical discharge capacity [10], faster charge and discharge speed, lower carbonization temperature and less energy loss, so it has become one of the research hotspots. Bamboo is planted in large quantities in China, with abundant sources and low prices. In this paper, bamboo pulp paper was used as raw material; hard carbon fiber was prepared by carbonizing at 800 °C [11], then ground into short bamboo carbon fiber. It was used as cathode material for lithium-ion batteries to test its charge-discharge performance. The results show that it has lithium storage capacity and good cycling performance. In addition, one-dimensional composites of nano-silicon @ short bamboo carbon fiber were prepared by a simple method. It was found that the electrochemical properties were greatly improved compared with pure short-cut bamboo-carbon fibers.
2. Experiment section

2.1. Raw Materials and Instruments
The purity of nano-silica powder (particle size 30 nm) used in this experiment is 99.9%. It was purchased from Zhongxin New Material Company. Bamboo pulp paper was marketed as Fanya brand bamboo pulp paper. Sodium carboxymethyl cellulose (CMC-Na) and styrene-butadiene rubber (SBR) were purchased from Cyber electrochemical material network. Analytical pure anhydrous ethanol was purchased from Chengdu Cologne Chemical Co., Ltd.

2.2. Material preparation
Bamboo paper was soaked in deionized water for 12 hours, taked out, and dried in an oven at 80 °C for 8 hours. Placing the treated bamboo paper into a vacuum carbon tube furnace and carbonizing at 800 °C in a vacuum environment for 8 hours to get bamboo carbon fibers. The bamboo fiber was grinded for 1 hour with agate mortar to obtain short hard carbon fiber. Nano silicon/ethanol sol with the mass percentage concentration of 0.8% was prepared by ultrasonic dispersion. Bamboo paper was soaked in deionized water for 12 hours, taked out, and dried in an oven at 80 °C for 8 hours. The bamboo paper was soaked in nano silicon/ethanol sol in an oven at 50 °C for 30 minutes, taked out, and dried in a vacuum oven at 80 °C for 3 hours. The bamboo paper with nano-silicon was carbonized in a vacuum carbon tube furnace at 800 °C for 8 hours to obtain the nano-silicon @ bamboo carbon fibers composite material. The heating rate is 8 °C/min. Grinding the nano silicon @ bamboo carbon fibers for 1 hour with an agate mortar to obtain the nano-silicon @ short hard carbon fiber composite material.

2.3. Battery assembly and electrochemical measurements
Active substances, sodium carboxymethylcellulose (cmc) and styrene butadiene rubber (SBR) are ground and prepared by using deionized water as a dispersant according to a mass ratio of 90: 5: 5, and are uniformly coated on copper foil by a scraper coating method after being ground uniformly. The copper foil is baked in an oven at 80 °C for 12 hours and then is punched by a punching machine to prepare a electrode with a diameter of 14 mm. A button cell (2016) was assembled in an argon filled glove box (Mikrouna (China) Co., Ltd., Super (1220/750/900),) filled with argon, in which the concentration of oxygen and water vapor was lower than 0.01 PPM. The electrolyte was 1 mol/L LiPF6 solution (the solvent was a mixed solvent of vinyl carbonate, methyl ethyl carbonate and diethyl carbonate with a volume ratio of 1: 1: 1). Celgard 232 was used as the separator; Li foil was used as both the counter and reference electrodes. The cells tested by LANHE CT2001A battery-test system (Wuhan LAND electronics Co., Ltd.) galvanostatic charge-discharge tests at various current densities in the voltage range of 0.01-3.0 V (versus Li/Li+).

3. Results and discussions

3.1. Morphology and structure
Figure 1 is an SEM photograph of the produced chopped hard carbon fiber. It can be seen from Figure 1(a) that the material is chopped fiber with a diameter of about 2-8 μm and a length of about tens of μm. The length of the fiber can be controlled by controlling the grinding time and strength. It can be seen from Figure 1(b) that there are irregular folds and cracks on the surface of the sample, which may be caused by cracking reaction at high temperature. These cracks and folds increase the specific surface area of the material.

Figure 2 is an xrd detection result diagram of chopped hard carbon fibers. From the diagram, it can be seen that the chopped bamboo charcoal fibers are amorphous structures, and the characteristic peak around 23° corresponds to the (002) crystal plane of carbon, which is formed by parallel stacking of
some graphitized sheets in the carbon material; The characteristic peak around 43° corresponds to the (100) crystal plane of the carbon material, which corresponds to the hexagonal lattice structure formed by the interaction of sp3 hybridization atoms in the carbon material [12].

Figure 3 is a SEM image of nano-silicon short hard carbon fiber with different magnification. The fluffy material attached to the short bamboo carbon fiber is nano-silicon. The distribution of nano-silicon on the bamboo charcoal fiber is sparse, which helps alleviating the volume expansion effect of nano-silicon during charging and discharging process. In addition, nano-silicon has a slight agglomeration phenomenon. Because the composite material has been under heat treatment at 800°C, thermal diffusion can strengthen the bonding strength between nano-silicon and short carbon fibers. Besides, the surface of nano-silicon will inevitably have some oxidation, and the oxygen atoms can be connected with oxygen-containing groups on the surface of short-cut bamboo charcoal fibers through vander Waals force, which also enhances the bonding strength between nano-silicon and short bamboo charcoal fibers. This is beneficial for the improvement of material cycling performance.

![Figure 1. SEM images of short hard carbon fiber](image1)

![Figure 2. XRD pattern of short hard carbon fiber](image2)

![Figure 3. SEM images of nano Si@short hard carbon fiber Composites](image3)

![Figure 4. XRD pattern of nano Si@short hard carbon fiber Composites](image4)

Figure 4 is the XRD test chart for Nano-silicon short bamboo carbon fiber composites. The diffraction peak in crystal silicon is very clear, but it is very weak in bamboo carbon. This is due to that the bamboo carbon is amorphous carbon and amorphous, and it has a very weak diffraction peak intensity, with the maximum intensity of about 350. Nano-silicon is a crystal with high intensity of diffraction peak, with a maximum intensity of about 400. Therefore, the diffraction peak of bamboo carbon is relatively weak when these two groups of peaks are in the same chart. In the graph, it can be observed that, in the range of 20 - 26°, the map base is relatively higher, which is caused by amorphous bamboo carbon.

3.2. Electrochemical performance analysis
Figure 5 shows the initial charge-discharge curve of the sample with a current density of 30 mA·g⁻¹ and a charge-discharge voltage range of 0.01~1 V. It can be seen from the diagram that the initial discharge specific capacity of the short bamboo carbon fiber is 607 mAh·g⁻¹. The initial charge specific capacity is 239 mAh·g⁻¹, and the first charge-discharge efficiency is 39%. It has been reported in the literature that the H/C of biomass hard carbon material carbonized at low temperature is higher, which leads to a lower first charge-discharge coulombic efficiency. The initial discharge specific capacity of nano-silicon@ short bamboo carbon fiber composites is 1267 mAh·g⁻¹, the first charge specific capacity is 764mAh·g⁻¹, and the first charge-discharge efficiency is 60%. The introduction of nano-silicon improves the first charge-discharge coulomb efficiency of anode materials. Compared with pure short bamboo carbon fiber, the introduction of high-capacity nano-silicon [13-15] is the fundamental reason for the improvement of electrochemical capacity of nano-silicon@ short bamboo carbon fiber composites. In the first discharge curve, there is an obvious voltage platform around 0.75 V, which corresponds to the formation of SEI film.

Figure 6 is a graph showing the charge-discharge cycle performance of the sample at a current density of 100 mA·g⁻¹. It can be seen from the graph that the cycle performance of chopped bamboo charcoal fiber is stable, but its capacity is not ideal and the first discharge specific capacity is only 193 mah g⁻¹. After nano-silicon is compounded on the chopped bamboo charcoal fiber, the capacity is obviously improved, the first discharge specific capacity reaches 428 mah g⁻¹, which is 121.76% higher than that of the chopped bamboo charcoal fiber and the cycle stability is not obviously reduced; after 50 cycles, the discharge specific capacity is still maintained at 400 mah g⁻¹, which is only reduced by 6.54%. Pure silicon active materials are accompanied by drastic volume changes [16] in the cycle process, which will lead to the destruction of the electrode structure, thus its capacity decays rapidly and its cycle performance is poor. In the nano silicon @ chopped bamboo charcoal fiber composite material, nano silicon is sparsely embedded in the chopped bamboo charcoal fiber, leaving enough space to relieve the volume change of nano silicon during charging and discharging, so the cycle performance of the composite material is not obviously reduced; In addition, the better connection between nano-silicon and chopped bamboo charcoal fibers can also alleviate the damage of electrode structure caused by the volume expansion of nano-silicon.

Figure 7 is a magnification performance chart of nano silicon/chopped hard carbon fiber composite material. It can be seen that when the current density gradually increases from 100mA·g⁻¹ to 400mA·g⁻¹, the specific discharge volume of the composite material decreases, but when it returns to 100mA·g⁻¹ again, the specific discharge capacity of the material basically returns to the original level. When hard carbon and silicon are respectively used as active materials of lithium battery cathode materials, their multiplying power performance is poor. However, when the two are combined together, nano silicon has higher lithium storage capacity and hard carbon fiber has excellent conductivity. The synergistic effect of the two improves the multiplying power performance of the composite material.
4. Conclusion
Short hard carbon fiber is successfully made from bamboo paper in the way of high temperature heat treatment in vacuum in this research. The preparation method for biomass-based short bamboo carbon fiber is simple and the raw material supply is wide. Bamboo paper is used as the template and soaked in silica sol. In the way of high temperature heat treatment in vacuum, compound material of nano-silicon @ short hard carbon fiber is prepared. The introduction of high-capacity nano-silicon improves the lithium storage capacity of active materials. Nano-silicon attaches on short-cut bamboo charcoal fiber sparsely. When it is made as pole pieces, nano-silicon is covered and buried into carbon fiber. This structure relieves the volume expansion in nano-silicon cycling and it is good for the improvement of cycling performance of compound materials. The preparation method in this research is simple and cost-effective. In such an era when the problems of environment protection and energy-saving are getting more and more serious, this method is of great research significance.

5. References
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