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Preparation and Lithium Storage Properties of Skewer-based Carbon Materials[1]

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Abstract

In daily life, bamboo sticks are widely used in the catering industry, resulting in significant waste. There is an urgent need to find sustainable methods for utilizing these discarded bamboo sticks. Traditional disposal methods, such as landfilling and incineration, can severely harm the environment. In this study, we focus on recycling waste bamboo sticks through a one-step high-temperature calcination process to prepare carbon-based anode materials. We fabricated electrodes and assembled lithium-ion batteries to conduct electrochemical cycling performance tests. The results indicate an initial discharge specific capacity of 326 mAh/g at a current density of 100 mA/g. After 100 cycles, the discharge specific capacity remains high at 260 mAh/g, demonstrating excellent cycling stability and effective lithium storage performance. This study provides a novel approach to the sustainable utilization of waste bamboo sticks.

Keywords

Bamboo sticks; High-temperature carbonization; Anode material; Cycling stability; Lithium-ion battery

The global environmental crisis is becoming increasingly severe, and taking the path of sustainable development has become a general consensus of the international community. Faced with problems such as resource depletion and environmental pollution, countries around the world are actively exploring new paths for energy transformation and green development [1]. In this context, rechargeable lithium-ion batteries, as the current mainstream energy storage and conversion equipment, are crucial to promoting the transformation process in the field of new energy by improving their cost-effectiveness [2-5]. Therefore, the development of low-cost, high-performance lithium-ion battery negative electrode materials has become a key demand for promoting the development of lithium-ion battery technology [6-7].

Biomass-based waste is a common waste in daily life. How to properly deal with biomass-based waste is an important environmental issue that today's society needs to face [8-13]. In the catering industry, bamboo sticks are widely used and consumed in large quantities. If waste bamboo sticks are landfilled at will, they will not only occupy precious land resources, but also cause a large amount of tree resources to be wasted; if they are incinerated, they will release a large amount of carbon dioxide, exacerbating global warming. Therefore, exploring high-value-added recycling methods for waste bamboo sticks is of vital significance for promoting resource recycling and reducing environmental pressure. This will not only help solve the problem of waste bamboo stick disposal but also contribute to the construction of a resource-saving and environmentally friendly society.

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[1] The Chinese version of this paper has been published in the *International Journal of Materials Science*, and this is an authorized translation of it.

Based on the above background, this research focuses on waste bamboo sticks, a biomass waste, and converts waste bamboo sticks into carbon-based negative electrode materials for lithium-ion batteries to achieve high-value-added reuse of waste bamboo sticks. This study uses a one-step method to calcine waste bamboo sticks at high temperature, treat waste bamboo sticks, and prepare amorphous carbon-based negative electrode materials. Through modern analytical methods such as scanning electron microscopy (SEM) and X-ray diffraction (XRD), the microstructure and properties of the material are characterized in detail, and electrochemical cycle performance tests are carried out to study its electrochemical performance as a negative electrode material for lithium-ion batteries. The results of this research will not only effectively avoid the environmental pollution caused by the landfill or incineration of a large number of waste bamboo sticks, but also provide new ideas for the recycling of waste bamboo sticks.

1. Experimental Section

1.1 Experimental materials and instruments

Experimental materials: waste bamboo sticks, conductive agent superconducting carbon black (SP), binder polyvinylidene fluoride (PVDF), N-methylpyrrolidone (NMP), metallic lithium, copper foil, diaphragm (model Celgrad2400), lithium-ion battery electrolyte (1.0 M LiPF6 1:1 EC: DMC), button battery shell (CR2016), etc.

Instruments: electronic analytical balance, tubular furnace, vacuum drying oven, blast drying oven, multi-channel battery testing system, inert atmosphere glove box, cutting machine, roller machine, button battery sealing machine, etc.

1.2 Experimental procedure

Material preparation: First, clean the recycled waste bamboo sticks, place them in a blast drying oven, and dry them at 80 °C for 24 hours. Then, cut the bamboo sticks into pieces and place them in a corundum crucible. In a tube furnace with a fixed nitrogen atmosphere, heat the temperature to 900 °C at a rate of 5 °C/min and calcine at this temperature for 2 hours. After cooling to room temperature, grind them evenly in an agate mortar to obtain bamboo stick-based carbon material powder.

Electrode preparation: According to the mass ratio of 8:1:1, weigh 80 mg of bamboo stick-based carbon material, 10 mg of conductive agent SP, and 10 mg of binder PVDF in an agate mortar and grind them evenly. Add an appropriate amount of NMP and stir evenly to obtain a viscous electrode slurry. Use a 100 μm wet film scraper to evenly scrape the electrode slurry on the clean copper foil current collector surface, dry it at 80 °C in a blast drying oven, transfer it to a vacuum drying oven, and dry it at 60 °C for 12 hours. Compact the dried electrode with an electric roller machine, cut a circular electrode with a diameter of 12 mm, weigh it, and set it aside.

Lithium-ion battery assembly: In a glove box filled with argon atmosphere, with metallic lithium as the counter electrode, the electrode sheet, diaphragm, electrolyte, and metallic lithium sheet are placed into a CR2016 battery shell in sequence [13], and sealed using a battery sealing machine to prepare a lithium-ion battery.

1.3 Characterization techniques

Physical characterization: The prepared carbon materials were tested by X-ray diffraction (XRD, D8 Advance Cu Kα), and the composition and phase analysis were performed using jade software; the morphology of the carbon-based materials was observed using SEM (FEI Nova NanoSEM 2300); the specific surface area and pore size of the materials were studied using N2 adsorption-desorption; and the carbon materials were analyzed and tested using Raman spectrometer (DXR).

Electrochemical performance characterization: The assembled lithium-ion battery was activated at room temperature for 5 h, and a cyclic voltammetry test was performed using an electrochemical workstation (CHI660E) (voltage range 0.01-3.0 V, scan rate 0.2 mV/s); the battery was subjected to constant current charge and discharge test (voltage range 0.01-3.0 V), rate performance test and long cycle charge and discharge test using a Newwell multi-channel battery test system (CT-4800).

2. Results and Discussion

The prepared bamboo stick-based carbon material was subjected to an X-ray diffraction test, and the results are shown in Figure 1. In the spectrum, there are two obvious peaks at 23° and 43°, which are compared with the standard PDF card and are attributed to the characteristic diffraction peaks of amorphous carbon. This means that the material prepared from waste bamboo sticks is an amorphous carbon material without impurity phases.

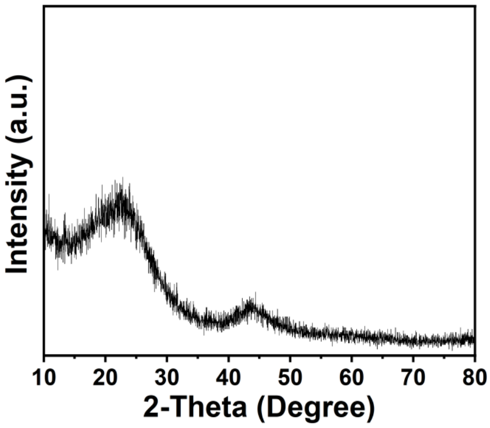

Figure 1. XRD pattern of bamboo stick-based carbon materials.

In order to observe the surface structure of bamboo stick-based carbon materials, an electron scanning microscope was used to analyze their surface. As shown in Figure 2, the carbon material made from waste bamboo sticks is irregular in shape, and the particle size is about 10 μm. Further magnification of the material shows that there are abundant pores on the surface of the bamboo stick-based carbon material, which almost cover the entire surface of the carbon material. At the same time, there are also abundant holes in the side section of the particles.

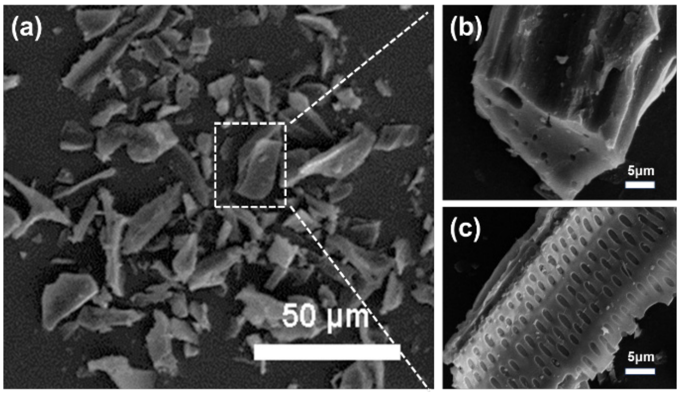

Figure 2. SEM image of bamboo stick-based carbon material.

The specific surface area and pore size of the material were studied by the N2 adsorption-desorption test. As shown in Table 1, the specific surface area of the bamboo stick-based carbon material is 140.98 m^2/g, and the average pore size is 3.59 nm. This test result shows that the bamboo stick-based carbon material has abundant pores. In the electrochemical process, this structure is conducive to the storage of electrolyte in the electrode material, providing convenient conditions for ion conduction. At the same time, the rich pore structure can also store additional ions, improve the specific capacity of lithium-ion batteries, and achieve good electrochemical performance.

Table 1. Specific surface area and pore size parameters of bamboo stick-based carbon materials

	Specific surface area (m^2/g)	Average pore size (nm)	Pore volume (cm^3/g)
Bamboo stick-based carbon material	140.98	3.59	0.00158

Raman spectroscopy was used to analyze the structural information of bamboo stick-based carbon materials, and the results are shown in Figure 3. There are two strong peaks at 1325 cm^{-1} and 1597 cm^{-1}. Among them, the D peak at 1325 cm^{-1} belongs to the C-C group in the carbon material; the G peak at 1597 cm-1 belongs to the C=C group.

The strong and narrow peak of the G peak indicates that the number of C=C groups in the carbon material increases, and more graphite structures are gradually formed [14]. Therefore, the Raman test results show that the material has a certain graphite structure and good conductivity.

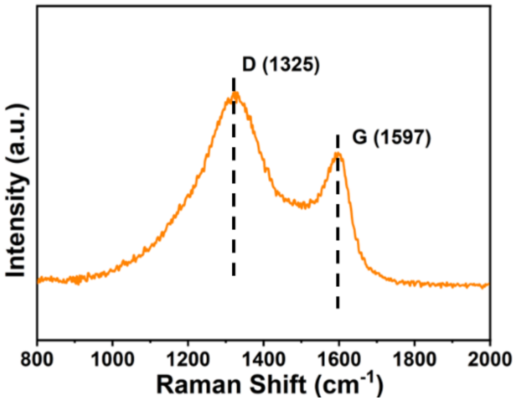

Figure 3. Raman spectrum of bamboo stick-based carbon material.

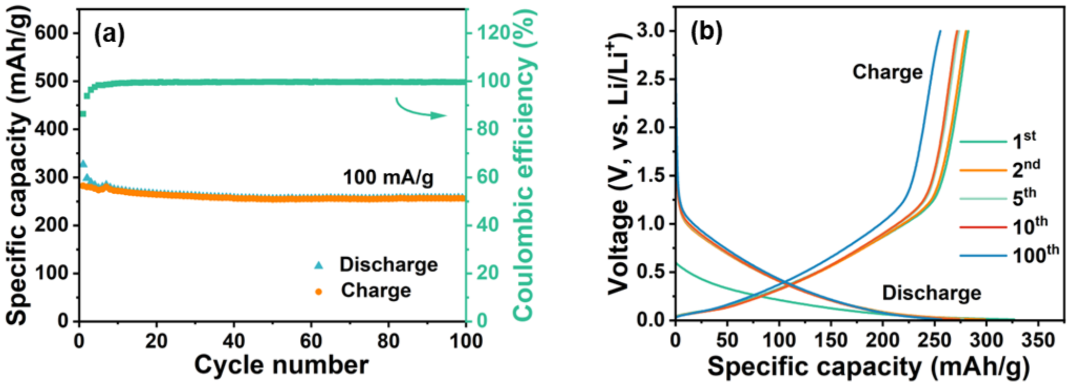

Figure 4. (a) Charge and discharge cycle diagram; (b) charge and discharge curve diagram.

The assembled lithium-ion battery was subjected to constant current charge and discharge tests, and the test results are shown in Figure 4a. At a current density of 100 mA/g, the battery's first charge capacity was 282 mAh/g, the first discharge capacity was 327 mAh/g, and the first coulombic efficiency was 86%. After 100 charge and discharge cycles, the discharge capacity was 256 mAh/g, and the capacity retention rate was 78% compared with the first time. The charge and discharge efficiency during the battery cycle was close to 100%, and the capacity did not fluctuate significantly throughout the process, showing good charge and discharge capacity and excellent cycle stability. Observing the charge and discharge curves (Figure 4b), the discharge process of the waste bamboo stick-based carbon negative electrode material can be divided into two stages when charged and discharged at a low current density of 100 mA/g: in the first stage, the voltage dropped rapidly from 3 V to 1 V and the discharge was small; in the second stage, the voltage dropped from 1 V to 0.01 V. In this stage, the voltage dropped slowly, and the discharge was stable. This is the main discharge platform stage of the battery, corresponding to the reaction of carbon material embedding lithium [15]. After one charge-discharge activation, the charge-discharge curves of the subsequent 2-100 cycles have a high overlap, showing good charge-discharge cycle stability. This proves the good charge-discharge performance of waste bamboo stick-based carbon materials in lithium batteries.

In order to further study the electrochemical reaction process of the electrode, the battery was subjected to a cyclic voltammetry test with a voltage range of 0.01 V to 3 V and a scan rate of 0.2 mV/s. The results are shown in Figure 5. From the figure, it can be seen that the reduction peak (1.1 V) and oxidation peak (0.8 V) during the battery charge and discharge process correspond to its lithium removal and lithium insertion processes, respectively.

After the first cycle of electrochemical activation, the curves of 2-5 cycles almost overlap, indicating that the waste bamboo stick-based carbon material electrode exhibits good electrochemical reversibility and excellent cycle stability. This result is consistent with the charge and discharge cycle results.

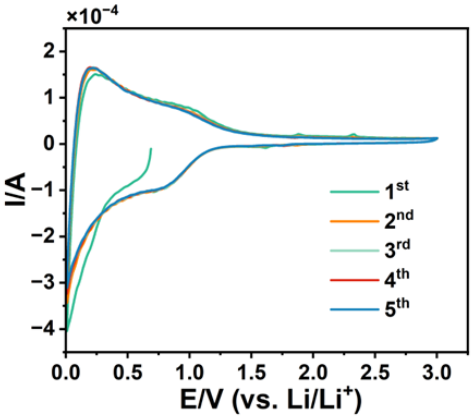

Figure 5. CV cycle diagram of bamboo stick-based carbon material for 5 cycles, with a scan rate of 0.2 mV/s and a voltage range of 0.01-3.0 V.

In order to verify the effect of the conductivity of carbon materials on rate performance, tests were carried out at different current densities (Figure 6a). When the current density was 50 mA/g, the discharge capacity was 376 mAh/g; as the current density gradually increased to 100, 200, 500, 1000 and 2000 mA/g, the discharge capacity was 302 mAh/g, 250 mAh/g, 204 mAh/g, 173 mAh/g and 137 mAh/g, respectively, showing a high discharge capacity. When the current density was restored to 100 mA/g, the discharge capacity returned to a considerable level, showing the good adaptability of the waste bamboo stick-based carbon material electrode to the changing current, indicating that the material has excellent rate performance, cycle stability, and stable reversibility. Under different current density test conditions, the charge and discharge curves of the electrode are shown in Figure 6b. The potential difference of the charge and discharge curves under different current densities is small, indicating that the battery polarization changes little, which also fully demonstrates that the waste bamboo stick-based carbon material electrode has excellent rate performance.

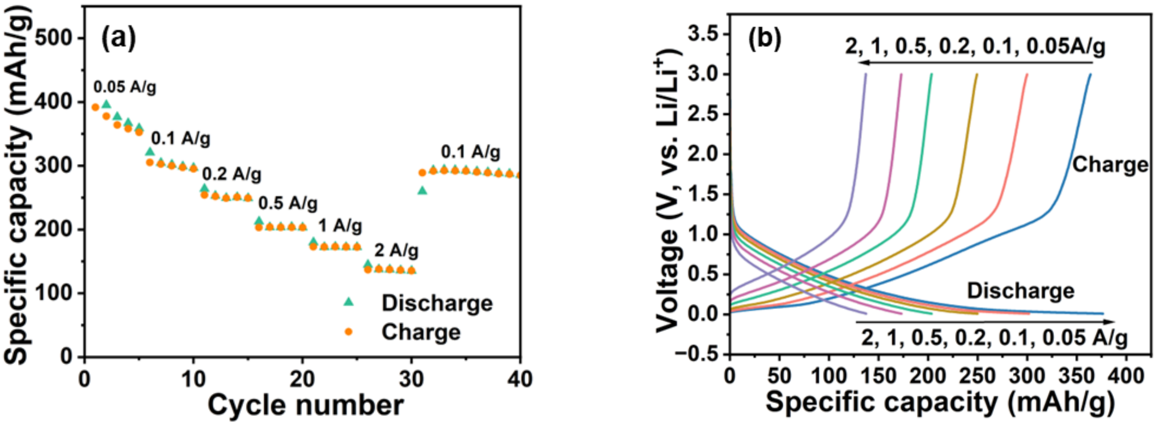

Figure 6. (a) Rate performance test diagram; (b) rate charge and discharge curve of bamboo stick-based carbon material electrode.

The battery assembled with waste bamboo stick-based carbon material electrodes was tested for long cycle life (Figure 7). At a high current density of 1000 mA/g, the battery's first charge capacity was 58 mAh/g, the first discharge capacity was 58 mAh/g, the first coulombic efficiency was close to 100%, and after 200 long charge and discharge cycles, the discharge capacity was 126 mAh/g. The battery capacity of this negative electrode material will gradually increase, which is attributed to the activation process of the lithium-ion battery. With continuous charging and discharging, its battery capacity tends to stabilize and eventually approaches 126 mAh/g, indicating that waste bamboo stick-based carbon materials have excellent long cycle life at high current density. Therefore, carbon-based negative electrode materials prepared with bamboo sticks are expected to become one of the candidates for negative electrode materials for lithium-ion batteries.

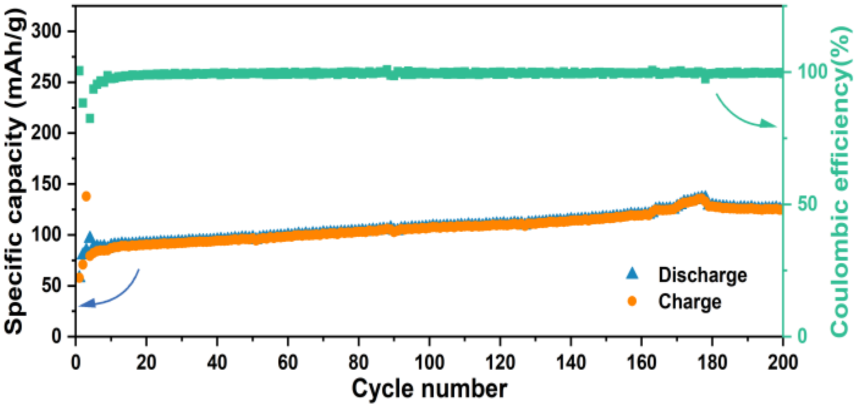

Figure 7. Long cycle test diagram.

As shown in Table 2, the specific capacity of bamboo stick-based carbon negative electrode materials is slightly inferior to that of commercial graphite electrodes. Compared with carbon materials prepared from other waste materials, they are competitive in terms of physical structure, preparation cost, raw material sustainability, and yield.

Table 2. Comparison of electrochemical properties of different materials

Number	Material	Current density (mA/g)	Specific capacity (mAh/g)	References
1	Graphite	100	360	[2]
2	Rice paper	500	565.4	[4]
3	Waste wine lees	100	1200	[10]
4	Waste cigarette butts	100	240	[12]
5	Tea dregs	372	244	[13]
6	Waste tires	117.7	353	[15]
Our work		100	260	

3. Conclusion

In order to solve the harm caused by waste bamboo sticks to the environment, this paper proposes to recycle waste bamboo sticks and prepare them into carbon-based materials for lithium-ion battery negative electrodes through a series of treatments and high-temperature carbonization processes. At a current density of 100 mA/g, the battery's first discharge capacity is 326 mAh/g, and the first coulombic efficiency is 86%. After 100 charge and discharge cycles, the discharge capacity remains at 260 mAh/g, and the capacity retention rate is 78% compared with the first time, showing good battery capacity retention ability. Under high current density charge and discharge, the battery's capacity does not show a significant attenuation, showing good rate performance. The experimental results show that the carbon negative electrode material made from waste bamboo sticks after calcination has potential commercial value. However, it still faces a series of challenges in large-scale production and practical applications. Especially in terms of the stability of raw material supply and quality control. As a kind of biomass resource, bamboo sticks may affect the consistency of the prepared carbon materials due to different categories and sources. The key to solving this problem is to establish a stable raw material supply chain and standardized quality control measures. For further optimization of material performance, we put forward the following suggestions: First, through surface modification, such as introducing nitrogen, phosphorus and other atomic doping to improve the conductivity of the material, or compounding with other high-performance materials (such as silicon, tin-based composite materials), further improve the specific capacity and cycle stability of the bamboo stick carbon negative electrode. Second, in-depth research on the relationship between the microstructure and electrochemical properties of bamboo stick carbon materials, and improve the lithium storage performance of the material by precisely controlling the pore structure and degree of graphitization.

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