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Preparation of straw porous carbon/graphite nanosheet composite and its electrochemical properties

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Straw porous carbon/graphite nanosheet composite (SPCG) was prepared by a hydrothermal method. The structures and morphologies of the material were characterized and analyzed. The surface of SPCG shows a tree-like support structure and a silk-like structure connected with a high specific surface area (1405 m²/g). The lithium storage performances of the material were studied. The first reversible specific capacity is 1136 mAh/g and initial coulomb efficiency is 63.5% at 100 mAh/g, the reversible specific capacity is 246 mAh/g after 200 cycles, which are better than those of straw porous carbon (SPC). The graphite nanosheet in the material can effectively improve the electrochemical performance of porous carbon materials. This study provided an effective way for the resource utilization of agricultural waste straw.

Keywords: agricultural waste straw, porous carbon, graphite nanosheet, lithium-ion batteries, electrochemical performances

1. INTRODUCTION

The utilization rate of agricultural waste straw is extremely low due to untimely treatment or improper disposal, resulting in environmental pollution and resource waste. How to avoid environmental pollution and resource waste caused by improper straw treatment and disposal has attracted extensive attention of researchers [1,2]. The resource utilization of straw has become a hot research topic [3]. Straw porous carbon has attracted widespread attention due to its high specific surface area, high porosity, and excellent electrical conductivity [4-7]. Porous carbon materials derived from agricultural waste not only solve the waste of renewable resources but also provide an inexpensive and easily available anode material for lithium-ion batteries [8].

Lithium-ion batteries are widely used as the power sources for mobile communication devices, portable electronic devices and electrical vehicles, owing to their high energy density, working voltage,

and light weight. The electrochemical performances of lithium-ion batteries are determined by both cathode materials and anode materials [9,10]. Straw porous carbon has a structural characteristics of loose pore structure, micro-mesoporous abundance and large specific surface area, which has attracted widespread attention in the field of energy storage [11,12]. Straw porous carbon as a lithium-ion batteries anode material, it has certain lithium storage properties. However, the electrode material will collapse and stack in the process of Li⁺ embedded and Li⁺ removal due to its low conductivity and low mechanical strength [13]. In addition, the accumulation density of straw porous carbon material is low, the porosity of straw porous carbon material is large, and the electrolyte will be filled into the pores, which is not conducive to improving the energy density of the electrode [14]. Therefore, how to improve the mechanical strength and graphitization degree of straw porous carbon, and control the straw porous carbon structure is the key to improving the performance of electrochemical lithium storage. Graphite nanosheet has a large specific surface area, high theoretical lithium storage capacity, high electrical conductivity, fast electron transmission, and high mechanical strength [15,16]. Therefore, straw porous carbon anode material can be modified by graphite nanosheet. The graphite nanosheet is supported on the surface or in large hole of straw porous carbon, so the mechanical strength of straw porous carbon anode material will be enhanced, which can reduce the collapse and stack of electrode material in the process of Li⁺ embedded and Li⁺ removal. In addition, the graphite nanosheet can provide a channel for the diffusion of lithium ions and electrolytes in the lithium-ion battery to improve the lithium storage performance of straw porous carbon.

2. EXPERIMENTAL

2.1 Preparation of straw porous carbon

The corn straw core was ultrasonic cleaned, dried at 60 °C, then crushed and sieved. A certain amount of corn straw core powder was weighed and pre-carbonized 1 h at 500 °C in a tube furnace under N_2 atmosphere. The heating rate was 5 °C/min. The resulting black powder was ultrasonic cleaned with absolute ethanol and dried to constant weight at 105 °C. The pre-carbonized material and KOH were mixed uniformly in a mass ratio of 1:3 and calcined at 750 °C for 2 h in a tube furnace under N_2 atmosphere. The product was washed with 5% dilute hydrochloric acid for 6 h and then washed with deionized water until neutral to obtain straw porous carbon.

2.2 Preparation of straw porous carbon/graphite nanosheet composite

The graphite nanosheet oxide was synthesized from natural large flakes graphite by the method reported in our previous work [17]. Weighed 0.3 g of straw porous carbon, added to 100 mL of aqueous graphite nanosheet oxide solution (1 mg/mL). After ultrasonic dispersion for 2h, putted them into a reactor and reacted for 12 h at 180 °C. The product was cleaned with deionized water to neutral, dried at 105 °C. Straw porous carbon/graphite nanosheet composite was prepared.

2.3 Sample characterization

The morphologies of the samples were characterized by scanning electron microscopy (SEM, Sigma 300), transmission electron microscopy (TEM, FEI TECNAI G2 F20). The structures of the samples were characterized by X-ray diffractometer (XRD, Bruker D8 Advance), X-ray electron spectrometer (XPS, Ultra DLD), Raman scattering spectra (Raman, Thermo Fischer DXR) and Fourier infrared spectroscopy (FTIR-8400s). The specific surface area and pore size distribution of samples were characterized by Surface Area and Microporous Analyzer (BSD, BSD-PM1/2).

2.4 Electrochemical measurements

The electrochemical measurements were carried out using CR2025 coin-type cells. The working electrode was prepared by the method reported in our previous work, which was coating slurry consisting of active material, PVDF (polyvinylidene fluoride) and acetylene black with a weight ratio of 80:10:10 in NMP (N-methyl-pyrrolidone) solvent [18].

3. RESULTS AND DISCUSSION

3.1 Microstructural characterization

Fig.1 is SEM images of samples. Fig.1 (a) is a cross-section SEM image of graphite nanosheet oxide (GO), and carbon nanosheets are stacked on top of each other to form graphite nanosheet oxide. Fig.1 (b) is graphite nanosheet after ultrasonic dispersion, the graphite nanosheet after ultrasound looks like transparent gauzes. Fig.1 (c) is SEM image of SPC, the pore structure of SPC is abundant, forming a large number of pores. Fig.1 (d) is SEM image of SPCG, it can be seen that the surface of SPCG is rough, the layers are thinned, forming a lot of cross-linked structures, and the structure presents tree-like supports, in addition to some filamentous hooks. The graphite nanosheet is supported on the surface or in large hole of straw porous carbon. Compared with the morphology of SPC, the number of large holes on the surface of SPCG is reduced, and the surface is mostly wrinkled, which may be due to the graphite nanosheet loading in the porous carbon material, filling the large pores, so that the surface large holes are reduced. The reduction of large holes will not reduce the reversible specific capacity of the material, but will provide more active sites for Li⁺ attachment, which can accelerate the transmission speed of Li⁺ and electrons [19]. In addition, the mechanical strength of SPCG can be enhanced due to graphite nanosheet and SPC support each other, which reduce the collapse and stack of electrode material in the process of Li⁺ embedded and Li⁺ removal.



Figure 1. SEM images of samples: (a) Graphite nanosheet section, (b) Graphite nanosheet after ultrasonic dispersion, (c) SPC and (d) SPCG.

Fig.2 shows the XRD patterns of GO, SPC and SPCG. From Figure 3-2, it can be seen that GO has a characteristic diffraction peak (001) near 11.5°, and the diffraction peak intensity is high. SPCG has a (002) crystal plane and a (100) crystal plane of graphite carbon material, corresponding to 22° and 44°, respectively. The diffraction characteristic peak strength and width of the (002) crystal surface of SPCG increase, which indicates that the crystallinity of SPCG has increased compared with SPC, the grain has become larger, and the diffraction peak of SPCG at a small angle is very strong, indicating that it has good graphitization degree [20].



Figure 2. XRD patterns of GO, SPC and SPCG

Fig.3 shows the Raman spectra of SPC and SPCG. As can be seen from Raman spectra, SPC and SPCG have typical Raman spectrogram peaks D and G peaks at wavelengths of 1354 cm⁻¹ and 1586 cm⁻¹. By calculation, the ratio of I_D/I_G of SPCG is 0.0.82, and the ratio of I_D/I_G of SPC is 0.93, indicating that it is consistent with the XRD result. Due to the addition of graphite nanosheet, the degree of graphitization of SPCG decreases, and the crystallinity rises.



Figure 3. Raman spectra of SPC and SPCG



Figure 4. FTIR spectra of GO, SPC and SPCG

Fig. 4 shows the FTIR spectra of GO, SPC, and SPCG. Graphite oxide exhibits characteristic peaks at around 1731 cm⁻¹ (C=O stretching vibrations from carbonyl and carboxylic groups), 1655 cm⁻¹ (C=C skeletal vibrations), 1404 cm⁻¹ (O–H deformation vibrations), 1226 and 1053 cm⁻¹ (C-O stretching

vibrations) [21,22]. Additionally, the broad peak at 3417 cm⁻¹ is attributed to O-H stretching vibrations of adsorbed water molecules and structural -OH groups [23]. For the SPCG, the expansion vibration peak of C=C increased significantly, the expansion and contraction vibration peak of C=O disappeared, which is consistent with the XRD result. Graphite oxide is reduced to graphite nanosheets.

In order to further verify the elemental components in the sample and their atomic valence states, XPS characterization analysis of the sample was performed. Fig.5 shows the spectral analysis of C, O and N elements in SPCG. As can be seen from Fig.5 (a), C and O elements are present in the sample, and the O elements are reduced from 16.46% of SPC to 15.61%, which is considered to be the redox reaction of GO in the hydrothermal process. The C/O value (5.37) is significantly increased. In the ternary organic electrolyte system, the higher C/O value can improve the hydrophobic characteristics of the material. From Fig.5 (b), the four peaks of C1s in SPCG correspond to the C-C (284.6 eV), C-O (286.8 eV), C=O (287.3 eV) and O-C=O (289.7 eV) structures, respectively. As can be seen from Fig.5 (c), the O1s spectrogram of SPCG has 4 O=R1, O=R2, C-O-C, and C=O functional groups at 529.8 eV, 531.1 eV, 532.5 eV, and 532.9 eV, respectively. From Fig.5 (d), the N1s spectrum of SPCG is not obvious because there is no N element in the sample. The addition of graphite nanosheet did not change the element type, but it had an impact on the content of each element. The reduction of oxygen content enhances the infiltration of the material in the organic electrolyte, and increases the effective contact area between the electrolyte ions and the material.

Description of sample	Name	Peak BE	FWHM eV	Area (P) CPS.eV	Atomic%
SPCG	C1s	281.98	3.28	244339.06	83.9
	O1s	529.61	3.9	109909.26	15.61
	N1s	397.74	-0.02	2211.35	0.49

Table 1. Energy spectrum analysis of C, O and N elements in SPCG

The nitrogen uptake and desorption curve of SPCG is shown in Fig.6. The curve is characterized by an ISOthermal type IV and an H4 between the adsorption and desorption curves, indicating that the micropores in the main SPCG are abundant. It can be calculated that the SSA of SPCG is 1405 m²/g, the total pore volume is 0.77 cm³/g, and the average pore diameter is 2.19 mm. Fig.7 is a pore size distribution of SPCG. From Fig.7, it can be seen that the pore size distribution of SPCG is concentrated between 1 and 3 nm. It is mainly micromesoporous. Compared with SPC, SPCG has a decrease in SSA, a decrease in TPV, and a decrease in the average pore size, which may be due to the action of π - π electrons in graphite nanosheet, resulting in agglomeration, reducing the specific surface area.



Figure 5. XPS spectra of (a) SPCG full spectra, (b) C1s spectra, (c) O1s spectra and (d) N1s spectra



Figure 6. SPCG plots of N₂ adsorption-desorption isotherms



Figure 7. SPCG plots of pore size distribution

3.2 Electrochemical performances

The electrochemical performances of SPC and SPCG at a current density of 100 mAh/g are shown in Fig.8. The first charge-discharge specific capacity of SPCG is 1136 mAh/g and 1962 mAh/g, respectively, which are much higher than SPC. During the first charge and discharge, a large loss of capacity is caused due to the generation of SEI membranes. After 100 cycles, its reversible specific capacity is 266 mAh/g, and its reversible specific capacity is maintained at 246 mAh/g after 200 cycles. The reversible specific capacity retention rate from the 100th charge and discharge to the 200th charge and discharge is 92.48%.



Figure 8. Charge-discharge curves of samples: (a) Charge-discharge curves of SPC and SPCG in the first cycle and second cycle, (b) Charge-discharge curves of SPCG

Fig.9 is the cyclic performances of SPC and SPCG. Although SPC has a large specific surface

area, because of the lack of graphite nanosheet support, SPC appears to collapse and stack collapse and stack in the process of lithium embedded and lithium removal. Therefore, its reversible specific capacity is reduced 144 mAh/g after 200 cycles. The reversible specific capacity of SPCG is maintained at 246 mAh/g after 200 cycles. The SPCG electrode material exhibits much better electrochemical lithium storage performance than the similar electrode materials [24-26]. The cyclic performance of SPCG was improved due to the addition of graphite nanosheet. In addition, the loss of irreversible capacity is reduced due to the mechanical strength of graphite nanosheet oxide. At the same time, graphite nanosheet and straw porous carbon play a synergistic role, which effectively prevents the collapse of electrode material and improves the cycle efficiency of SPCG.



Figure 9. Cycle performance of sample SPC and SPCG

Fig.10 is the coulomb efficiency of SPC and SPCG, it can be seen that the initial coulomb efficiency of SPCG is 63.5%, and the coulomb efficiency of SPCG is more than 90% in the second cycle. The charge and discharge of SPCG gradually tends to be stable, which is consistent with the performance of charge and discharge curve. The preparation of straw porous carbon material supported by graphite nanosheet skeleton can improve the specific capacity and coulomb efficiency of straw porous carbon.



Figure 10. Coulombic efficiency of SPC and SPCG

4. CONCLUSIONS

In this paper, straw porous carbon/graphite nanosheet composite was prepared by a hydrothermal method. Straw porous carbon/graphite nanosheet composite has good pore structure with a specific surface area of 1405 m²/g, a total pore volume of 0.77 cm^3 /g, and an average pore diameter of 2.19 mm. As an anode material of lithium-ion batteries, straw porous carbon/graphite nanosheet composite has good electrochemical performance. The first charge-discharge specific capacity is 1136 and 1962 mAh/g, and initial coulomb efficiency is 63.5%. The reversible specific capacity is 266 mAh/g after 100 cycles, and remains at 246 mAh/g after 200 cycles. The improvement of SPCG electrochemical lithium storage performance is due to unique tree-like support structure and the electrical conductivity of graphite nanosheet. In the process of Li⁺ embedded and Li⁺ removal, graphite nanosheet plays a supporting and reinforcing role in the straw porous carbon, and effectively prevents the collapse of the porous carbon electrode material of the straw during the charge and discharge process.

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