



High capacity hard carbon derived from lotus stem as anode for sodium ion batteries



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HIGHLIGHTS

- Hard carbons were derived from lotus stems with naturally hierarchical structures.
- The obtained hard carbons exhibit excellent sodium storage performance.
- The excellent performance is closely related to the large closed pore ratio.

ARTICLE INFO

Keywords:

Biomass
Hard carbon
Closed pore ratio
Anode
Sodium ion batteries

ABSTRACT

Porous hard carbons are synthesized via carbonizing lotus stems with naturally hierarchical structures. The hard carbon carbonized at 1400 °C (LS1400) delivers a total capacity 350 mAh g⁻¹ in the current density of 100 mA g⁻¹ and a plateau capacity of 250 mAh g⁻¹. Even cycled at 100 mA g⁻¹ after 450 cycles, the capacity still retains 94%. Further investigation shows that the sodium storage of LS carbons involves Na⁺ adsorption in the defect sites, Na⁺ insertion and Na metal deposition in the closed pores. However, the Na metal deposition in closed pores mainly contribute to the plateau capacity, leading to the excellent sodium storage performance of LS1400 with a large closed pore ratio of 66%. The results show that the intrinsic structure of natural biomass can inspire us to design hard carbon with large closed pore ratio as excellent anode for sodium ion batteries.

1. Introduction

Sodium ion batteries (SIBs) have recently shown great potential in the applications of large scale energy storage due to the abundant Na resource, low cost and similar electrochemistry to lithium ion batteries (LIBs) [1–3]. However, the research on the electrode materials for SIBs is still sluggish because of the large Na⁺ radius, which may result in the large volume change, slow ion diffusion and structure collapse during cycling. Till now, many materials have been explored as anode in SIBs, such as oxides [4–6], metal/alloying metal [7], organic materials [8–11], and non-metal substance [12–17]. These materials usually exhibit high redox potential and poor cycling performance.

Hard carbon is a dominant anode material for SIBs because of its considerable capacity (200–300 mAh g⁻¹) and low operating potential

(below 0.1 V vs. Na/Na⁺) [18]. It is generally supposed that hard carbon can accommodate Na⁺ via surface adsorption in the defect sites, Na⁺ insertion into graphitic layers and deposition of Na clusters in microvoid [19,20]. The electrochemical performance of hard carbon is closely related to the microstructures, such as heteroatoms doping, pore size distribution and graphitization degree.

Recently, natural biomass derived carbons have attracted great attentions due to their intrinsic characteristic of naturally hierarchical structures. Zhang et al. synthesized the hard carbon using switchgrass as a biomass example [21]. The carbon materials obtained at 2050 °C intrinsically inherit its three-dimensional porous hierarchical architecture and exhibit a reversible capacity of 210 mAh g⁻¹ with initial coulombic efficiency of 64%. Additionally, Liu et al. reported a hard carbon material derived from corn cobs, which can deliver a reversible

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capacity of 275 mAh g⁻¹ at a current rate of 0.2 C after 100 cycles [22]. Till now, a variety of hard carbons have been synthesized from biomass such as banana peel [23], apple peel [24], cotton [25], orange peel [26], pomelo peels [27] and wood [28].

Lotus stem is an abundant and reproducible raw material. The lotus stem in nature intrinsically consists of macroporous vascular bundles in the longitudinal dimensions, which can transport water and mineral nutrients from roots upward. Such macroscopic structure makes lotus stem an ideal precursor to produce three-dimensional (3D) porous carbon material with excellent electrochemical properties. In this work, the lotus stem (LS) was carbonized at different temperature to synthesize the hard carbon as anode for SIBs. The obtained LS carbons exhibit high plateau capacity, excellent rate capability and cycling performance, showing great potential as anode in SIBs. The effects of closed pores on the electrochemical performance are discussed for the first time.

2. Experimental

2.1. Materials synthesis

The fresh lotus stems were cut into pieces and dried at 100 °C for 24 h. The dried LS pieces were then carbonized at 1200, 1400 and 1600 °C in Ar atmosphere. The carbonized products were washed by HF solution and deionized water to remove impurities and then dried at 80 °C for 12 h. The finally obtained carbon materials were denoted as LS1200, LS1400 and LS1600, and their physical parameters are summarized in Table 1. The detailed experimental procedure is displayed in Fig. S1.

2.2. Materials characterization

The structure and morphology were characterized with X-ray diffractometer (XRD, PANalytical B.V., Holland), field-emission scanning electron microscope (FE-SEM, SIRION200) and transmission electron microscope (TEM, JEOL 2100F). Raman spectra were obtained on a Lab RAM HR 800 (Horiba Jobin Yvon). X-ray photoelectron spectroscopy (XPS) was performed on a VG Multi-Lab 2000 system (Germany) with a monochromatic Al K X-ray source (ThermoVG Scientific). Nitrogen adsorption and desorption isotherms were conducted at 77 K on a Micromeritics ASAP 2020 analyzer. The true density is measured by He pycnometry.

2.3. Electrochemical measurements

The working electrode was prepared by casting a slurry containing 90 wt% active materials and 10 wt% PVDF binder onto a copper foil, and vacuum dried at 80 °C for 12 h. The solvent is N-methyl-2-pyrrolidone (NMP). The average mass loading was ~ 1.0 mg cm⁻². The coin cells were assembled in an argon-filled glovebox with water and oxygen content lower than 1 ppm. Sodium foil with thickness of around 1 mm was used as counter electrode. The separator and electrolyte were glass

fiber from Whatman and 1 mol L⁻¹ NaClO₄ in a mixed solvent of ethylene carbonate (EC) and diethyl carbonate (DEC) (v/v = 1:1), respectively. The charge and discharge were conducted on a battery testing system Land CT2001 battery tester (Wuhan Land Electronic Co. Ltd., China) in a range of 0.01–2 V (vs. Na⁺/Na). Cyclic voltammetry (CV) was conducted on an electrochemical workstation (CHI760E, China) between 0 and 3 V (Na⁺/Na) at a scan rate of 0.1 mV s⁻¹. Electrochemical impedance spectra (EIS) was obtained on a PARSTAT 2273 potentiostat with the frequency ranged from 0.01 Hz to 100 kHz and an amplitude of 5 mV.

3. Result and discussion

Fig. 1 shows the SEM and TEM images of LS carbons. Obviously, the parallel channel array structure in the longitudinal dimensions of LS is well maintained after thermal treatment up to 1600 °C (Fig. 1a–c). This structure is beneficial for the electrolyte infiltration and Na⁺ ions diffusion. However, the thickness of tube walls decreases with the increasing carbonization temperature, which can be ascribed to the graphitization and removal of heteroatoms. The structure shrinkage of LS carbons also leads to the increasing true density (Table 1). HRTEM images reveal a significant improvement of local structure ordering with the elevation of carbonization temperature. In LS1200, only turbostratic graphitic structure can be observed, matching the typical “house of cards” model [18] (Fig. 1d). However, the short range ordering structure can be clearly detected in LS1400 and LS1600, indicating the improved graphitization degree (Fig. 1e and f). The sharpness of dispersing diffraction rings in selected-area electron diffraction (SAED) patterns also increases with the increasing carbonization temperature, further confirming the improvement of local structure ordering degree.

The microstructures of LS carbons are further analyzed by XRD (Fig. 2a). Two broad peaks can be observed at around 25° and 45° in the XRD patterns, corresponding to the crystallographic planes of (002) and (100), respectively. With the increasing carbonization temperature, the peak intensity increases accordingly due to the improvement of structure ordering. Meanwhile, the (002) peak gradually shift to larger angles with the elevation of temperature. The d₀₀₂ spaces of LS1200, LS1400 and LS1600 are calculated to be 3.69, 3.68 and 3.61 Å based on Bragg equation, respectively.

Fig. 2b shows the Raman spectra of LSs carbons. All LS carbons show two characteristic peaks at around 1324 and 1590 cm⁻¹, corresponding to the disordered carbon band and the graphitic band, respectively. The L_a calculated from the I_D/I_G ratio slightly decreases with the elevation of temperatures (Table 1), indicating the decrease of graphite microcrystals in the direction of (100). This result accords with the previous reports [25,29].

Fig. 2c and d displays the N₂ adsorption/desorption isotherm and the derived pore size distribution of LS carbons. The specific surface area of LS carbons decreases with the elevation of carbonization temperature. All the LS carbons show a relatively low specific surface area of 25.81, 24.37 and 23.73 m² g⁻¹ for LS1200, LS1400 and LS1600,

Table 1
Physical parameters of LS products.

Samples	D ₀₀₂ (Å)	L _c (nm)	L _a (nm)	S _{BET} (m ² g ⁻¹)	ρ _{true} ^a (g cm ⁻³)	ρ _{trueABM} ^b (g m ⁻³)	R _{closed pores} ^c (g m ⁻³)	Pore volume (cm ³ g ⁻¹)
LS1200	3.69	0.76	15.95	25.81	1.65	2.65	37.7%	0.0102
LS1400	3.68	0.79	14.35	24.37	2.26	6.73	66.4%	0.0088
LS1600	3.61	1.46	13.19	23.73	2.29	4.00	42.7%	0.0083

The ratio of closed pores is calculated by the following equation.
The ratio of closed pores = $\frac{(\text{True density after ball-milling}) - \text{True density}}{\text{True density after ball-mixing}}$

^a ρ_{true}: true density.

^b ρ_{trueABM}: true density after ball-milling for 30 min.

^c R_{closed pores}: the ratio of closed pores.

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