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High-yield humic acid-based hard carbons as promising anode materials for sodium-ion batteries

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ABSTRACT

A low-cost and sustainable anode material is essential for the future commercialization of sodium-ion batteries (SIBs). Among all proposed anode materials for SIBs, hard carbons are considered to hold the most promise. However, high cost and low carbon yield of precursors limit its industrialization process. Here the synthesis of a biomass-derived hard carbon from leonardite humic acid (LHA) through a facile process was reported. The obtained hard carbons with an amazing high carbon yield of 60.73% were evaluated as anode for SIBs. The LHA-based hard carbons exhibit a promising anode performance with a sodium storage capacity of 345 mAh g^{-1}, an initial coulombic efficiency up to 73% and superior cyclic stability. Combined with the facile synthesis process and abundant resource, the LHA-based hard carbons may hold a promising future as anode materials for SIBs.

1. Introduction

Because of the advantages of high reversible capacity and good cyclic stability, lithium-ion batteries (LIBs) have been the most widely applied power for portable electronics and electric vehicles [1–3]. However, with the ever-growing application of LIBs, the cost and continued availability of lithium have raised increasing concern [4]. Another secondary battery, sodium-ion batteries (SIBs), have been considering as alternatives to LIBs in view of the abundance of sodium sources [5–8].

Although sodium has similar intercalation chemistry as lithium, different ionic radius makes it challenging to design a suitable host material for SIBs like graphite for LIBs [9–11]. Much effort has been made to fabricate appropriate anode materials for SIBs, such as numerous carbonaceous materials [12–16], alloys [17–21], oxides [22,23] and phosphorus [24,25]. Unfortunately, there are still some drawbacks including low capacity, poor cycle life or high volume expansion caused by the Na insertion/extraction, limiting their industrialization. Among various anode materials for SIBs, hard carbons hold the most promise considering their high reversible capacity, low operating voltage and excellent cycle stability [10,15,26–29]. Nevertheless, high cost caused by the price and low carbon yield of precursors, to a great degree, hinders the industrialized process of hard carbons.

Owing to the low cost and environmentally friendly characteristics, various biomass materials have been adopted as precursors for carbon materials that are used in energy storage field [30,31]. Some of them, such as cotton [5], banana peels [6], grass [32], lignin [33,34], leaf [35] and peat moss [36], have been adopted as precursors for hard carbons. Among various biomass materials, humic acids (HAs) are potential candidates for hard carbon anode materials considering their carbon-rich characteristic (more than 40 wt %) and abundance. As the principal composition of humic substances, humic acids exist widely in soil, coal, peat and et al. [37]. Typically, HAs are described as tricky mixture of organic species and polymers with molecular weights varying from 10^3 to 10^6 g mol^{-1}, though the precise molecular formula of HAs is still under debate [38]. Given their biological and carbon-enriched characteristics, HAs have been used to prepare chemically modified electrodes [39–41] and activated carbons for supercapacitor [38,42,43], but there are few study of hard carbons directly made from HAs [44]. In our previous work [14], carbon nanofibers from composites of humic acids and PAN were prepared by electrospun for SIBs anode materials, but the synthetic technology is too complex to realize the large-scale commercialization.

Herein, we report an economical and efficient route to fabricate hard carbons by utilizing leonardite humic acid (LHA). Compared

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with other HAs, LHA has higher thermal stability and chemical stability because of its higher aromaticity and larger molecular weight. The as-prepared hard carbons present a promising anode performance with high reversible capacity as well as excellent cycle stability. Effects of the pyrolysis temperature on the microstructure and electrochemical properties of the LHA samples was investigated. This work should contribute to better understand the mechanism of sodium storage in hard carbons and probably provide good chance to deeply explore the leonardite resources.

2. Experimental

2.1. Materials synthesis

LHA based-hard carbons were simply fabricated by one-step pyrolysis of LHA (Tianjin guangfu chemical Co., Ltd). Firstly, a purification process containing alkali dissolution and acid precipitation was conducted to remove the salts and ash in LHA. The refined LHA was then carbonized at different temperature (900 °C, 1100 °C, 1300 °C, 1500 °C and 1600 °C) in a tube furnace under inert atmosphere. The finally hard carbon samples were donated as LHA-900, LHA-1100, LHA-1300, LHA-1500 and LHA-1600.

2.2. Materials characterization

Elemental analysis was conducted on Galbraith Laboratories. Thermogravimetric analysis (TGA) was obtained by a TA-50 instrument from room temperature to 1000 °C at 5 °C min^{-1} under a nitrogen atmosphere. The morphology and texture characteristics were performed on a scanning electron microscope (SEM, Hitachi S-4800). Transmission electron microscopy (TEM) characterization was taken on a FEI Tecnai F20 microscope. X-ray diffraction (XRD) (Rigaku D/Max 2500) on CuK$_\alpha$ radiation ($\lambda = 1.54056$ Å) and Raman spectra (Renishaw MKI-2000) were carried out to investigate the microstructure of the samples. The X-ray photoelectron spectroscopy (XPS) was obtained by a PHI-1600ESCA equipment (America PE Company) on a spectrometer with a high performance Al monochromatic source. Nitrogen adsorption measurements were done on a Tristar 3000 analyzer.

2.3. Electrochemical measurements

The electrochemical measurements of the LHA samples were conducted by assembling CR-2032-type coin cells. The working electrodes were fabricated by coating the mixture of active material, carbon black and polyvinylidene fluoride (PVDF) in N-methypyrrolidine (NMP) (8:1:1 wt %) onto a copper foil current collector and then dried at 85 °C for 10 h in a vacuum oven. The electrolyte was 1 M NaClO$_4$ which dissolved in a mixture of ethylene carbonate (EC) and diethyl carbonate (DEC) (1:1 v/v) and the separator is glass fiber. The fabrication of the coin cells was conducted under argon atmosphere in a glove box. Cyclic voltammetry (CV) and electrochemical impedance spectroscopy (EIS) tests were conducted on CHI660E electrochemical measurement system. The scan rate is 0.1 mV s^{-1} with a voltage range of 0.0–2.5 V. EIS tests were conducted in the frequency range of 100 kHz to 0.01 Hz. The charge and discharge tests were performed by a LAND CT2001A battery-testing instrument in the potential range of 0.001–2.5 V.

3. Results and discussion

Table 1 shows the chemical element composition of LHA. The high carbon content (66.2 wt %) indicates its carbon rich nature. It also can be seen that LHA possesses high O elements with little H, N and S elements. XPS was conducted to further confirm the surface chemistry of LHA, which are shown in Fig. 1a–c. There are two obvious peaks at ~285 eV (C1s) and ~533 eV (O1s) in the XPS spectra, indicating that C and O are the dominant elements in LHA. After deconvolution, there are three types of carbon species shown in C$_{1s}$ spectrum: C–C (284.4 eV, 46.37%), C–O (285.1 eV, 16.66%) and O–C=O (288.7 eV, 10.71%). The O$_{1s}$ is decomposed into peaks located at 531.1, 532.1 and 533.1 eV, which corresponds to C=O (30.46%), C–O (21.39%) and O–C=O (48.15%). Thermo-gravimetric analysis (TGA) (Fig. 1d) shows that the carbon yield is 60.73 wt %. We compared the carbon yield of different carbon precursors at 1000 °C as summered in Table 2. The results indicate that the LHA sample has the highest carbon yield. The element analysis combined XPS and TGA analysis demonstrates LHA an excellent carbon precursor for hard carbon.

Table 1
Element composition of the carbon precursor.

Sample	Element analysis (wt %)					Ash (wt %)[b]	Surface atom analysis (at. %)			
	C	H	N	O[a]	S		C	O	N	S
LHA	66.5	4.0	0.6	28.6	0.3	2.09	78.6	19.6	1.4	0.4

[a] Oxygen tested by difference.

[b] The ash was obtained by heating at 1000 °C for 2 h in air.

After carbonization, the morphology and texture of the LHA-based hard carbons are shown in Fig. 2. They were found to present irregular granular morphology with a size distribution varying from 2 μm to 5 μm. The porosity structure of the LHA samples was measured by nitrogen adsorption/desorption and the surface area was calculated by the Brunauere Emmette Teller (BET) equation. As shown in Table 3, all the LHA samples have a low BET surface area (below 10 m^2 g^{-1}), especially the LHA-1100 sample. XPS spectra shown in Fig. S1 manifests that there are few heteroatoms in the LHA samples after high temperature treatment. As shown in Table S1, the carbon content increases from 92 at. % at 900 °C to 97.2 at. % at 1600 °C while the oxygen content decreases from 6.9 at. % to 2.6 at %. There is a little nitrogen on the surface, which may be beneficial to the electrical conductivity and capacity of LHA samples [6].

XRD and Raman spectroscopy were conducted to investigate various microstructures of the LHA samples. As shown in Fig. 3a, it can be observed that all samples have two broad peaks around 24° (the 002 bond) and 43° (the 100 bond), which confirm their amorphous nature. With the pyrolysis temperature increasing, the (002) bond is found to shift to higher angle and become narrow, implying a decrease of d_{002} and an increase of L_c because of the structure arrangement from disordering to short-range ordering. The d_{002} interlayer distance (shown in Table 3) of the LHA samples is 3.99 nm, 3.90 nm, 3.72 nm, 3.68 nm and 3.62 nm, respectively, which are larger than that of graphite. Such larger interlayer space would be conducive to the insertion and extraction of Na$^+$ and thus improve the sodium storage behavior. Raman spectroscopy patterns of the LHA samples, as shown in Fig. 3a, present two peaks at about 1350 cm^{-1} and about 1580 cm^{-1}, which correspond to the D-band (the defect-induced mode) and the G-band (the crystalline graphite band). The half width decreased obviously with the carbonization temperature increasing, which means the improvement of order degree of local carbon layer [12]. Raman spectrum was deconvoluted into four Lorentzian peaks, which are shown Fig S2. The integral intensity ratio, I_G/I_D, is 0.6 for LHA-900, 0.62 for LHA-1100, 0.66 for LHA-1300, 0.89 for LHA-1500 and 0.92 for LHA-1600, respectively. The increasing I_G/I_D value indicates that the defects decreases with increasing annealing temperature and the orientation of the samples becomes better.

The microstructure of the LHA materials was further characterized by HRTEM (as shown in Fig. 4). As expected for hard carbon,