Carbon 126 (2018) 85–92

Contents lists available at ScienceDirect

Carbon

journal homepage: www.elsevier.com/locate/carbon

Ultrahigh level nitrogen/sulfur co-doped carbon as high performance anode materials for lithium-ion batteries

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ARTICLE INFO

Article history:
Received 27 July 2017
Received in revised form
24 September 2017
Accepted 28 September 2017
Available online 29 September 2017

Keywords:
Electrode materials
Co-doping
Porous carbon
Anode
Lithium

ABSTRACT

Ultrahigh level nitrogen and sulfur co-doped disordered porous carbon (NSDPC) was facilely synthesized and applied as anode materials for lithium-ion batteries (LIBs). Benefiting from high nitrogen (14.0 wt%) and sulfur (21.1 wt%) doping, electrode fabricated from $NS_{1/3}$ showed a high reversible capacity of 1188 mA h g^{-1} at 0.1 A g^{-1} in the first cycle with a high initial columbic efficiency (>75%). In addition, prolonged life over 500 cycles and excellent rate capability of 463 mA h g^{-1} at 5 A g^{-1} have been realized. The preeminent electrochemical performance is attributed to three effects: (1) the high level of sulfur and nitrogen; (2) the synergic effect of dual-doping heteroatoms in cooperation with each other; (3) the large quantity of edge defects and abundant micropores and mesopores that can provide extra Li storage regions. These unique features of NSDPC electrodes suggest that they can serve as a practical substitute for graphite as a high performance anode material in LIBs.

1. Introduction

With the rapid development of portable devices, renewable energy harvesting, and electric vehicles [1,2], safe energy storage devices with improved power and energy densities are becoming increasingly important [3]. Among these devices, lithium-ion batteries (LIBs) are promising choices for their high energy density and power density, additionally with long lifespans [4]. However, application of LIBs in large-scale electric energy storage requires further improvements in energy density, rate capability, safety, and electrode durability. To a large extent, these issues rely on several determinants. One of them is the development of novel anode materials. Graphite is the main commercial anode material used in currently available LIBs. But the low theoretical specific capacity of 372 mA h g^{-1} cannot meet the increasing demands of rapidly developing markets [5]. Therefore, it's urgently to develop new anode materials with high theoretical capacities and excellent rate and cycling performance for the next-generation LIBs.

Various nanostructured products containing Si [6–8], P [9], or Sn [10–12], as well as alloy [13,14] and some transition metal oxides/sulfide [15–23], have been reported as high capacity anode materials for LIBs. Unfortunately, intrinsic problems such as huge volume expansion, relatively low conductivity, and large voltage hysteresis, exist in these materials during the lithiation process [24]. These deficiencies severely limit their commercialization in LIBs. Therefore, novel carbon-based anode materials, with enhanced electrochemical performance for lithium storage, are still a major focus of research worldwide [25]. Applied them as anode materials, high energy LIBs with elevated specific capacity, excellent cycling stability and rate performance have been realized. Significant efforts have been made to design novel nanostructures of carbonaceous materials with larger specific capacity for lithium storage [25–27]. However, for amorphous carbon materials, although activating agents (such as KOH) has been applied to increase the specific surface area, inferior stability and poor rate performance still occur due to the low degree of graphitization [28]. Therefore, a novel strategy of artificial doping with heteroatoms, such as N [26], B [29] or S [30], have being proposed. With this method, the electronic properties and electrochemical activity of amorphous carbon materials can be effectively improved, leading to excellent Li ion storage capacity. Nevertheless, most reported results related to this field are based on the single element doping but co-doping and their synergistic influence to the

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https://doi.org/10.1016/j.carbon.2017.09.100

electrochemical property is less studied.

Although nitrogen doped carbon-based materials have been extensively studied, sulfur and especially nitrogen/sulfur dual-doping are far less exhaustive [31]. When doped with nitrogen the electronic properties of carbon-based materials can be improved [32]. As a complement to nitrogen, sulfur doping has attracted increasing attention in recent carbon materials research. While sulfur has a larger atomic radius, it can enlarged the interlayer spacing (d_{002}) of the carbon matrix [31]. The doped sulfur substantially increases the charge capacity with the enlarged graphite crystallite size (Lc) and creates more micropores, improving the electrochemical properties of the carbon [30]. Meanwhile, its easily polarizable lone pairs can change the charge state of neighboring carbon atoms. Hence, it can be used to tune chemical reactivity and catalytic activity of the carbon materials. Therefore, as a doping heteroatom, sulfur can be incorporated into carbon-based anode materials, improving their reversible capacity in LIBs [33]. Importantly, when both highly interactive elements of nitrogen and sulfur are simultaneously doped into the carbon matrix, synergistic effects can be aroused [34]. In addition, it has been reported that the binding state of sulfur and nitrogen in the carbon matrix can be tuned when different sulfur and nitrogen sources were used [31]. Most studies property on sulfur/nitrogen dual-doped carbon materials is about their enhanced electrocatalyst ability [31,35]. Few reports focus on dual-doped carbons for LIBs. Therefore, we were inspired to investigate the favorable influences of dual-doped heteroatoms in LIBs systems.

Herein, we applied a “dual-doping” strategy to synthesize an amorphous porous carbon with nitrogen and sulfur at an ultrahigh doping level. In this way, the synergistic effects of heteroatom co-doping and a disordered porous structure has been achieved. The nitrogen and sulfur co-doped disordered porous carbon (NSDPC) was employed as a preeminent anode material for high-performance LIBs. By a facile synthesis method, an amorphous porous structure was formed. In the sample of $NS_{1/3}$, micropores and mesopores were homogenously embedded with a nitrogen content of 14.0 wt% and a sulfur content of 21.1 wt%. Benefitting from the convenient transport pathway for Li-ions and electron, as well as the abundant pores for extra Li storage in the carbon framework, the $NS_{1/3}$ electrode exhibits excellent rate performance with superior cycling stability. The reversible specific capacity achieved as high as 1188 mA h g^{-1} at a current density of 0.1 A g^{-1}, and even after increasing the rate to 5 A g^{-1} high capacity of 463 mA h g^{-1} can still be obtained, the capacity still remains at 653 mA h g^{-1} after 500 cycles at 1 A g^{-1}.

2. Experimental section

2.1. Synthesis of cystine aggregates

10 mM L-Cysteine was dissolved in 100 mL ultrapure water (18.0 MΩ cm^{-1}) under ultrasonication for about 10 min. The pH value of the L-Cysteine aqueous solution was rapidly adjusted to 8.0 using Na_2CO_3 aqueous solution. 5 mL H_2O_2 solution (30 wt%) was added drop by drop slowly to the L-Cysteine solution with a syringe (10 mL). The whole reaction process was kept at room temperature with stirring. After 10 min, the resulting solution was incubated at room temperature without interruption for 24 h. The resulting precipitation was centrifuged and washed several times with water and ethanol and finally the white powder of cystine aggregates were obtained after dried under oven at 60 °C for 24 h.

2.2. Preparation of NSDPC

In order to adjust the elemental composition of the obtained NSHPC, varied concentrations of melamine and sulfur were added to a constant amount of cystine aggregates harvested in front. The nitrogen/sulfur co-doped carbon was synthesized by the following synthetic route. In a typical experiment: 8.0 g of cystine aggregates and x g ($x = 3.0, 2.4, 2.0, 1.6$, or 1.0) of melamine and y g ($y = 1.0, 1.6, 2.0, 2.4$, or 3 corresponding to x) of sulfur were mixed thoroughly. Followed by annealing at 500 °C for 2 h in the atmosphere of Ar with a heating ramp of 2 °C min^{-1} and the obtained sample were labeled according to the following scheme: $NS_{X/Y}$ where X and Y denotes the integer proportion of x and y. $NS_{3/1}$ hence corresponds to an experiment in which 3.0 g of melamine and 1.0 g sulfur were added to 8.0 g of cystine aggregates.

2.3. Material characterization

The powder X-ray diffraction (XRD) patterns of all samples were recorded with an X-ray diffractometer (D8 Advance of Bruker, Germany) with filtered Cu Kα radiation over the 2θ range of 10–60°. Field emission scanning electron microscopy (FE-SEM) images were collected on a JSM-7800 F scanning electron microscope. The amounts of doped nitrogen and sulfur in the synthesized materials were determined by a CHNOS Elemental Analyzer (vario EL cube, Germany). Transmission electron microscopy (TEM) images were taken on a JEM-2100 transmission electron microscope using an accelerating voltage of 200 kV, and high-resolution transmission electron microscope (HRTEM) (JEOL-2011) was operated at an acceleration voltage of 200 kV. The specific surface area was evaluated at 77 K (Quantachrome NOVA1200e) using the Brunauer-Emmett-Teller (BET) method, while the pore volume and pore size were calculated according to the Barrett-Joyner-Halenda (BJH) formula applied to the adsorption branch. Thermogravimetric analysis (TGA) was carried out using a STA409PC from 0 °C to 800 °C at a heating rate of 10 °C min^{-1} under Ar. X-ray Photoelectron Spectrum (XPS) was performed on an ESCALAB 250 X-ray Photoelectron Spectrometer with Al Ka radiation. Raman spectra were obtained using a Digilab FTS3500 from Bio-Rad with a laser wavelength of 632.8 nm.

2.4. Electrochemical measurements

The electrochemical performance of the NSDPC was examined by using CR 2032 coin-type cells which assembled in an argon-filled glovebox, using lithium foils as the counter electrodes, Celgard 2500 membrane as the separator, 1 M $LiPF_6$ in a 1:1 (v/v) mixture of ethylene carbonate and dimethyl carbonate as the electrolyte. To prepare a working electrode, active materials (NSDPCs, 70 wt%), conductive material (acetylene black, 20 wt%), and binder (Sodium Alginate (SA), 10 wt%) were milled in ultrapure water to form slurries and then coated onto the surface of a copper foil current collector. The electrode capacity was measured by a galvanostatic discharge–charge method in the voltage range between 0.01 and 3.0 V on a battery test system (Land CT2001A, China). Cyclic voltammetry (CV) from 0.01 to 3.0 V (vs. Li/Li^{+}) at 0.1 mV s^{-1} and electrochemical impedance spectroscopy (EIS) in the frequency range 100 MHz to 0.01 Hz and with an amplitude of 5 mV were performed using an electrochemical workstation (CHI660A). All electrochemical measurements were carried out at room temperature.

3. Results and discussion

3.1. Synthesis and characterizations of the NSDPC

It has been demonstrated that H_2O_2 can oxidize the –SH group of cysteine to form disulfide bonds and lead to the formation of