



Nitrogen-doped nanostructured porous carbon derived from monosodium glutamate for high-performance lithium sulfur battery

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ABSTRACT

Carbon host materials play an important role in improving the electrochemical performances of lithium-sulfur batteries. In this work, we have successfully prepared nitrogen-doped porous carbon nanosheets (NPCN) by using low-cost raw materials (monosodium glutamate) via a facile carbonization approach without any activation process. The obtained NPCN-800 possesses a special micro/mesoporous structure, with a relatively high BET surface area and appropriate nitrogen doping. By employing the NPCN-800 as a reservoir to impregnate sulfur as the cathode material of lithium-sulfur batteries, the resulting sulfur/carbon composite with 65.5 wt% sulfur exhibits an initial discharge capacity of 1070 mAh g⁻¹ at 0.2 C and enhanced capacity retention of 680 mAh g⁻¹ after 150 cycles. Moreover, a capacity of 452 mAh g⁻¹ at 0.5 C is achieved over 200 cycles with 98.6% Coulombic efficiency. The superior electrochemical performance is attributed to the synergistic effect of the hierarchical porous structure (physisorption) and N-doping (chemisorption).

1. Introduction

To meet the demands of emerging electric vehicles, it is an urgent need to explore renewable energy sources for large-scale energy storage. Lithium-sulfur (Li-S) batteries have received an exciting attention recently and become one of the most attractive candidates better than current lithium-ion batteries (LIBs), owing to a high theoretical charge capacity of 1675 mAh g⁻¹ and a high theoretical energy density of 2600 Wh kg⁻¹ [1]. However, there are still challenges to hinder the commercial application of Li-S batteries. This arises from the poor conductivity (5×10^{-30} S cm⁻¹ at 25 °C) caused by the insulating nature of sulfur, a serious “shuttle effect” induced by a soluble intermediate discharge products of long chain polysulfides (Li₂S_n, 4 < n < 8) and terrible stability of the electrode led by the huge volume expansion (as high as 80%) during lithiation [2,3]. All of these defects pose a threat to the specific capacity and cycling stability of sulfur cathode.

Therefore, many approaches have been explored to address the above-mentioned problems, such as designing new cathode nanostructures, new electrolyte, and so on [4]. Among them, fabricating porous carbon-sulfur composite has been found to be more effective because the excellent electric conductivity and large pore volume of

porous carbon can surmount the electrical insulation of sulfur and render enough space for volume change of sulfur. Recently, chemical modification of the carbon matrix by heteroatom doping (such as N, P, O and S) can greatly improve the electrochemical performances of Li-S batteries. Nitrogen-doped porous carbon with substantial wettability, adsorptive capacity, surface polarity and conductivity has shown major potential in improving the performance of carbon hosts [5–8]. Up to now, various N-doped carbon materials have been prepared and used as a sulfur supporter to enhance electrochemical properties. For example, Zhou et al. reported N-doped carbon nanofiber webs-sulfur composites via a modified oxidative template route and carbonization-activation process, which showed a high initial discharge capacity of 1564 mAh g⁻¹ and a good cycling stability [9]. Qu et al. synthesized a nitrogen-rich mesoporous carbon derived from gelatin with SBA-15 as hard template [10]. However, these synthetic methods of porous carbon are usually cumbersome with harsh experimental conditions and relatively high cost.

Herein, we report novel N-doped porous carbon nanosheets which can be applied as cathode hosts for Li-S batteries. We adopt the direct carbonization of monosodium glutamate to prepare N-doped porous carbon without using chemical activation. The direct carbonation method is low-cost, simple, facile, and suitable for large-scale industrial

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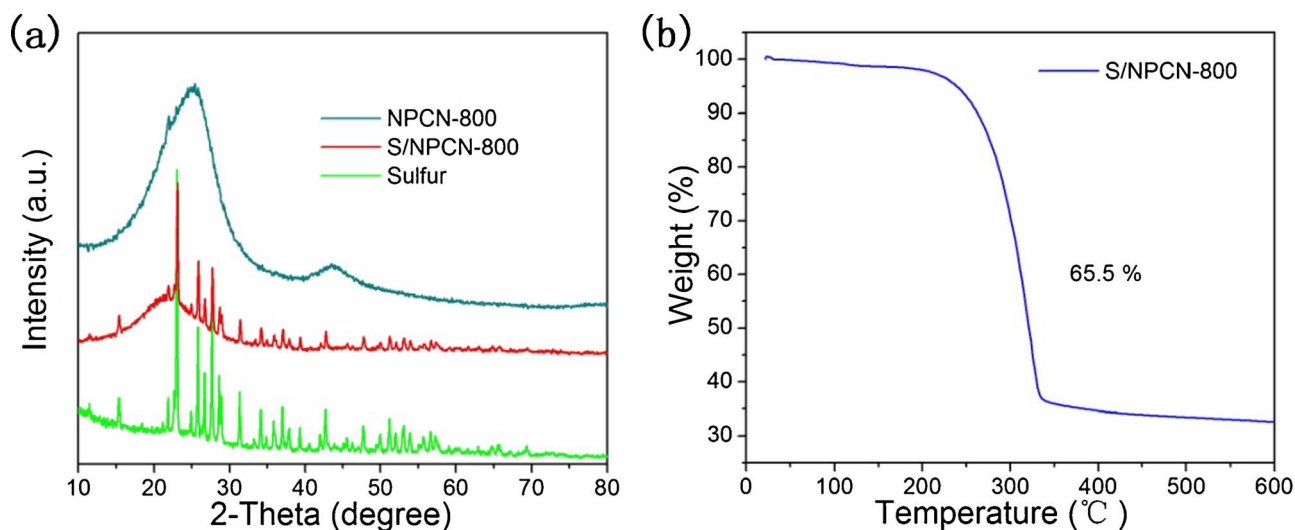


Fig. 1. (a) XRD pattern of sulfur, NPCN-800 and S/NPCN-800 composite; (b) TG curve of S/NPCN-800 composite.

production. To date, a few of organic salts, such as tetrasodium salt of ethylenediamine tetraacetic acid [11] and citrates [12] have been carbonized through this way. Selecting the appropriate organic salt (Na, K, Ca, and so on) is beneficial for the specific metals that generate after heat treatment and operate as activating agents in formatting porous carbon materials [13]. In our design, we use the MSG as the precursor to prepare N-doped porous carbon (NPCN) to encapsulate sulfur, and trap the dissolved polysulfides to improve the electrochemical performance of Li-S battery.

2. Experimental

2.1. Sample preparation

The monosodium glutamate (MSG, $\geq 99\%$) used in this work was purchased from local supermarket (Jinhua, China). The NPCN was prepared by a simple pyrolysis of MSG. In a typical synthesis, 10 g of MSG was heated at 800 °C (or 700 °C) for 90 min in a sealed vessel under N_2 protection at a heating rate of 7 °C min^{-1} . Then, the obtained samples were washed first with diluted hydrochloric acid to remove inorganic impurities and then with distilled water to reach neutral pH value. After filtration, the product was dried at 80 °C for 24 h and the NPCN was thus obtained, which was labeled as NPCN-800 and NPCN-700 in terms of the heating temperature.

Sulfur loaded NPCN (designated as S/NPCN-X where X = 800 or 700) was obtained by melt-diffusion strategy. The sublimed sulfur and NPCN with a weight ratio of 2:1 were thoroughly mixed in a quartz mortar and then heated at 155 °C for 12 h to obtain S/NPCN-800 and S/NPCN-700 composites.

2.2. Material characterization

The morphologies of the obtained samples were characterized using scanning electron microscopy (SEM, Hitachi S-4800) and transmission electron microscopy (TEM, JEM 2010F). The X-ray diffraction (XRD) was recorded with a Philips PW3040/60 X-ray diffractometer using $Cu K\alpha$ ($\lambda = 1.5418 \text{ \AA}$) radiation. The specific surface area was calculated using the Brunauer-Emmett-Teller (BET) equation and the pore size distribution was determined by using the Density Functional Theory (DFT) based on the adsorption branch. The sulfur content in the composites was determined by a thermogravimetric analyzer (Netzsch STA 449C) under N_2 atmosphere with a heating rate of 5 °C min^{-1} from 25 to 600 °C. The composition of the NPCN was examined by X-ray photoelectron spectra (XPS) on an ESCALAB 250Xi Spectrometer (Thermo

Scientific).

2.3. Electrochemical measurements

To evaluate the electrochemical performance, the as-prepared S/NPCN-X composites, conductive carbon black, and polyvinylidene difluoride (PVDF) were mixed in *N*-methyl Pyrrolinone (NMP) solvent at a weight ratio of 7:2:1. The slurry was stirred continuously for 4 h and then coated onto aluminum (Al) foam current collector and dried at 60 °C overnight. The average sulfur loading is 0.9–1.2 $mg\ cm^{-2}$. The CR2025-type coin cells were assembled in an argon-filled glove box to test the electrochemical properties. The electrolyte was 1 M lithium bis(trifluoromethanesulfonyl)imide in a 1:1 v/v mixture of 1,3-dioxolane (DOL) and 1,2-dimethoxyethane (DME) with 0.1 $mol\ L^{-1}$ $LiNO_3$ additive. The amount of electrolyte used in the cells is about 50 μl for each cell. The cyclic voltammetry (CV) was performed on a CHI 660C electrochemical workstation. Galvanostatic charge/discharge performance test and the rate capability at different current densities were performed by a Neware battery test system (Shenzhen Neware Co. Ltd., China) in the voltage range from 1.5 to 3.0 V.

3. Results and discussion

The structures of the NPCN-800 and S/NPCN-800 composites were studied by XRD as shown in Fig. 1a. The broad specific diffraction peak from 20° to 30° is observed for NPCN-800, suggesting the formation of partially graphitized carbon during pyrolysis process [14,15]. The pristine sulfur shows a well-crystallized orthorhombic type and the distinct diffraction peaks can be indexed as sulfur with the JCPDS card no. 08-0247. After encapsulating sulfur into the NPCN-800 composite, only weak characteristic peaks of sulfur were observed for the composite. Therefore, it can be reasonably inferred that most sulfur has been successfully spread into the pores of NPCN-800 and a small amount of crystalline sulfur existed on the carbon surface.

Thermogravimetric analysis (TGA) was used to determine the weight contents of sulfur in S/NPCN-800 composites under the atmosphere. From the TG curve, we can see that the S/NPCN-800 composite has a slope between 200 and 340 °C, which suggests a rapid evaporation of sulfur. Subsequently, the curve achieves a platform, indicating that impregnated sulfur has been completely evaporated at high temperature. As shown in Fig. 1(b), the sulfur content in the sample is 65.5 wt%.

The SEM images of the samples are shown in Fig. 2(a–f). It can be seen from Fig. 2(a, b, d, e) that the NPCN-700 and NPCN-800 exhibit a

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