



Nitrogen-doped porous “green carbon” derived from shrimp shell: Combined effects of pore sizes and nitrogen doping on the performance of lithium sulfur battery



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ABSTRACT

Nitrogen-rich porous “green carbons” derived from abundant shrimp shell shows good performance for Li–S batteries. The strategy in this work is highlighted to selective removal of intrinsic CaCO₃ in shrimp shell followed by KOH activation to tune the pore sizes of the obtained carbons. On the basis of the different porous structures, the discharge capacity of the obtained carbons as Li–S cathodes follows the order of micro-mesoporous carbon > mesoporous carbon > microporous carbon. The high capacity of the micro-mesoporous carbon is attributed to its positive characters such as the coexistence of micro-mesoporous structure, the large pore volume and the high specific surface area. Furthermore, well-dispersed nitrogen in the porous carbons is naturally doped and inherited from shrimp shell, and can help to enhance cycle stability when used as cathodes. As a result, all carbon cathodes exhibit the good cycle stability (>78%) due to their nitrogen doping induced chemical adsorption of sulfur on the surface areas of the porous carbons. Among them, mesoporous carbon cathode shows the best cycle stability with 90% retention within 100 cycles, which is mainly attributed to the synergistic effects of its both large pore size (5.12 nm) and high nitrogen content (6.67 wt %).

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1. Introduction

Lithium-sulfur (Li–S) batteries are considered to be a promising energy-storage solution for the rapidly growing hybrid electric vehicle and renewable energy owing to their extremely high theoretical specific capacity (1672 mA h g⁻¹) and energy density of 2500 Wh kg⁻¹ of sulfur [1–3]. In addition, sulfur is low cost, natural abundance and environmental friendliness. Despite those considerable advantages, the commercial applications of Li–S batteries are still far away hampered by shuttling effect and volumetric change of lithium polysulfides and sulfur [4–9]. To overcome those problems, a variety of strategies have been explored to advance Li–S batteries, including optimization of the organic electrolyte, preparation of conductive polymer-sulfur composites, and

fabrication of carbon-sulfur composites [10–13]. Carbon materials are particularly attractive to improve the utilization of sulfur and restrain the solubility of lithium polysulfides due to their excellent conductivity, large surface area, suitable pores, low cost as conductive matrix and strong adsorbent agents [14,15]. It is widely reported that sulfur particles embedded in the pores of the conductive carbon matrix could increase the electrical conductivity of the sulfur cathode, while retarded the polysulfide shuttle phenomenon. Some efforts have been focused on different porous carbons such as mesoporous carbon (Meso-C), microporous carbon (Micro-C) and micro-mesoporous carbon (Micro-Meso-C) for the fabrication of carbon-sulfur cathodes with high capacity [11,16–18]. For example, Nazar et al. succeeded in immobilizing sulfur in 3 nm ordered carbon pores and achieving promising cycle stability over 20 cycles and high initial discharge capacities of 1005 mAh g⁻¹ at 168 mA g⁻¹ rate [19]. Zhang et al. reported that carbon-sulfur composite with 42 wt% sulfur presented a long electrochemical stability up to 500 cycles based on the constrained electrochemical reaction inside the narrow micropores of carbon spheres [20]. 3D hierarchically ordered porous carbon with mesoporous walls and

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interconnected macropores exhibited a stable capacity of 884 mAh g⁻¹ after 50 cycles [21]. Although the developments of carbons-sulfur composites are encouraging, the effect of the pore sizes of porous carbon on the performance of Li–S batteries need to be studied in detail.

Recently, much effort has been spent on tuning the pore sizes of the porous carbon by two strategies including chemical activation and hard-templating strategies [22]. The chemical activation is widely used in preparation of Micro-C to increase the surface area and porosity of carbon materials with KOH, NaOH or ZnCl₂ as the activation agent [23]. The hard-templating strategy is widely studied for the fabrication of Micro-C, Meso-C or hierarchically porous carbons using the hard template such as nanostructured silica, MOF, or metal oxide to impregnate with an appropriate carbon source, followed by the carbonization of the composites, and subsequent removal of the template [24]. For example, Hu et al. reported that the macroscopic carbon monoliths with both mesopores and macropores were successfully prepared by using meso-/macroporous silica as the template [25]. However, the hard-templating method for tailoring the pore sizes of the carbons always suffers from the drawbacks such as the design of complicated template and the massive use of template agents. Alternatively, the combination of chemical activation and hard-templating provides another method for tuning the porosity of the carbon. In this field, He et al. prepared hierarchically porous carbons using Fe₂O₃ as the template coupled with KOH activation [26]. It's obvious that the currently effective templates suffer from the drawbacks of either high costs or tedious steps. White et al. have reported studies on prawn shell derived Meso-C with its intrinsic mineral scaffold (natural inorganic CaCO₃) as the template [27]. Inspired by their work, the discovery of inexpensive and abundant template derived from renewable biomass for tailoring of the porous carbon is still in great demand.

Additionally, recent studies have also demonstrated that surface functional groups or doped heteroatoms (such as N and O) in the porous carbons play an important role in improving the electrochemical performances of the carbon-sulfur composite [28–32]. Such functional carbon with the ability to chemically adsorb sulfur or Li₂S promotes good electrical contact and effectively confines polysulfides in the cathode by preventing dissolution. For example, Song et al. reported that the doped nitrogen in the carbon could effectively promote chemical adsorption between sulfur atom and oxygen functionalities on the carbon [33]. Because of the advantage of nitrogen-doped carbon on the improved performance of Li–S battery, some techniques have been focused on the introduction of nitrogen species into the carbon framework, which are achieved either by using nitrogen-containing precursors such as melamine and polyvinylpyridine or via treating carbon materials with ammonia gas [14,34]. Despite the great efforts on the synthesis of nitrogen-doped carbon electrodes with high capacitive performance, the exploration of renewable biomass with lots of heteroatoms as the raw material to produce electrode materials would be more worthwhile considering the potential scale of electrochemical applications. Waste shrimp shell, which is composed of nitrogen containing polysaccharide named as chitin (poly-β(1/4)-N-acetyl-D-glucosamine), is expected to be an excellent candidate precursor for producing nitrogen-rich carbon [27]. The synthesis of nitrogen-doped carbon from shrimp shell would not only be beneficial from an economic standpoint, but also allow a simple route to make different carbon structures in high value application.

Herein, we report the nitrogen-doped porous “green carbons” with good performance as the cathode material of Li–S batteries. The porous carbons including Micro-C, Meso-C and Micro-Meso-C were prepared by coupling selective removal of intrinsic CaCO₃ in the shrimp shell with KOH activation. Naturally occurring nitrogen

element was preserved as the dopant to enhance the cycle stability of Li–S batteries. The combined effects of pore sizes and the nitrogen contents of the carbons on the performance of Li–S batteries have been investigated in detail.

2. Experimental

2.1. Synthesis of shrimp shell-derived porous carbons

In this study, “Bohai shrimp shell” was used as the raw precursor. The synthesis of the nitrogen-doped porous carbons included demineralization followed by KOH activation. In the case of demineralization, 13.87 g of pristine shell was suspended in 10 wt % HCl solution at 60 °C for 4 h to remove CaCO₃ completely. Samples were subsequently rinsed with deionized H₂O. The KOH activation was performed as the following procedures. Firstly, 5.5 g demineralized shrimp shell was refluxed at 80 °C for 22 h after immersed in the mixture of 49.4 mL water and 9.7 g KOH. Secondly, the obtained mixture was freeze-dried and then calcinated at 700 °C for 1 h with the heating rate of 3 °C min⁻¹ under argon flow. The resultant carbon was denoted as Micro-C. In the case of the synthesis of the Micro-Meso-C, 13.87 g of pristine shell was suspended in 10 wt % HCl solution for 40 min to remove CaCO₃ partly, and the following KOH activation process was similar to that of Micro-C synthesis. The synthesis of Meso-C followed the reversed order as that of Micro-C. It should be mentioned that the pyrolysis procedure during KOH activation was performed at 600 °C for 1 h under argon flow. The residual CaCO₃ and KOH in all of the samples were removed by 10 wt% HCl solution after KOH activation, filtered and washed thoroughly with water (until neutral pH), and dried overnight at 80 °C.

2.2. Preparation of carbon-sulfur composites

The carbon-sulfur composites were prepared by a melt diffusion method. Typically, the porous carbons and sublimed sulfur were mixed according to a mass ratio of 1:1.7 to grind a black mixture. The mixture was then sealed in a reaction kettle in argon flow and heated at 149 °C for 6 h, allowing sulfur to flow into the pores of the carbons. The resultant composites were denoted as Micro-C/S-X, Micro-Meso-C/S-X and Meso-C/S-X, where X was the weight percentage of sulfur in the composites.

2.3. Electrochemical measurements

To prepare the working electrodes, the as-prepared composite was mixed with acetylene black and polyvinylidene difluoride in a mass ratio of 80:10:10 with N-methyl pyrrolidone (NMP) as a dispersant. The paste was compressed into a thin piece with a roller, followed by cutting into a film disk of 14 mm in diameter. The as-obtained film disk was dried in a vacuum oven at 50 °C overnight. The electrolyte was 1M LiTFSI in 1, 2-dimethoxyethane/1, 3-dioxolane (1:1 v/v) with 10 wt% LiNO₃. The separator was a Celgard 2300 membrane. A lithium sheet was used as both counter and reference electrode. Cyclic voltammogram (CV) data were recorded on a CHI660D electrochemical workstation (Shanghai Chenhua) between 1.5 and 2.8 V to characterize the redox behavior and the kinetic reversibility of the cell. Cells were discharged and charged on a LAND system at room temperature. The specific capacities mentioned in this article were calculated based on the mass of sulfur.

The morphologies and structures of the as-obtained products were examined using field emission scanning electron microscopy (SEM, Hitachi Ltd SU8010), powder X-ray diffraction (XRD, Rigaku D/max-2500 diffractometer with Cu K α radiation),

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