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Sulfur-impregnated 3D hierarchical porous nitrogen-doped aligned carbon nanotubes as high-performance cathode for lithium-sulfur batteries

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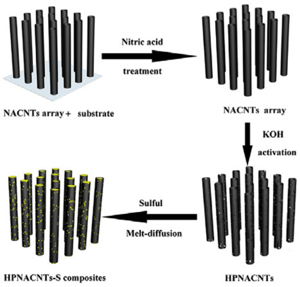
HIGHLIGHTS

- A rational HPNACNTs array is designed as scaffolds to infuse sulfur.
- The HPNACNTs array shows a hierarchical porous morphology and robust structure.
- The HPNACNTs-5-S electrode retains a high capacity of 817 mAh g^{-1} at 5 C.
- Its 3D structure with 1D conductive electron paths enables high-rate capability.

GRAPHICAL ABSTRACT



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ABSTRACT

A rational 3D hierarchical porous nitrogen-doped aligned carbon nanotubes (HPNACNTs) with well-directed 1D conductive electron paths is designed as scaffold to load sulfur. The HPNACNTs have abundant micropores, mesopores and macropores with a relatively high specific surface area and a large total pore volume. The sulfur-HPNACNTs composite is synthesized for lithium–sulfur batteries by a melt-diffusion of sulfur powders into HPNACNTs scaffolds. Electrochemical tests reveal that the sulfur-HPNACNTs (68.8 wt% sulfur) composite exhibits a high initial discharge capacity of 1340 mAh g^{-1} at 0.1 C and retains as high as 979 mAh g^{-1} at 0.2 C after 200 cycles. More importantly, it shows high reversible capacity at high rates (817 mAh g^{-1} at 5 C). Its enhanced electrochemical performance can be attributed to the excellent electrical conductivity of aligned carbon nanotubes, the synergetic effect of its hierarchical porosity and the restraint of the shuttle effect due to the SxLi … N interactions via the N lone-pair electron.

1. Introduction

In recent years, lithium–sulfur (Li–S) batteries have attracted a great deal of interest due to its high theoretical specific capacity (S: 1675 mAh g^{-1}) and excellent theoretical energy density (2600 Wh kg^{-1}), as well as its low cost, environment friendliness

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and abundance [1–3]. However, the current investigation of Li–S batteries still faces some basic obstacles: the intrinsic insulativity of sulfur, the dissolution of intermediate polysulfides, their notorious shuttle effect in the electrolyte and large volume expansion of the sulfur (~80%) cathode, which lead to its poor rate performances and severe capacity fade [4–7].

To overcome these problems, many strategies have been carried out, including the design of conductive polymer/sulfur composites [8–10] and the construct of carbon/sulfur composites such as carbon spheres/sulfur [11,12], hollow carbon spheres/sulfur [13,14], carbon nanotubes/sulfur [15–18], carbon nanofiber/sulfur [19–21], graphenes/sulfur [22–24] and porous carbon/sulfur [13,25–30]. Among them, porous carbon materials have been proved effective and facile candidates for Li–S batteries to improve the sulfur utilization and alleviate the dissolution of lithium polysulfides because the conductive carbon skeleton can not only provide efficient and rapid pathways for electron and ion transport but also can immobilize sulfur due to its capillary force of the pores [26]. For example, Nazar et al. [31] pioneered the developments of ordered mesoporous carbon for sulfur encapsulation and achieved an impressive capacity of 1320 mAh g^{-1} at 0.1 C. However, with the ordered pore structure, the C/S composites usually suffer from kinetic inhibition to Li^+ diffusion within the framework due to carbon pores fully or partially filled with sulfur, which causes inferior rate capability [32].

To address this issue, the effort to synthesize hierarchical porous carbon for sulfur encapsulation has been made to enhance the electrolyte permeability and electrolyte accessibility [32–34]. In the hierarchical porous structure, the macropores can provide large space voids for electrolyte reserve [35]; the mesopores not only offer a reasonable pore volume for high sulfur loading, but also permit fast electrolyte ingress and diffusion for enhanced ion-transport kinetics [36,37]; and the micropores facilitate the immobilization of sulfur and its intermediate polysulfides due to their confined spaces [38,39]. Inspired by the unique functions of different kinds of pores, considerable efforts have been devoted to the design of hierarchical porous carbon architectures [40]. Liang et al. designed a meso-micro porous carbon with a bimodal structure to act as a host for encapsulating sulfur, which exhibited much more excellent cycling stability than the one with only microporous or mesoporous carbon structure [37]. However, generally, the hierarchical porous carbon prepared by common methods shows a low graphitization degree and often exhibits poor electrical conductivity, which limits the electron transfer and thus restricts the rate performance to a certain extent for Li–S batteries [41,42].

To further enhance the electrical conductivity of C/S electrodes, carbon nanotubes (CNTs) have been developed to act as the sulfur accommodation skeleton due to its excellent conductivity, porosity and mechanical properties [43,44]. In particular, compared with disordered aligned CNTs, nitrogen-doped aligned CNTs (NACNTs) have been demonstrated to significantly improve electrolyte accessibility and charge transport capability because of its well defined regular pore structure and the well 1D directed conductive electron paths, as well as the additional electron transport pathways created by the N-doped graphite layers in the NACNTs [12,45,46]. However, the NACNTs/S composite exhibits low sulfur loading and relatively high decay rates, which is resulted from relatively low specific surface areas (S_{BET}), specific total pore volume (V_T) of NACNTs [47] and the weak interface bonding between S and the NACNTs [16,48]. According to the advantages of hierarchical porous structure in Li–S batteries, therefore, it is necessary to create hierarchical pores in NACNTs to increase S_{BET} and V_T and achieve high-electrochemical performance for sulfur-CNT electrode.

Based on this promising strategy, we report a rational 3D hierarchically porous nitrogen-doped aligned carbon nanotubes (HPNACNTs) array with 1D conductive electron paths to encapsulate sulfur. The synthetic procedure for the HPNACNTs–S composite was schematically illustrated in Fig. 1. Firstly, NACNTs were purified with nitric acid and then activated with KOH. Hierarchical pores were introduced into nanotube walls; meanwhile, the inner cavities of bamboo-like structure NACNTs were opened and the interconnected macro/mesopores were achieved. Secondly, HPNACNTs-S composite was obtained by a typical melt-diffusion method. Such a unique 3D HPNACNTs structure was used to encapsulate sulfur with several advantages: (1) the space between the nanotubes and the interconnected mesopores not only contributed to load sulfur but also facilitated Li^+ transport at high rates so as to ensure high rate capability; (2) the 1D directed conductive electron path and the graphite layers inside the cavities provided rapid pathways for electronic transport to enhance the electrical conductivity; (3) the opened bamboo-like NACNTs provided high pore container and large pore volume for sulfur encapsulation; (4) more importantly, the unique hierarchical micro-meso-macro architectures are beneficial for high sulfur loading and for ion-transport kinetics enhancing. Therefore, the hierarchical porous HPNACNTs-S composites with high electronic conductivity are expected to show an excellent electrochemical performance.

2. Experimental

2.1. Preparation of the composite

2.1.1. Synthesis of NACNT array

NACNT array was prepared as previously reported [43]. In brief, 0.08 g ferrocene was ultrasonically dispersed into 40 ml mixtures of xylene and cyclohexylamine (65:35 in volume). The solution was atomized by an ultrasonic nebulizer and then was passed into the quartz tube at a temperature of 900 °C under a flow rate of 650 sccm Ar. A quartz slice (3 mm × 30 mm × 30 mm) was used as a substrate for the NACNT array. The as-synthesized NACNT array was heated to 120 °C in nitric acid (70%, 30 mL) for 9 h. After that, the resulting solid was washed with deionized water until a neutral pH and the sample was dried in vacuum at 80 °C overnight.

2.1.2. Preparation of HPNACNT array

The HPNACNTs array was obtained by 7 M aqueous KOH solution with different KOH/NACNTs mass ratios of 3, 5, 7 and 11. The NACNTs were impregnated into aqueous KOH solution and stirred for 4 h at a speed of 400 rpm, followed by another 24 h of static soaking. Then the mixture solution was dried at 80 °C for 24 h. The activation process was carried out at 800 °C for 2 h in a tubular furnace under flowing Ar with a heating rate of 3 °C min^{-1}. To assure a complete removal of KOH, the resulting sample was washed with 0.1 M HCl and followed by deionized water until the pH of the filtrate was approximately 7. The final HPNACNT array was obtained after drying at 80 °C for 24 h. The resultant HPNACNT array were denoted as HPNACNTs-3, HPNACNTs-5, HPNACNTs-7 and HPNACNTs-11, according to the mass ratios of KOH/NACNTs.

2.1.3. Preparation of HPNACNTs-S composites

The as prepared HPNACNTs-3, HPNACNTs-5, HPNACNTs-7 and HPNACNTs-11 were mixed with sulfur (Aldrich, with a purity of >99.995%) in a mass ratio of 1:2 and heated to 155 °C for 10 h in a closed glass container under air atmosphere to facilitate sulfur diffusion into the carbon scaffold to obtain the HPNACNTs-3-S, HPNACNTs-5-S, HPNACNTs-7-S and HPNACNTs-11-S composite, respectively.