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Three-dimensional hierarchical porous tubular carbon as a host matrix for long-term lithium-selenium batteries

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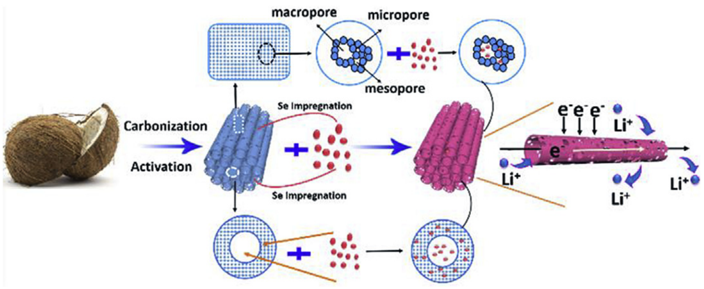
HIGHLIGHTS

- 3D hierarchical porous carbon with a hollow tubular structure is synthesized.
- Dual scale pores (micro-, meso- and macropores) co-existed in HPTCs.
- HPTC/Se composite exhibits a good stability at 2 C over 900 cycles.

GRAPHICAL ABSTRACT



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ABSTRACT

Lithium-selenium (Li-Se) batteries are of great interest as a representative family of electrochemical energy storage systems because of their high theoretical volumetric capacity and considerable electronic conductivity. However, the main drawback of Se electrodes is the rapid capacity fading caused by the dissolution of polyselenides upon cycling. Here, we report a simple, economical, and effective method for the synthesis of three-dimensional (3D) hierarchical porous carbon with a hollow tubular structure as a host matrix for loading Se and trapping polyselenides. The as-obtained porous tubular carbon shows a superior specific surface area of 1786 m^2 g^{-1}, a high pore volume of 0.79 cm^3 g^{-1}, and many nano-structured pores. Benefiting from the unique structural characteristics, the resulting hierarchical porous carbon/Se composite exhibits a high capacity of 515 mAh g^{-1} at 0.2 C. More importantly, a remarkable cycling stability over 900 cycles at 2 C with a capacity fading rate of merely 0.02% per cycle can be achieved. The 3D hollow porous tubular carbon can be also used for other high-performance electrodes of electrochemical energy storage.

1. Introduction

In recent years, lithium-ion (Li-ion) batteries have been widely favored as the portable instrument for energy storage and power supplies of various kinds of devices due to their high energy density and long cycle life [1–4]. However, with the rising demand for plug-

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in hybrid electric vehicles and smart grid community systems, Li-ion batteries have become demonstrably unfit in view of limited theoretical capacity [5–7]. As an alternative, lithium-sulfur (Li-S) batteries have attracted many attentions due to their high theoretical capacity of 1675 mAh g^{-1} and energy density of 2600 Wh kg^{-1}, which are attractive properties for modern electrochemical energy storage [8–10]. Unfortunately, the commercialization of Li-S batteries has been frustrated by the low electronic conductivity of sulfur, fast capacity fading, and low coulombic efficiency [11,12]. Like sulfur, selenium originating from the same group of elements is a better candidate as a cathode material in industrial batteries based on several notable properties. First, the chemical property of selenium is similar to that of sulfur, giving rise to similar electrochemical reaction mechanisms during the charging/discharging processes. Furthermore, selenium possesses a higher electrical conductivity of 10^{-5} S cm^{-1} when compared to sulfur, enabling more efficiently utilization of active materials and fast electrochemical reactions [13,14]. Finally, selenium exhibits a theoretical volumetric capacity of 3253 A h L^{-1} based on the density of 4.82 g cm^{-3}, which is comparable to that of sulfur (3461 A h L^{-1} and 2.07 g cm^{-3}), and a broader output voltage with higher volumetric energy density [15].

In view of these advantages, lithium-selenium (Li-Se) batteries have recently begun to attract increasing interest from prospective developers and investors. However, Li-Se batteries are not exempt from persistent issues of rapid capacity decay and low utilization of selenium cathode materials [13]. Therefore, several methods have been put forward to solve these problems to strengthen the conductivity of cathode material and trap the polyselenides. One of the promising methods is to insert active materials within a host matrix, such as porous carbons [16], conductive polymers [13], and graphene [17]. Among these, porous carbon materials with unique structure are of great important such as microporous carbon nanosheets [18], microporous carbon [19], porous hard carbons [20], carbon nanoparticles [21], nitrogen-rich porous carbon [22], and disordered carbons [23,24]. Specifically, biomass-derived carbon is under active study due to its low cost and unique porous structure.

Here, we report a simple, economical, and effective method to synthesize three-dimensional (3D) hierarchical porous carbon with a hollow tubular structure from coconut shells for Li-Se batteries. As compared with other carbonaceous matrixes [13,16–24], the as-prepared low-cost and environmentally-friendly sample provides abundant hierarchical hollow channels, yielding a combination of advantages including loading selenium, transporting electron and ion, infiltrating electrolyte, and entrapping polyselenides. When used as cathode for Li-Se batteries, the resulting 3D hierarchical porous hollow carbon/Se composite cathode shows high capacity, excellent rate capability, and superior cycling stability over 900 cycles without any clear capacity fading.

2. Experimental

2.1. Material preparation

All of the reagents were of analytical-grade purity and directly used without alteration. To prepare the 3D hierarchical porous tubular carbons (HPTCs), a raw coconut shell was first carbonized at 600 °C for 2 h. Next, the as-synthesized porous carbon (PC) was introduced into a 10 M KOH solution, dried at 120 °C for 10 h, then heated at 300 °C for 1.5 h and at 750 °C for 2 h at a heating rate of 5 °C min^{-1} under Ar flow, leading to the formation of HPTCs. Se (Sigma Aldrich, 99.9%) was introduced to the porous carbon host by heating the Se-porous carbon mixture at approximately 260 °C under argon to yield HPTCs/Se composites.

2.2. Material characterization

The morphological characteristics of the as-prepared samples were analyzed by field-emission scanning electron microscopy (FESEM, SM-7800N) and transmission electron microscopy (TEM, JEM-2100). An X-ray diffractometer (Maxima-X XRD-7000) with Cu K-alpha radiation ($\lambda = 1.5406$ nm) was used to examine the crystal structures of the samples between 10° and 80 °C. Thermogravimetric analysis (TGA, Q50) was conducted to obtain the amount of Se content in the sample under N_2 atmosphere, with a heating rate of 10 °C min^{-1}. The nitrogen adsorption/desorption isotherms and pore size distributions of the prepared samples were measured with a Quadrasorb evo 2QDS-MP-30 (Quantachrome Instruments, USA). Finally, X-ray photoelectron spectroscopy (XPS) was conducted to analyze the elemental at different states using a Thermo Scientific ESCALAB 250Xi electron spectrometer.

2.3. Electrochemical measurements

To characterize the electrochemical properties of the HPTCs/Se composite cathodes, the working electrodes were prepared by coating aluminum foil with a slurry containing our active material (80 wt%), carbon black (10 wt%), and sodium alginate (SA) binder (10 wt%) dissolved in deionized water. The coated electrodes were dried at 60 °C for 15 h in a vacuum and the mass loading of selenium was about 0.6 mg cm^{-2}. CR3025 coin cells were used to conduct electrochemical tests, with Li foil as the counter electrode. The electrolyte was 1 M of $LiPF_6$ dissolved in a mixture of ethylene carbonate (EC) and diethyl carbonate (DEC), with a volume ratio of 1:1. The cells were assembled in an argon-filled glove box and then aged for about 6 h before charging-discharging. Charging–discharging characteristics were galvanostatically tested between 1.0 V–3.0 V (vs. Li/Li^{+}) at room temperature, using a Land instruments testing system. The capacity of the prepared materials was calculated based on the weight of Se in the carbon host.

3. Results and discussion

The morphologies of the as-prepared PCs are shown in Fig. S1 with their typical cut surfaces at various magnifications. As shown in Fig. S1a, the PC is composed of long tubular structures with an average diameter of nearly 30 μm. The surface of the PC is relatively rough, as shown in Fig. S1b. Many pores with the sizes ranging from 2 to 10 μm can be found in the PC sample displayed in Fig. S1c. After the activation by KOH, FESEM images of the HPTCs sample are shown in Fig. 1a–f. Although the general structure of the HPTCs is strongly similar to that of the PCs sample (Fig. 1a), visible differences can be still seen. The surface texture of HPTCs is slightly looser compared to that of PCs, as well as in the presence of the obvious porous structure of the HPTCs, with unevenly sized pores shown in Fig. 1b. The partially enlarged detail in Fig. 1c shows an average pore size in the nanometer range. Fig. 1d reveals the broken structure of the HPTCs and obviously tubular structure could be seen. The trend of similarity is further corroborated by the low and high-magnification FESEM images (Fig. 1e and f), revealing the high similarity pore structure and configuration compared with the PCs.

The nature of the morphology and related elemental mappings of the HPTCs/Se composite are shown in Fig. 2a–i and Fig. S2. After the selenium powder was loaded, the surface of the HPTCs/Se composite experienced no significant changes in comparison to that of the HPTCs sample, and no large aggregation of selenium was found on any cross section surface. This observation, compounded with the elemental mappings of elements C and Se, implies that a good dispersion of selenium was present within the HPTCs host.