Confine sulfur in double-hollow carbon sphere integrated with carbon nanotubes for advanced lithium–sulfur batteries

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Abstract

The lithium–sulfur (Li–S) batteries are promising because of the high energy density, low cost, and natural abundance of sulfur material. Li–S batteries have suffered from severe capacity fading and poor cyclability, resulting in low sulfur utilization. Herein, S-DHCS/CNTs are synthesized by integration of a double-hollow carbon sphere (DHCS) with carbon nanotubes (CNTs), and the addition of sulfur in DHCS by melt impregnations. The proposed S-DHCS/CNTs can effectively confine sulfur and physically suppress the diffusion of polysulfides within the double-hollow structures. CNTs act as a conductive agent. S-DHCS/CNTs maintain the volume variations and accommodate high sulfur content 73 wt%. The designed S-DHCS/CNTs electrode with high sulfur loading (3.3 mg cm^{-2}) and high areal capacity ($5.6 \text{ mAh mg cm}^{-2}$) shows a high initial specific capacity of 1709 mAh g^{-1} and maintains a reversible capacity of 730 mAh g^{-1} after 48 cycles at 0.2 C with high coulombic efficiency (100%). This work offers a fascinating strategy to design carbon-based material for high-performance lithium–sulfur batteries.

Keywords Energy storage · Lithium–sulfur battery · Polysulfide · Double-hollow carbon sphere

Introduction

Researchers have been investigating to meet the increasing demand for high capacity energy storage devices, as well as looking for new technologies that will help to minimize the effects of global warmings, such as reducing energy consumption or facilitating the transition to renewables [1, 2]. In recent years, Li–S battery has been attracted much attention because of its high energy density (2600 Wh kg^{-1}), lower environmental impacts, low manufacturing costs, abundant supply of materials, ease of processing, and reduced environmental footprint [3–5]. However, Li–S battery has been firstly hampered by the low electrical conductivity of both sulfur ($5 \times 10^{-30} \text{ S cm}^{-1}$) and the discharge product (Li_2S), which lead to restricting the electron transport and the utilization of the active sulfur [6]. Second, the dissolution of

polysulfides in the conventional organic electrolyte (Li_2S_x , $4 \leq x \leq 8$) provides low coulombic efficiency and short cycle life [7, 8]. Third, the volume change of sulfur (about 80%) during the charge–discharge process leads to the pulverization of sulfur cathode and gives up a rapid capacity decay [9, 10].

Carbon materials have been intensively used as hosts for sulfur because they can increase the electrical conductivity of sulfur and immobilize the soluble polysulfides [11, 12]. However, due to the presence of weak interactions between sulfur and the carbon materials, the carbon-based cathode suffers from a capacity decay over long-term cycling. Besides, owing to their tendency to adsorb soluble polysulfides, polar metal oxide (MnO_2) [13], metal WS_2 – WO_3 heterostructure [14], and metal sulfide (MoS_2) [15] also have been developed as sulfur hosts. However, the polar inorganic metallic compounds possess poor electrical conductivity, leading to limit the electron transport and diminish the electrochemical performance of the batteries [16]. In these aspects, it is still very important to design carbon-based electrodes which can provide adequate space for the storage of the active materials and soluble polysulfides, leading to fast electron transport and oxidation–reduction reaction.

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It has been confirmed that combining porous carbon with sulfur increase the cyclic performance and rate capability of Li–S battery. Besides, sulfur with graphene [17], carbon nanotubes [18], hollow carbon nanofibers [19], and conducting polymers [20] are the most common ways to enhance the electronic conductivity of sulfur and also as volume change barriers. The hollow structures have received much attention as hosting of large amount of sulfur. This leads to accommodate the volume expansion of the sulfur. Specially, the double-hollow structure enhances the advantages of hollow material, which could confine, store sulfur and retard the outward diffusion of soluble polysulfides. Hence, integrating the DHCS with carbon nanotubes will improve the conductivity and also helps to transfer the electron and ions. For example, Lou et al. found that the double-shelled hollow carbon spheres can effectively confine sulfur and also improved the accommodation of volume variation [21].

In this work, we report a rational design and synthesis of confining sulfur in double-hollow carbon spheres integrated with carbon nanotubes (S-DHCS/CNTs). The CNTs serve as a conducting agent and support the DHCS. The combination of DHCS and CNTs accelerates the electron transport and enhances the kinetics of the electrochemical reactions. The synergistic effects provide an outstanding cycling performance of S-DHCS/CNTs with high sulfur content (73%) and high loading (3.3 mg cm^{-2}).

Experimental

Preparation of DHCS/CNTs composites

The preparation of DHCS/CNTs is concisely illustrated in Fig. 1. In a typical experiment, 0.3 g resorcinol was dispersed into a solution containing 3 mL of tetraethyl orthosilicate (TEOS), 60 mL methanol, 20 mL distilled water, 0.2 g carbon nanotubes (CNTs), and 0.1 g sodium dodecyl sulfate (SDS). Afterward, 3 mL of ammonia solution (30 wt%) was added, and stirred for 30 min. Subsequently, a 1 mL formaldehyde solution was added to the dispersion under stirring. After 5 h, the above steps were repeated without the addition of CNTs. $\text{SiO}_2@\text{RF}@\text{SiO}_2@\text{RF}/\text{CNTs}$ composites were

collected by centrifugation and washed three times with distilled water and methanol, and dried at 110°C for 8 h. The DHCS/CNTs composites were obtained by pyrolysis $\text{SiO}_2@\text{RF}@\text{SiO}_2@\text{RF}/\text{CNTs}$ at 800°C for 2 h under argon atmosphere with a heating rate of 5°C min^{-1} . DHCS/CNTs were obtained by etching the as-product with 2 M NaOH aqueous solution for 5 h.

Preparation of S-DHCS/CNTs and S-CNTs composites

The S-DHCS/CNTs and S-CNTs composites were prepared with melt impregnations under pressure. A mixture of sulfur and DHCS/CNTs powder (8:1 by weight) was placed in a Teflon-lined steel autoclave and heated to 155°C for 8 h. The preparation process of S-CNTs was the same as the method mentioned above.

Materials characterization

The morphology of the as-prepared materials was characterized by transmission electron microscopy (TEM, FEI Titan G2 60–300, USA). Thermogravimetric analysis (TGA, SDT Q600 V8.0, TA Instruments, USA) was conducted under an argon atmosphere to determine the sulfur content in the composites. The crystalline of sulfur was studied with X-ray diffraction (XRD, Rigaku, Dmax/2550VB, Japan) with Cu $K\alpha$ radiation. The surface composition and chemical bonds were investigated by X-ray photoelectron spectroscopy (ThermoFisher Scientific, ESCALAB 250XI, USA).

Electrochemical measurements

The electrochemical measurements of the cathodes made from S-DHCS/CNTs and S-CNTs were carried out using CR2025 coin-cells with lithium foil as an anode, fabricated in an argon-filled glove box. The active materials (S-DHCS/CNTs and S-CNTs) were mixed with acetylene black (AB) and polytetrafluoroethylene (PTFE) binder uniformly in a mass ratio of 8:1:1 in isopropyl alcohol, respectively. The prepared cathode membrane was cut and compressed at 10 MPa onto stainless-steel wire mesh with 0.8 cm in diameter. The sulfur loading of the cathode is from 3.0 to

Fig. 1 Schematic illustrations for the preparation of S-DHCS/CNTs composite

3.3 mg cm^{-2} . Celgard 2300 used as the separator and lithium bis(trifluoromethane) sulfonamide (1.0 M) (LiTFSI, Novolyte Technology Co., Suzhou, China) in 1,3-dioxolane (DOL) and 1,2-dimethoxyethane (DME) (2:1 by weight) containing 1 wt% of LiNO_3 as the electrolyte. The amount of electrolyte added was 50 mL g^{-1} for every cathode. Cyclic voltammetric measurement was performed with an electrochemical workstation (CHI 660E, Chenhua, Shanghai, China) in a voltage range from 1.5 to 3.0 V at a scan rate of 0.1 mV s^{-1} . Galvanostatic charge–discharge tests were conducted with a LAND CT2001A battery test system (Jinnuo Electronic Co., Wuhan, China). All specific capacities of the cathode were calculated according to the weight of sulfur in the active material.

Results and discussion

The double-hollow carbon spheres with carbon nanotubes composites (DHCS/CNTs) have been prepared by polymerization of resorcinol with formaldehyde under the basic medium. The TEOS was added to form a hard template

(SiO_2) by in situ method. RF resin is used as a carbon precursor. Moreover, the CNTs are added to serve as a conducting and supporting agent. After carbonization, SiO_2 was removed by etching in aqueous sodium hydroxide. Sulfur is added to DHCS/CNTs with melt impregnations (see in Fig. 1).

The morphology of the S-DHCS/CNTs composites was studied with transmission electron microscopy (TEM) (see Fig. 2). The unique hollow spheres with two shells interconnected with CNTs have been observed and the inner space of DHCS/CNTs is dark after sulfur loading as shown in Fig. 2a. The high-resolution TEM image of S-DHCS/CNTs also shows a porous structure (see Fig. 2b). The S-DHCS/CNTs spheres reveal the diameter from 50 to 200 nm. The two concentric shells supported with CNTs furnishing an excellent carbon matrix for high sulfur loading. To determine the sulfur content in S-DHCS/CNTs and S-CNTs composites, thermogravimetric analysis (TGA) was executed. The sulfur content in the S-CNTs and S-DHCS/CNTs is 62% and 73%, respectively, as indicated in Fig. 2c. The higher sulfur content in S-DHCS/CNTs manifests the formation of strong sulfur binding interaction with the host material

Fig. 2 TEM image of S-DHCS/CNTs at **a** low, **b** high magnifications. **c** TGA of S-DHCS/CNTs and S-CNTs. **d** XRD of DHCS/CNTs and S-DHCS/CNTs

with high evaporation temperature [22]. This confirms that DHCS/CNTs have strong physical interactions with sulfur. The crystal structure of S-DHCS/CNTs was also investigated with X-ray diffraction (Fig. 2d). The characteristic peaks at 26° and 43° are attributed to the graphitic carbon [23], resulted due to the carbonization of the material at high temperatures. The characteristic peaks of the sublimed sulfur (PDF # 78-1889) can be observed in the S-DHCS/CNTs, confirming the presence of sulfur in the material.

X-ray photoelectron spectroscopy (XPS) was adopted to further verify the surface composition of S-DHCS/CNTs (see Fig. 3). In the survey XPS spectrum of S-DHCS/CNTs (Fig. 3a), two obvious peaks centering at 284.8 and 532.5 eV, correspond to C 1s and O 1s [24], respectively. Besides, the peaks at 169 and 232 eV are represented the S 2p and S 2s, respectively. The obtained atomic percentages of carbon, oxygen and sulfur in S-DHCS/CNTs are 77.45%, 19.49% and 3.05%, respectively. C 1s peak deconvoluted into three species, corresponding to the C–C/C=C bonds with sp^3 and sp^2 hybridizations (284.5 eV), the covalent C–S bond formed upon sulfurization (285.3 eV), the covalent C–O bond (286.4 eV) and the O–C=O (288.2 eV) [25]. The high-resolution O 1s spectrum of S-DHCS/CNTs shows

the interactions of oxygen with carbon, sulfur and hydrogen (see Fig. 3c). As illustrated in Fig. 3d, the high-resolution S 2p peak which consists of two doublets at 165.1 eV (S 2p_{1/2}) and 163.9 eV (S 2p_{3/2}) suggests the presence of S–S species [26]. The S–O peak at 168.6 eV could result from a certain amount of sulfate existing in the sample because of the oxidation of sulfur in the air.

The cyclic voltammetry profile of the cell is illustrated in Fig. 4a at the scan rate of 0.1 mV s^{-1} , showing the oxidation–reduction processes. Two prominent cathodic peaks at 2.30 and 2.02 V could be attributed to the reduction of sulfur to higher-order soluble lithium polysulfides (Li_2S_n , $4 \leq n \leq 8$) and ultimately to insoluble $\text{Li}_2\text{S}/\text{Li}_2\text{S}_2$, respectively. In the succeeding anodic scan, only one peak at about 2.46 V is observed, as a result of the oxidation of Li_2S to lithium polysulfides [16, 27, 28]. During the first four cycles, there are no significant changes for both anodic and cathodic peaks, confirming the high reversibility and electrochemical stability of the cathode. This validated that the unique structure S-DHCS/CNTs effectively confines the soluble polysulfides and maintains high utilization of the active material in the multistep reactions.

Fig. 3 XPS spectra of **a** survey, **b** C 1s, **c** O 1s, and **d** S 2p

Fig. 4 CV of S-DHCS/CNTs cathode at different **a** cycle numbers, **b** scan rates

Fig. 5 Charge/discharge profile of S-DHCS/CNTs for LSBs obtained at 0.2 C

CV analysis of the S-DHCS/CNTs cathode was investigated to evaluate the lithium-ion diffusion coefficient (D) of the cathode using the Randles–Sevcik equation [29],

$$I_p = 2.69 \times 10^5 n^{3/2} A D^{1/2} \nu^{1/2} C, \quad (1)$$

where I_p is the peak current in ampere (A), n is the number of electrons transferred, A is the surface area (cm^2), D is diffusion coefficient (cm^2/s), ν is the scan rate (V/s), and C is the lithium-ion concentration (mol/cm^3).

When the scan rate increases, the charge current also increases and actual capacitance is constant for the materials. This implies that when the scan rate increases, it is allowing more current to flow (i.e., flowing of electrical charge carriers) is indicated in Fig. 4b. The calculated D values are $3.16 \times 10^{-7} \text{ cm}^2 \text{ s}^{-1}$, $4.5 \times 10^{-7} \text{ cm}^2 \text{ s}^{-1}$ and $6.32 \times 10^{-6} \text{ cm}^2 \text{ s}^{-1}$ at 2.3, 2.02 and 2.46 V, respectively.

The galvanostatic discharge–charge profile was carried out at a current rate of 0.2 C (Fig. 5). The discharge curve consists of two reduction plateaus about 2.03 and 2.34 V,

respectively; while the charge curve consists of one oxidation plateau about 2.4 V. This information is similar to the data obtained by CV.

The electrochemical properties of the cathode prepared from S-DHCS/CNTs are shown in Fig. 6. To study the cyclic and rate performances of the S-DHCS/CNTs cathode material, the Li–S batteries using S-DHCS/CNTs cathode material were tested. As shown in Fig. 6a, the initial capacity of S-DHCS/CNTs at 0.2 C is as high as 1709 mAh g^{-1} , and maintain a reversible capacity of about 730 mAh g^{-1} after 48 cycles with high coulombic efficiency of about 100%. This proposing that the reversibility of Li^+ insertion and extraction is high [30]. The sulfur loading of S-DHCS/CNTs cathode is 3.3 mg cm^{-2} with a high areal capacity of $5.6 \text{ mAh mg cm}^{-2}$, indicating that the high utilization of the active material. Besides, it could also physically suppress the soluble polysulfides and the volume expansions [31, 32].

The rate performance of the S-DHCS/CNTs cathode was evaluated at different current rates (Fig. 6b). The capacities of the S-DHCS/CNTs cathode are 551, 574, 548, and 840 mAh g^{-1} at the high current rate of 3, 4, 5, and 0.5 C, respectively. When the current rate of S-DHCS/CNTs is restored to 3 C, the electrode produces a highly stable specific capacity of 573 mAh g^{-1} . Thus, the S-DHCS/CNTs cathode provides good conductivity and material utilization with 3.0 mg cm^{-2} sulfur loading.

Thus, the CFP fibers provide better conductivity and better active material utilization was achieved at high cycling rates.

The comparison of the cycling performance of the S-DHCS/CNTs and cathodes at 0.5 C with 3.2 mg cm^{-2} ($1 \text{ C} = 1675 \text{ mA h g}^{-1}$) was studied (see Fig. 6c). The S-DHCS/CNTs electrode delivers an initial capacity of 1224 mA h g^{-1} with the areal capacity of $5.4 \text{ mAh mg cm}^{-2}$ and maintains 615 mAh g^{-1} after 160 cycles, elucidating that the cathode possesses excellent electrochemical performance

Fig. 6 Electrochemical tests of S-DHCS/CNTs. **a** Cyclic performance, **b** rate performance at different rates, **c** long cyclic performances of S-DHCS/CNTs and S-CNTs, and **d** cyclic performances at 2 C after activation at 1 C

in respect of the reversible capacity and cycling stability (stable and higher coulombic efficiency). However, the ordinary S-CNTs electrode shows lower cyclability and lower coulombic efficiency under similar test conditions. Besides, the S-CNTs cathode exhibits rapid capacity fading and the reversible capacity decreases to 339 mA g^{-1} after 148 cycles. The superior capacity of S-DHCS/CNTs is due to the double-hollow structure of the carbon spheres interconnected with CNTs, which enhances the encapsulation of the active material. The novel structure could also suppress the volume expansion and outward diffusion of soluble polysulfides resulting a high coulombic efficiency. Figure 6d shows that both the capacity and cycle performance obtained by the S-DHCS/CNTs in our study surpass many other related works on S-DHCS/CNTs, delivered a high initial capacity of 1145 mAh g^{-1} at 1 C and 507 mAh g^{-1} at 2 C after 150 cycles.

Conclusion

In summary, a double-hollow carbon sphere integrated with CNTs as a sulfur host for Li-S batteries was prepared. RF resin is used as a carbon precursor and the SiO_2 spheres are prepared by the in situ method. The unique DHCS/CNTs structure can effectively confine sulfur and exhibit high sulfur content (73 wt%). The CNTs serves as a conductive

agent. Owing to the unique structure, the S-DHCS/CNTs electrode performs an outstanding electrochemical performance. The S-DHCS/CNTs cathode with 3.3 mg cm^{-2} sulfur loading achieves as high as 1709 mA h g^{-1} , and maintains a reversible capacity of about 730 after 48 cycles at 0.2 C with high coulombic efficiency of about 100%. Besides, the cathode with 3.2 mg cm^{-2} sulfur loading provides a high areal capacity of $5.4 \text{ mA h mg cm}^{-2}$. This attributed that the DHCS/CNTs effectively confine sulfur and physically suppress the soluble polysulfides during cycling. Therefore, our work demonstrates the potential application of the material with high sulfur loading for high-performance Li-S batteries.

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Compliance with ethical standards

Conflict of interest The authors declare no conflict of interest.

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