

Core-shell meso/microporous carbon host for sulfur loading toward applications in lithium-sulfur batteries

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Abstract

Lithium-sulfur (Li-S) batteries belong to one of the promising technologies for high-energy-density rechargeable batteries. However, sulfur cathodes suffer from inherent problems of its poor electronic conductivity and the shuttling of highly dissolvable lithium polysulfides generated during the cycles. Loading sulfur into porous carbons has been proved to be an effective approach to alleviate these issues. Mesoporous and microporous carbons have been widely used for sulfur accommodation, but mesoporous carbons have poor sulfur confinement, whereas microporous carbons are impeded by low sulfur loading rates. Here, a core-shell carbon, combining both the merits of mesoporous carbon with large pore volume and microporous carbon with effective sulfur confinement, was prepared by coating the mesoporous CMK-3 with a microporous carbon (MPC) shell and served as the carbon host (CMK-3@MPC) to accommodate sulfur. After sulfur infusion, the as-obtained S/(CMK-3@MPC) cathode delivered a high initial capacity of up to 1422 mAh·g⁻¹ and sustained 654 mAh·g⁻¹ reversible specific capacity after 36 cycles at 0.1 C. The good performance is ascribed to the unique core-shell structure of the CMK-3@MPC matrix, in which sulfur can be effectively confined within the meso/microporous carbon host, thus achieving simultaneously high electrochemical utilization.

Key words

core-shell structure; microporous carbon coating; mesoporous carbon; lithium-sulfur batteries; sulfur cathode

1. Introduction

Rechargeable batteries with high energy densities and long-lasting life have elicited considerable research attentions because of the urgent demand for energy storage devices for electric vehicles, as well as interest in smart power grids [1–5]. Among the various types of rechargeable batteries, lithium-sulfur batteries are promising owing to their high theoretical energy density of 2600 Wh·kg⁻¹ calculated on a Li anode (approximately 3860 mAh·g⁻¹) and a sulfur cathode (approximately 1675 mAh·g⁻¹) [6–8]. Despite extensive investigations on the Li-S batteries for several decades, the Li-S batteries are still fatigued with a variety of problems that hinder their commercial utilization. The problems include poor electronic/ionic conductivity of elemental sulfur, causing low utilization of the active material, as well as the high solubility of polysulfides (Li₂S_n, 4 ≤ n ≤ 8), which are sulfur reduction intermediates in liquid organic electrolytes. The dissolved

polysulfide ions shuttle between the sulfur cathode and the lithium anode, causing precipitation of insoluble and insulating Li₂S₂/Li₂S on the surface of the electrodes. These issues result in low utilization of the active material, poor cycle life, and low Coulombic efficiency [9–11].

Porous carbon materials have been proved to be effective and facile candidates to solve the above problems because of their excellent electrical conductivity and the electrochemical affinity with sulfur [12–15]. Among them, ordered mesoporous carbons (OMCs) are promising carbon matrixes for sulfur accommodation, based on their large pore volume and highly ordered pore structure. The former facilitates a high sulfur loading rate and the latter is favorable for homogenous sulfur infusion. CMK-3, which has been successfully utilized to host sulfur in Li-S batteries by Nazar and colleagues [16], possesses a large pore volume (2.1 cm³·g⁻¹), with a uniform pore size of 3.3 nm, and consequently accommodates sulfur with a high loading rate of up to 70%. The as-obtained sulfur-CMK-3 composite (S/CMK-3) manifests high sulfur

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utilization. However, the problem of polysulfide dissolution still exists, arising from the open pore architecture of CMK-3, which leads to an obvious capacity decay of approximately 10% for the first 20 cycles. To overcome this issue, various coating shells, such as PEO (polyethylene oxide), conducting polymers and SiO_x , were attached to OMCs [16–21]. Although these coating shells have confinement on polysulfides, they usually have poor electronic conductivities. As a result, these coated S/CMK-3 composites show an increased interfacial charge transfer resistance [22]. Therefore, the ideal coating material should not only function as a block layer, but also be ionically and electronically conductive.

Apart from mesoporous carbons, microporous carbon materials have also been investigated as the loading hosts for sulfur in Li-S batteries. Compared with mesoporous carbons, microporous carbons show much improved confinement for polysulfides. It is worth to note that chain-like sulfur molecules stored in microporous carbons with 0.5 nm micropores can completely avoid the formation of soluble polysulfide intermediates and thus deliver impressive electrochemical properties with high capacity, good cycle stability, and superior rate capability [23]. However, the implementation of microporous carbons in Li-S batteries is limited by their small pore volume, which will decrease the loading amount of sulfur, thus reducing the specific capacity of the entire S/C composite.

Herein, we report a meso/microporous carbon material with a core-shell structure by coating CMK-3 with a thin microporous carbon layer, which acts as an ideal carbon host to contain sulfur for Li-S batteries. On the one hand, the inner large mesopores provide sufficient space to gain a high sulfur loading rate, and on the other hand, the outer microporous carbon shell can effectively constrain polysulfide dissolution towards the electrolyte. Owing to the unique core-shell structure of S/(CMK-3@MPC), the cathode can achieve high reversible capacity and stable cycle performance.

2. Experimental

2.1. Synthesis of CMK-3@MPC carbon host

The carbon host of CMK-3@MPC was prepared for subsequent sulfur accommodation. Typically, silica template of rod-like SBA-15 was first prepared as described in the literature [16]. Then, a carbon precursor (CP) was filled inside the mesopores of SBA-15 via a solution-evaporation impregnation to obtain the SBA-15@CP. Thereafter, the carbon-coating process was performed on the SBA-15@CP. In a typical synthesis, 200 mg of SBA-15@CP was ultrasonically dispersed in 45 mL of aqueous solution containing 400 mg of D-glucose for 4 h to form a homogenous brown suspension. Then, the suspension was sealed in a 70 mL Parr autoclave with a quartz tube and heated at 180 °C for 15 h. After the hydrothermal reaction, the dark-brown precursor was collected by centrifu-

gation, washed with deionized water thrice, and then dried at 60 °C overnight. The dried precursor was calcined under argon at 800 °C for 1 h, with a heating rate of 3 °C·min⁻¹ and a flow rate of 50 mL·min⁻¹. To remove the SBA-15 template, the composite was stirred in a 5% HF solution at room temperature for 24 h to obtain the CMK-3@MPC composite. For comparison, mesoporous carbon of CMK-3 without any coating shell was prepared similarly [16].

2.2. Synthesis of S/(CMK-3@MPC) composite

Sulfur and the as-prepared CMK-3@MPC carbon host were thoroughly mixed according to a mass ratio of 7 : 3. Then, the mixture was put into a glass tube, with both sides sealed, and heated at 400 °C for 10 h to obtain the S/(CMK-3@MPC). For comparison, a sulfur-CMK-3 (S/CMK-3) composite was prepared through the same sulfur-infiltration process.

2.3. Materials characterization

SEM (6701F, operating at 10 kV), TEM (Tecnai F20) and EDX elemental mapping (Tecnai F20) were used to investigate the morphologies, particle sizes, structure and elemental compositions of the materials. XRD analysis of the as-obtained samples was carried out with a Rigaku D/max-2500 with Cu K_α radiation ($\lambda = 1.54056 \text{ \AA}$) operated at 40 kV and 200 mA. Thermogravimetric analysis of S/(CMK-3@MPC) was applied on TG/DTA 6300 to obtain the sulfur content in the composite. Nitrogen adsorption and desorption isotherms were measured at 77.3 K on an Autosorb-1 specific surface area analyzer from Quantachrome Instruments.

2.4. Electrode fabrication and electrochemical measurements

Electrochemical measurements were performed using Swagelok-type cells assembled in an argon-filled glove-box. To prepare S/(CMK-3@MPC) electrodes, a mixture of an active material, super-P acetylene black and poly(vinyl difluoride) at a weight ratio of 70 : 20 : 10 was pasted on an Al foil. The sulfur cathode had a diameter of 1 mm and an active material load of approximately 1 mg·cm⁻². Lithium foil was used as the anode. The organic electrolytes comprised solutions of Bis-(trifluoromethane) sulfonimide lithium (LiTFSI) (99.95% trace metals basis) in a mixed solvent of 1,3-dioxolane (DOL) and dimethoxyethane (DME) with a volume ratio of 1 : 1 (purchased from Zhangjiagang Guotai-Huarong New Chemical Materials Co. Ltd.). Galvanostatic cycling of the assembled cells was carried out using an Arbin BT2000 system in the voltage range of 1.0 V to 3.0 V (vs. Li⁺/Li). Cyclic voltammetry (CV) measurements were performed on an Autolab PG302N with a scanning rate of 0.1 mV·s⁻¹ in the potential range of 1.0 V to 3.0 V (vs. Li⁺/Li).

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