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Mesoporous carbon materials prepared from litchi shell as sulfur encapsulator for lithium-sulfur battery application

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HIGHLIGHTS

- Mesoporous carbon materials (MCMs) were synthesized from waste litchi shells.
- The as-prepared MCMs exhibit a similar conductivity to conductive carbon black.
- MCMs-S cathode delivers a very high initial specific capacity of 1667 mAh g^{-1}.
- The MCMs-S cathode material treated at 300 °C remains 612 mAh g^{-1} after 200 cycles.

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ABSTRACT

Novel mesoporous carbon materials (MCMs) with excellent electron conductivity and high surface area are successfully synthesized from waste litchi shells. The as-prepared MCMs possess a narrow pore size distribution (0.5–2.0 nm) and exhibit similar electron conductivities to conductive carbon black (Super P, Timcal). Because of the unique properties of MCMs, they are used as host matrixes to encapsulate sulfur for lithium-sulfur cathodes. The obtained MCMs-sulfur (MCMs-S) composite cathodes deliver a high initial specific capacity of 1667 mAh g^{-1}. Moreover, 300 °C treated MCMs-S composite cathode shows a more stable discharge capacity than the untreated MCMs-S composite cathode, it remains 612 mAh g^{-1} after 200 cycles at a high current density of 0.5 C.

1. Introduction

Lithium-sulfur batteries are considered as one of the most promising candidates for the next generation high-energy storage system owing to a high theoretical capacity of 1672 mAh g^{-1} and a high energy density of 2500 Wh kg^{-1} of sulfur cathode on the basis of complete reaction of sulfur with lithium to lithium sulfide (Li_2S) [1]. Additionally, the advantages of the natural abundance, low cost and environmental friendliness of elemental sulfur make it attractive for large-scale practical applications [2,3]. However, there are two major challenges that hinder the practical application of this attractive cathode material [4]. One is the low electrical conductivity of elemental sulfur (5×10^{-30} S cm^{-1}) and its discharge product of Li_2S at room temperature, which results in low utilization of the active material and low rate capability [5,6]. The other problem is the high solubility of intermediate products of lithium polysulfides (Li_2S_x, $4 \leq x \leq 8$) in the organic electrolyte solution. The polysulfide intermediates dissolve in the organic electrolyte and shuttle between the sulfur cathode and the metal lithium anode, causing precipitation of insoluble and insulating Li_2S_2 and/or Li_2S on the surface of electrodes [7]. The dissolution and shuttle effect of the polysulfide intermediates leads to irreversible active material loss and rapid capacity decay [7–9]. Thus, how to effectively improve the electrical conductivity of sulfur cathode and

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Table 1
Mesoporous carbon materials (MCMs) prepared from litchi shell.

Sample	Weight ratio (litchi shell/KOH)	Carbonization temperature (°C)	Carbonization time (h)
MCM1	1:1	900	1.5
MCM2	1:1.5	900	1.5
MCM3	1:2	900	1.5
MCM4	1:3	900	1.5

suppress the diffusion of polysulfide intermediates has become the focus of research in the field of lithium–sulfur batteries.

To overcome these shortcomings, many approaches have been proposed to improve the electrochemical performance of the sulfur cathode. Among them, the most widely used method is to encapsulate sulfur with various porous carbon materials [10–19], particularly mesoporous carbon. Because of the excellent electron conductivity and some adsorption property of porous carbon materials, the electronic conductivity of the sulfur composite is greatly improved, and the dissolution of polysulfide intermediates into the electrolyte is also restrained effectively, which results in high active material utilization and improved cycle stability. For example, Nazar et al. [10] synthesized nanostructured polymer-modified mesoporous CMK-3 carbon-sulfur composite cathode materials, which exhibited a high initial reversible capacity of 1320 mAh g^{-1}. In previous work [11], mesoporous carbon materials were synthesized from silk cocoon, and mesoporous carbon-sulfur composite was prepared and used as a cathode material, which delivered a high initial discharge capacity of 1443 mAh g^{-1} and retained a capacity of 804 mAh g^{-1} after 80 cycles at a rate of 0.5 C.

Because mesoporous carbon materials possess a much smaller pore size, using mesoporous carbon as a sulfur supporter may be helpful to suppress the dissolution of polysulfides into electrolyte. Previous studies have suggested that the sulfur cathode based on mesoporous carbon gives a significantly improved cycling stability [20–22]. Furthermore, Based on theoretical calculation results of sulfur allotropes by Guo et al. [20], the size of S_8 molecule in at least two dimensions are <0.7 nm. Thus, S_8 can be accommodated into the mesopores (0–2.0 nm). In this work, mesoporous carbon materials (MCMs) were prepared by carbonization of waste litchi shells. Compared with the reported porous carbon materials [23,24], the as-prepared MCMs possess a narrow pore size distribution (from approximately 0.5 to 2.0 nm) and exhibit similar electron conductivities to conductive carbon black (Super P, Timcal). Moreover, MCMs contain certain amount of nitrogen, which could improve the wettability, surface polar and adsorption ability of the carbon material. When elemental sulfur was encapsulated into the narrow mesopores of MCMs, a certain amount of C–S chemical bonds could be formed in MCMs-S composite. Consequently, sulfur is trapped in the narrow mesopores and the MCMs-S composites exhibit superior electrochemical performance.

2. Experimental section

2.1. Preparation of mesoporous carbon materials (MCMs) from litchi shell

The waste litchi shell was collected, and then cleaned using deionized water and dried at 80 °C for 24 h. The dried litchi shells were pre-carbonized at 300 °C for 3 h with a heating rate of 1 °C min^{-1}. The obtained pre-carbonized litchi shells were grinded and mixed with KOH (w/w = 1:1, 1:1.5, 1:2 and 1:3) in ethanol. The obtained mixture was stirred and stood for 12 h at room temperature, and then dried at 120 °C in an oven and carbonized in a tubular furnace at 900 °C for 1.5 h with a heating rate of 5 °C min^{-1} under a nitrogen atmosphere. The obtained carbon materials were treated with 1 M HNO_3 aqueous solution three times, and washed several times with deionized water and vacuum dried at 120 °C for 24 h. The final products were labeled as MCM1, MCM2, MCM3 and MCM4, respectively and listed in Table 1.

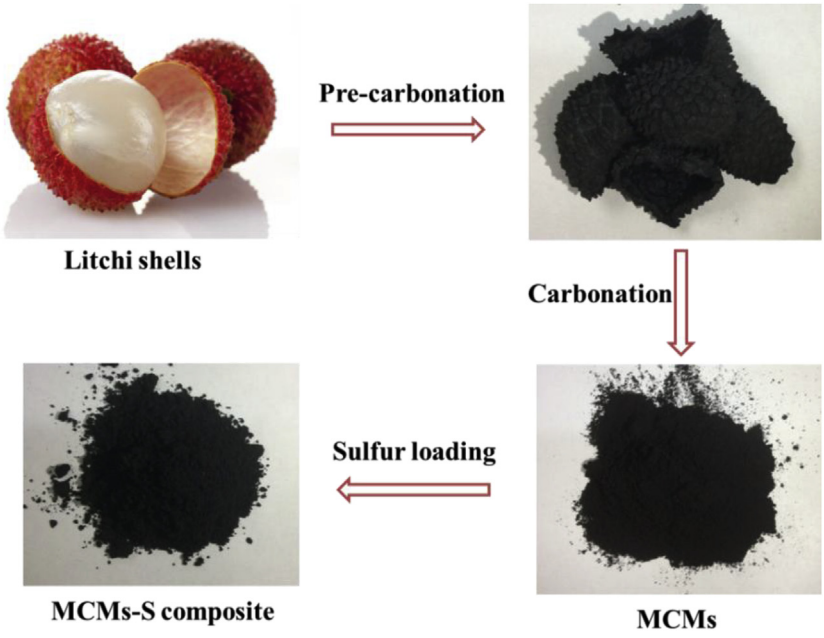

Fig. 1. Schematic illustration for the MCMs-S composite fabrication.