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Enhanced performance of lithium sulfur battery with polypyrrole warped mesoporous carbon/sulfur composite☆

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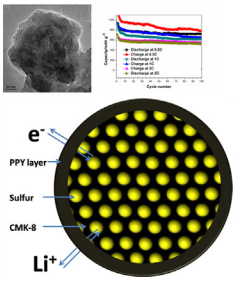
HIGHLIGHTS

- A novel approach for high-rate lithium sulfur batteries.
- 3D cubic mesoporous carbon CMK-8 was used as the matrix of the sulfur.
- A wrapping microstructure was designed and obtained with PPy as the coating layer of the CMK-8/S composite.
- This work makes much sense to the structure designing of novel sulfur-based materials.

GRAPHICAL ABSTRACT



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ABSTRACT

A sulfur cathode is designed with three-dimensional (3D) cubic mesoporous carbon CMK-8 as the matrix of sulfur, and polypyrrole (PPY) as the wrapping layer. CMK-8 provides perfect 3D conductive network. Furthermore, PPY is coated onto the surface of CMK-8/sulfur (CMK-8/S) composite to inhibit the migration of lithium polysulfide and offer better lithium ion conductive channels. The microstructure and electrochemical performance of the PPY@CMK-8/sulfur (PPY@CMK-8/S) cathode are investigated systematically. The results show that PPY layer with about 50 nm thickness is coated uniformly on the surface of CMK-8/S. The Li–S battery with PPY@CMK-8/S as cathode material presents a discharge capacity of 937.8 mAh g^{-1} at 20 cycles and is stabilized at about 860 mAh g^{-1} after 100 cycles at 0.2C.

1. Introduction

Li-ion battery is one of the most important rechargeable batteries in modern society. However, it still can't meet energy requirements for many applications, such as electric vehicle, large scale energy storage et al. [1,2]. The relatively low capacity of cathodes is one of the main obstacles achieving the high specific energy. As known, sulfur cathode has a theoretical capacity of 1675 mAh g^{-1} and a theoretical specific energy of 2600 Wh kg^{-1}, which are much higher than that of the commercialized $LiCoO_2$ system [3]. Therefore, in combination with the natural abundance, low cost and environmental friendliness of sulfur, the Li–S high

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energy density battery system becomes a promising candidate for the next generation power source.

Lithium sulfur (Li–S) battery has been studied for almost 50 years since Herbt and Ulam first introduced the concept of elemental sulfur as a positive electrode material in 1962. However, the spotlight hasn't returned to this battery system until there is a renewed interest in electric vehicles in recent years. The major impediments to the development of Li–S battery are low active material utilization rate, poor cycle life and low coulombic efficiency [4,5]. The insulating nature of sulfur and lithium sulfides decreases the utilization rate of active material. And the high solubility of lithium polysulfides generated during the electrochemical-reduction reaction process, results in severe capacity loss. The so called shuttle mechanism resulting from the migration of lithium polysulfides in the liquid electrolyte, even penetrating through the separator, followed by immediate reaction with metallic-lithium anode and the formation of Li_2S, is considered as the major reason for the low coulombic efficiency. Moreover, the gradually deposition and aggregation of insulating Li_2S on the cathode's surface results in a poor high-rate capacity and cycle stability.

To overcome these problems, sulfur embedding in the conductive carbon matrix has been adopted frequently. Various carbon materials such as active carbon [6], mesoporous carbon [7–10], carbon nanotubes [11,12], grapheme [13,14], microporous carbon [15,16], and porous hollow carbon [17,18] have been applied to achieve the purpose.

It was reported that with CMK-3, an ordered mesoporous carbon with high specific surface area and large pore volume, acting as the absorbent and matrix of sulfur, the Li–S battery exhibited reversible capacities up to 1350 mAh g^{-1} [8,10]. However, polysulfide can still dissolve in the electrolyte without any kinetic and chemical constraints, leading to a poor cycle performance. To inhibit the shuttle behaviors, conductive polymers such as PEDOT:PSS [19], PEO-PPO [20] and PANi [21] were adopted as coatings onto the surface of S/C composite. Since the good conduction feature of the conductive polymer, the coating layer affords the sulfur cathode low interfacial polarization, and hinders the polysulfides dissolution.

CMK-8 is a kind of 3-dimensional highly conductive mesoporous carbon, which has been widely used in supercapacitors [22] and catalytic [23,24]. However, there are few reports about the application of CMK-8 in the Li–S battery. Polypyrrole is another kind of conductive, whose dual conductive is beneficial to improve the rate ability [25]. Furthermore, the rich functional groups of PPY owe chemical trapping of polysulfides. In addition, the mechanical properties of PPY allows for better accommodation of volume expansion than pure carbon coatings [26]. Herein, the mesoporous carbon CMK-8 is prepared and acts as the matrix to load sulfur. PPy [25,27] is coated onto the surface of CMK-8/sulfur composite using a simple chemical oxidative polymerization method, then a wrapping micro-structure composite could be realized as shown in Fig. 1. In the obtained PPy@CMK-8/S composite, the sulfur nano-particles were penetrated into the channels of cubic mesoporous carbon CMK-8, and the CMK-8/S composite was wrapped with PPy. The 3D conductive networks and the coating layer for sulfur active material are favorable to improve the utilization rate of sulfur and coulombic efficiency, moreover to decrease the interfacial polarization.

2. Experimental

2.1. Preparation of PPY@CMK-8/S composite

The mesoporous carbon CMK-8 was prepared by the nanocasting process using sucrose as a precursor, mesoporous silica

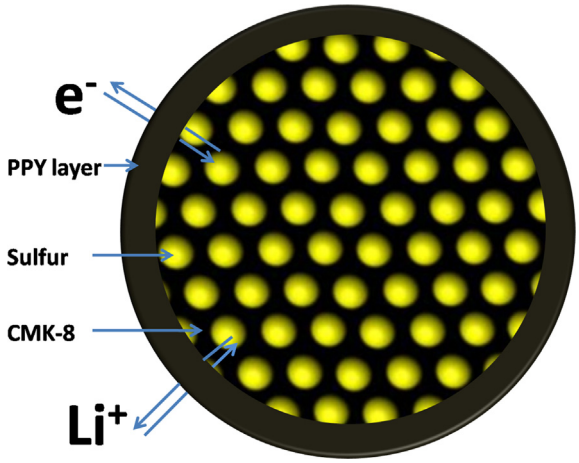

Fig. 1. The schematic diagram of the wrapping micro-structure composite.

KIT-6 as the hard template and sulfuric acid as the carbonization catalyst according to the literature [22,28]. The CMK-8/sulfur composite (CMK-8/S) was prepared by a melting-diffusion strategy with a mixture of sulfur and CMK-8 in the weight ratio of 3:1 and 3:2 respectively was sealed in a glass tube under vacuum followed by co-heating at 155 °C for 3 h and 300 °C for 2 h. The pitaya like PPY@CMK-8/sulfur composite (PPY@CMK-8/S) was prepared as follows: 0.4 g CMK-8/S (sulfur and CMK-8 in the weight ratio of 3:1) was dispersed in 200 ml deionized water by sonication for 30 min. Then, 0.1 g pyrrole was added into the solution and stirred for 30 min. After that, proper amount of $FeCl_3$ was added dropwise and stirred for 12 h, the chemical reaction was controlled under 2 °C. The product was washed and filtered until the filtrate was colorless. Finally, the products were dried under vacuum at 60 °C for 12 h. In order to obtain close sulfur contents in CMK-8/S and PPY@CMK-8/S composite, more content of sulfur in CMK-8/S composite is used to be wrapped with PPY.

2.2. Preparation of the sulfur cathode and coin-type cell

To prepare the cathode, the slurry was prepared by mixing 80 wt % PPY@CMK-8/S composite, 10 wt% acetylene black (AB), 5 wt% carboxy methyl cellulose (CMC), 5 wt% (styrene-butadiene rubber) SBR with deionized water was first prepared by ball milling. For comparison, the slurry of CMK-8/S composite (sulfur and CMK-8 in the weight ratio of 3:2) was prepared in the same way. The slurries were casted onto aluminum foil substrates. After the solvent was evaporated, the electrode was cut into discs with 14 mm in diameter and then dried at 60 °C under vacuum for 12 h. CR2025 type coin cells were assembled in a glove box with oxygen and water contents less than 1 ppm. A solution of 1 M LITFSI dissolved in DOL/DME/PYR_{14}TFSI (v/v/v, 2/2/1) was employed as the electrolyte. The cells contained Celgard 2400 as the separator and lithium foils as both the counter and reference electrodes.

2.3. Characterization

Thermogravimetry (TG) (NETZSCH 409 PC) was applied under N_2 atmosphere to determine the components of the composite. FTIR spectra were carried out on the Thermo Nicolet 7000-C Fourier Transform Spectrometer with ±2 cm^{-1} resolution between 4000 and 400 cm^{-1} using KBr disk method. Specific surface area was tested using the Brunauer–Emmett–Telley (BET) method on the Micromeritics Tristar 3000. SEM images were measured by field emission scanning electron microscope (FESEM JSM-6700) and

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