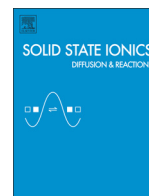




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Mesoporous carbon/sulfur composite with polyaniline coating for lithium sulfur batteries

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ABSTRACT

Polyaniline coated mesoporous carbon/sulfur composite (CMK3/S-PANI) was prepared by an in-situ polymerization of aniline monomer on the surface of CMK3/S composite. The CMK3/S-PANI composite exhibits much better electrochemical performance than the uncoated CMK3/S composite and delivers initial discharge capacity of 1103 mAh g^{-1} and maintains 649 mAh g^{-1} after 100 cycles at 1C rate. The coating layer can suppress the diffusion of discharge intermediate product into electrolyte and improve the cycling performance of the composite cathode.

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1. Introduction

With the development of electric vehicles and smart grids, high energy density lithium ion batteries have attracted much attention [1]. Elemental sulfur is considered as one of the most promising cathode candidates for next generation lithium secondary battery [2]. Lithium sulfur battery is very attractive for its natural abundance, low cost, high theoretical specific capacity (1675 mAh g^{-1}) and energy density (2600 Wh kg^{-1}). However, sulfur is a natural insulating material and the polysulfide intermediate can dissolve into organic electrolytes, which leads to a limited real capacity and rapid capacity fading of the batteries. To overcome these problems, various conductive matrixes have been designed [3–8]. For example, Ji et al. [9] reported the highly ordered nanostructured carbon–sulfur cathode, which provided access to Li^+ ingress/egress for reactivity with the sulfur and inhibited the diffusion of polysulfide. Yang et al. [10] explored the application of conducting polymer to minimize the diffusion of polysulfides out of the mesoporous carbon matrix by coating

poly(3,4-ethylenedioxythiophene)–poly(styrene sulfonate) (PEDOT:PSS) onto mesoporous carbon/sulfur particles. The discharge capacity with the polymer coating was ~10% higher than the bare counterpart, with an initial discharge capacity of 1140 mAh/g and a stable discharge capacity of $>600 \text{ mAh/g}$ after 150 cycles at C/5 rate. Enshrouding porous-carbon/sulfur composites with an inorganic thin film shell formed by the surface-initiated growth of oxides can more effectively inhibit the dissolution of polysulfides [11].

Recently, various conductive polymers with different structures have been widely used as conductive matrix for lithium sulfur batteries [6,12–14]. Polyaniline nanotube/S molecular composite synthesized for lithium sulfur battery could retain a discharge capacity of 837 mAh g^{-1} after 100 cycles at 0.1C rate. Even at a high discharge rate of 1C, the electrode manifested very stable cycling capacity up to 500 cycles [7]. Conductive polyaniline coated sulfur–carbon composite shows improved rate and cycle performance for lithium sulfur batteries [15]. PANI@S/C composite delivered a maximum discharge capacity of 635.5 mAh g^{-1} after activation at 10C rate [16], demonstrating that PANI is a superior performance conductive matrix.

In this study, we present a quick route for preparing PANI coated CMK3/S composite. Compared with other conductive carbon materials, mesoporous structure of the CMK3 can ensure good electrical contact with sulfur and act as micro-reactor for electrochemical reaction. In addition, optimized sulfur content in the CMK3 can ensure sufficient space for volume effect during charge–discharge process. Meanwhile, the conductive PANI coating physically prevents the dissolution of lithium polysulfides from the CMK3. The CMK3/S-PANI composite

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with double barrier effect can trap soluble polysulfide intermediates, which can further improve electrochemical performance of lithium sulfur battery.

2. Experimental

2.1. Preparation of the CMK3/S-PANI composite

The synthesis steps are shown in Fig. 1. Firstly, a mixture of 0.4 g mesoporous carbon CMK3 and 0.6 g sublimed sulfur was sealed in a glass tube under vacuum. Subsequently, the mixture was heated at 155 °C for 3 h and 300 °C for 2 h, to allow the melted sulfur to diffuse into the pores of CMK3 and vaporize the remaining sulfur on the outer surface of CMK3. The CMK3/S-PANI composite was prepared by an in-situ rapid polymerization method at room temperature. In a typical experiment, 0.3 g CMK3/S composite was dispersed in a water–ethanol mixture system (20 ml distilled water and 10 ml ethanol) by ultrasound. Then, 0.1 g aniline monomer and 10 ml 1 M HCl were added into the mixture solution under continuous stirring. After stirring for 30 min, an aqueous solution of $(\text{NH}_4)_2\text{S}_2\text{O}_8$ (0.245 g $(\text{NH}_4)_2\text{S}_2\text{O}_8$ dissolved in 20 ml H_2O) was added dropwise to the above mixture solution. After constant stirring for 2 h, the mixture was filtered and washed repeatedly with distilled water. The DeepGreen powder was dried at 60 °C for 12 h.

2.2. Material characterization

XRD measurements were performed using a Rigaku X-ray diffractometer at a scan rate of 6 min^{-1} . The sulfur content in the composite was detected using thermogravimetric analyzer (Netzsch STA 409PC) under N_2 flow from room temperature to 600 °C at a heating rate of 5 °C min^{-1} . Nitrogen sorption isotherms and BET surface area were measured at 77 K with a Micrometrics Tristar II analyzer (USA). The morphology of the composite was obtained by transmission electron microscopy (TEM).

2.3. Electrochemical measurements

CMK3/S and CMK3/S-PANI composite cathode were prepared by mixing the active material with acetylene black and water based binder (SBR:CMC = 1:1 w/w) in a weight ratio of 80:10:10 to form homogeneous slurry, and then casting onto aluminum foil. After being dried under vacuum at 60 °C for 10 h, the cathode electrode was cut into disks of 14 mm in diameter. CR2025 coin cells were assembled using lithium foil and Celgard separator in an Ar-filled glove box. In order to obtain high coulombic efficiency, concentrated 3 M LiTFSI DOL/DME (1:1, v/v) was used as an electrolyte for lithium sulfur battery [17–19].

Cyclic voltammetry (CV) of the cell was measured on an Autolab PGSTAT302N electrochemical workstation at a scanning rate of 0.5 mV s^{-1} between 1.5 and 3.0 V. Galvanostatic charge–discharge

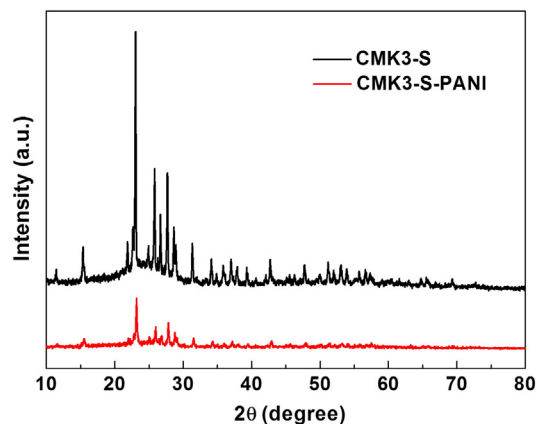


Fig. 2. XRD patterns of the CMK3/S and CMK3/S-PANI composite.

tests were carried out based on the active sulfur on a LAND-CT2001A battery test system.

3. Results and discussion

Fig. 2 presents the XRD patterns of CMK3/S and CMK3/S-PANI composite. The peaks of the composite match well with the orthorhombic pristine sulfur, indicating that the treatment process of the composite did not bring any structure change for sulfur. The obvious diffraction signals of bulk sulfur may be due to inhomogeneous distribution of sulfur outside the carbon. The BET specific surface area decreased significantly due to sulfur impregnation from initial value of $771 \text{ m}^2 \text{ g}^{-1}$ to $3.1 \text{ m}^2 \text{ g}^{-1}$ and pore volume decreased from $0.956 \text{ cm}^3 \text{ g}^{-1}$ to $0.011 \text{ cm}^3 \text{ g}^{-1}$. Furthermore, low peak intensity of CMK3/S-PANI demonstrates a complete coating of PANI on the surface of CMK3/S composite.

As seen from Fig. 3, the sulfur content of the composites was obtained by thermogravimetric analysis (TGA) under a N_2 flow from room temperature to 600 °C at a heating rate of 5 °C min^{-1} . The sulfur content in the CMK3/S composite of 53 wt.% indicated that the sulfur on the surface of CMK3 was evaporated under heat treatment. After PANI was coated on the surface of CMK3/S composite, the sulfur content decreased to 41% in the CMK3/S-PANI composite. It also showed that aniline delivered high chemical oxidative polymerization efficiency at room temperature.

The TEM result presented in Fig. 4a showed that the CMK3/S composite prepared via heat treatment under vacuum reserved the pore structure of mesoporous carbon CMK3. No significant large agglomeration was observed on the surface of the CMK3/S particles, indicating a uniform distribution of sulfur in the pore of CMK3. However, small amounts of sulfur presented on the surface of the particles will

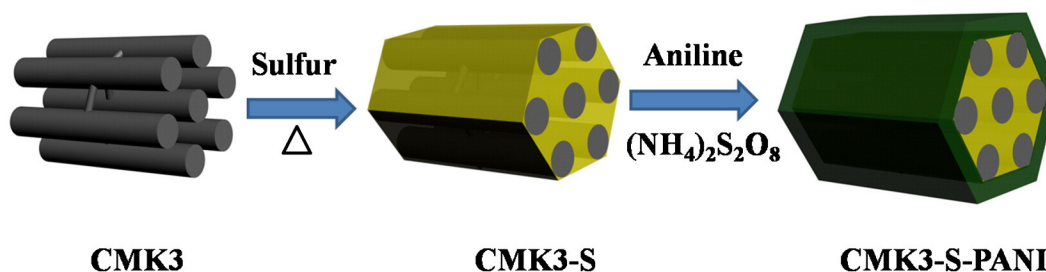


Fig. 1. Schematic of the preparation process for CMK3/S-PANI composite.

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