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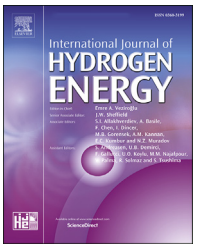

Mesoporous MnO_2 fibers as an efficient bifunctional absorber for high-performance lithium-sulfur batteries

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ABSTRACT

A novel morphology of mesoporous MnO_2 fibers (MOF) are successfully prepared for the first time as host materials for lithium-sulfur (Li–S) batteries. The as-prepared mesoporous MnO_2 fibers can restrain the polysulfides dissolution via chemical bonding and physical trapping at the same time. As a result, the mesoporous MnO_2 fibers sulfur (MOF/S) composites exhibit excellent cycle performance. The MOF/S composite electrodes deliver a high initial capacity of 1015 mAh g^{-1} and maintain 815 mAh g^{-1} after 200 cycles at 0.1 C.

Introduction

Lithium-sulfur batteries are one of the promising energy storage systems that can be applied to portable electronic equipment and electric vehicles due to their high energy theoretical specific capacity (1675 mAh g^{-1}) and energy density (2600 Wh Kg^{-1}) [1–5]. Despite these considerable advantages, many issues still remain in developing a practical lithium-sulfur battery for commercialization. Especially, the dissolution of intermediate lithium polysulfides into the electrolytes during cycling process, which results in capacity fading and poor coulombic efficiency, causes loss of active material and the polysulfides shuttle effect.

Over the past decades, much attention has been paid on the carbonaceous materials for sulfur encapsulation [19–21]. This method has been proved to successfully enhance the electrochemical performance of sulfur-based cathode. However, the nonpolar carbonaceous materials immobilize the polar polysulfides via weak physical absorption, which is insufficient for improving the cycle stability. The polysulfides are still able to diffuse out of the carbonaceous materials [6–8]. Therefore, it is particularly urgent to design optimized structure of host materials for suppressing polysulfides dissolution via strong interactions between host material and polysulfides [9,22,23].

In this paper, for the first time we have prepared mesoporous MnO_2 fibers as a bifunctional absorber for Li–S batteries. Different from previous research about sulfur host materials, the as-prepared mesoporous MnO_2 fibers sulfur composite (MOF/S) possesses two advantages: (a) the mesopores in MnO_2 fibers can absorb the polysulfides via physical

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trapping, (b) the presence of MnO_2 fibers provides enough binding to the polysulfides by chemical interactions [10,17]. Therefore, the synergistic effect of chemical bonding and physical trapping contribute to the high performance of Li–S battery.

Experimental

Materials preparation

First, 20 ml $MnSO_4$ aqueous solution (concentration 10 mM) and 60 ml $KMnO_4$ aqueous solution (concentration 2 mM) was mixed and stirred for 30 min to prepare mesoporous MnO_2 fibers (MOF). Then, the as-prepared MOF was added into a 100 mL aqueous solution of $Na_2S_2O_3 \cdot 5H_2O$ (1 g). Finally, while mildly stirring the solution, 0.6 mL concentrated HCl was added dropwise. After that, the obtained MOF/S composites were heated at 155 °C for 12 h in a tubular filled with argon gas.

Materials characterization

The morphology information were obtained from scanning electron microscopy (SEM, Ultra 55). TEM was conducted on an FEI Tecnai F20 transmission electron microscope operating at 200 kV. X-ray diffraction (XRD) measurements were carried out on a D8 Advance (Bruker, Ltd). Thermal gravimetric analysis (TGA, TA SDT-Q600) was conducted under nitrogen flow with a heating rate of 5 °C min^{-1}. The N_2 adsorption–desorption were determined by BET measurements using an Quantachrome instrument surface area analyzer.

Electrochemical measurements

The electrochemical performance of sulfur and MOF/S composite electrodes were evaluated by using CR2016 coin batteries. The galvanostatic charged/discharged tests were performed in the voltage range of 1.5–3.0 V on LAND battery tester. Cyclic voltammetry measurements and electrochemical impedance spectra (EIS) measurement were carried out on an electrochemistry workstation (CHI660E).

Results and discussion

The fabrication processes of MOF/S composites are schematically illustrated in Fig. 1. The as-prepared MOF was added into aqueous solution of $Na_2S_2O_3 \cdot 5H_2O$. Then, concentrated HCl was added dropwise. Finally, the obtained MOF/S composites were heated at 155 °C to ensure the sulfur particles dispersed uniformly in the MOF.

Fig. 2 shows the nitrogen adsorption–desorption isotherms and pore size distribution curves. As shown in Fig. 2a, the adsorption–desorption isotherms demonstrates that MnO_2 fiber possess a mesoporous structure, which can absorb polysulfides by physical trapping. The pore size distribution curve of the MnO_2 fibers (Fig. 2b) indicates that the size of the mesopores mainly centers at 12 nm, which is consistent with the adsorption–desorption isotherms analysis. Compared to the MnO_2 fibers, the isotherm of MOF/S composites shows low adsorption volume, which indicates that most pores are occupied with sulfur particles [11,12].

In order to confirm the sulfur content in the MOF/S composite, TG analysis is conducted. As shown in Fig. 3a, the mass loss of MOF/S composites is up to 74.35 wt%. Fig. 3b shows the XRD patterns of MOF, sulfur and MOF/S composite. Sulfur exhibits typical reflection pattern of a-orthorhombic type. A strong peak at 36° and two weak peaks at 62° and 65° are observed in the XRD pattern of MOF. The intensity of the sulfur peaks in the MOF/S composite becomes weaker than pure sulfur, due to the stronger interactions between mesoporous MnO_2 fibers and sulfur.

Fig. 4a shows the morphology of mesoporous MnO_2 fibers, it can be seen that the surface of MOF has large amounts of pores. After sulfur infiltration, the pores of MOF are filled with sulfur particles, as shown in Fig. 4b. In line with the SEM image, TEM image of MOF/S composites confirm that sulfur particles are dispersed uniformly in the MOF structure (Fig. 4c). Further, it has been demonstrated by STEM image and elemental mapping images (Fig. 4d–g) that Mn, O, S are well dispersed uniformly in the MOF/S composite.

The first discharge/charge curves of sulfur and MOF/S composite electrodes are shown in Fig. 5a. The MOF/S composite electrodes deliver a high specific capacity value of 1015 mAh g^{-1}, while the sulfur electrodes only display 862 mAh g^{-1} at a current density of 0.1 C. Fig. 5b shows the cyclic voltammogram profiles of sulfur electrodes and MOF/S composite electrodes. Similarly, there are two reduction peaks at 2.3 and 2.0 V for sulfur electrodes and MOF/S composite electrodes, respectively. The peak at 2.3 V is ascribed to the transformation of sulfur to soluble polysulfide. Further, the peak at 2.0 V represents the reduction of soluble polysulfide to insoluble Li_2S_2 and Li_2S. However, one main oxidation peak at 2.3 V and another shoulder peak at 2.4 V are clearly observed

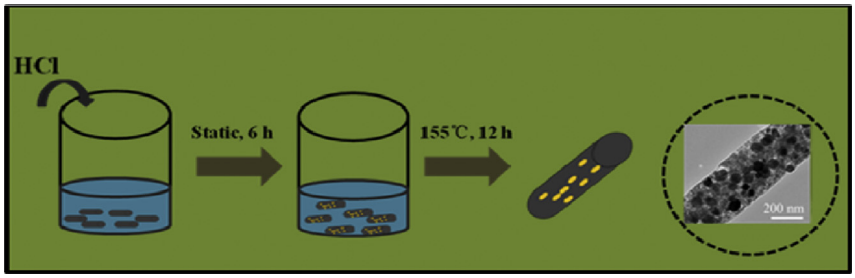

Fig. 1 – Illustration of the preparation of MOF/S composites.

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