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Short Communication

Mesoporous TiO_2 Nanofibers as Advanced Sulphur Host Materials for Lithium Storage

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With the development of the science and technology, many electric vehicles have been emerged in the markets. Therefore, advanced energy storage systems must provide sufficient energy for the electric vehicles. Among many energy systems, Li-S batteries are the most suitable system for them due to their high specific capacity and energy density. However, the poor cycle stability is the main obstacle for the application into electric vehicles. Herein, mesoporous TiO_2 nanofibers are prepared and used as advanced host materials for sulfur in the Li-S batteries. The mesoporous TiO_2 nanofibers could adsorb the polysulfide and promote the transport or electronics during discharge and charge cycles. As a result, the MTO/S composites show excellent electrochemical performance.

Keywords: Nanofibers, Li-S batteries, Polysulfide, Mechanical, Electrical Vehicle

1. INTRODUCTION

With the development of science and technology, some issues have been emerged in our society. Among many issues, the air pollution is the most severe due to fossil fuel combustion [1, 2, 3]. As we all known, gasoline is the main energy resource for the cars and buses [4, 5]. Therefore, it is urgent for us to develop new energy system, which could provide energy for the cars. In the past decades, many researchers focus on the employment of lithium-ion, lithium-sulfur batteries and so on [6, 7]. These energy storage systems, which are used in the electrical vehicles, could protect our environment to the utmost extent [8]. Among various battery systems, Li-S batteries are the most promising candidate for the electrical vehicles, due to their high specific capacity and high energy density [9, 10].

However, there are two main problems in the Li-S battery system, which inhibit the application of them for the electrical vehicles. First, the sulfur has poor electronic conductivity. Second, the polysulfide causes shuttle effect during electrochemical process [11]. Therefore, the key factors are improving the electronic conductivity and restrain the dissolution of polysulfide in the electrolyte. To solve these problems, many methods have been applied, including cathode design, anode protection and electrolyte modification [12, 13].

In this paper, mesoporous TiO_2 nanofibers are prepared and used as advanced host materials for sulfur in the Li-S batteries. The mesoporous TiO_2 nanofibers could adsorb the polysulfide and promote the transport or electronics during discharge and charge cycles at the same time. As a result, the MTO/S composites show excellent electrochemical performance.

2. EXPERIEMENTAL

2.1. Preparation of MTO/S composites

The MTO was prepared via an sol-gel method. Firstly, 20 ml ethanol and 10 ml water were mixed and stirred for 5 min. Then, 1.6 g tetraethyl titanate was added into the above solution under stirring for 20 min. At last, 1.2 g NH_3H_2O was added into the mixture drop and drop. As a result, it could be seen that the white solid is precipitated. This is the mesoporous TiO_2 nanofiber. Finally, the mixture of MTO and sulfur were heated at 155°C for 10 h to prepare MTO/S composite.

2.2. Materials Characterization

The morphologies and structure of the as-prepared samples were characterized by using scanning electron microscope (SEM, EVO 18) and the X-ray diffractometer (XRD, D8 Advance, BRUKER). X-ray photoelectron spectroscopy (XPS) was performed on a Thermo ESCALAB 250Xi for juding the element valence. BET measurements were conducted for measuring the pore structure of the samples.

2.3. Electrochemical Measurements

The electrochemical performance of the cathode materials was measured by employing CR 2016 coin batteries. For the process of preparing slurry, 80 wt.% cathode materials, 10 wt.% super black and 10 wt.% PVDF with NMP were mixed. Then, the slurry was uniformly coated on the surface of Al foil. After that, the prepared-film was placed under the temperature of 80°C for 24 h. Finally, the film was cut into circular electrodes. The cells were assembled in an Ar-filled glove box. The coin battery is used ithium foil as anode. The electrolyte was consisted of 1.0 M LiTFSIand DOL/DME. Dicharging/charging profiles were carried out on a battery testing system (Land CT2001A) in the voltage between 1.5 V and 3 V.

3. RESULTS AND DISSCUSSION

Figure 1is the XRD patterns of the pristine sulfur, mesoporous TiO_2 nanofiber and MTO/S composites. As shown in Figure 1, the MTO demonstrates typical anatase structure. The peaks at 25° and 40° are corresponding to the plane of (111) and (101), respectively, proving that the purity of the as–prepared mesoporous TiO_2 nanofiber. As for the pristine sulfur, the diffraction peaks show the typical crystal structure. After heated with the element sulfur, the intensity of the diffraction peaks for the MTO/S composites is much weaker than pristine sulfur. This result is according to the previous reports about S-based composite materials [14].

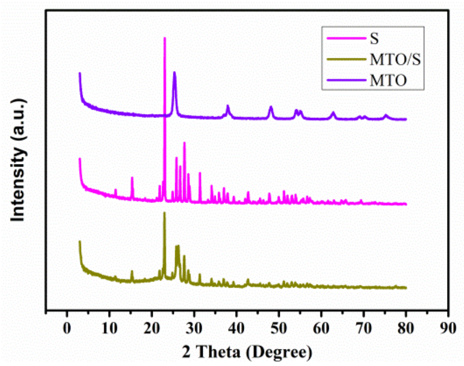

Figure 1. The XRD pattern of the S, MTO and MTO/S composites.

The porous structure is good for the transport of the li-ions and the wetting of the electrolyte. To test the porosity of the samples, BET analysis was used in the experiment under N_2 atmosphere. As shown in Figure 2a, the as-prepared MTO/S composites show typical mesoporous structure. The mesoporous structure has positive effect on the wetting of electrolyte and is beneficial for the transport of li-ion. While for the pristine sulfur, there is no porous structure to store the electrolyte. To confirm the presence of element Ti in the MTO/S composites, XPS test was conducted for the samples. As shown in Figure 2b, the Ti 2p demonstrates two main peaks at 459 ev and 464 ev, respectively. They are corresponding to the Ti $2p_{3/2}$ and Ti-S bond, respectively. From the Ti-S bond at 464 ev, it can be inferred that the chemical bond could be generated between metal oxide and pristine sulfur. This is good for the absorption of polysulfide, which is soluble in the electrolyte during electrochemical process [15].

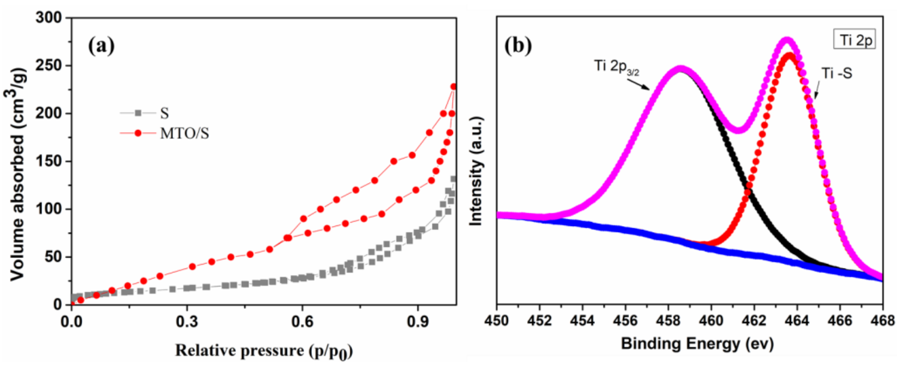

Figure 2. (a) BET curves of the sulfur and MTO/S composites. (b) The XPS of Ti 2p for the MTO/S composites.

To observe the morphology of the as-prepared MTO/S composites, SEM was applied for the MTO/S composites. As shown in Figure 3a, the TiO_2 shows mesoporous nanofiber structure with a dimeter of 10 nm. After heated with pristine sulfur, there is no obvious change on the morphology of MTO/S composites. This indicates that the sulfur particles are dipping into the mesoporous structure of the TiO_2 nanofiber. EDS could clearly observe the presence of various elements in the composites. As shown in Figure 3c-f, it can be seen that the element Ti, O and S are uniformly dispersed in the TMO/S composites. In conclusion, the MTO/S composites are prepared successfully. As we all know, the performance depends on the structure of the materials. Therefore, this unique mesoporous nanofiber structure is beneficial for the improvement of the electrochemical performance [16, 17].

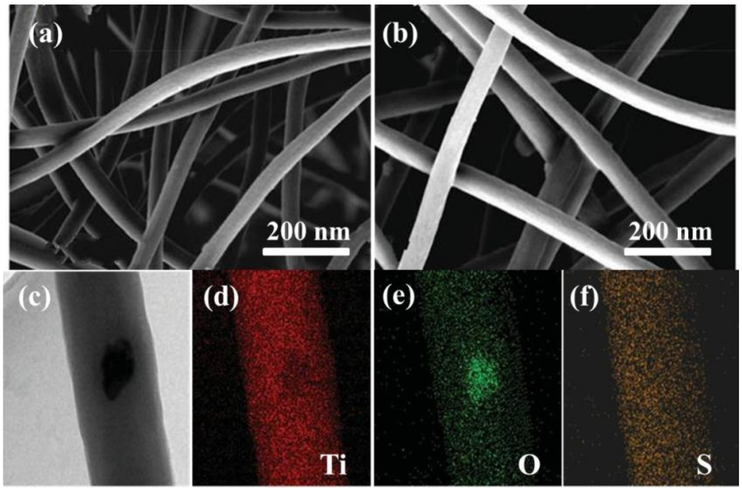

Figure 3. (a), (b) SEM images of the mesoporous TiO_2 nanofiber and MTO/S composites, (c-f) TEM iamge of MTO/S composite and corresponding elemental mapping of Ti, O and S.

The specific capacity is an important index for the Li-S batteries. The high capacity could provide sufficient energy for the electric vehicles. Therefore, constant discharge charge profiles are tested for the two cathode materials. As shown in Figure 4, the as-prepared MTO/S composite delivers initial specific capacity of 1186 mAh/g at the current density of 0.2 C. Moreover, it could be observed that the discharge capacity is equal to the charge capacity, demonstrating high coulombic efficiency. While the pristine sulfur shows the initial specific capacity of 695 mAh/g, which is much lower than the MTO/S composites. Besides, the voltage platform at 2.1 V of MTO/S composites is longer than pristine sulfur. As a result, the MTO/S composites display higher specific capacity value than pristine sulfur. Clearly, the as-prepared MTO/S composites cathode show excellent specific capacity value, which is significant for the Li-S battery that used in electric vehicles [18]. As for the improvement of capacity value, it is ascribed to the unique structure of the cathode materials, which could enhance the conductivity. Besides, the presence of metal oxides provides sufficient absorption ability between the MTO and polysulfide [19, 20].

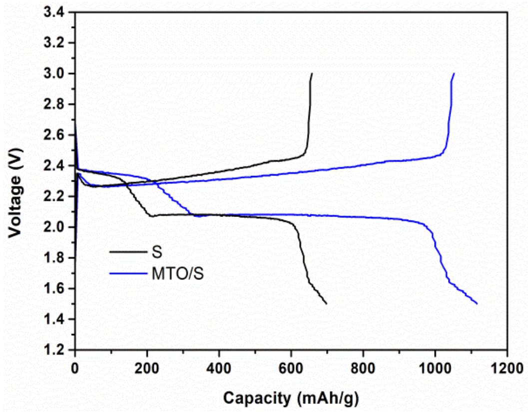

Figure 4. The constant discharge/charge profiles of the S and MTO/S cathode.

Cycle stability is another important factor for the Li-S batteries that used in the electric vehicles. The electric vehicles must have sufficient mileage. To study the cycle performance of the samples, long cycle performance is tested for 200 cycles. As shown in Figure 5, the MTO/S composites deliver specific capacity of 1206 mAh/g. This value is at 1100 mAh/g after 200 cycles at the current density of 0.5 C. In terms of the pristine sulfur used as cathode in the Li-S battery, the specific capacity value is only 726 mAh/g after 200 cycles at the current density of 0.5 C. Besides, the coulombic efficiency of the MTO/S composite cathode is about 98% all the time, which is much higher than pure sulfur cathode. From the cycle performance test, it can be seen that the MTO/S cathode materials exhibit superior cycle stability than the pure sulfur cathode. Cycle stability have direct influence on the employment of the Li-S battery which will be used in electric vehicles [21]. Perfect electric vehicles must have long enough range [22].

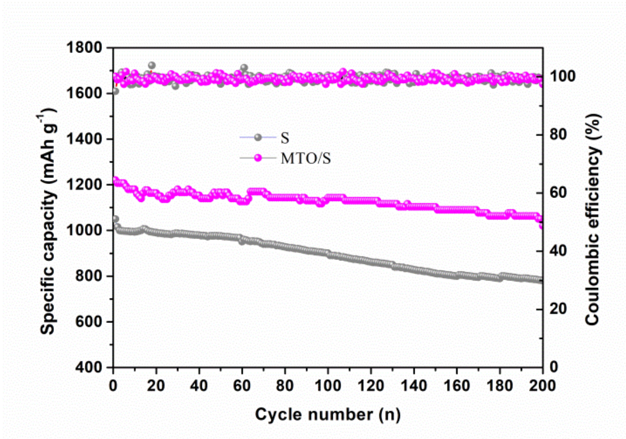

Figure 5. The cycle performance of the S and MTO/S cathode at the current density of 0.5 C.

Rate capability of the samples is tested at various kinds of current densities from 0.1 C to 2 C. As shown in Figure 6, the MTO/S composites display superior rate performance from 0.1 C to 2 C. It shows specific capacity of 996 mAh/g at the current density of 1C in the cycle process. When the current density is at 2 C, its specific capacity is 868 mAh/g, demonstrating excellent ability at various kinds of current densities. Finally, when the current density comes back 0.1 C, the specific capacity value recovers as its initial capacity value. However, it can be seen that the specific capacity of pristine sulfur fades rapidly with the increase of the current density. Therefore，the MTO/S cathode materials have more excellent electrochemical performance than the pristine sulfur cathode. As a result, the MTO/S cathodes could be used as a promising energy storage system for the electric vehicles.

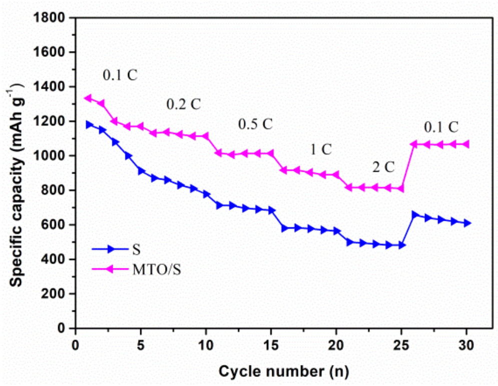

Figure 6. Rate performance of the S and MTO/S composite at various kinds of current densities.

To further understand the excellent electrochemical performance of the as-prepared MTO/S composites, various kinds of cathode materials are listed in the Table 1. As shown in Table 1, it could be seen that the MTO/S composites shows the most superior electrochemical performance. This is attributed to the presence of metal oxide TiO_2, which could modify the electronic conductivity. Besides, the Ti-S bond in the MTO/S composites is beneficial for the absorption of soluble polysulfide in the electrolyte.

Table 1. Comparison of the electrochemical performance between the MTO/S composites and other reported cathode materials.

Sample	Current	Specific Capacity	Ref
rGO/WS_2-S	0.5 C	883 (200)	23
S/Al_2O_3/PPy	0.5 C	730 (100)	24
Mo_2N/S	0.5 C	995 (100)	25
MTO/S	0.5 C	1100 (200)	This Work

4. CONCLUSIONS

In summary, mesoporous TiO_2 nanofibers are prepared and used as advanced host materials for sulfur in the Li-S batteries. The mesoporous TiO_2 nanofibers could adsorb the polysulfide and promote the transport or electronics during discharge and charge cycles. As a result, the MTO/S composites show excellent electrochemical performance. The initial specific capacity of MTO/S composites is as high as 1368 mAh g^{-1} at the current density of 0.1 C. Moreover, the MTO/S composites show stable cycle stability for 300 cycles at the current density of 0.5 C.

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