The application of Li-S battery is hindered mainly due to the shuttle effect of the polysulfide, which is produced via discharge process. Most recently, metal oxides are applied for inhibiting this shuttle effect. In our work, mesoporous Ti$_4$O$_7$/S composites are prepared and employed into Li-S battery. The mesoporous Ti$_4$O$_7$ layer in the Ti$_4$O$_7$/S composites could provide both physical absorption and chemical bond between the polysulfide and cathode material. As a result, the electrochemical results show that the Ti$_4$O$_7$/S composites have excellent cycle stability and high specific capacity. This excellent electrochemical performance is attributed to the presence of Ti$_4$O$_7$ layer in the composite.

**Keywords:** Cathode; S@Ti$_4$O$_7$; Cycle stability: Capacity; Electrochemical performance

1. **INTRODUCTION**

During the past decades, many achievements have been obtained in the electrochemical energy storage system [1, 2]. These energy storage systems included Li-ion batteries, Li-Air batteries, Li-S batteries and so on [3, 4, 5, 6]. Among these batteries, Li-S batteries are the most promising candidate for the next generation energy storage system. This is mainly due to the high specific capacity (1675 mAh g$^{-1}$) and energy density (2600 Wh Kg$^{-1}$) of Li-S batteries [7, 8, 9]. Moreover, the sulfur has advantage of resource abundance and no pollution for the environment [10, 11]. Consequently, much attention has been paid on the research of Li-S batteries.

However, several issues hindered the application of Li-S batteries. First, the poor electronic conductivity of sulfur lead to the low discharge capacity value during discharging process [12]. Second, the soluble polysulfide will produce during the electrochemical reaction [13]. This polysulfide caused shuttle effect which had negative effect on the cycle stability. Therefore, the key factor is enhancing the
conductivity and inhibiting the shuttle effect at the same time [14].

To address these problems, the scientists have proposed many strategies in the literature. Linda Nazar first reported the application of SBA-15 in the Li-S batteries [15]. Due to the employment of SBA-15, the as-prepared Li-S batteries showed perfect cycle stability. After that, the works about the various carbon materials become more and more, such as mesoporous carbon, carbon fiber, carbon nanotube and graphene. Until the emergence of MnO₂ in the Li-S batteries, the researchers put their eyes from the carbon to the metal oxides. The most interesting work is that Lou prepared MnO₂ nanosheet and applied it as host material for sulfur [16].

In this work, Ti₄O₇ coated sulfur composites were successfully prepared via heat treatment method. The as-prepared S@Ti₄O₇ composites exhibited excellent capacity value and cycle stability. This superior electrochemical performance is attributed to the presence of Ti₄O₇ layer in the composite. The Ti₄O₇ layer could enhance the conductivity and inhibit the shuttle effect at the same time.

2. EXPERIMENT

2.1. Preparation of S@Ti₄O₇ Composite

In this experiment, the sulfur was firstly prepared. 1.2 ml HCl was added into 120 ml Na₂S₂O₃ solution at the condition of stirring for 3 h. After that, the surfactant of 20 g hexadecyl trimethyl ammonium bromide (CATB) was added into the mixed solution. The next step is the growth of Ti₄O₇ layer on the sulfur particle. Typically, 20 ml titanium isopropoxide (TIP) solution was added into the above solution. Then, 2.1 ml ammonia was gradually added for the reaction with TIP forming TiO₂ layer on the surface of sulfur. After that, the sample was reduced under H₂ atmosphere for 3 h. Finally, the sample was washed and dried to obtain S@Ti₄O₇ composite.

2.2. Materials Characterization

The as-obtained samples were characterized by using a transmission electron microscope (TEM, Tecnai F20), an X-ray diffractometer (XRD, D8 Advance, BRUKER). The content of sulfur in the composite was tested by thermogravimetric analysis (TG, TA Q600 instrument).

2.3. Electrochemical Measurements

The electrochemical performance was measured by using coin-type half batteries. A slurry was prepared by mixing 80 wt.% samples, 10 wt.% super black and 10 wt.% Poly(vinylidene fluoride) PVDF with N-Methyl pyrrolidone (NMP). Then, the slurry was uniformly casted onto Al foil. The film was dried for 12 h under vacuum at 80°C and was cut into circular electrodes. The cells were assembled in an Ar-filled glove box with lithium foil, and a solution of 1.0 M bis-trifluoro methane sulfonimide lithium salt (LiTFSI) was dissolved in ethylene carbonate (EC)/ diethyl carbonate (DEC) as the electrolyte. Dicharging/charging profiles were
carried out on a battery testing system (Xin Wei) in the potential between 1.5 V and 3 V. Electrochemical impedance spectroscopy was tested on an electrochemistry workstation.

3. RESULTS AND DISCUSSIONS

To understand the morphology of the as-prepared S@Ti4O7 composite, SEM was conducted. As shown in Figure 1a, the S@Ti4O7 composite exhibits spheres structure with a diameter of ~230 nm. To further confirm the Ti4O7 layer in the S@Ti4O7 composite, TEM was tested. As shown in Figure 1b and Figure 1c, it can be clearly seen that the S@Ti4O7 composite shows core-shell structure, in which the sulfur particle is coated by the Ti4O7 layer. Moreover, the corresponding elemental mapping (Figure d-g) of S@Ti4O7 composite was tested to determine the component. From the Figure e-g, it can be observed that the elements of Ti, O, S are dispersed uniformly in the whole S@Ti4O7 composite [17].

Figure 1. (a) SEM image, (b) and (c) TEM image of S@Ti4O7 composite, (d), (e), (f), (g) SEM image of S@Ti4O7 composite and corresponding elemental mapping of Ti, O, S.

Figure 2. (a) The XRD patterns of pure sulfur and S@Ti4O7 composite. (b) TG curve of S@Ti4O7 composite.

Figure 2a is the XRD pattern of all samples. As shown in the Figure, the sulfur shows strong typical reflection pattern of S8 molecule [18]. When the sulfur was coated by Ti4O7 layer, the S@Ti4O7 composite displays the same diffraction peak as pure sulfur. However, the peak intensity of S@Ti4O7
composite is weaker than the pure sulfur. This is mainly due to the presence of Ti$_4$O$_7$ layer on the surface of sulfur. Because the sulfur is covered by the Ti$_4$O$_7$ layer. Therefore, this will lead to the decrease of peak intensity. To determine the sulfur content in the S@Ti$_4$O$_7$ composite, thermogravimetric analysis was tested under Ar atmosphere. As shown in Figure 2b, the sulfur mass loss is about 56%, which demonstrates that the sulfur content in the S@Ti$_4$O$_7$ composite is 56%.

Figure 3 shows the initial discharge-charge profiles of pure sulfur and S@Ti$_4$O$_7$ composite at the current density of 0.05 C. From the figure, some information can be obtained. First, the S@Ti$_4$O$_7$ composite exhibits discharge capacity value of 1205 mAh g$^{-1}$, which is much higher than the pure sulfur (802 mAh g$^{-1}$). Second, in terms of the shape of the profiles, it can be seen that the discharge profile has two voltage platforms from 1.5 V to 3.0 V. These two voltage platforms represent two step reaction of S$_8$, which include the formation of soluble polysulfide and insoluble Li$_2$S. During the two voltage platforms, the second platform at 2.1 V provides much higher capacity value than the first platform at 2.3 V. This improved capacity value has close correlation with the presence of Ti$_4$O$_7$ layer in the S@Ti$_4$O$_7$ composite. This is because the metal oxide Ti$_4$O$_7$ could enhance the electronic conductivity of the cathode materials [19].

![Figure 3. The initial discharge-charge profiles of pure sulfur and S@Ti$_4$O$_7$ composite.](image)

![Figure 4. The rate performances of pure sulfur and S@Ti$_4$O$_7$ composite.](image)

Rate performance is a key index for judging the electrochemical performance of the Li-S battery. Therefore, we have tested the rate performance of pure sulfur and S@Ti$_4$O$_7$ composite at various current
densities from 0.05 C to 1 C. As shown in Figure 4, the S@Ti₄O₇ composite displays capacity value of 1205 mAh g⁻¹, 1192 mAh g⁻¹, 1086 mAh g⁻¹, 1003 mAh g⁻¹ at the current densities of 0.05 C, 0.1 C, 0.2 C and 0.5 C, respectively. More importantly, the discharge capacity value of S@Ti₄O₇ composite is 753 mAh g⁻¹ at the current density of 1 C. However, for the pure sulfur electrode, the all capacity values of pure sulfur are lower than the S@Ti₄O₇ composite. Moreover, it can be clearly observed that the S@Ti₄O₇ composite could keep the capacity value when the current densities increase. Rate performance is related to the conductivity of the electrode materials. Therefore, the S@Ti₄O₇ composite shows more excellent rate performance than the pure sulfur electrode [20, 21].

The cycle performances of pure sulfur and S@Ti₄O₇ composite are shown in Figure 5a. As it can be seen from the Figure, the S@Ti₄O₇ composite demonstrates superior cycle stability than the pure sulfur. The capacity value of S@Ti₄O₇ composite remains 708 mAh g⁻¹ after 100 cycles. While the capacity value of pure sulfur is only 483 mAh g⁻¹ after 100 cycles. Although the capacity fade rapidly at first 20 cycles for S@Ti₄O₇ composite, however, after that, the capacity value becomes stable. In a word, the S@Ti₄O₇ composite shows more excellent cycle stability than the pure sulfur.

Electrochemical impedance spectroscopy was measured on an electrochemistry workstation. As shown in Figure 5b, the as-prepared S@Ti₄O₇ composite has a smaller diameter of the high frequency semicircle, demonstrating much lower interface layer resistance than pure sulfur. This result further confirms that the S@Ti₄O₇ composite exhibits more superior conductivity than the pure sulfur electrode. As a result, the electronics could easily transport in the channels of the cathode materials. Besides, it is beneficial for the Li⁺ transfer in the electrolyte between electrode surface and electrolyte [22, 23].

![Figure 5](image.png)

Figure 5. (a) The cycle performances of pure sulfur and S@Ti₄O₇ composite. (b) The electrochemical impedance spectra of pure sulfur and S@Ti₄O₇ composite.

Table 1 lists the electrochemical performance of similar cathode materials for Li-S battery. As shown in Table 1, it can be clearly seen that the S@Ti₄O₇ composite displays superior cycle stability...
among these similar cathode materials. This indicates that the S@Ti₄O₇ composite would be a promising cathode material for the Li-S battery.

**Table 1.** The comparison between S@Ti₄O₇ composite and other similar cathode materials

<table>
<thead>
<tr>
<th>Samples</th>
<th>Current Density</th>
<th>Capacity</th>
<th>Reference</th>
</tr>
</thead>
<tbody>
<tr>
<td>S@MnO₂@GO</td>
<td>0.2 C</td>
<td>405 (100)</td>
<td>24</td>
</tr>
<tr>
<td>S/C-SnS₂</td>
<td>0.2 C</td>
<td>698 (100)</td>
<td>25</td>
</tr>
<tr>
<td>PEDOT/TiO₂/S</td>
<td>0.1 C</td>
<td>532 (100)</td>
<td>26</td>
</tr>
<tr>
<td>S@Ti₄O₇</td>
<td>0.2 C</td>
<td>708 (100)</td>
<td>This Work</td>
</tr>
</tbody>
</table>

4. CONCLUSIONS

a) The yolk-shell structure S@Ti₄O₇ composite was successfully prepared and used as cathode materials for Li-S batteries.

b) The S@Ti₄O₇ composite showed high capacity value and excellent cycle stability.

c) The superior electrochemical performances are attributed to the yolk-shell structure, which could protect the polysulfide in the cathode side. Moreover, the metal oxide Ti₄O₇ layer could improve the electronic conductivity.

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References


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