

Short Communication

## Sulfur/Graphene Oxide Composites as Cathode Materials for Lithium- Sulfur Batteries

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The sulfur/graphene oxide composites were synthesized via hummers and melt diffusion method. The sulfur/graphene oxide composites were characterized by means of XRD and SEM, and the electrochemical studies were characterized by constant current charge-discharge tests. The sulfur/graphene oxide composites exhibited the initial discharge capacity of  $1411 \text{ mAhg}^{-1}$  and it sustained  $680 \text{ mAhg}^{-1}$  at the 30th cycles. The results indicate that the composites exhibit more better electrochemical property than that of the sulfur.

**Keywords:** Graphene oxide, sulfur, cathode materials, lithium-sulfur batteries

### 1. INTRODUCTION

Sulfur has many advantages of high energy density, low cost and environmental-friendly [1]. Nevertheless, the sulfur is insulated and the irreversible dissolution of the polysulfides in the process of charge and discharge make the discharge capacity fade significantly. In order to solve the issues, we should prepare a conductive, unique structure and functional materials which is combined with the sulfur [2, 3].

Graphene oxide is the typical derivative of the graphene which has good conductivity, high surface area and chemical stability [4-6]. Graphene oxide has a mass of oxygen-containing functional groups, such as hydroxyl groups, epoxide, carboxyl groups and carbonyl groups, which play the role of immobilizers that keep intimate contact of the conducting matrix with sulfur species, and effectively suppressing the dissolution of polysulfides into electrolyte [7-9].

By the hummers method, graphene oxide was synthesized. And then the sulfur/graphene oxide composites were synthesized by melt diffusion method. Sulfur/graphene oxide composites as cathode

materials for lithium- sulfur batteries exhibited more better electrochemical property than that of the sulfur [10,11].

## 2. EXPERIMENTAL

Graphene oxide was prepared by Hummers method [12].

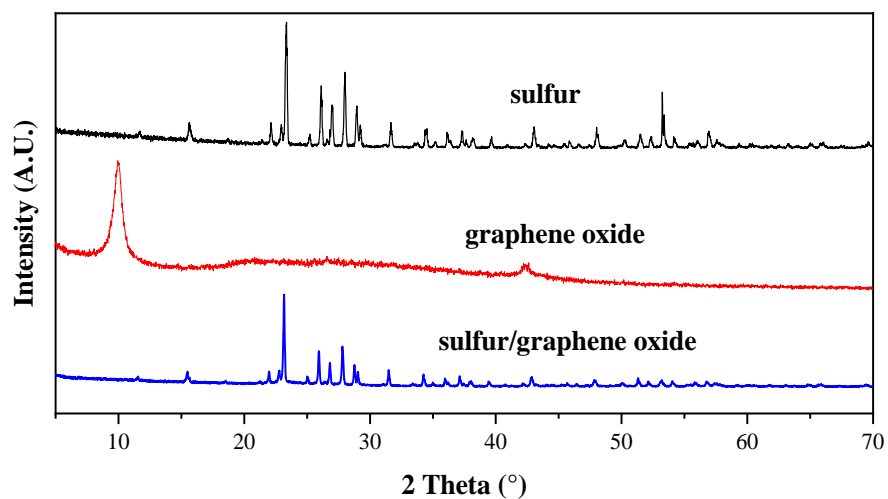
Graphene oxide and sulfur powders (99.5% purity) were grinded together (1:3, wt %). The melt diffusion method was carried out under an argon atmosphere. The mixture was placed in a quartz tube. The mixture was heated to 150 °C (3 °C/min) , and kept the 150 °C for 18 h, Sulfur/graphene oxide composites powders were obtained.

The phase of the composites was tested by XRD (Bruker D8, 5 °-70 °). The morphology of the composites was observed by SEM (Hitachi S-4800).

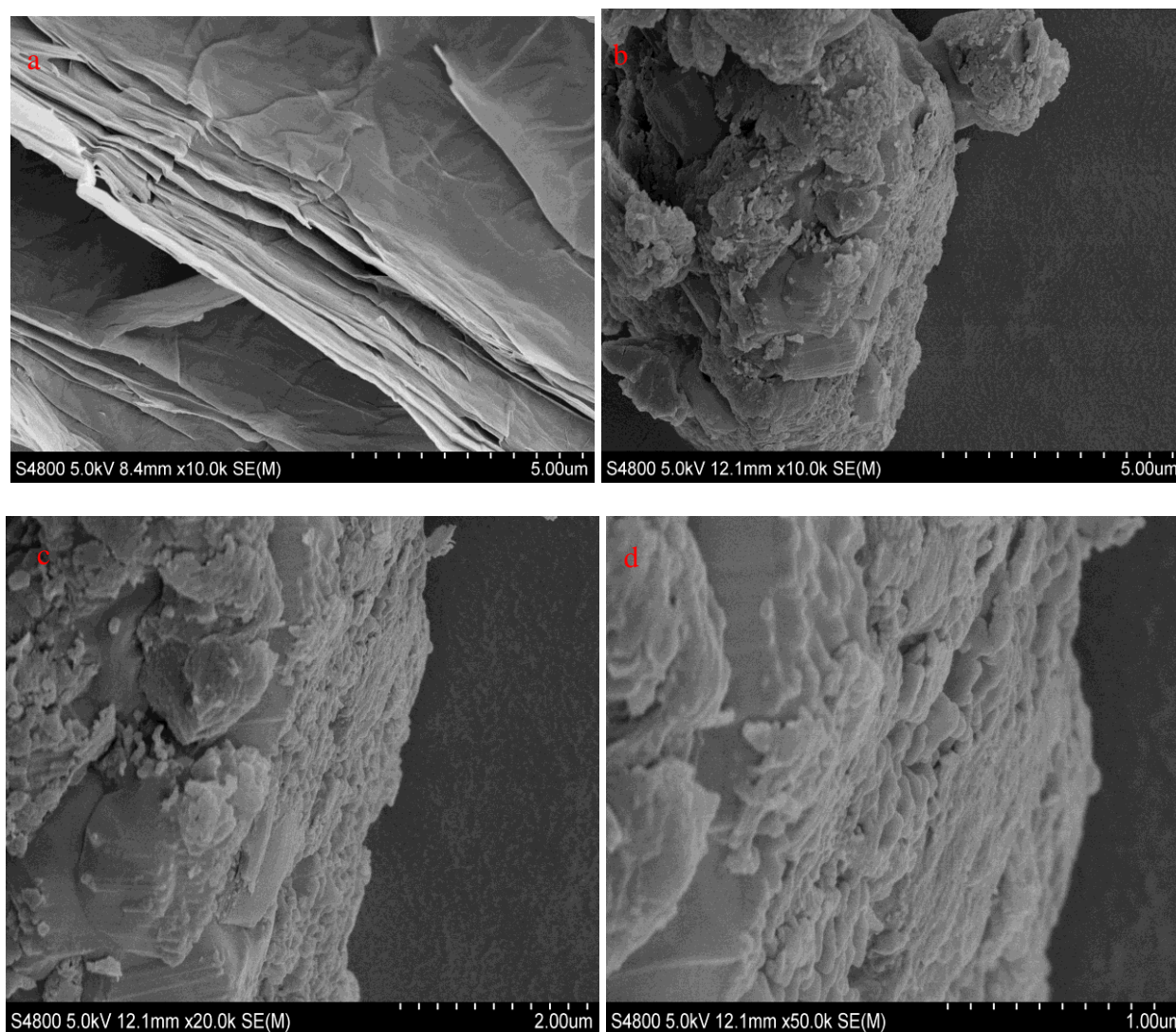
Charge-discharge tests were studied by CR2025 coin cells. A cathode slurry of the composites, PVDF and acetylene black was prepared and dispersed in NMP solvent on a copper foil and dried in a vacuum oven at 80 °C for 12 h. The electrolyte was 1.0 M lithium LiTFSI in DME and DOL (volume ratio 1:1) with 1 wt% LiNO<sub>3</sub> additive. Separator was the Celgard 2400 microporous polypropylene film. Anode was Li foil. Charge-discharge property tests were studied by Neware BTS (1.5V-2.8V, 0.1C).

## 3. RESULTS & DISCUSSION

In Fig. 1, the XRD patterns of the sulfur, the graphene oxide and the sulfur/graphene oxide composites are shown. The strong and sharp peaks of sulfur show orthorhombic structure (JCPDS No. 08-0247). Graphene oxide powder shows a characteristic peak near 10(2θ) [13]. This is due to the oxidation process in which the oxygen-containing functional groups are on the graphene oxide [14]. The oxygen-containing groups are beneficial for the strongly adsorbed polysulfides during charge-discharge process. The peak of sulfur/graphene oxide composites vanishes at 10(2θ), and a broad diffraction peak at 23(2θ) appears, indicating that on the surface and in the interlayers of graphene oxide the sulfur is dispersed highly, which can also be obviously observed in Fig.2 (b. c. d) .



**Figure 1.** XRD patterns of graphene oxide, sulfur and sulfur/graphene oxide.



**Figure 2.** SEM images of graphene oxide (a), sulfur/graphene oxide composites (b, c, d)

In Fig. 2, the SEM images of the graphene oxide and the sulfur/graphene oxide composites are shown. The interlayer structure of the graphene oxide (Fig. a) provide abundant position for the sulfur between the interlayers which he is beneficial to faster transport of  $\text{Li}^+$ . In the Fig. 2 ( b, c, d), the sulfur is on the surface and in the interlayers of the graphene oxide owing to the melt diffusion process between sulfur and graphene oxide [15].

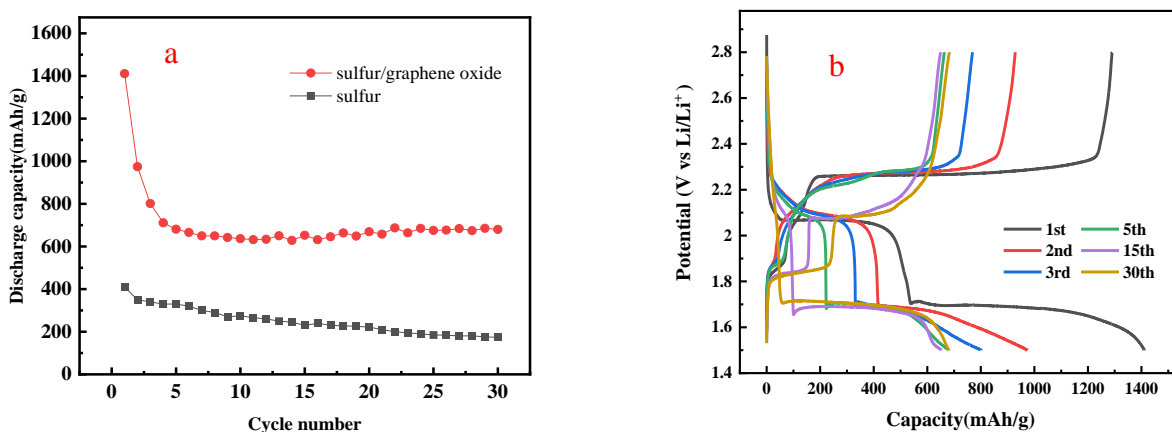
The cycling performance of the sulfur/graphene oxide composites and the sulfur are shown in Fig. 3(a), which were tested in the voltage range of 1.5–2.8V at a constant current of 0.1 C. It can be seen that the sulfur/graphene oxide composites exhibit remarkably enhanced initial discharge specific capacity of  $1411\text{mAhg}^{-1}$  and the specific capacity is  $680\text{mAhg}^{-1}$  at the 30th cycle, the capacity of the sulfur cathode is enhanced significantly. Owing to the unique interlayer structure of graphene oxide, it preventing the polysulfide out of the interlayer structure during the cycles. In comparison with the first discharge, there is a capacity fade for the second discharge capacity. The reasons for the capacity fade are described as following: (1) the irreversible reaction of the polysulfide (2) the formation of the solid electrolyte interphase (SEI) layer (3) the decomposition of electrolyte on the surface of the electrode [16].

In Fig. 3(b), the charge-discharge profiles of the composites are depicted, the first discharge shows the specific capacity of  $1411\text{mAhg}^{-1}$  and the retention specific capacity of the composites is  $680\text{mAhg}^{-1}$  at the 30th discharge, it implies the enhanced utilization of the sulfur in the sulfur/grapheme oxide composites. Furthermore, the electrochemical performance of sulfur/graphene oxide composites cathode is better in comparison with the similar sulfur based cathodes in Table 1 [17–20].

**Table 1.** Comparison of electrochemical performance of lithium sulfur batteries with different cathodes

Cathode material	Current density	Initial discharge capacity(mAh/g)	Discharge capacity at nth cycle(mAh/g)	Capacity retention(%)	Ref.
AC/S	0.05C	1120	486(20th cycle)	43	17
S/AB	0.1C	934	500(50th cycle)	53	18
S/GA	0.1C	1100	500(60th cycle)	45	19
S@PPy	0.1C	1145	370(50th cycle)	32	20
S/GO	0.1C	1411	680(30th cycle)	48	This work

The oxygen-containing groups on the surface of the graphene oxide can effectively prevent the polysulfides from dissolution and diffusion into the electrolyte. In the cycle process, several sequential steps are shown, there are two obvious plateaus at 2.1 V and 1.7 V, assigning to the two-step reaction, high-order polysulfides and low order polysulfides are formed respectively.



**Figure 3.** Cycling performance curves of the composites and the sulfur (a) the charge-discharge curves of the composites (b)

#### 4. CONCLUSIONS

By hummers and melt diffusion method, we have synthesized the sulfur/graphene oxide composites. The structure of the sulfur/graphene oxide composites is obviously changed in the process of the melt diffusion. With the unique interlayers structure, the sulfur/graphene oxide composites exhibit good electrochemical performance. The initial discharge specific capacity is  $1411 \text{ mAhg}^{-1}$  and the retention specific capacity of the composites is  $680 \text{ mAhg}^{-1}$  at the 30th discharge. The above results reveals that the combination with the graphene oxide is a better way to improve the electrochemical performance of the sulfur, and it could be developed to meet the demand of next generation lithium ion batteries.

#### ACKNOWLEDGEMENTS

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