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微波法制备硫/膨胀石墨复合材料及其锂硫电池性能

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摘要: 采用简单的微波辅助的方法成功制备了硫/膨胀石墨复合材料。膨胀石墨可以用作锂硫电池中阴极的微型容器及集流体。通过控制硫与膨胀石墨的配比成功控制了复合材料中硫颗粒的大小。当硫与膨胀石墨的比例为 10:1 时, 可以得到相对较均匀的硫颗粒。同时研究了不同条件下所制样品的锂硫电池性能。结果表明, 硫的含量与硫颗粒的大小对锂硫电池的容量非常重要。当硫与膨胀石墨的比例为 10:1 时, 在 0.1 C 放电速率下, 复合材料具有最高的放电容量 1 020 mAh·g⁻¹。

关键词: 膨胀石墨; 锂硫电池; 微波; 硫颗粒尺寸

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Microwave assisted preparation of expanded graphite/sulfur composites as cathodes for Li-S batteries

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Abstract: Expanded graphite/sulfur (EG/S) composites were prepared by microwave irradiation of mixtures of sulfur and expanded graphite with S/EG ratios from 4:1 to 12:1. Sulfur was sublimed and entered the EG pores when the mixtures were heated and was condensed to form particles within the pores during cooling. The pores of the EG acted as microcontainers to host the sulfur, and the material, with its interconnected and conductive pore walls, acted as a current collector for the cathode of the Li-S battery. The size of sulfur particles in the EG pores could be controlled by the S/EG mass ratio. When the ratio is 10:1, relatively uniform size sulfur particles could be obtained. Both the S/EG ratio and the sulfur particle size have an important effect on the capacity increase of the Li-S battery. Using a composite with a S/EG ratio of 10:1 as the cathode gives the highest capacity of 1 020 mAhg⁻¹ at a rate of 0.1 C.

Key words: Expanded graphite; Lithium-sulfur batteries; Microwave; Sulfur particles size

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1 Introduction

Lithium-sulfur (Li-S) battery is a very attractive battery. Compared with the traditional lithium ion batteries, it has many merits^[1]. For example, the battery has a high theoretical specific capacity of 1 672 mAh/g and a high theoretical specific energy of 2 600 Wh/kg based on the reaction between lithium and sulfur^[2]. Moreover, sulfur is easily available and

environmentally friendly^[3-4]. However, Li-S battery has obvious two drawbacks. On one hand, the low electronic/ionic conductivity of sulfur would limit the operating current of the battery^[5]. On the other hand, sulfur as the active materials would easily dissolve into the liquid electrolyte during the discharge process and then transform into insoluble Li₂S and Li₂S₂^[6,7]. Li₂S and Li₂S₂ will finally adhere onto the surface of cathode materials, which will occur in ev-

ery charge/discharge cycle, restrict the reaction of the inner sulfur^[1], and lead to the loss of the capacity.

To overcome these problems, several technological contributions are attempted, such as the optimization of the organic electrolyte via introducing room temperature ionic liquid or fabrication of the sulfur composites with the electronic conductors^[8]. The electronic conductors include nano metal oxides^[9], solid solutions^[10], transition metals^[11], carbon materials^[12] and conductive polymers^[13]. Since the carbon materials have high specific surface area, high pore volume, extensive pore structure and good conductivity, they are proved to be effective and facile candidates to improve the sulfur utilization and restrain the solubility of lithium polysulfides^[8]. Lots of carbon materials are used to modify the sulfur cathode, such as mesoporous carbon^[9], carbon nanotubes^[13], carbon nanofibers^[14], and graphene^[15], all of which have shown improved performance. Among these, graphene sheets, one-atom-thick layers of sp²-hybridized carbon atoms packed in a honeycomb lattice, are advantageous for wrapping sulfur owing to their large lateral size, good conductivity and the flexible structure^[16]. And some graphene-based material is more suitable for improving the performance. But the preparation for some carbon-sulfur materials includes complicated multi-steps with strict synthetic conditions^[17]. Li et al^[18] have prepared a graphene-wrapped carbon/sulfur composite for lithium-sulfur battery by changing the hydrophilicity of graphene oxide during reduction, in which the hydrophobic graphene closely wraps around the hydrophobic carbon surface. And the first discharge capacity is about 1 578.3 mAh·g⁻¹ (0.15 A·g⁻¹), higher than the pure carbon/sulfur composite. Li^[19] have prepared a graphene/sulfur composite by chemical deposition sulfur on the graphene oxide. And the first discharge capacity is 1 320 mAh·g⁻¹ (0.02 C). Tang^[20] have prepared a nitrogen-doped carbon nanotube/graphene-sulfur composite, by the chemical vapor deposition for the nitrogen-doped carbon nanotube/graphene followed by a melt-diffusion infiltration strategy. The initial discharge capacity is 1 152 mAh·g⁻¹ and nearly 76% capacity is retained after 80 cycles. Above all the composites show excellent performance, but the materials preparation involves complicated multi-steps with strict synthetic conditions.

Expanded graphite which has a hierarchical pore structure is low in cost and easily to obtain, so it can be used as the cathode material for Li-S batteries. Expanded graphite is prepared by expanding intercalated graphite, which is an exothermic process. So it is beneficial for the preparation sulfur/expanded graphite

(S/EG) composites. In this paper, a facile method is successfully used to prepare the S/EG composites assisted with microwave. The sulfur and expanded graphite is mixed and the S/EG composites is easily obtained during the graphite expanding process by microwave irradiation. The S/EG composite as a Li-S battery cathode has a high discharge capacity. This method provides an experimental basis for the subsequent preparation of sulfur/carbon composites.

2 Experimental

2.1 Preparation of S/EG composite

Firstly, the EG was prepared by expanding the graphite intercalated compound through rapid thermal expansion at 800 °C in a muffle furnace. In brief, the natural flake graphite was mixed with concentrated sulfuric acid (98%) and concentrated nitric acid (65%) (4:1, v/v), then the mixture was vigorously stirred for 12 h to ensure the formation of expandable graphite intercalation compound. After that the intercalated graphite was washed with deionized water to neutral and then dried. The dried expandable graphite intercalation compound was rapidly expanded at 800 °C for 20 s in a muffle furnace. Then the expanded graphite and sulfur was mixed together with different mass ratios (S:EG = 4:1, 6:1, 8:1, 10:1, 12:1, m/m), and the mixture was put into a microwave oven and irradiated for 2 min at about 400 W. In this process, expanded graphite was used as the heat producer and the heat transfer medium. And the heat can be transferred to the sulfur surface, leading to the sublimation of sulfur that was loaded into the pore of the expanded graphite when the sulfur was cooled.

2.2 Characterization

The morphology and microstructure of the S/EG composite was characterized by scanning electron microscopy (FESEM, JSM 6701F). The microstructure of the S/EG material was also analyzed by powder X-ray diffraction (XRD, Cu K α radiation, Panalytical X'Pert Pro). The thermal gravimetry (STA 449F3) was used to analyze the quantity of loaded sulfur from 25 to 500 °C at a heating rate of 10 °C/min under the protection of nitrogen.

2.3 Electrochemical measurements

The S/EG composite and acetylene black (electrical conductor) with polyvinylidene fluoride binder (8:1:1, weight ratio) were grinded with a mortar into N-methyl-2-pyrrolidone (NMP) to form a slurry. In this process, the NMP and polyvinylidene fluoride are used as a diluent and binder, respectively. The S/EG composite could be ground to form a uniform

slurry. Then the slurry was coated onto aluminum foil and dried under vacuum to form the working electrode at 60 °C for 12 h. 2032-type coin cells were assembled in an argon-filled glove box using lithium foil as the counter electrode. The electrolyte was 1 M bis (trifluoromethane) sulfonimide lithium salt (LiTFSI) dissolved in a mixture of 1 β -Dioxolane (DOL) and Dimethoxyethane (DME) (1:1 v/v) containing LiNO₃ (1 wt%). The cathode, separator, and anode were pressed by a sealing machine to ensure a tight contact. The batteries were cycled between 1.5 and 3.0 V with a battery test instrument Land CT2001A battery test system at 0.1 C (1 C = 1 672 mA \cdot g⁻¹) at room temperature. CV tests were performed on a CHI660D electrochemical workstation at a scan rate of 0.2 mV \cdot s⁻¹ from 1.5 to 3.0 V. The calculation of specific discharge capacities was based on the mass of elemental sulfur.

3 Results and discussion

The microstructure of the S/EG composites after microwave at different mass ratios of sulfur to EG is characterized by SEM. As illustrated in Fig. 1, the SEM images indicate that all the S/EG composites possess an ideal layer-by-layer structure with a hierarchical pore structure. There are some particles embedded into the layers or pores of expanded graphite.

When the ratios of sulfur to expanded graphite is 4:1, 6:1, 8:1 and 10:1, no large sulfur particles are found and the particles are about tens to hundreds of nanometers as shown in the red rectangle. Lots of large sulfur particles about 1 μ m are found when the ratio is 12:1.

The temperature of EG is increased by absorbing microwave energy when it is irradiated by microwave. The sulfur is sublimed when it is heated by EG. When the mixture is cooled down the sulfur vapor enter into the pores of the particles and deposited on EG. The higher is the content of sulfur, the more are the sulfur particles formed, but when the sulfur content increases to a limit, the sulfur can not sublime completely, so the particle size increases. So the size of sulfur particles is controlled by controlling the amount of sulfur.

To further obtain the particle size distribution, we randomly select one hundred sulfur particles in the red rectangle in Fig. 1. The result is shown in Fig. 2. It is found that the percentage of sulfur particles between 20 and 50 nm reaches a maximum of 79% at the S/EG mass ratio of 10:1. While the particles between 50-100 nm and 100-150 nm are found in all the samples, but their percentages in the sample at 10:1 is the lowest.

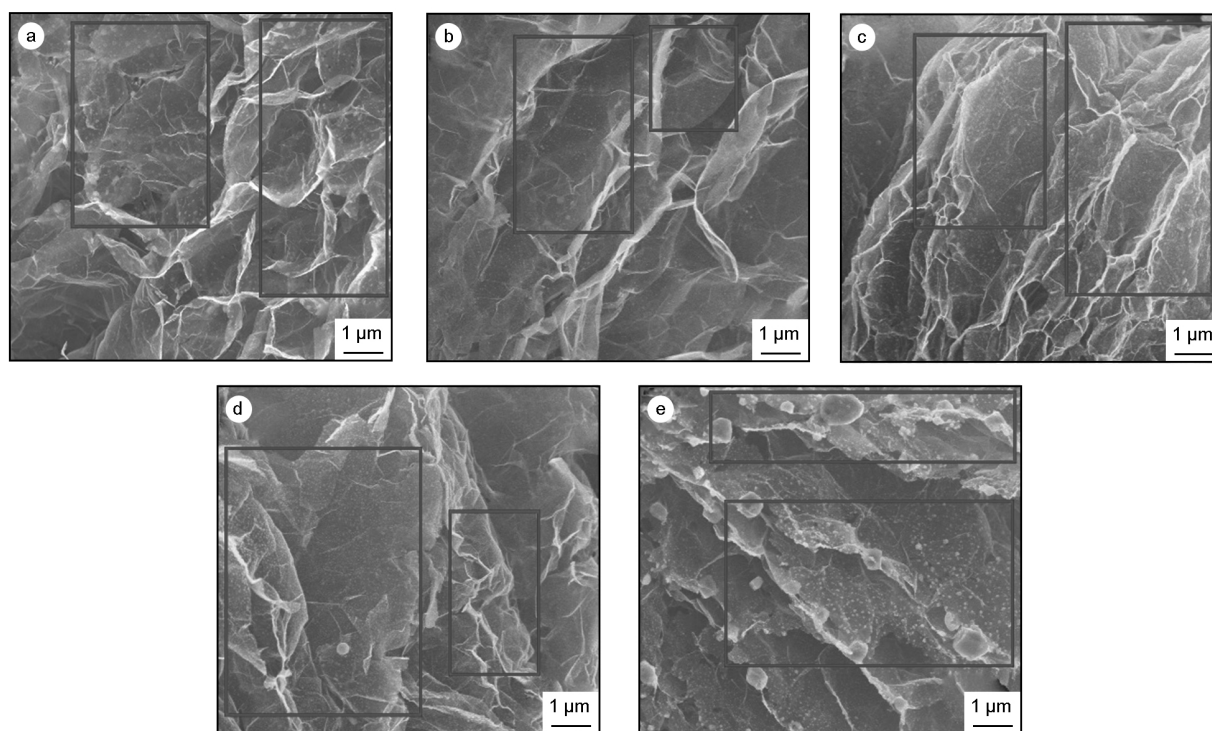


Fig. 1 SEM images of the S/EG composites with different mass ratios of S/EG after microwave irradiation. (a) 4:1, (b) 6:1, (c) 8:1, (d) 10:1 and (e) 12:1.

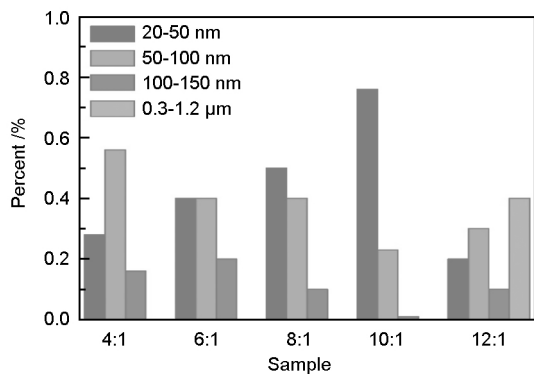


Fig. 2 The particle size distribution of sulfur at different ratios of S/EG.

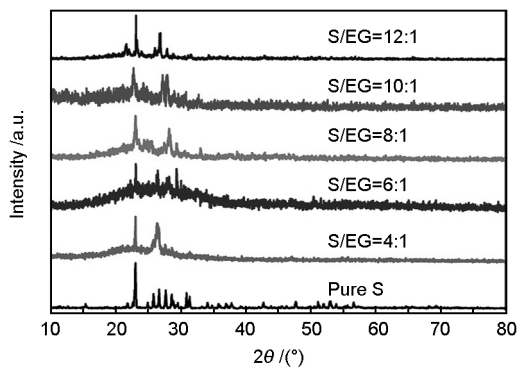


Fig. 3 XRD patterns of the S/EG composites at different mass ratios of S/EG after microwave irradiation.

To investigate the state of the sulfur in the S/EG composite after microwave irradiation XRD patterns are recorded. Firstly, the pure sulfur displays sharp diffraction peaks that agree well with the characteristic pattern of S_8 ^[21]. Compared with the pure sulfur sample, all of the S/EG composites at different ratios of S/EG after microwave irradiation show the diffraction peaks of bulk crystal sulfur in the form of S_8 . This is also consistent with the SEM images.

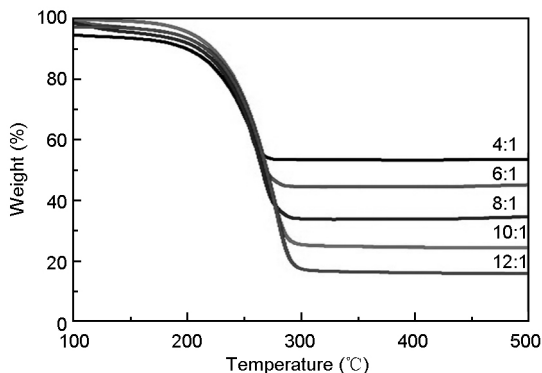


Fig. 4 Thermo gravimetric analysis (TGA) curves of the S/EG composites at different ratios of S/EG after microwave irradiation.

The thermal decomposition characteristic of the S/EG composites at different ratios of S/EG after mi-

crowave irradiation under nitrogen atmosphere is investigated by TGA. The expanded graphite is prepared at 800 °C, so here, the weight loss of the composites is caused by sulfur. The TGA curves in Fig. 4 show that the weight loss of the S/EG composites after microwave irradiation is about 50, 55, 64, 71 and 76% at the S/EG ratios of 4:1, 6:1, 8:1, 10:1 and 12:1, respectively. This result indicates that in the composites, the quantity of sulfur increase with the S/EG ratio. For testing the electrochemical properties of the S/EG composites, the batteries assembled were investigated by galvanostatic charge-discharge measurement. Fig. 5a shows the cyclic performance of the S/EG cathodes with different S/EG ratios. The initial discharge capacity increases from 347 to 950 $\text{mAh}\cdot\text{g}^{-1}$ with the S/EG ratios from 4:1 to 10:1. With a further increase of the S/EG ratio to 12:1, the capacity is decreased to 556 $\text{mAh}\cdot\text{g}^{-1}$.

From the results of Fig. 2 and Fig. 3, it is found that both the sulfur content and the sulfur particle sizes are the main factors for capacity. The S/EG composite with a S/EG ratio of 10:1 is the best, so we choose this ratio for the next discussion. To identify all the electrochemical reactions in the S/EG composite, the CV and galvanostatic discharge-charge curves are shown in Fig. 5b and 5c, respectively. As shown in Fig. 5b, one oxidation peak and two reduction peaks are observed, which are attributed to the multi-step reaction of sulfur with lithium^[3]. The transformation of sulfur to lithium polysulfide (Li_2S_n , $2 < n < 8$) is the first step at a high potential of about 2.3 V, and the polysulfides dissolve into the electrolyte, which leads to the loss of the capacity. The second step is ascribed to the reduction of high order lithium polysulfides to lithium sulfide (Li_2S_2 , Li_2S) at a lower potential about 2.0 V. The oxide peak at about 2.47 V is caused by the lithium sulfide conversion to lithium polysulfide (Li_2S_n , $n > 2$)^[22]. The charge-discharge curves of the S/EG composite is shown in Fig. 5c. Two typical plateaus at 2.3 V and 2.1 V are observed in the discharge process, which can be assigned to the two-step reaction of sulfur with lithium in the discharge process, only one plateau is observed in the charge process at about 2.47 V. The positions of the plateaus agree well with the results of the CV curves (Fig. 5b). Next, the rate performance of the S/EG cathode is shown in Fig. 5d. The capacity and C rates are based on the mass of sulfur ($1\text{ C} = 1\ 672\ \text{mAh}\cdot\text{g}^{-1}$). The initial discharge capacity is as high as 1 020 $\text{mAh}\cdot\text{g}^{-1}$ at 0.1 C.

Yang^[23] prepared composites using a conductive polymer as coating to improve the performance of lithium-sulfur batteries, and the results show that the

performance of the composites with the conductive polymer coating is better than the composites without the coating. Based on this observation, we are going

to coat conductive coating on the material to restrain the solubility of lithium polysulfides to improve the performance.

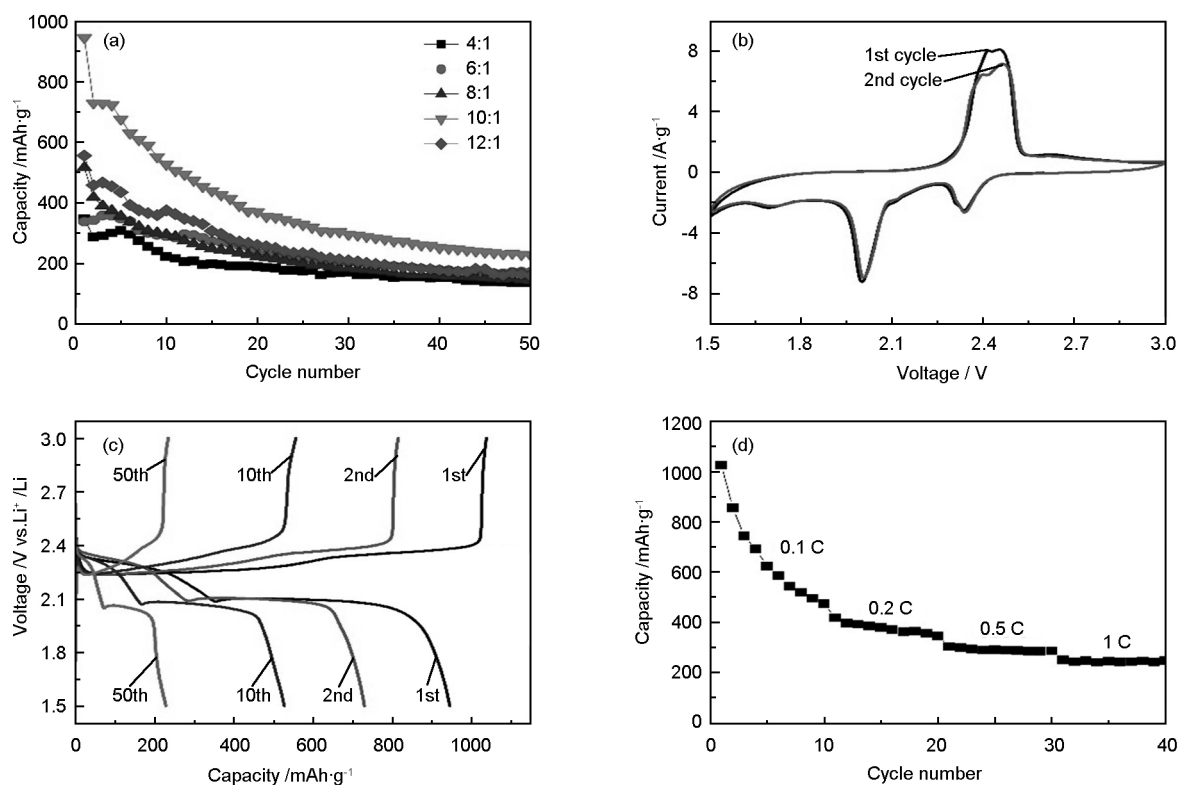


Fig. 5 (a) The cyclic performance of the S/EG composites at different S/EG ratios; (b) Cyclic voltammogram of the S/EG cathode at the ratio of 10:1 with a scan rate of $0.2 \text{ mV} \cdot \text{s}^{-1}$; (c) The discharge-charge curves of the S/EG composite at the ratio of 10:1 at 0.1 C; (d) Capacity at different C rates of the S/EG composite at the ratio of 10:1.

4 Conclusions

We successfully prepared the S/EG composites by microwave irradiation method. The size of sulfur particles loaded in the composites can be easily controlled by the S/EG mass ratio. When the ratio is 10:1, relatively uniform sulfur particles are obtained. Both the S/EG ratio and the sulfur particle size play an important role for capacity in Li-S battery. It has been confirmed that the cathode with the ratio of 10:1 shows the highest capacity ($1020 \text{ mAh} \cdot \text{g}^{-1}$) at 0.1 C rate. Such facile method is a promising means for preparing the cathode of Li-S batteries.

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