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Preparation and properties of Sulfur/Mesoporous Carbon Composite Cathode Materials

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Abstract. A sulfur /mesoporous carbon composite is prepared by thermally treating a mixture of sublimed sulfur and mesoporous carbon. The microstructure of the mesoporous carbon is characterized by BET analysis and X-ray diffraction (XRD). The electrochemical performance of the S /C composite as cathode materials is evaluated by the galvanostatic method. The results confirmed that the mesoporous carbon could not only greatly enhance the electrochemical activity of sulfur electrode, but also effectively confine the diffusion of dissolved polysulfides in organic electrolyte. As a result, the S /C composites showed high capacity, good cycle performance and excellent rate capability. The specific capacity of the S /C composite is more than 1200 mAh /g for the first discharge, and remained at 800 mAh /g after 100 cycles even at a high current density of 800 mA/g.

1. Introduction

Sulfur electrode has high theoretical specific capacity (1675 mAh/g), and rich in resources, the advantages of low cost, and environmental friendly[1], is a kind of extremely has the application prospect of lithium secondary battery cathode material. However, due to the poor electronic conductivity of elemental sulfur and exist in the conventional organic electrolyte of the intermediate dissolve erosion[2], lead to the sulfur electric pole electrochemical activity and cycle stability is poor, limits its practical application. To solve the problem of sulfur electrode of the above, the people had extensive exploration in recent years, Including optimization of electrolyte composition, using room temperature ionic liquid electrolyte to avoid losses of the intermediate dissolve[3-4], the preparation of conductive polymer/sulfur composites and sulfur/carbon composite material so as to enhance the electrochemical activity of sulfur electrode and cyclic stability[5-8]. Given the mesoporous carbon has good electrical conductivity, high specific surface and rich the pore structure, strong adsorption ability, this work presents the preparation of mesoporous carbon materials as elemental sulfur carrier S/C composite electrode, is to improve the sulfur electrode electrochemical activity and cycle stability.



2. Experiment

2.1. Preparation and characterization of mesoporous carbon

Reference to literature[9] and [10], mesoporous carbon is prepared by template enantiation method. First, the triblock copolymer P123 ($\text{EO}_{20}\text{PO}_{70}\text{EO}_{20}$, $M_n = 5800$, Aldrich) is used as the template, and tetraethyl orthosilicate (TEOS, A.R) is used as the silicon source, and 1, 3, 5-tritoluene (TMB, C.P) is a co-soluble agent. Mesoporous silica (SBA-15) is synthesized by launching heat under acidic conditions. Steps as follows: P123 (4g) and TMB (4g) are dissolved in 150 mL 1.6 mol/L HCl solution and magnetic stirring for 2 hours in 40 °C. 11.4 g of TEOS is added to the solution drop by drop and continue stirring for 20 hours. High pressure water thermal crystallization under 100 °C for 48 hours. Then, the product is filtering, washing, drying and calcining in 550 °C for 5 hours. The mesoporous silica material SBA-15 is obtained after removing the polymer material from silica.

Mesoporous carbon materials are prepared by using SBA-15 as template and sucrose as carbon source. 1.25 g sucrose is dissolved in 5 g distilled water, 1 g mesoporous silica template is added, and 0.14 g concentrated sulfuric acid is added slowly. And the mixture is carbonization for 6 hours under 100 °C and 160 °C respectively. After that, 0.75 g of sucrose is dissolved in 5 g of distilled water and added to the above products, and 0.7g of concentrated sulfuric acid is slowly added. The preliminary carbide products is obtained by another carbonization for 6 hours under 100 °C and 160 °C respectively. The preliminary carbide products is transferred to the tube furnace, and high temperature carbonized for 5 hours under nitrogen atmosphere at 850 °C. The high temperature carbonization products placed in the solution of sodium hydroxide in water and ethanol mixed solution and reflux 12 hours under 80 °C. After removing the silica template in carbon, the mesoporous carbon material is obtained after drying.

The adsorption-desorption isotherm of N_2 at 77K on mesoporous carbon is measured by ASAP 2002-m (Micro meritics, USA). The structure of SBA-15 and mesoporous carbon is characterized by small-angle X-ray diffraction, and the instrument is D8 ADVANCEX-ray diffractometer.

2.2. Preparation and electrochemical properties of sulfur/carbon composites

Mesoporous carbon and sublimed sulfur are mixed by mass ratio of 3 to 7. The material is ground for 10 h in qm-3a high-speed oscillating pendulum ball mill. Tablet is heated for 10h under 150 °C and 2 h under 300 °C. After cooling and grinding, the sample S/C composite material is obtained, in which the sulfur content is 48.11% (by mass).

The composite material, acetylene black and teflon are respectively weighed with mass ratio of 8.5:0.5:1. After mixing, adding suitable amount of isopropyl alcohol and rolling into a thickness of about 0.1 mm film, which is drying in vacuum under 80 °C for 2 hours. The disc with an area of about 2 cm² is rolled onto the aluminum grid to serve as the positive electrode of the battery.

A 2016 type button battery is assembled in a glove box filled with dry air using the above film as positive pole, lithium metal sheet as negative pole, polypropylene microporous film as diaphragm, electrolyte as DME/DOX (4:1, by Vol.) solution dissolved with 1 mol/L LiTFSI.

CT2001A battery tester (Wuhan LAND co., LTD.) is used to test the charge-discharge capacity of the button battery, the current density is 800 mA/g, and the charge-discharge voltage range is 1.0 ~ 3.0 V.

3. Results and discussion

3.1. Mesoporous carbon structures

Referring to the method described in literature[9,11], a certain amount of 1,3,5-trimethylbenzene (TMB) is added as a co-solvent during the formation of the template agent SBA-15. In this way, the pore size of the template agent can be increased and its regularity can be reduced. Figure 1 shows the SBA-15 template of mesoporous silica and the small Angle XRD diffraction pattern of mesoporous carbon.

According to relevant literature reports[9], none of the three characteristic peaks appeared in the diffraction spectral lines. This indicates that the synthesized template agent SBA-15 and mesoporous carbon do not have regular structure. Compared with conventional template method, this method is more favorable for sulfur infiltration than conventional template method, which produces mesoporous carbon with small hole diameter, long pipeline and regular length [9].

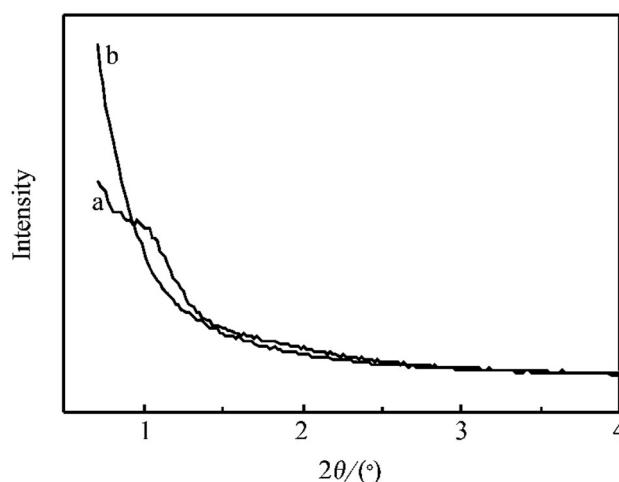


Figure 1. XRD patterns of the mesoporous silica SBA-15 (a) and mesoporous carbon (b)

Figure 2 shows the adsorption-desorption isotherm of nitrogen on mesoporous carbon. As shown in the figure, there is an obvious h1-type hysteresis loop at high relative pressure, which presents typical mesoporous adsorption characteristics, indicating that the sample has rich mesoporous structure. Figure 3 shows the pore size distribution curve of mesoporous carbon. It can be seen from the figure that the pore size of mesoporous carbon can be distributed at the left and right of 50 nm. The specific surface area of the mesoporous carbon is $975.4 \text{ m}^2 / \text{g}$, distributed in the capacity of $1.26 \text{ cm}^3 / \text{g}$, micro distributed capacity for $0.12 \text{ cm}^3 / \text{g}$, The average diameter of the middle hole is 51.6 nm.

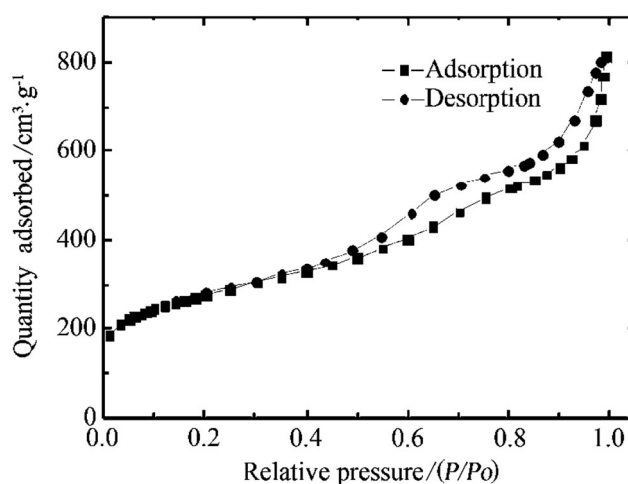


Figure 2. Nitrogen adsorption desorption isotherms at mesoporous carbon 77 K

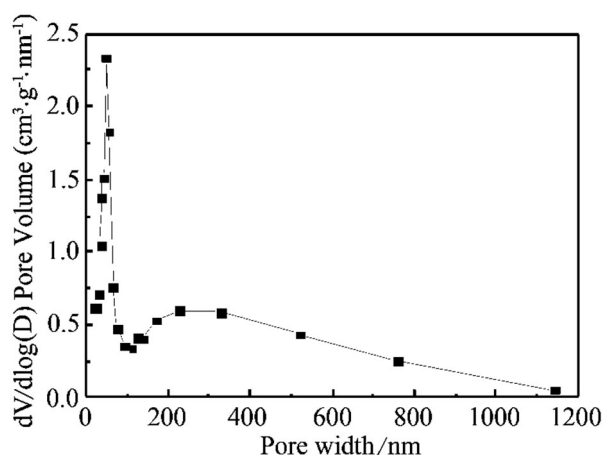


Figure 3. Pore size distributions curve of the mesoporous carbon

3.2. The electrochemical properties of composites

Figure 4 shows the first-cycle charge-discharge curve of S/C composite at current density of 800 mA/g. As can be seen in the figure, three distinct voltage platforms appear during the first cycle of discharge. Among them, 2.3V, 2.1V in the platform for the voltage consistent with the literature[12], correspond to the S to much sulfur ions Li_2S_x ($x = 4 \sim 5$) and sulfur ions to Li_2S_2 , Li_2S further reduction[13,14]. 1.9 V point of the discharge voltage platform and after process may be distributed in mesoporous channel is deep and a small amount of the reduction of elemental sulfur in pores. Because of the Li^+ spread in hole is relatively difficult, increased the polarization reaction, In the subsequent charging process, the platform is stable at 2.3 ~ 2.4 V.

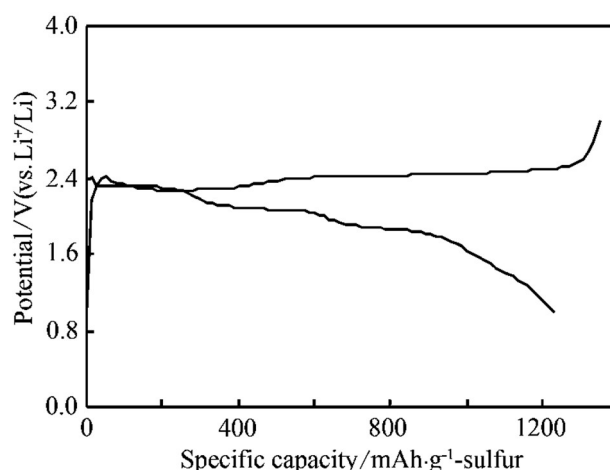


Figure 4. The first charge / discharge curves of S / C composite electrode at current density of 800 mA / g

Figure 5 shows the charging and discharging efficiency of the composite electrode under the current density of 800 mA/g. It can be seen that the charging and discharging efficiency is 92% in the 1st cycle. As you progress through, the cycle efficiency gradually reduce to 76% in 5th cycle. After the 6th cycle, efficiency and gradually recovered with the increase of cyclic number, and the efficiency rise to nearly 100% in 23th cycle, and in the loop always stay in the high efficiency state. Possible causes of this phenomenon is: S/C composite material, the outer surface of the mesoporous carbon, inevitably, there is a small amount of elemental sulfur. Sulfur surface cannot be fixed, in the initial stage, its discharge

intermediate gradually to dissolving electrolyte loss, and have a Shuttle effect in the process of charging, Lead to five cycles before charging and discharging efficiency decrease. As the surface completely dissolved loss of sulfur and more sulfur ions in the solution of gradual deactivation, electrode cycle efficiency and rising gradually, and to stabilize after 23 cycles. Because of the mesoporous carbon pore structure effectively limits the sulfur in the discharge of the intermediate dissolve erosion, in the subsequent loop, electrode showed high filling put electricity efficiency.

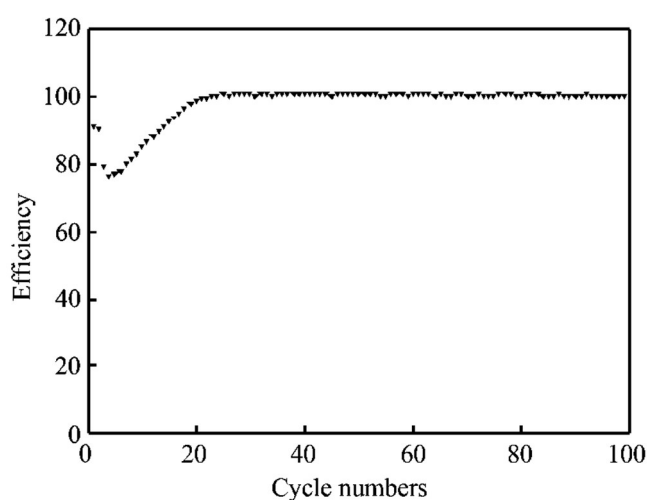


Figure 5. Charge-discharge efficiency of the S / C composite electrode at current density of 800 mA / g

Figure 6 shows the cyclic performance curve of the S/C composite electrode under the current density of 800 mA/g. After a cycle of 5 cycles, the capacity gradually recovered and basically stabilized after 20 cycles, reaching more than 850 mAh/g. After cycling for 100 cycles with the current density of 800 mA/g, the electrode capacity remained above 800 mAh/g, which fully demonstrated that the composite had strong current charge-discharge performance and good circulation performance.

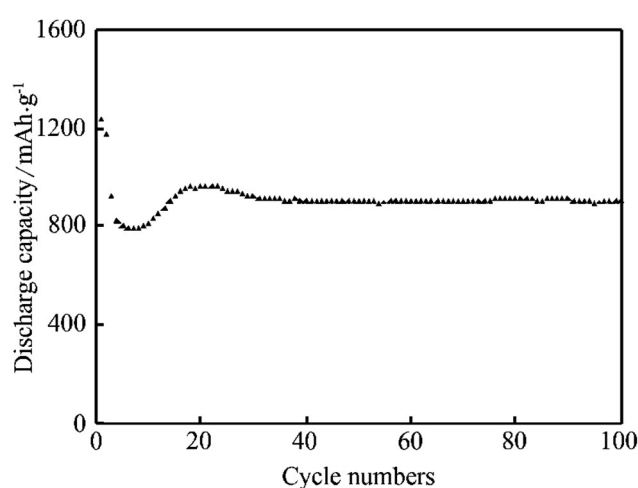


Figure 6. The cycling performances of S / C composite electrode at current density of 800 mA / g

4. Conclusion

The mesoporous carbon with TMB reaming has high specific surface area and abundant pore structure, which can effectively improve the electrochemical activity of elemental sulfur and its cyclic stability.

Acknowledgments

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