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A novel suspension polymerization process to prepare sulfur composite cathode materials for lithium/sulfur batteries

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Abstract

The sulfur-containing PAN composite cathode materials for lithium/sulfur batteries were prepared by suspension polymerization method and electrochemical properties of lithium/sulfur cells were investigated. The sulfur composite cathode was characterized by X-ray diffraction (XRD) and scanning electron microscopy (SEM). The structure analysis showed that the sulfur composite is constituted by homogenous flake-like crystallites with the size about 100 nm. The sulfur composite cathode showed a not very high initial capacity of 546.6 mAh•g⁻¹, but the cycle performance was excellent and had a slowly capacity fade after the second cycle, and remained at a reversible capacity of 400mAh•g⁻¹ after 30 cycles.

Keywords: lithium/sulfur batteries, cathode materials, cycle performance, capacity

1. Introduction

The rapid advancement of electronic technology and the widespread use of mobile devices have been continuously demanding a next generation battery. Lithium/sulfur battery is very attractive because of its high theoretical specific capacity of 1675mAh•g⁻¹sulfur. Besides, elemental sulfur is very cheap, abundant resources and nontoxic material [1,2]. Despite of those advantages, lithium/sulfur battery is difficult to commercialize due to low sulfur utilization and poor cycle performance. Those problems are caused by soluble polysulfides, which generate during charge/discharge process. Because of polysulfides dissolution into the liquid electrolytes cause the active material loss and the viscosity increase of liquid electrolyte as well as the morphology change of sulfur cathode [3-6]. Additionally, 100% sulfur cathode cannot be made due to very low electrical conductivity of sulfur.

To enable a reversible electrochemical reaction at high current rates and polysulfides dissolution, various carbon-sulfur composites have been used for this purpose. Composites with sulfur embedded in conducting polymers have shown some promising results. Wang et al. [7-9] reported composites with highly dispersed sulfur embedded in the polyacrylonitrile (PAN) as cathode materials for rechargeable sulfur composite cathode, which showed novel performances compared to the elemental sulfur cathode and overcame the abovementioned problems in some extent.

In this paper, we developed a novel method to prepare the sulfur-containing PAN composite cathode materials for lithium/sulfur batteries of a wet chemical method-suspension polymerization using acrylonitrile (AN) and sulfur as source material.

2. Experimental

2.1 Preparation of the sulfur composite cathode materials

Analytical grade AN, sublimation sulfur, polyvinyl alcohol (PVA), dimethyl formamide (DMF) and azodiisobutyronitrile (AIBN) were selected for use in

this work. The diagram of the experimental device is shown in Fig.1. Firstly, dispersing agents PVA was added into the flask with 100 ml deionized water to make a homogenous solution. Then, set the temperature of the water bath on a invariable reactive temperature of 65° C, 5ml DMF, 20ml AN and 8 g sublimation sulfur was added into the above solution in sequence and the mixtures were agitated violently continuously. Next, AIBN was added into the flask piece by piece to promote the reaction. After 3h reaction, the precipitates were separated from the mother liquor by filtration and washed with deionized water 4 times. The filtrates were dried sufficiently in an oven at 60° C.

The above precursor was heated to 300° C under a nitrogen atmosphere at a heating rate of 5 $^{\circ}$ C·min⁻¹. After keep the temperature at 300 $^{\circ}$ C for 8h, the furnace was cooled to room temperature and the final product of the sulfur-containing PAN composite cathode materials was ground and sieved.



Figure 1: Sketch diagram of the suspension polymerization equipment used in this work

2.2 Preparation of cathode and coin-type cell

The composite materials were mixed with acetylene black and polytetrafluoroethylene (PTFE), using ethanol as a dispersant. The weight ratio of the sulfur composite, acetylene black and PTFE was 70:20:10. The mixture was then coated onto nickel foam current collectors and cut into disks with a diameter of 12 mm. The electrodes were then dried at 80 °C under vacuum for 24 h. CR2025-type coin cells were assembled in a glove box with H₂O and O₂ content below 1 ppm. A lithium foil was used as the anode and separated by a Celgard 2400 microporous film. The electrolytes were 1.0 M LiPF₆ dissolved in a mixture of ethylene carbonate and diethyl carbonate (1:1, v/v).

2.3 Measurements

The phase compositions of the as-prepared sulfur composite materials were identified using XRD with a scan rate of $2^{\circ} \cdot \text{min}^{-1}$. The microstructures were analyzed using SEM (Model JSM-5800, JEOL, Tokyo). The charge and discharge performances of the

cells were tested at 0.1C between 1.0 and 3.0 V with a LAND cycler (Wuhan, China) at room temperature.

3. Results and discussions

Fig.2 shows the XRD patterns of the prepared sulfur composite materials. It is clearly seen that the composite materials show the characteristic of an amorphous structure, with a broad peak at $2\theta=25^{\circ}$. No characteristic peaks of sulfur can be observed, that is to say the sulfur have embedded in the framework of PAN sufficiently. And the element analysis demonstrates the sulfur content of the composite materials is 33.41%.



Figure 2: X-ray diffraction patterns of the prepared sulfur composite material

Fig.3 presents the particle morphology of the sulfur composite materials. The composite is composed of nonuniformity particles with the size about 3-5 μ m on the lowly magnification (Fig.3(a)). With the increase of magnification(Fig.3(b)), it is clearly that the composite is actually constituted by homogenous flake-like crystallites in nanometer grade and no dissociative sulfur can be found. This indicates that sulfur is well dispersed in the framework of the conducting polymers. The above analysis is in accord with XRD result.



Figure 3: SEM photographs of sulfur composite materials

The charge and discharge voltage profiles for selected cycles of the cells are shown in Fig.4. We can see that the initial discharge capacity is 546.6 mAh• g^{-1} , which is mainly generated by the voltage range of 1.2-1.3. In the following cycle, there is an appreciably increase of the discharge plateau and an appreciably decrease of the charge plateau. It demonstrates the decrease of the electrochemical reaction resistance of

the two electrodes, just the decrease of the electrodes inner resistance. Cycle life properties of lithium/sulfur cells are given in Fig.5. A dramatic discharge capacity drop to 416.4 mAh•g⁻¹ is observed following the first discharge. The big capacity loss in the initial lithium insertion/extraction can be attributed to some irreversible conversion of the active materials. There is nearly no obvious capacity fades upon cycling with a charge-discharge efficiency of 100% after the second cycle, remaining about 400 mAh•g⁻¹ after 30 cycles. Sulfur utilization is high according to the composite initial sulfur content (33.41%). The particle size of the prepared sulfur composite materials is about 100nm from the Fig.3, it concludes that the smaller particle size and the distinguishingly microstructure decide the favorable cycle performance, which is similar to Choi's research results [10].



4. Conclusion

A novel suspension polymerization method has been found to provide a simple and economic route for the preparation of the sulfur-containing PAN composite cathode materials for lithium/sulfur batteries. The prepared sulfur composite cathode material is constituted by homogenous flake-like crystallites with the size about 100 nm. The first discharge showed a not very high capacity of 546.6 mAh•g⁻¹, but it shows an excellent cycle properties and remains at a reversible capacity of $400 \text{mAh} \cdot \text{g}^{-1}$ after 30 cycles.

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