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Polysulfide rubber-based sulfur-rich composites as cathode material for high energy lithium/sulfur batteries

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ABSTRACT

Novel sulfur-rich polymer composites were prepared from the commercial polysulfide rubber through facile vulcanization methods and were firstly used as cathode material for lithium/sulfur batteries. The sulfur enriched in the composites includes three parts, the first part was inserted into the main chains of the polysulfide rubber, the second part formed insoluble polysulfide (-S_n-)through self-polymerization and the third part was trapped inside the network of the above two polymer chains. The obtained sulfur-rich polymer composites have high sulfur content over 80%. Compared with the pure sulfur electrode, the composites showed better cycle stability and coulomb efficiency.

Introduction

With the development of the portable electronic device, great attention is given to lithium–sulfur(Li–S) battery due to it's high energy density and theoretical capacity. With lithium and sulfur employed as anode and cathode separately, lithium sulfur battery has a high theoretical energy density of 2600 Wh/kg, which shows great potential among rechargeable batteries. Moreover, S is resource-abundant and environmentally friendly. Thus, Li–S batteries have garnered worldwide interest in the up-surging EVs and large-scale energy storage applications. However, Li–S batteries have two major drawbacks. One is the low electrical conductivity of Sand its discharged products, which will undesirably lower the utilization of the sulfur material, severely affecting the rate capability of the battery; the other drawback is the dissolution of the discharge products, for example lithium polysulfide, in electrolyte, causing irreversible loss of active materials and poor cycle performance.

In order to prevent the loss of the active substances and improve the reversibility of sulfur material, some researchers tried to employ sulfur-contained polymer as the cathode material. Trofimov [1]et al. synthesized ethynedithiol-based polyeneoligosulfides by the reaction of sodiumacetylides and elemental sulfur through the Na-C_{sp} bond in liquid ammonia. The oligosulfides obtained, being redox systems capable of reversible redox processes, provide high values of discharge

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capacity (345–720 mAh/g) of rechargeable lithium–sulfur batteries. A novel conducting sulfur-polypyrrole composite material was prepared by the chemical polymerization method in Wang's group [2]. For the synthesized sulfide-polypyrrole as cathode material in Li–S battery, the conductivity, specific capacity and cycle performance were significantly improved. The initial discharge capacity was 1280 mAh/g, after 20 cycles, the discharge capacity remained stable at 600 mAh/g or more. According to Ref. [3], conductive polymer polyacrylonitrile-based sulfur-containing heterocyclic compounds were prepared in Wang's group. At room temperature, sulfide-polyacrylonitrile was employed as the cathode, a lithium metal as the anode, the measured initial discharge capacity was up to 850 mAh/g. Its specific capacity remained above 600 mAh/g after 50 cycles, about five times that of $LiCoO_2$. Michael's group also prepared the sulfur-polyacrylonitrile composite as the positive electrode material, the carbonate of $LiPF_6$ was used as an electrolyte solution, and after 40 cycle's charge–discharge, the specific capacity of the obtained battery was 370 mAh/g polymer [4]. Novel sulfur/polythiophene composites with core/shell structure composites were synthesized via an in situ chemical oxidative polymerization method in Wu's group [5],a suitable ratio for the composites was found to be 71.9% sulfur and 18.1% polythiophene as determined by CV and EIS results. The initial discharge capacity of the active material was 1119.3 mAh/g, sulfur and the remaining capacity was 830.2 mAh/g sulfur after 80 cycles. The capacity retention rate was 74.2%. The sulfur utilization, the cycle life, and the rate performance of the S–PTh core/shell electrode in a lithium–sulfur battery improved significantly compared to that of the pure sulfur electrode.

Although all of these reports demonstrated high specific capacity, the cycle performance was still not stable enough, and the synthesis process was also too complex, with high energy consumption.

Considering the progress as above, we have some idea about the sulfur-containing polymer. We want to explore a kind of sulfur-rich polymer material with inexpensive raw material by simple preparation procedure. The energy storage and release could be achieved through the splitting and recombination of S–S chemical bonds in the sulfur-rich polymer. The discharge intermediate could be confined by the polymer chain network either through chemical bond or through physical wrapping, thus the decrease of discharge products dissolution and consequently better cycle performance of the battery will be expected.

In this work, we tried to use existing linear sulfur-containing polymeric material as raw material to prepare the sulfur-rich polymer. Polysulfide rubber drew our attention because it is commercial available with low price. What's more it can react with sulfur to extend S–S bond between two carbons, obtaining a sulfur-rich polymer as a cathode material for lithium–sulfur battery. In our study, the sulfur enriched in the composites was existed in three states: (i) the sulfur was inserted into the main chains of the polysulfide rubber(-C_4–S_2-)in form of (-C_4–S_m-, $8 > m > 2$); (ii) the sulfur was in form of insoluble polysulfide (-S_n-,$8 < n < 100$)by self-polymerization; and (iii)the sulfur was trapped inside the network of the above two polymer chains in the third state. It could be clearly seen from Fig. 1. Thus, the interactions are different from others' reports. There were two kinds of interactions reported; one was polymerization with sulfur which usually had lower sulfur content and mostly no more than 50 wt%, and the other was the physical interaction such like coating method. For our work, as described above, the means of the interaction among the different compositions included (i) chemical bond in the sulfide polymer, (ii) chemical bond in the polysulfide and (iii) physical wrapping among the polymer chains. The chemical bond played a major role in those interactions, only small amount of un-reacted elemental sulfur was trapped the polymer chains, and the sulfur content was higher.

Experimental

Preparation of sulfur-rich polymer composites

The sulfur-rich polymer composites were prepared through vulcanization methods in a flask. The polysulfide rubber JLG-200 ([-S–CH_2–CH_2–CH_2–CH_2–S-]$_x$) was used as received from Jinxi Research Institute of Chemical Industry, Huludao City. A certain amount of polysulfide rubber (for example 4.00 g) was put into the shredder with liquid nitrogen and was

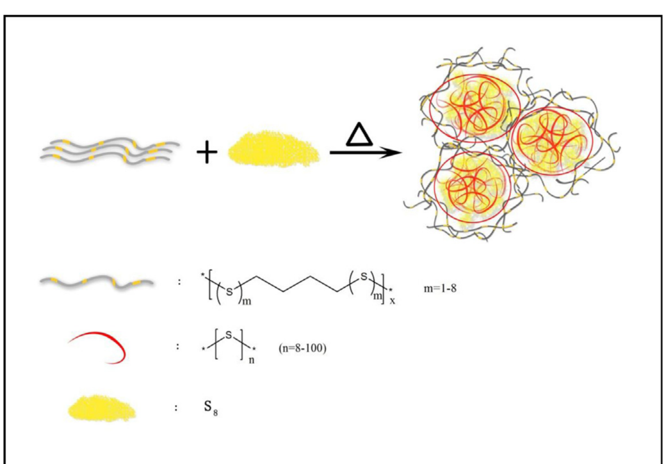

Fig. 1 – Schematic diagram of the sulfur-rich polymer composites.