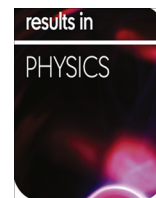




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Reduced graphene oxide encapsulated sulfur spheres for the lithium-sulfur battery cathode

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ABSTRACT

Reduced graphene oxide (rGO) encapsulated sulfur spheres for the Li-S batteries were prepared via the redox reaction between sodium polysulfide. XRD spectra showed that the diffraction peak of graphite oxide (GO) at 10° disappeared, while the relatively weak diffraction peak at 27° belongs to graphene emerged. FT-IR spectra showed that the vibrations of the functional groups of GO, such as 3603 cm⁻¹, 1723 cm⁻¹ and 1619 cm⁻¹ which contributed from –OH, C–O–C and C=O respectively, disappeared when compared to the spectra of GSC. SEM observations indicated that the optimum experimental condition followed as: mass ratio of GO and S was 1:1, 10% NaOH was used to adjust the pH. EDX analysis showed that the sulfur content reached at 68.8% of the composite material. The resultant electric resistance was nearly less than GO's resistance in three orders of magnitude under same condition. Further electrochemical performance tests showed a coulombic efficiency was 96% from the first cycle capacity was 827 mAh g⁻¹, to 388 mAh g⁻¹ in the 100 cycles. This study carries substantial significance to the development of Li-S battery cathode materials.

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Introduction

In the face of increasing demands for high energy and high power for use in electric vehicles and electronic devices, the next generation of power supplies, especially high performance rechargeable batteries are attracted wide attentions worldwide [1,2]. Lithium-sulfur (Li-S) battery, composed of sulfur composite cathode, electrolyte, and lithium anode, has attracted the attention of numerous researches nowadays due to its unique properties. Sulfur firstly is a promising positive electrode material for Li-S battery on account of its high theoretical specific capacity of 1675 mA h g⁻¹ and the Gibbs energy of the Li/S reaction is more than five times the theoretical energy of a Li-ion system, approximately 2600 Wh kg⁻¹ [3,4]. Moreover, elemental sulfur benefits from the advantages such as natural abundance, low cost and non-toxicity [3–5]. There has been strong incentive to develop a rechargeable Li-S battery as well [6,7].

Although the Li-S battery has considerable advantages, there are two main concerns with it that have impeded its practical

application. First, the intermediate reduction products polysulfides (Li₂S_x, 3 ≤ x ≤ 6) are highly soluble in the electrolyte which leads to active materials mass loss and lowered coulombic efficiency through the well known sulfur shuttle mechanism [8–12]. Another problem urgently needed to be solved is the poor electronic conductivity of sulfur (5 × 10⁻³⁰ S cm⁻¹), which causes poor electrochemical contact of the sulfur and leads to low utilization of the active materials in the cathode [13]. Therefore, conductive material is required when making the sulfur cathode. In order to address the issue involved with the poor electrical conductivity of a sulfur cathode, recent researches on the Li-S battery have focused on the addition of conductive carbon matrices [14–19] and conducting polymers [20–22]. Liang et al. synthesized the carbon/sulfur composite material that embedded in the nanopores of the carbon matrix, not only were the electrical and ionic conductivity of sulfur cathode elevated, but also the shuttle effects were suppressed simultaneously [23]. Qiu et al. made a nano-sized S/PPy (poly (pyrrole-co-aniline)) composite material which showed a high discharge capacity and acted as a good conductive matrix favorable for the Li-S battery [24].

The use of graphene-enveloped sulfur particles as the cathode material in the Li-S battery has also been reported [25]. As a com-

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mon approach to improve the electrical and ionic conductivity of Li-S battery, graphene-enveloped sulfur method consists of two steps as follows: 1. wrap the sulfur with graphene oxide; 2. deoxidize the graphene oxide to make the graphene-enveloped sulfur composite material. However, the researches focused on the specific process of the redox reaction between element sulfur and graphene oxide were relatively few and the mechanisms are still not quite clear.

In this work, we prepared the graphene-enveloped sulfur composite material via the redox reaction between sodium polysulfide and graphene oxide without any extra reducing agents. The sulfur spheres were perfectly wrapped by the graphene to form the idea composite material, and no aggregation of sulfur particles was attached to the graphene surface. The results prove that the graphene sulfur composite (GSC) material is substantially promising in the applications of the Li-S battery cathode materials.

Experimental

Chemicals and materials

Graphite oxide (AR, 99.0%), sublimed sulfur (CP, 98.0%) and sodium sulfide nonahydrate (AR, 99.99%) were obtained from Aladdin. NaOH (AR, 96%) and HCl (AR, 38%) were purchased from Sino-pharm Chemical Reagent Co., Ltd. Distilled water was home-made. All the chemicals purchased were used as received.

Preparation of well-dispersed graphene oxide

0.02 g NaOH was added into 100 mL distilled water in a 200 mL beaker to make 5 mM NaOH solution. Four amounts of graphene oxide (GO) powders (mass ratio, 1:1:1:5) were added into four separated bottles with 20 mL of 5 mM NaOH. Later on sonicate the mixed solution for 1 h to prepare the well-dispersed GO solution.

Preparation of sodium polysulfide solution

Analogously four amounts of the sublimed sulfur powders and sodium sulfide monohydrate (mass ratio, 1:2) were added into four separated beakers entitled A, B, C, D with 100 ml distilled water to prepare the sodium polysulfide solution. According to the quantities of GO weighted in the last step, make sure the corresponding mass ratio of GO and S (from sublimed sulfur and sodium sulfide monohydrate) were 1:10, 1:1, 1:1, 10:1. Subsequently 10% NaOH was mixed respectively with the solutions contained from beaker A, B, D and 5% NaOH was for beaker C. Homogenize the solution by stirring for 1 h at 60 °C.

Preparation of graphene sulfur composite (GSC)

Briefly, the graphene sulfur composite (GSC) was prepared as following: Pour the GO solution into corresponding beakers, and then homogenize the mixture by stirring for 4 h at 60 °C. Later on 5% HCl solution was added to lower the pH to 2. The GSC composite was obtained after filtration and drying (named as GSC-A, GSC-B, GSC-C and GSC-D). Samples A, B and D were used to study the reduction affects caused by different mass ratio of GO; B and C were used to study the alkalinity affects caused by proportional amount of NaOH.

Electrochemical performance tests

Coin-type (CR2035) cells were prepared using polypropylene separator between a cathode and lithium metal foil in glove box. The slurry was prepared by mixing the GSC, carbon black, and

PVDF ratio of 8:1:1 (by weight %) in NMP as the solvent. The resultant slurry was stirred under magnetic stirring for 1 h before uniformly spread on pure aluminum foil and dried at 60 °C for 6 h under vacuum. The electrolyte used was 1 M LiTFSI in a solvent mixture of DOL/DME (1:1 v/v), 1 wt% LiNO₃. The cells were discharged and charged on a battery test system (LAND, Wuhan) from 1.6 to 3.0 V at a current density of 0.2 C to test the cycle life.

Characterization

Samples of GO, GSC, NaCl were tested by X ray diffractometer (X Pert Power), which was purchased from Panalytical Ltd.; Samples of GO, GSC were tested by Fourier transform infrared spectrometer (Bruker TENSOR27) and the samples were processed through KBr pellets; Scanning Electron Microscope (FEI Quanta 400 FEG) equipped with Energy Dispersive X-ray microanalysis (Apollo 40 SDD) was used to characterize the GO and GSC powders; Laser Micro-Raman Spectrometer (Renishaw in Via) was a specially used instrument to characterize the grinded GSC powder; finally the resistances of GO and GSC were measured by volometer (MB 194E), the specimen were processed by the tableting machine.

Results and discussion

Sodium polysulfide solution was prepared via the reaction between sulfur and sodium sulfide nonahydrate under the alkali environment. GO was turned into rGO after the reduction reaction of GO and sodium polysulfide, as illustrated Fig. 1. HCl solution was subsequently added into the solution and rGO was transformed into graphene sulfur composite (GSC) which made up of graphene and sulfur. In this procedure, sulfur spheres were uniformly enveloped by rGO.

XRD was used to verify the redox reaction between sodium polysulfide and GO. As can be seen in Fig. 2, a clear diffraction peak appeared at 10° which belongs to GO. However, compared to the XRD pattern of GSC, the peak at 10° disappeared and the characteristic peak at 27° belongs to rGO emerged of the spectra of GSC-A, B and D. There were several peaks among 22–30° of GSC-D which refer to the diffraction of sulfur attached to the surface of rGO. Unfortunately, the impacts on the reduction degree caused by different quantities of S were not indicated from the patterns, since no characteristic peaks belong to rGO and GSC turned up simultaneously. These results indicate that GO can be reduced into graphene successfully by sodium polysulfide under alkaline environment.

Further tests were applied to study the effects caused by different alkaline conditions when GSC was synthesized. The XRD patterns of GSC-B and C synthesized under 10% and 5% NaOH respectively was showed in Fig. 3, the characteristic peak at 27° appeared in both patterns. However, compared to the GSC-B, there were several peaks among 22–30° of GSC-B which refer to the diffraction of sulfur attached to the surface of rGO. The spectra indicate that, when the alkaline condition was adjusted by 10% NaOH, the rGO was reduced completely.

FT-IR spectra results showed in Fig. 4. From the spectrum of GO, we can see vibrations at 1619 cm⁻¹ and 1723 cm⁻¹ which contributed from C=O and C—O—C group, respectively. The vibration at 3600 cm⁻¹ can also be observed that contributes to —OH. Compared with the spectra of GSC and pure graphene, the characteristic vibrations of GO disappear in the spectrum of GSC, which is also extremely similar to the spectrum of pure graphene. These results indicate that GO was reduced successfully using sodium polysulfide.

The scanning electron microscope (SEM) was used to observe microstructure of GO and GSC. At low magnification, we can see

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