Short communication

A sulfur–polyacrylonitrile/graphene composite cathode for lithium batteries with excellent cyclability

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HIGHLIGHTS

- A sulfur–polyacrylonitrile/reduced graphene oxide (SPAN/RGO) composite was prepared.
- The composite consists of RGO decorated by SPAN particles of 100 nm average size.
- It exhibits ∼85% retention of the initial reversible capacity of 1467 mAh g^{-1} over 100 cycles.
- It retains 1100 mAh g^{-1} after 200 cycles.
- It displays an 828 mAh g^{-1} reversible capacity at 2C rate.

ARTICLE INFO

ABSTRACT

A sulfur–polyacrylonitrile/reduced graphene oxide (SPAN/RGO) composite with unique electrochemical properties is prepared via deposition of PAN on the surface of RGO sheets followed by ball milling with sulfur and heat treatment. Infrared spectroscopy and microscopy studies indicate that the composite consists of RGO decorated by SPAN particles of 100 nm average size. The SPAN/RGO composite shows good overall electrochemical performance when used in Li—S batteries. It exhibits ∼85% retention of the initial reversible capacity of 1467 mAh g^{-1} over 100 cycles at a constant current rate of 0.1C and retains 1100 mAh g^{-1} after 200 cycles. In addition, the composite displays excellent Coulombic efficiency and rate capability, delivering up to 828 mAh g^{-1} reversible capacity at 2C. The improved performance stems from the composition and structure of the composite, wherein RGO renders a robust electron transport framework and PAN matrix help suppresses the shuttle effect by absorbing sulfur/polysulfides.

1. Introduction

Rechargeable lithium sulfur (Li—S) batteries are safe, environmentally friendly and economical alternative energy storage systems that can potentially be combined with renewable sources including wind, solar and wave energy. Sulfur has a high theoretical specific capacity of ∼1680 mAh g^{-1}, attainable through the reversible redox reaction denoted as $S_8 + 16Li \leftrightarrow 8Li_2S$, which yields an average cell voltage of ∼2.2 V [1]. However, two detrimental factors prevent the achievement of the full potential of the Li—S batteries. First, the poor electrical/ionic conductivity of elemental sulfur and Li_2S/Li_2S_2 severely hampers the utilization of active material for obtaining full capacity of the electrode [2]. Second, dissolution of intermediate long-chain polysulfides (Li_2S_n,

$2 < n < 7$) into the electrolyte and their shuttle between cathode and anode leads to fast capacity degradation and low Coulombic efficiency [3]. As a result of this shuttle process, insoluble and insulating Li_2S/Li_2S_2 precipitates on the surface of electrodes causing loss of active material and rendering the electrodes surface electrochemically inactive [4].

Extensive research efforts have been devoted to overcome the aforementioned problems, such as combination of sulfur with conductive polymers [5—9], and encapsulation or coating of elemental sulfur in different nanostructured carbonaceous materials [10—21]. Noteworthy, sulfur—polyacrylonitrile (SPAN) composites, wherein sulfur is chemically bond to the polymer backbone and PAN acts as a conducting matrix, have shown some success in suppressing the shuttle effect [21,22]. However, due to the limited electrical conductivity of polyacrylonitrile, the capacity retention and rate performance of the SPAN systems are still very modest. Recently, graphene has been intensively investigated for enhancing the rate and cycling performance of lithium sulfur

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batteries. Graphene, which has a two-dimensional, one-atom-thick nanosheet structure offers extraordinary electronic, thermal and mechanical properties [23–29]. Herein, we report on a sulfur–polyacrylonitrile-reduced graphene oxide (SPAN/RGO) composite prepared by a low-cost and environmentally benign solvent exchange approach. The electrochemical performance of the composite as a cathode material for Li–S batteries was also investigated.

2. Experimental section

2.1. Materials

Natural graphite (Alfa Aesar), hydrazine (35 wt.% in water), ammonia solution (28 wt. % in water), polyacrylonitrile (average molecular weight 150,000), sulfur, dimethylformamide, sodium chloride, sulfuric acid (concentrated), sodium nitrate, potassium permanganate, hydrogen peroxide (30 wt.%), hydrochloride acid (37 wt.%) (Sigma–Aldrich) were used without further purification, Katjen Black 600 (AkzoNobel), polyvinyldifluoride (Sigma–Aldrich), N-methylpyrrolidone (Sigma–Aldrich). Milli-Q grade water was used in all experiments.

2.2. Synthesis procedure

2.2.1. Preparation of reduced graphene oxide (RGO) aqueous suspension

Graphite oxide (GO) was prepared through a modified Hummers method [30]. 0.8 g natural graphite was stirred in 23 ml concentrated H_2SO_4 (98%) for 24 h, and 3 g $KMnO_4$ were added to the dispersion while the temperature was kept below 20 °C. The mixture was then diluted and heated up to 100 °C for 15 min. The reaction was terminated by addition of 10 ml H_2O_2 solution (30%) and 140 ml water. The resulting graphite oxide was then repeatedly washed with 5% HCl aqueous solution and water. A brown-colored dispersion was achieved. The graphite oxide dispersion was ultrasonicated for 30 min using a Hielscher Ultrasonics (UIP 1000hd, 150W, 50% amplitude).

Next, a reduced graphene oxide (RGO) dispersion was achieved through chemical reduction of GO with the presence of ammonia, which was used to preserve the functional group on reduced graphene oxide to obtain maximal charge density for a stable dispersion of RGO [31]. The GO dispersion was diluted with water to 0.05 wt.%. 100 ml of the homogeneous dispersion was then mixed with 100 ml water, 100 μl hydrazine solution (35 wt.% in water), and 0.7 ml ammonia solution (28 wt.% in water) in a 250 ml round bottom flask. The weight ratio of hydrazine to graphene oxide was 7:10. The flask and its contents were immersed into an oil bath, kept at 95 °C, for 1 h. The excess hydrazine was thoroughly removed by dialysis against 0.5% ammonia solution.

2.2.2. Polyacrylonitrile/reduced graphene oxide composite (PAN/RGO)

100 ml of the as prepared RGO dispersion were mixed with 64 ml of a 5.88 gL^{-1} PAN/DMF solution. After vigorous stirring for 10 min, 600 ml 0.5 wt.% ammonia aqueous solution was added to the beaker and stirred for 24 h. About 0.4 g PAN/RGO sediment was obtained by centrifugation, and repeatedly washing with ethanol and water.

2.2.3. Sulfur–polyacrylonitrile/partially reduced graphene oxide composite (SPAN/RGO)

The PAN/RGO composite obtained by centrifugation was immediately subject to wet ball milling with 1.6 g sulfur at 500 rpm for 3 h. The mixture was then dried in a vacuum oven at 60 °C,

followed by heat treatment at 320 °C for 5 h under argon atmosphere.

2.3. Characterization

The sulfur content in all the composites was determined with a CHNOS Elemental Analyzer (Vario Micro Cube, Elementar Americas). The morphology of the composites particles was evaluated by scanning electron microscopy (SEM, Leo FESEM). Atomic force microscopy (AFM, Agilent 4500 Series) imaging was detected under tapping mode. Zeta potential of graphene was determined using a laser electrophoresis zeta potential analyser (Zetasizer 3000HSA, Malvern Instruments). Powder X-ray diffraction (XRD, Bruker D8 Discover) analysis was carried out using Cu–Ka 1.1446 Å radiation at 40 kV. Fourier transformed infrared spectroscopy (FTIR, Bruker Vertex 70) analysis of KBr pellets were recorded in transmission mode. Thermogravimetric analysis (TGA, TA Instruments SDT Q600) was performed in nitrogen atmosphere at heating rate of 10 °C min^{-1} to investigate the thermal stability of the composites.

The electrochemical performance of the composites was evaluated using lithium metal as counter and pseudo-reference electrode. The cathode was prepared by mixing active material, Katjen Black 600, and polyvinyldifluoride (PVDF) with a weight ratio of 8:1:1 using N-methylpyrrolidone (NMP) as solvent. The resulting slurry was painted onto nickel foam current collector (Φ12 mm) and dried at 60 °C for 12 h. The final electrode loading density was around 6–8 mg cm^{-2} (total cathode material). CR2025 coin cells were assembled in an argon-filled glove box (Mbraun) using 1.0 M LiPF$_6$ in 1:1:1 v/v EC/DC/DMC as electrolyte and Celgard 2250 as separator. The cells were galvanostatically charge–discharged between 1 V and 3 V (vs Li/Li$^+$) using a battery tester (Neware Shenzhen, China). The specific capacities and rates reported here are based on the mass of sulfur. Cyclic voltammetry (CV) and electrochemical impedance spectroscopy (EIS) measurements were carried out on a Biologic VMP3 electrochemistry workstation. EIS was handled over the frequency range of 100 kHz–0.1 Hz and CV analysis was performed at scan rate of 0.1 mV s^{-1}.

3. Results and discussion

The preparation procedure of SAPN/RGO composite is illustrated in Fig. 1. Through the process, the exfoliated GO sheets in water are converted back to graphene by chemical reduction.

Zeta potential measurements confirmed the anionic charge of graphene sheets in water. The exfoliated GO shows a zeta potential of −55.7 mV, whilst that of hydrazine reduced RGO is −43.2 mV. This result implies that the carboxylic acid groups of GO are partially preserved when the reduction is conducted in the presence of ammonia. As a result, RGO can be dispersed due to the electrostatic forces.

RGO sheets cast on a silicon wafer were examined by AFM under tapping mode. Fig. 2 shows flat RGO sheets with a thickness of ~1 nm, implying the successful exfoliation from graphite to graphene sheets.

Fig. 3 depicts typical TGA curves of GO and RGO. The onset of mass loss for GO occurs at 200 °C, due to the pyrolysis of the labile oxygen containing functional groups leading to total decomposition of the material. The reaction is accompanied by an exothermic peak at 200 °C in the heat flow curve. Conversely, RGO shows about 65 wt.% residual mass after heating to 800 °C, and no obvious exothermic peak is detected in its heat flow curve. This is likely due to an increased thermal stability of the RGO after reduction of the oxygen functional groups and implies the successful formation of graphene.

The FTIR spectra of intermediates and composites materials are displayed in Fig. 4. After reduction of GO, the carboxylic and ketone