



Synthesis of a ternary polyaniline@acetylene black-sulfur material by continuous two-step liquid phase for lithium sulfur batteries



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ABSTRACT

A ternary polyaniline/sulfur/acetylene black (PANi@S-C) composite cathode with variable PANi content has been synthesized by a continuous two-step liquid phase route. Different ratios of the PANi@S-C composite are characterized by SEM, TEM, FTIR, XRD and electrochemical methods. The conductive polyaniline plays multiple roles in the composite, acting as a conducting additive and a porous adsorbing agent. It is uniformly coated onto the surface of a S-C composite powder to form a core/shell structure, which significantly enhances the electrochemical performance and cycle life of the sulfur cells. The PANi@S-C composite with 12.5 wt% PANi presents optimum electrochemical performance, where the initial discharge specific capacity is 1257 mAh g⁻¹ and remains ~600 mAh g⁻¹ after 100 cycles at 0.16 mA cm⁻². After a rate test from 0.1 to 1 mA cm⁻², the cell remained at ~600 mAh g⁻¹ sulfur after 50 cycles when the current density returned to 0.1 mA cm⁻².

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1. Introduction

Lithium sulfur batteries are attractive due to their high theoretical specific energy (2600 Wh kg⁻¹), which is much higher than that of conventional lithium ion batteries based on intercalation chemistry. In addition, sulfur is abundant and inexpensive. Therefore, Li-S batteries show great potential for the next generation of lithium batteries and are capable of offering high energy density as power sources for electric vehicles [1–3].

Unfortunately, many challenges remain in developing practical Li-S batteries for commercialization. First, the low electrical conductivity of elemental sulfur as the electrode active material (~5 × 10⁻³⁰ S cm⁻¹, 25 °C) causes poor electrochemical utilization. Second, the high solubility of the intermediate polysulfides (Li₂S_n) results in the loss of active material and an irreversible capacity fade. Third, the large volumetric expansion (~80%) upon lithiation gives rise to deteriorating cycle performance [4–8].

To overcome these problems, considerable attempts have been made to optimize the organic electrolyte [9–11], to prepare carbon/sulfur composites [12–21], to fabricate polymer/sulfur composite [22–30], etc. Carbon/sulfur composites have been the most extensively studied due to their light weight and good electrical conductivity. However, the synthesis of such composites faces many

difficulties, such as the creation of special templates, complicated processes and tough conditions, which have prevented successful deployment on a commercial scale. Similarly, the chain-like structure and many functional groups of polymers facilitate the trapping of polysulfides while maintaining good electrical conductivity. Moreover, polymer-based processes are feasible below 100 °C because polymers are either soluble or dispersible in various solvents. In addition, polymers have good mechanical resilience, solving issues associated with volumetric expansion and material pulverization [31]. Considering the merits of both carbon and polymer host materials, the preparation of multicomposites of sulfur with carbon and a conductive polymer should enhance the electrochemical performance of sulfur cathodes.

Polyaniline (PANi) has gained popularity among conductive polymers owing to its electrical, electrochemical, and optical properties, as well as its free volume and excellent environmental stability [32,33]. A recent boom in PANi-related energy research has been triggered by the emerging focus on Li-S batteries because it is stable and moderately rigid in the electrochemical environment. At present, incorporating carbon with PANi as a sulfur host has been found to exhibit excellent electrochemical performance. However, the synthesis of these ternary composites includes processing by a sulfur melting route, resulting in additional energy consumption and poor dispersion of the multicomposite [22,34–36].

We therefore present here a facile and scalable continuous two-step liquid phase route to synthesize ternary PANi@acetylene black-S composites, aiming to improve Li-S cell electrochemical

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performance. Through an in situ sulfur deposition route, the chain-like acetylene black was integrated with sulfur particles to increase electrical conductivity. A conductive PANi layer was then coated onto the surface of the S-C composites using an in situ chemical oxidative-polymerization method. The effective conductive network provided by the acetylene black, together with the strong affinity to sulfur and polysulfides provided by PANi, enables the homogenous dispersion of the sulfur, facilitates the transportation of ions and improves the cycling performance of the lithium sulfur battery. The optimum amount of PANi in the ternary PANi@acetylene black-S composites is discussed. We also note that the use of the low-cost and commercially available conductive acetylene black as a conductive matrix will be highly significant to the mass production of S-C composites and Li-S batteries in the future.

2. Experimental

2.1. Preparation of the composites

S-C composites: The synthesis of S-C composites by in situ sulfur deposition has been reported by Su *et al.* [34]. In a typical reaction, acetylene black (1 g) was dissolved in sodium thiosulfate pentahydrate (19.38 g, 40 mL) with magnetic stirring. Hydrochloric acid (1 M) was then added dropwise. The reaction proceeded at room temperature for 3 h, after which the product was filtered and washed several times with deionized water until a neutral pH was reached. The dark gray S-C composites were collected and dried in an air-oven at 60 °C for 24 h. Meanwhile, pristine sulfur was also synthesized by the same means.

PANi@S-C composites: The PANi@S-C composites were prepared by an in situ chemical oxidative polymerization at freezing temperature in a mixed solution. In a typical experiment, a mixed solution containing aniline monomer (without any pre-treatment) and dilute hydrochloric acid (20 mL, 1.5 M) was treated in an ultrasonic cleaner for 30 minutes, followed by the addition of S-C composites (1.4 g, see above) with magnetic stirring. As an oxidant, $(\text{NH}_4)_2\text{S}_2\text{O}_8$ dissolved in dilute hydrochloric acid (20 mL, 1.5 M) was added dropwise to the above reactant mixture. In the polymerization, the mole ratio of aniline monomer and $(\text{NH}_4)_2\text{S}_2\text{O}_8$ should be kept at 1:1. After constant stirring for 12 h at 0–5 °C, the precipitate was filtered and washed repeatedly with ethanol and distilled water until the washing solution became transparent. The product was then dried in a vacuum oven at 60 °C for 24 h for subsequent use. The samples where the aniline content was 0.02 g, 0.1 g, 0.2 g, and 0.3 g were marked as PANi@S-C1, PANi@S-C2, PANi@S-C3, and PANi@S-C4, respectively. For comparison, pure PANi was also synthesized by the same means.

2.2. Materials characterization

The morphology of the composite materials was observed with an SU8010 high-resolution field emission scanning electron microscope (SEM). X-ray diffraction (XRD) patterns of the S, acetylene black, PANi and composite materials were measured on a D8-FOCUS powder diffraction system operating at 40 kV using Cu-K α radiation. Fourier transform infrared (FTIR) spectra were collected using a Nicolet6700 FT-IR spectrometer by dispersing S-C, PANi@S-C3, and PANi in KBr pellets. The sulfur content of the composites was calculated from the thermal gravimetric analysis (TGA) data collected with a STA449F Thermogravimetric Analyzer at a heating rate of 10 °C min⁻¹, from 30 °C to 400 °C, in a nitrogen atmosphere.

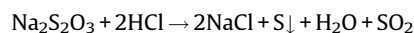
2.3. Electrochemical measurements

The cathodes containing S-C or PANi@S-C composites were prepared by mixing the active material (80 wt%) with acetylene

black (10 wt%) and a poly(vinylidene fluoride) binder (10 wt%) and then dispersing the mixture in NMP to form a slurry. The electrode slurry was then pasted on Al foil by means of a doctor blade method, followed by evaporation of the NMP at 60 °C in an air-flow oven for 5 h. Next, the electrode film was cut into sheets measuring 15 mm in diameter. The film disk was dried in a vacuum oven at 60 °C for 24 h before assembling the testing cells. Handmade Teflon cells were then assembled in a glove box filled with argon. Lithium metal was used as the counter electrode and the reference electrode, and a microporous polypropylene film (Celgard 2300) was used as a separator. The electrolyte consisted of 0.1 M anhydrous lithium nitrate and 1 M $\text{LiN}(\text{CF}_3\text{SO}_2)_2$ in a mixed solvent of 1,3-dioxolane and dimethyl ether at a volume ratio of 1:1. The cells rested for 12 h before testing. Galvanostatic charge/discharge tests were then performed in a voltage range of 1.5–2.8 V with a BT-2000 Arbin Battery Testing System. Cyclic voltammetry (CV) experiments were conducted with a VMP3 electrochemical workstation at a scanning rate of 0.1 mV s⁻¹ with a voltage range from 1.5 to 2.8 V. Electrochemical impedance spectroscopy (EIS) data were collected with the VMP3 electrochemical workstation over the frequency range from 10⁻² to 10⁵ Hz at potentiostatic signal amplitudes of 5 mV.

3. Results and Discussion

The entire synthesis of ternary PANi@S-C composites by the continuous two-step liquid phase route is illustrated in Fig. 1. In the first step of the synthesis, sulfur was synthesized in the presence of acetylene black to generate uniform S-C composites by the following reaction in aqueous solution:



Sulfur was thus highly dispersed in acetylene black (matrix), which provided the main conductive framework. In the second step of the synthesis, the PANi particles agglomerated to build a cover layer on the surface of the S-C composite by oxidation polymerization. Sulfur easily connects with the PANi networks through hydrophobic–hydrophobic interactions. In the designed structure, the severe shuttle reaction of soluble lithium polysulfides is effectively blocked by the PANi-coating layer. Meanwhile, the structural stability of the entire electrode is maintained during long cycling due to the good conductivity and compatibility of PANi.

Fig. 2 shows SEM micrographs of the S-C composites and PANi@S-C composites with differing PANi contents. As shown in Fig. 2a, the sulfur in the S-C composites contains floc-like particles with a diameter of a few microns, while acetylene black appears as a loose particle aggregation of uniform carbon particles with a size of less than 100 nm. Sulfur particles are uniformly distributed throughout the network structure formed by the acetylene black; however, the sulfur particles are too large for the acetylene black particles to be completely enveloped. The PANi-coated S-C composites with increasing PANi content are shown in Fig. 2b–d. It can be seen that the floc-like sulfur particles gradually became invisible with increasing PANi content. In the case of PANi@S-C3, the floc-like sulfur particles were completely invisible; in other words, the S-C composites were almost fully covered by the PANi layer. With the PANi content increased in PANi@S-C4, the outer particles were larger than acetylene black, indicating that the excessive PANi was not only coated on the surface of the sulfur but also on the surface of the conductive acetylene black particles. The TEM micrograph in the right inset of Fig. 2d shows that the PANi is coated uniformly on the surface of the S-C composite forming a core/shell structure with a thickness of ~5–10 nm.

It was difficult to identify the presence of a PANi-coating layer from observations in SEM images. Taking PANi@S-C3 as an example, elemental mapping was used to evaluate the distribution

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