



Nonfilling polyaniline coating of sulfur/acetylene black for high-performance lithium sulfur batteries



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ABSTRACT

A kind of nonfilling polyaniline coating of sulfur/acetylene black composite is prepared via a facile and eco-friendly approach in consideration of the different solubility of sulfur in the liquid phases and at the proper temperature. Acetylene black particles with the particle size of 50 nm are partially infiltrated with sulfur, just the outer surface are coated with polyaniline shell. When using as a cathode material for lithium sulfur batteries, it exhibits significantly enhanced rate capability (initial capacity of 810 mAh/g at 2C, 486 mAh/g at 5C), and rate stability after 500 cycles (> 351 mAh/g at 5C). This considerable electrochemical performance could be attributed to the highly uniform distribution of sulfur in the nanopores of the conductive acetylene black and the physical isolation of the sulfur with electrolyte by conductive polyaniline. This renders it to be a promising candidate for practical application in lithium sulfur batteries.

1. Introduction

Great academic and industrial efforts have been devoted to exploit rechargeable lithium sulfur batteries with high energy density, long cycle life and low cost for various technological applications, ranging from consumer devices to electric vehicles [1–3]. Nonetheless, particle pulverization, loss of electrical contact and shuttle effect have long been acknowledged as primary barriers for the commercialization of sulfur-based cathode [4–8]. Numerous works have been done to solve these problems (see Table 1). Surface coating, adding interlayer between cathode and separator, Li₂S-based cathode are considered effective ways to improve the electronic conductivity and prevent sulfur dissolution [9–11]. But for sulfur with large volume change (up to 100%) during extended charging/discharging cycles, it is challenging to coat a stable protection layer since a large volume change will rupture the coating [12,13]. Significant progress has been achieved to address these issues by combining surface coating with internal void space [14–16]. Such as sulfur/graphitic carbon nanocage [17], pomegranate-like sulfur/carbon structure [18], polyaniline/sulfur yolk-shell structure [19]. Although these reported structures substantially improve the cycling life of sulfur-based cathode, they require expensive and multistep synthesis. Otherwise, the sulfur content and the final distribution of sulfur remain challenging [20,21].

In recent years, syntheses of sulfur/carbon [22], sulfur/graphene [23] composites with low-temperature (155 °C) sulfur injection method

have attracted growing attention and have been widely used due to the facile preparation procedures. It allowed the sulfur to melt and infuse into carbon or graphene. But the poor mobility led to a large proportion of the sulfur aggregated on the surface of the composites. Another promising solution is to attempt a two-step process to load sulfur [9]. A prolonged heating process at 155 °C was adopted, followed by the high-temperature (300 °C) step. Notably, the high-temperature (300 °C) step during sulfur loading is essential to the sulfur infusion into the internal region and the distribution of sulfur. This, however, comes at the expense of decreased sulfur content. In addition, Xiao group [24] have reported the use of toxic CS₂ as solvent to fabricate PANI/S composite, which was not beneficial for practical application in lithium sulfur batteries.

To address these concerns, here we designed a simple and environmental friendly approach to synthesize the nonfilling polyaniline coating of sulfur/acetylene black composite, for which sulfur nanoparticles were uniformly anchored in the pores of acetylene nanoparticles, and then the confining polyaniline layer coated only the outer surface of the interconnected acetylene nanoparticles. Such a design offered multiple attractive features for sulfur cathode: (1) A commercially available sulfur source and a simple synthesis procedure make the process highly cost-effective and scalable. (2) Sulfur nanoparticles were uniformly distributed in the pores of acetylene black, allowing for good electronic conductivity; (3) Polyaniline was coated the exterior surface of the acetylene black, benefiting electrolyte diffusion into the interior

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Table 1
Decrease the charge transfer resistance and mitigate the shuttling problem.

Modification	Capacity (mAhg ⁻¹)	Advantages	Issues
Surface coating [9]	1470 at C/20	Low cost, Good cycle life	Low coulombic efficiency
Adding interlayer [10]	1100 at 3C	Low charge transfer resistance, No shuttling problem	High cost of production
Li ₂ S cathode [11]	1144 at C/50	Non-lithium anode, high safety	Electrical insulation
Poros adsorption [12,14–16]	> 1000 at C/10	High sulfur content, High power capability	Low coulombic efficiency
Chemical adsorption [21]	> 1200 at C/10	Strong binding, High surface diffusion	Low sulfur content

space, allowing Li⁺ to pass through, and restricting solubility of intermediate lithium polysulfides. (4)The nonfilling coating retained enough internal void space to accommodate the volume expansion of sulfur nanoparticles and kept the polyaniline shell intact during the electrochemical cycling. As a result, the as-synthesized nonfilling polyaniline coating of sulfur/acetylene black composite exhibited improved cycling stability and rate capability.

2. Experimental

2.1. Material synthesis

320 mg of sulfur was vigorously dissolved in 160 mL of ethanol at 70 °C, then poured into 40 mL deionized water to form sulfur sol. Continue adding 137 mg acetylene black to the prepared sol under ultrasound dispersion for 0.5 h, let it aging for one night and dry overnight at 50 °C. Then, 400 mg of the above powder, 26 mL de-ionized water and 4 mL acetone were blended through ultrasonic for 3 min, following by adding 0.1 g aniline and 15 mL (2 mol/L) HCl for 15 min to form solution A. Another solution was prepared by dissolving 0.245 g (NH₄)₂S₂O₈ in 30 mL deionized water. Under Ar atmosphere, the later solution was added dropwise into the solution A at 0 °C for 6 h via magnetic stirring. The precipitate was collected by centrifugation, washed with acetone and dried at 60 °C overnight.

2.2. Materials characterization

The crystalline phases of the obtained products were identified by powder X-ray diffraction (Rigaku Ultima IV XRD with Cu K α radiation, $\lambda = 1.54178 \text{ \AA}$). The morphologies and structures of the samples were characterized with scanning electron microscopy (SEM; JSM-6610LV, 30KV) and transmission electron microscopy (TEM, JEM-2100F, Japan). The specific surface area was calculated using the Brunauer-Emmett-Teller (BET) method based on adsorption data in the partial pressure (P/P_0) range 0.10–0.20, and total pore volume was determined from the amount of nitrogen adsorbed at $P/P_0 = 0.99$. The pore size distribution was calculated by the original density functional theory (DFT) included in the software of ASAP 2020 system. Thermogravimetric analysis (TGA) was conducted on a TGA Q50 V20.8 Build 34 instrument from 20 °C to 800 °C at a temperature ramp of 5 °C/min in air.

2.3. Electrochemical measurements

To explore the electrochemical performance of the composite, coin-type half cells (CR2016) were carried out, and the working electrode was made of active materials, conductive agent (acetylene black), and polymer binder [poly (vinylidene fluoride), PVDF, Aldrich] in a weight ratio of around 7:2:1. Cells were assembled in an Ar-filled glove box,

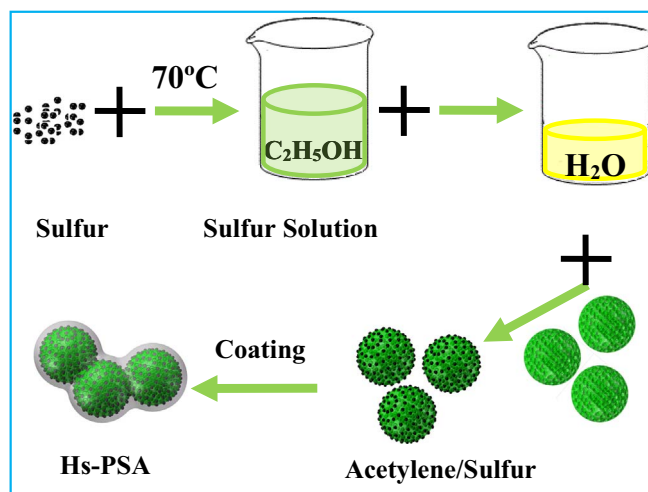


Fig. 1. Schematic illustration of the synthesis procedure of the nonfilling polyaniline coating of sulfur/acetylene black composite.

using the pure lithium metal foil as the counter electrode, and 1.0 mol/L Lithium bis(trifluoromethylsulfonyl)imide (LiTFSI) in 1, 3-dioxolane/Dimethoxyethane (1:1 in volume ratio) as the electrolyte. The galvanostatic charge/discharge tests were carried out in the potential range from 1.5 to 3 V (vs. Li⁺/Li) at various rates using the NEWARE battery testing system under room temperature. Cyclic voltammetry (CV) measurements and AC impedance measurements were conducted on a CHI600D electrochemical workstation.

3. Results and discussion

Fig. 1 illustrated that the synthesis of the nonfilling polyaniline coating of sulfur/acetylene black composite consists of four main steps: typically, sulfur solution was formed in ethanol at 70 °C, then the solution was transferred in de-ionized water at room temperature to form the impalpable particle size of sulfur sol in consider of its different solubility in this two solvents. Meanwhile, the added acetylene black was homogeneously dispersed through ultrasonic, so that sulfur sol could immerse into the pores of acetylene black through physical absorption. Subsequently, polymerization and coating happened on the outer surface of sulfur/acetylene black powder by adding the aniline monomer at 0 °C to achieve the nonfilling polyaniline coating of sulfur/acetylene black precipitate.

Sulfur was infiltrated into the acetylene black through a solution-based precipitation method. **Fig. 2(a-c)** exhibited the SEM images of acetylene black, sulfur/acetylene black and the nonfilling polyaniline coating of sulfur/acetylene black composite. There was no conspicuous difference among the three samples, which suggested that sulfur was successfully dispersed in the internal of the nonfilling polyaniline coating of sulfur/acetylene black composite. The thickness of polyaniline shell was almost unable to observe compared with the diameter of acetylene. To visually probe the presence and distribution of sulfur, the elemental mapping analysis was performed. In the selected region (**Fig. 2d**), no noticeable change in the strength of the sulfur signal was observed, as displayed in **Fig. 2e**, which confirmed the homogenous dispersion of sulfur. The uniform distribution of sulfur was helpful for electronic conductivity [25,26].

Fig. 3 (a, b) demonstrated the TEM images of typical acetylene black before and after sulfur absorption. The pure acetylene black consisted of a homogeneous distribution of spherical nanoparticles, had smooth surfaces and diameters in 40 nm. Large quantities of disordered nanopores confined and interconnected in the core region of acetylene black. The sulfur/acetylene black nanoparticles were completed through elemental sulfur immersion into acetylene black. The sulfur/acetylene

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