



Short communication

Polar cross-linked polystyrene as polysulfides anchor enhanced cycle performance and coulombic efficiency for lithium sulfur batteries

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ABSTRACT

Lithium-sulfur (Li-S) batteries have the theoretical energy density up to 2600 Wh/kg, but its commercialization is limited by poor cyclic performance, low coulombic efficiency and high material cost. In this work, the polar cross-linked polystyrene/sulfur (PCP/S) composite with a sulfur content of 58 wt% is firstly synthesized as the cathodes for Li-S batteries, in which these polar cross-linked polystyrene agents effectively adsorb polysulfides with a large specific surface area and various functional groups, resulting in an enhancement of the cycle performance and coulombic efficiency for Li-S batteries. The first specific discharge capacity of the PCP/S cathode is 1309.7 mAh g⁻¹ at 0.2 C, which can remain as high as 659.7 mAh g⁻¹ after 400 cycles with a low capacity decay of 0.124% per cycle.

1. Introduction

With the development of science and technology, batteries have played an increasingly important role in our daily life. As one of the most promising energy storage devices, lithium-sulfur (Li-S) batteries have attracted enormous attention due to their high theoretical capacity up to 1672 mAh g⁻¹ and specific energy density up to 2600 Wh kg⁻¹, 3–5 times larger than that of traditional Li-ion batteries [1, 2]. However, their practical applications are limited by several drawbacks [3], the major of which is the diffusion of polysulfides during the electrochemical reduction process. This problem induces the polysulfides shuttle reaction and resultant reduction of battery capacity [4, 5]. Therefore, a great quantity of efforts have been devoted to overcome this challenge. One practical way is to physically restrain polysulfides dissolution by sulfur host materials, including mesoporous carbons [6], microporous carbon [7, 8], CMK-3 [9], carbon nanotubes [10], graphene [11, 12] and conductive polymers [13]. These materials can effectively suppress the diffusion of polysulfides into the electrolyte by trapping them in the nanostructured pores. Besides of suppressing the polysulfides shuttle, these carbonaceous materials can also provide additional pathways for electrolyte and Li⁺ diffusion, so that better cycling performance have been obtained. However, due to the repulsion between the polar reactants and the nonpolar conductive surface [14], the nonpolar carbonaceous hosts cannot strongly adsorb the polar polysulfides, leading to the loss of active materials and unspecific deposition of discharged products. The alternative way is to chemically

restrain polysulfides dissolution using sulfur host materials that can chemically interact with polysulfides, such as functionally modified surfaces [15], polymers [16] and carbides [17]. Among them, polar-polar strategy is widely used to provide strong chemical bindings between functionally modified materials and polysulfides, which allow higher sulfur loading and improves the probability of trapping polysulfides. For instance, Chen et al. [18] anchored inherently polar polymer Triton X-100 on the surface of carbon materials to suppress the polysulfides shuttle effect and improved the overall performance of Li-S batteries. Their results showed a high discharge capacity of 1432 mAh g⁻¹ in the first cycle, a capacity retention of 76% after 50 cycles at a rate of 0.2 C with an excellent coulombic efficiency of 95%. The key factor to improve the cycling performance with the high capacity of Li-S batteries relies on the interactions between polysulfides and sulfur host materials. For this propose, cross-linked polystyrene agents formed by synthetic organic polymers with three-dimensional porous structure and various functional groups [19] have attracted great attention in recent years. Such agents are widely used in the fields of chemistry [20], catalyst [21], adsorbent [22] and environmental protection [23] because of their special physicochemical properties and strong physical and chemical adsorption characteristics. In this work, the polar cross-linked polystyrene/sulfur (PCP/S) composite with a sulfur content of 58 wt% is firstly synthesized as the cathodes for Li-S batteries. The first specific discharge capacity of the PCP/S cathode is 1309.7 mAh g⁻¹ at 0.2 C, which can remain as high as 659.7 mAh g⁻¹ after 400 cycles with a low capacity decay of 0.124% per cycle.

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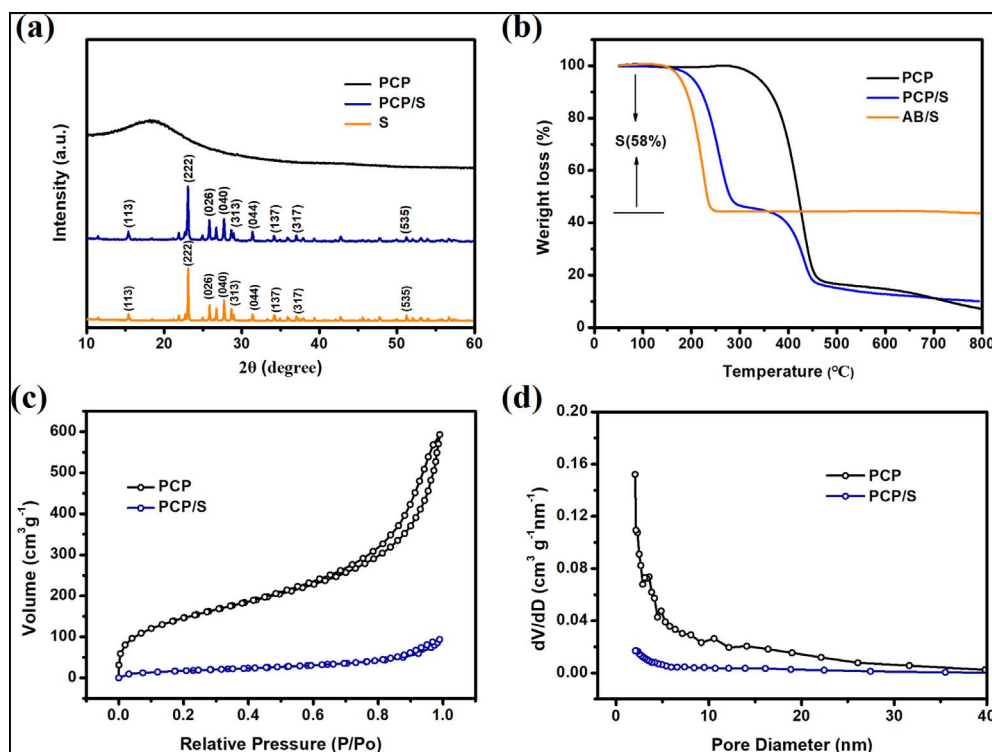


Fig. 1. (a) XRD patterns of PCP, PCP/S composite and pure S; (b) TGA profiles of PCP, PCP/S composite and AB/S composite; (c) Nitrogen adsorption-desorption isotherms at 77 K of PCP and PCP/S composite; (d) BJH pore size distribution of PCP and PCP/S composite.

2. Experimental

2.1. Sample preparation

The styrene (St), divinylbenzene (DVB), polyvinyl pyrrolidone (PVP) and 2,2'-azobisisobutyronitrile (AIBN) with analytical grade were purchased from Tianjin Haoju Resin Technology Co., Ltd. (Tianjin, China) and acetylene black (AB, 99.9%) was purchased from Hefei Kejing material technology Co., Ltd. (Hefei, China). First of all, 20 g St, 1.4 g PVP, 0.2 g AIBN, 100 mL ethanol (95 wt%) and 20 mL deionized water were added to a 250 mL, three-necked flask equipped with a gas supply. After a homogeneous solution formed at room temperature, nitrogen was injected into the reaction system at room temperature for 30 min. The flask was then suspended in a 70 °C water bath and stirred at 120 rpm for 2 h or 2 h, followed by 2.3 g DVB dissolved in 5 mL ethanol, slowly adding to the reaction system for 3 h. The latexes were filtered and washed by ethanol, and the remaining precipitates were rinsed by centrifugations for five iterations before they were dried under vacuum at 60 °C for 12 h to get PCP powders. The PCP powders were grinded and screened through a 200-mesh sieve before they were mixed with sulfur (Aladding, 99.95%) by grinding with mortar and pestle, the weight ratio of sulfur was controlled at 60 wt%. Finally, the mixed powders were heated under vacuum (1–100 Pa) at 125 °C for 3 h to get the polar cross-linked polystyrene/sulfur (PCP/S) composite. As a reference, acetylene black/sulfur (AB/S) composite with the same ratio of sulfur was also synthesized in the same way.

2.2. Li_2S_6 solution preparation

The solution of Li_2S_6 was synthesized according to the literature [24]. In short, sulfur and lithium sulfide (Li_2S , Sigma Aldrich, 99.9%) with a molar ratio of 5:1 were added into a mixed solvent of 1,3-dioxalane (DOL, Sigma Aldrich, 99.8%) and 1,2-dimethoxyethane (DME, Sigma Aldrich, 99.5%) at a volume ratio of 1:1, and the solution was then stirred for 12 h in an argon-filled glove box to form Li_2S_6 (0.1 M) solution.

2.3. Characterizations

The characterizations of the samples were conducted by X-ray diffraction (XRD, Rigaku D/max-2400), Raman spectra (Horiba JY LabRAM HR Evolution) with an excitation wavelength of 532 nm, scanning electron microscopy (SEM, FEI Helios Nanolab 600i) coupled with energy dispersive X-ray spectroscopy (EDS) and X-ray photoelectron spectroscopy (XPS, Escalab 250 Xi). The sulfur contents were determined by thermogravimetric analysis (TGA, Q50) in the temperature range of 25–800 °C and N_2 atmosphere at a heating rate of 10 °C/min, and the specific surface area and pore size distribution were measured by nitrogen adsorption-desorption at 77 K (BET, JW-BK122W).

2.4. Electrochemical test

The cathode electrodes comprised of 70 wt% PCP/S composites, 20 wt% AB and 10 wt% polyvinylidene fluoride binders were homogeneously mixed in an *N*-methyl-2-pyrrolidone (NMP) solvent under continuous magnetic stirring for 12 h, then the slurry was coated uniformly onto an aluminum foil by Dr. Blade and the gap was 150 μm . The electrodes were dried under vacuum at 60 °C for 12 h. The mass loading of the active sulfur in the electrode ($\Phi 12$ mm) was 1.3–1.6 mg cm^{-2} . 2016-type coin cells were assembled in an argon-filled glove box, in which the water and oxygen contents were < 0.1 ppm. Li metal (99.9%, Hefei Kejing material technology Co., Ltd.) with a thickness of 0.25 mm and a diameter of 14 mm was used as the counter electrode. Polypropylene membrane (Celgard 2400) was used as the separator. The cell was then injected with an electrolyte solution (50 μL) consisting of 1 M Li bis (trifluoromethanesulfonyl) imide (LiTFSI, Sigma Aldrich, 99.95%) in a mixed solvent of 1,3-dioxalane (DOL) and 1,2-dimethoxyethane (DME) at a volume ratio of 1:1. The charging/discharging curves of the coin cells were measured between 1.0 and 3.0 V on a BTS-5V20mA battery test system (Neware, Shenzhen, China) at room temperature. The electrochemical performance was measured on a CHI660D electrochemical workstation (Chenhua, Shanghai, China). Cyclic voltammetry (CV) tests were conducted within the voltage window of 1.0–3.0 V at a scan rate of 0.2 mV/s. The electrochemical

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