

Enhanced cycle performance of hollow polyaniline sphere/sulfur composite in comparison with pure sulfur for lithium–sulfur batteries



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ARTICLE INFO

Article history:

Received 27 April 2015
Received in revised form
16 July 2015
Accepted 2 August 2015
Available online xxx

Keywords:

Lithium sulfur battery
Cycle performance
Cathode
PANI/S composite

ABSTRACT

Sulfur deposited on a hollow polyaniline sphere was prepared through in situ synthesis and used to investigate the electrochemical properties of lithium/sulfur cells. The fabricated hPANIs@S composite presented an excellent reversible capacity of 601.9 mAh g⁻¹ after 100 cycles at 170 mA g⁻¹. The capacity increased with the cycle increase, especially at high charge/discharge current. For example, the capacity had only approximate 270 mAh g⁻¹ after initial 121th cycle at 510 mA g⁻¹, and the capacity steadily increased to 380 mAh g⁻¹ after 180th cycle at similar current. These results indicated that cycle property improved compared with that of pure sulfur prepared through in situ synthesis under similar conditions. The enhanced cycle property of the hPANIs@S composite could be due to the homogeneous distribution of fine sulfur particles on the PANI surface, which stabilized the nanostructure of sulfur and enhanced its conductivity during charge/discharge cycles.

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1. Introduction

The demand for clean and efficient energy storage devices has urgently increased with heightened concerns on limited global energy supply and environmental changes [1]. Lithium–sulfur batteries are a promising rechargeable battery system that can boost the capacity fivefold higher than commercially available lithium-ion batteries because of the high theoretical capacity of sulfur (1673 mAh g⁻¹, energy density of ~2600 Wh/kg) [2]. Lithium–sulfur batteries also satisfy the requirements for large-scale production because of their simple preparation technology, natural abundance of source materials, and low cost [3]. However, applications of lithium–sulfur batteries face several serious challenges, such as low electrochemical utilization of sulfur, poor cycling stability, and poor rate capability [4,5]. These limitations are primarily caused by the solubility of polysulfide anions (S_n²⁻) produced through reduction of cyclooctasulfur (S₈) or oxidation of Li₂S during charge/discharge process. The resolved S_n²⁻ results in active mass loss, capacity fading [6], and lithium corrosion, thereby leading to self-discharge. Another factor could be the inherent poor

electrical conductivity of sulfur (5 × 10⁻³⁰ S cm⁻¹ at room temperature) [7] and agglomeration of insulating Li₂S₂/Li₂S; these factors reduce utilization of the active material and results in serious capacity fading in the battery.

Numerous studies have focused on enhancing the performance of lithium–sulfur batteries. Different structures of carbon, such as conductive porous carbons [8,9], carbon nanotubes [10], graphene, and nitrogen-doped graphene [11,12], function as matrices to improve the electrical conductivity of the sulfur cathode. Coating or blending conductive materials, such as polymers, metals, and metal oxide, is also an effective method to improve the electrochemical performance of lithium–sulfur batteries. The combination of conductive polymers, such as polyaniline (PANI) [13,14] and polypyrrole [15,16], and carbon materials forms highly conductive polymer/sulfur composites, which present excellent electrochemical property. The improved electrochemical performance could be attributed to the core/shell structure of the PANI@S/C composite [17]. PANI presents a flexible nanostructure and contains an internal void space inside the polymer shell, which can accommodate the volume expansion of sulfur during lithiation [18]. Nevertheless, the detailed electrochemical performance of the PANI/S composite has been rarely reported.

In this study, we designed and prepared a hollow PANI sphere@sulfur (hPANIs@S) composite, in which sulfur was well-distributed on the surface of the PANI sphere. The low

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conductivity and volume change of sulfur during the charge/discharge cycles was improved by regulating the particle size and distribution of sulfur on the hPANI surface. Therefore, the electrochemical performance of the hPANI@S composite was enhanced and the related mechanism was elucidated for future design of sulfur-based cathode materials.

2. Experimental

2.1. Materials and methods for hPANI@S composite

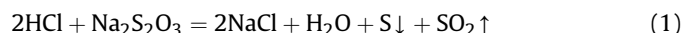
2.1.1. Materials

The initial materials included aniline (AR), tetraethyl orthosilicate (98%), ammonium hydroxide ($\text{NH}_3 \cdot \text{H}_2\text{O}$, 28%), pure ethanol (AR), CTAB (AR), $\text{Na}_2\text{S}_2\text{O}_8$ (AR), HCl (38 wt%), $\text{Na}_2\text{S}_2\text{O}_8$ (AR), HF (24 wt%), deionized water, which mostly came from the reagent company of China. The materials were used in the experiment process without any pretreatment.

2.1.2. Preparation process of hPANI@S composite

hPANI@S composite was prepared via a three-step process to synthesize lithium–sulfur batteries. First, aniline (An) monomer decorated the silicon sphere (SS) through Stöber synthesis [19] in situ polymerization. A solution containing 10 ml of ammonium hydroxide ($\text{NH}_3 \cdot \text{H}_2\text{O}$, 28%), 15 ml of pure ethanol, and 25 ml of deionized water were stirred for 30 min. About 5 ml of tetraethyl orthosilicate (98%) and 45 ml of pure ethanol were added to the solution, and the mixed solution was stirred for 3 h. The SS was acquired after the remaining solution was centrifuged and washed three times with deionized water. The obtained SS, 0.025 mol CTAB, and 0.5 ml of An were added to 200 ml of diluted hydrochloric acid (HCl, mass fraction of 3.5%) and sonicated for 1 h. About 1 g of $\text{Na}_2\text{S}_2\text{O}_8$ (AR) was added dropwise to the mixture and stored at 0°C with constant magnetic stirring for 3 h. The mixture was then filtered and dried to obtain SS/PANI composite.

Second, sulfur was deposited on the SS/PANI surface through the between $\text{Na}_2\text{S}_2\text{O}_3$ and acidic suspension, as shown in the following equation:



The SS/PANI, 0.01 mol CTAB and 0.03 mol $\text{Na}_2\text{S}_2\text{O}_3$ were added to 250 ml of deionized water through ultrasonic agitation and magnetic stirring for 30 min each. About 100 ml of diluted HCl (mass fraction of 2%) was added dropwise to the solution. The reaction was allowed for 3 h with magnetic stirring to deposit sulfur on the SS/PANI surface.

Lastly, hPANI@S was obtained after the SS@PANI/S composite was etched in hydrofluoric acid (HF) solution. The SS@PANI/S composite was added to the HF solution and stored for 24 h. The hPANI@S composite was acquired after filtration, cleaning, and drying. The detailed synthesis of the hPANI@S composite is described in Fig. 1.

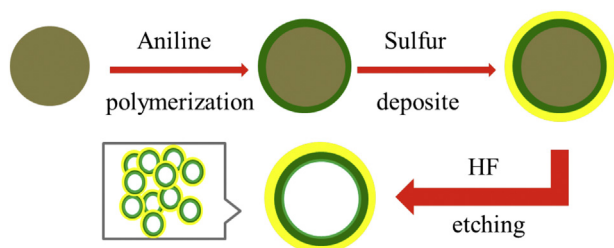


Fig. 1. Synthesis of the hPANI@S composite.

Separate sulfur particles and PANI were also prepared for comparison using similar processes.

2.2. Structural characterization

Powder X-ray diffraction (XRD) patterns of the as-prepared samples were obtained using an X-ray diffractometer (RIGAKU, Japan, model, D/MAX2550 V/PC). Surface morphology was characterized through scanning electron microscopy (SEM, JSM-5610LV) and transmission electron microscopy (TEM, JEOL JEM-2100). EDS analysis was also performed. Thermogravimetric analysis (TGA, METTLER Toledo SMP/PF7548) was conducted to determine the sulfur content in the composite under argon atmosphere, with a temperature increase rate of $10^\circ\text{C}/\text{min}$.

2.3. Electrochemical measurements

Electrochemical characterization was performed using a CR2025-type coin cell. The cathode was prepared by mixing the hPANI@S composite (80 wt%), acetylene black (10 wt%), and polyvinylidene fluoride binder (10 wt%) in N-methylpyrrolidinone solvent. The slurry was uniformly scribed onto the aluminum foil and dried at 60°C under vacuum for 10 h. The button cell, which included a lithium metal anode, a Celgard 2400 separator, and a cathode, was assembled in an argon-filled glove box. Subsequently, 1 M bis(trifluoromethane) sulfonamide lithium salt (Sigma Aldrich) and 0.1 M LiNO_3 in a mixture of 1, 3-dioxolane and 1, 2-dimethoxyethane (volume ratio of 1:1) were used as electrolyte.

The galvanostatic charge/discharge tests of sulfur were conducted within the potential range of 1.5–3.0 V by using a LAND CT2001A battery-testing system. The cells were first discharged to 1.5 V, and then the cycle number was counted. The charge/discharge current density was set to 170, 340, and 510 mA g^{-1} . All electrochemical tests were conducted at room temperature and carried out at least four coin cells. The results should promise to be repeated in the experiments.

Cyclic voltammetry (CV) test and electrochemical impedance spectroscopy (EIS) measurement were performed in the CHI660E electrochemical measurement system. CV tests were conducted between 1.3 and 3.2 V versus Li^+/Li at a scanning rate of 0.2 mV s^{-1} . EIS was determined within the frequency range from 100 kHz to 0.01 Hz with an AC voltage amplitude of 5 mV at open-circuit voltage.

3. Results and discussion

3.1. TGA

Fig. 2 shows the changes in the weight curves of sulfur, PANI,

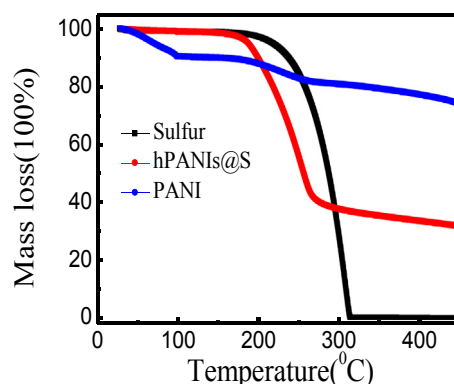


Fig. 2. TGA curves of S, PANI and hPANI@S composite.

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