Dual-shell hollow polyaniline/sulfur-core/polyaniline composites improving the capacity and cycle performance of lithium –sulfur batteries

Yanling An^a, Pan Wei^a, Meiqiang Fan^{a*}, Da Chen^a, Haichao Chen^a, QiangJian Ju^a,
Guanglei Tian^a, Kangying Shu^a

^aDepartment of Materials Science and Engineering, China Jiliang University,
Hangzhou 310018, PR China,

E-mail: fanmeiqiang@126.com, kangyingshu@163.com

Abstract

In this study, a dual-shell hollow polyaniline/sulfur-core/polyaniline (hPANI/S/PANI) composite was prepared by successively depositing PANI, S, and PANI on the surface of a template silicon sphere. The electrochemical properties of this composite were evaluated using a lithium plate as an anode in lithium/sulfur cells. The hPANI/S/PANI composite showed a discharge capacity of 572.2 mAh g⁻¹ after 214 cycles at 0.1 C, and the Coulombic efficiency was above 87% in the whole charge/discharge cycle. The improved cycle property of the hPANI/S/PANI composite can be ascribed to the fine sulfur particles homogeneously deposited on the PANI surface and sprawled inside the two PANI layers during the charge/discharge cycle. This behavior stabilized the nanostructure of sulfur and enhanced its conductivity.

Keywords: lithium–sulfur battery; cycle performance; cathode; dual-shell hollow polyaniline/sulfur-core/polyaniline ANI/S/PANI composite

1. Introduction

Lithium–sulfur batteries are promising low-cost rechargeable battery systems requiring simple preparation because of the high theoretical capacity (1672 mAh g^{-1}) of sulfur [1–3]. However, some problems should be addressed before the commercial application of sulfur cathode; these limitations include the insulating nature and large volume expansion of sulfur, as well as the dissoluble polysulfide species formed during discharge [4, 5]. Such difficulties may lead to active material loss and side reactions on the lithium metal anode, which can directly result in faded capacity, decreased Coulombic efficiency, and low C rate. These setbacks have been a subject of great concern over the past 10 years.

Various sulfur-based nanocomposites, particularly sulfur composites, carbon materials, and conductive polymers, which can effectively anchor sulfur inside and prevent polysulfide dissolution, have been designed to address the abovementioned problems [6, 7]. Many studies have shown that the combination of sulfur, conductive polymers, and carbon materials can achieve excellent electrochemical properties, which are attributed to the core-shell structures of the composites [8–10]. Polymers and carbon materials act as electrical and ion-conducting agents with stable network-like structures for sulfur cathode. Wu F performed rapid in situ chemical oxidation polymerization of polyamine to coat carbon-core/sulfur-shell structures. The composite of 70% sulfur, 20.2 PANI, and 9.8% carbon yielded 932.4 mAh g^{-1} after 80 cycles [11]. However, the commercialization of high-performance carbon materials was limited by their high-cost complex manufacturing process.

Recent works reported that sulfur cathode coated or modified with electropolymerized conductive polyaniline (PANI) and polypyrrole (PPY) improved the electrochemical performance of Li-S batteries [12, 13]. Qiu L.L. prepared a nano/sulfur/poly(pyrrole-co-aniline) (S/PPyA) composite material by co-heating a mixture of PPyA and sulfur at 160 °C for 24 h [14]. The S/PPyA composite yielded 866 mAh g⁻¹ after 40 cycles. Moreover, this polymer exhibits a flexible nanostructure and contains an internal void space inside the polymer shell, which can accommodate the volume expansion of sulfur and prevent polysulfide dissolution during lithiation [15]. The electronically conductive polymer matrix may also act as a distribution agent or absorbing agent to enhance the electrochemical performance of sulfur cathode, replacing expensive carbon materials. However, co-heating method requires long periods of time for uniform mixing of sulfur and polymer, and excessive heat may damage the polymer structure.

In the present study, we designed and prepared an hPANI/S/PANI composite by successively depositing PANI, sulfur particles, and PANI on the surface of a template silica sphere via chemical reaction. PANI was selected because side reactions rarely occur in this material, and film-like polymer was strongly deposited on the particle surface via chemical oxidative polymerization [16, 17]. Double PANI layers were expected to provide many paths for lithium-ion permeation but may suppress the polysulfide into the organic solution. The flexible nanostructure of PANI improved the low conductivity and volume change of sulfur during lithiation. Thus, the electrochemical performance of the hPANI/S/PANI composite was enhanced, and the

potential mechanism was elaborated for the future design of sulfur-based cathode materials.

2. Experimental

2.1 Materials

The main materials used in the experiment, including aniline (An, analytical reagent), cetyltrimethylammonium bromide (CTAB, analytical reagent), Na₂S₂O₈ (analytical reagent), and HCl (38 wt%), were purchased from Aladdin Reagent Company. These materials were used without any pretreatment. The template silicon sphere (SS) was prepared through Stöber synthesis [18].

2.2 Preparation of hPANI/S/PANI composite

The hPANI/S/PANI composite was prepared through a four-step process. First, 0.1 g of SS with approximately 100 nm to 200 nm diameter, 0.091 g of CTAB, and 0.1 ml of An were added to 200 ml of diluted HCl with a mass fraction of 3.5% and then stirred for 1 h. Up to 1 g of Na₂S₂O₈ was added dropwise to the mixture and stored at 0 °C with constant magnetic stirring for 3 h. The mixture was subsequently filtered and dried to obtain the SS/PANI composite. Second, the SS/PANI composite, 0.091 g of CTAB, and 4.74 g of Na₂S₂O₃ were added to 250 ml of deionized water, and the mixture was stirred for 5 h. Approximately 100 ml of diluted HCl (mass fraction of 2%) was added dropwise to the mixture while stirring continuously at room temperature. Sulfur was successively deposited on the SS/PANI surface through the reaction of Na₂S₂O₃ and HCl in the following equation:

The mixture was filtered and dried to obtain the SS/PANI/S composite. Third, PANI was deposited again on the surface of the SS/PANI/S composite, and the conditions were similar to those in the first step, except that the SS/PANI/S composite replaced 0.1 g of silica. Afterward, the reaction product was filtered and dried to obtain the SS/PANI/S/PANI composite. Finally, the hPANI/S/PANI composite was obtained after the SS/PANI/S/PANI composite was etched in a hydrofluoric acid (HF) solution, filtered, and dried. The detailed synthesis of the hPANI/S/PANI composite is described in Fig. 1. Sulfur and PANI were individually synthesized under similar conditions for comparison.

2.3 Microstructure characterization

Powder X-ray diffraction (XRD) patterns of the hPANI/S/PANI composite were collected on an X-ray diffractometer (RIGAKU, Japan, model, D/MAX2550V/PC). Surface morphology evolution was characterized via scanning electron microscopy (SEM, JSM-5610LV), along with EDS analysis and transmission electron microscopy (TEM, JEOL JEM-2100). The sulfur content in the hPANI/S/PANI composite was measured by thermogravimetric analysis (TGA, METTLER Toledo SMP/PF7548) under argon atmosphere, with a temperature increase rate of 10 °C/min.

2.4 Electrochemical measurements

CR2025-type coin cells were assembled in an Ar-filled glove box and used for electrochemical characterization. Details of electrode preparation technology and assembly were introduced in our previous work [19]. The hPANI/S/PANI composite (80 wt%), acetylene black (10 wt%), and polyvinylidene fluoride binder (10 wt%)

were mixed in a N-methylpyrrolidinone solvent, and the mixture was stirred for 10 h at 25 °C. The mixture was uniformly printed on the surface of an aluminum foil and vacuum dried at 60 °C for 10 h. The cathode was generated containing approximately 10 mg of sulfur with standard deviation of 1 mg. The coin cell, which contained a lithium metal anode, a Celgard 2400 separator, and a cathode, was assembled in the Ar-filled glove box. Additionally, 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 electrolytes.

The galvanostatic charge/discharge performance tests of the sulfur cathode were performed within the potential range of 1.5 V to 3.0 V by using a LAND CT2001A battery-testing system at room temperature. All cells were discharged to 1.5 V before the test started. Specific capacities and charge/discharge current densities were calculated on the basis of sulfur weight in the cathode. Cyclic voltammetry (CV) and electrochemical impedance spectroscopy (EIS) measurements were performed using the CHI660E electrochemical measurement system. CV tests were conducted under voltages of 1.5 V to 3.0 V versus Li^+/Li at a scanning rate of 0.2 mVs^{-1} . EIS values were determined within a frequency range of 100 kHz to 0.01 Hz, with an AC voltage amplitude of 5 mV at an open-circuit voltage.

3. Results and discussion

3.1 Microstructure analysis

Fig. 2 shows the XRD patterns of PANI, sulfur, and the hPANI/S/PANI composite. A wide peak corresponding to an amorphous phase in the XRD patterns of PANI also

existed. The amorphous phase of PANI was attributed to its low crystallinity [20]. All the peaks identified for sulfur were determined in the XRD patterns of sulfur particles (JCPDS: 08-0247). The thin peak line showed high crystallinity of sulfur particles, which was also observed in the XRD patterns of the hPANI/S/PANI composite. Sulfur peak lines of the hPANI/S/PANI composite were slightly wider than those of the sulfur particles. This finding was confirmed by comparing the grain size, which was calculated using the peak line at 24° (Fig. 2). The grain sizes of sulfur were 88.3 and 59.3 nm for the sulfur particles and the hPANI/S/PANI composite, respectively.

To observe the morphological evolution of the hPANI/S/PANI composite during preparation, detailed morphologies of sulfur, PANI, hPANI/S, and the hPANI/S/PANI composite were collected (Fig. 3). The sulfur particles were flat and irregularly shaped, with sizes ranging from several micrometers to tens of micrometers (Fig. 3a). PANI exhibited nanofibers and formed a hollow flexible network structure. The nanofibers were tens of nanometers wide and hundreds of nanometers long (Fig. 3b). However, after sulfur was deposited on the PANI surface, PANI nanofibers became wider than PANI, and some flat particles of sulfur were observed on the PANI surface (Fig. 3c). The particle sizes of sulfur deposited on the PANI surface ranged within tens of nanometers, which implied that the presence of PANI prevented the agglomeration of sulfur particles. Thin PANI nanofibers and numerous pores were observed on the surface of the hPANI/S/PANI composite (Figs. 3d and 3e), which reflected that PANI was deposited on the surface of hPANI/S. The particle size of the hPANI/S/PANI composite was approximately $1\ \mu\text{m}$, which is significantly smaller

than that of sulfur or PANI. The particle sizes can be further confirmed in Fig. 4, which shows the TEM images of the hPANI/S/PANI composite. Black circles with a diameter of approximately 1 μm were observed, corresponding to the particle size of the hPANI/S/PANI composite. Many particles with diameters in the order of 10 nm, which might be PANI or sulfur, were found in the circle. The distribution of PANI and sulfur is shown in Fig. 5, illustrating the elemental mapping of the hPANI/S/PANI composite. Element N was uniformly distributed around element S, implying that PANI was uniformly deposited on the sulfur surface.

Fig. 6 shows the TG-DSC curves of sulfur, PANI, and the hPANI/S/PANI composite. Sulfur underwent a 100 wt% weight loss in the temperature range of 200 $^{\circ}\text{C}$ to 320 $^{\circ}\text{C}$ (Fig. 6a). The hPANI/S/PANI composite showed a similar weight-loss curve to sulfur below 285 $^{\circ}\text{C}$ but underwent significant weight loss at 170 $^{\circ}\text{C}$, which is approximately 30 $^{\circ}\text{C}$ lower than the weight-loss temperature range of sulfur. The low weight-loss temperature of sulfur is related to the fine sulfur particles formed on the PANI surface. Weight-loss temperatures were correspondingly observed in the DSC curves (Fig. 6b). Sulfur melting was detected at 100 $^{\circ}\text{C}$ to 200 $^{\circ}\text{C}$. The hPANI/S/PANI composite presented a low sulfur-melting temperature at 110 $^{\circ}\text{C}$, which is significantly lower than that of sulfur. The low sulfur-melting temperature stimulated sulfur diffusion because of the heat generated in the charge/discharge cycles. This behavior may influence the electrochemical performance of the hPANI/S/PANI composite. Given the weight-loss curve of PANI in Fig. 6a, the weight-loss values of sulfur, PANI, and the hPANI/S/PANI composite

were 100 wt%, 19.84 wt%, and 78.75 wt% at 320 °C, respectively. The sulfur content in the hPANI/S/PANI composite was determined to be 73.49 wt% by using the following equation:

$$(M_s + M_p) \times 78.75\% = M_s \times 100\% + M_p \times 19.84\% \quad (2)$$

where M_s is the mass fraction of sulfur in the composite material, and M_p is the mass fraction of PANI.

3.2 Electrochemical performance

The electrochemical performances of sulfur and the hPANI/S/PANI composite were measured using a coin cell with a lithium plate as anode. Fig. 7 shows the cycle performances of sulfur and the hPANI/S/PANI composite, in which the capacities were obtained via repeated charge/discharge currents at 0.1 C. The increased charge/discharge capacities were observed for sulfur and the hPANI/S/PANI composite during the first 30 cycles. This behavior was attributed to the activation caused by gradual sulfur distribution on the hollow PANI or carbon black in the cathode, wherein heat was generated and sulfur was melted during the charge/discharge process [21, 22]. The charge/discharge capacities decreased with the increased number of cycles. However, the sulfur particles and hPANI/S/PANI composite remained different. The charge and discharge capacities of sulfur increased from 326.7 and 268.5 mAh g⁻¹ during the first cycle to 526 and 384.1 mAh g⁻¹ during the 30th cycle of the activation process, correspondingly. The charge and discharge capacities then decreased irreversibly and remained at low values. For instance, the charge and discharge capacities of sulfur were 378.8 and 306.7 mAh g⁻¹, respectively,

in the subsequent 70 cycles or up to the 100th cycle. The charge and discharge capacities of the hPANI/S/PANI composite increased from 549.6 and 497.9 mAh g⁻¹ during the first cycle to 716.1 and 638.4 mAh g⁻¹ during the 30th cycle of the activation process, correspondingly. Afterward, the charge and discharge capacities decreased slightly and remained constant at approximately 640 and 572.2 mAh g⁻¹ for the next 184 cycles or up to the 214th cycle. The charge and discharge capacities of the hPANI/S/PANI composite were significantly higher than those of sulfur under similar conditions. Thus, the addition of double PANI layers increased the capacity of the cathode.

The faded capacity of sulfur was attributed to the dissolution of polysulfide anions (Sx²⁻) [5]. On the one hand, sulfur presented a discharge capacity of 306.7 mAh g⁻¹ after 100 cycles, which is approximately 18.2% of its theoretical capacity. On the other hand, the hPANI/S/PANI composite exhibited a discharge capacity of 572.2 mAh g⁻¹ after 214 cycles, which is approximately 69.9% of its theoretical capacity. The introduction of double PANI layers prevented the diffusion of polysulfide species to a certain degree. This finding can be further confirmed by the Coulombic efficiencies of sulfur and the hPANI/S/PANI composite (Fig. 7). Sulfur demonstrated a large-span Coulombic efficiency of 60% to 80% for 100 charge/discharge cycles. The low Coulombic efficiency was attributed to the internal redox shuttle of polysulfide anions [23]. The hPANI/S/PANI composite showed a stable Coulombic efficiency with a value maintained at 87% to 89% for 214 charge/discharge cycles. The improved Coulombic efficiency was ascribed to the

double PANI layers, which acted as physical barriers to prevent polysulfide diffusion. The PANI nanowires used to coat the sulfur surface also avoided active material agglomeration during the charge/discharge cycles.

Fig. 8 shows the capacity rate of the hPANI/S/PANI composite. The charge and discharge capacities of the hPANI/S/PANI composite increased, and the values remained stable at above 710 and 620 mAh g⁻¹ at 0.1 C during the first 21 cycles, respectively, which agreed well with the cycle performance in Fig. 7. The composite yielded stable capacity rates at 0.2 C and 0.5 C for the subsequent cycles. The charge and discharge capacities were stabilized above 610 and 530 mAh g⁻¹ at 0.2 C, correspondingly, for the 20 subsequent cycles. Afterward, the charge and discharge capacities remained stable above 350 and 300 mAh g⁻¹ at 0.5 C for another 20 cycles. Finally, the charge and discharge capacities increased to more than 650 and 570 mAh g⁻¹ at 0.1 C, respectively, in the succeeding cycles. The Coulombic efficiency for hPANI/S/PANI remained above 87% for different rates of 0.1, 0.2, and 0.5 C. Overall, the hPANI/S/PANI composite demonstrated good rate capacities with the introduction of double PANI layers.

The first three cycles of the CV curves are presented in Fig. 9. These CV curves showed lithiation and delithiation peaks for the lithium–sulfur batteries. Significant lithiation peaks of sulfur were observed at 2.05 V in the first cycle, which shifted to 2.13 V in the second and third cycles. The delithiation peaks of Li₂S were found at 2.7 V in the first cycle and shifted to approximately 2.75 V in the second and third cycles. The lithiation and delithiation peaks became stable after the first

charge/discharge cycle. Comparison of the CV curves of sulfur showed that the two typical lithiation peaks of sulfur at 1.8 and 2.3 V were changed to only one lithiation peak of the hPANI/S/PANI composite at 2.05 V. Moreover, S_8 distributed in the two PANI layers; thus, it was easily reduced to lithium sulfide. By contrast, the hPANI/S/PANI composite exhibited a delithiation peak of up to 2.75 V, which was significantly higher than that of sulfur. Hence, the lithiation product of lithium sulfide in the two PANI layers was more easily oxidized than that of sulfur. CV results showed that the transition between S_8 and lithium sulfide (Li_2S_2 or Li_2S) on the hPANI/S/PANI composite easily occurred compared with that of sulfur.

EIS measurements were conducted to demonstrate the cycle performance improvement of the hPANI/S/PANI composite. Fig. 10 shows the typical Nyquist plots of the hPANI/S/PANI composite at different charge/discharge cycles. The Nyquist plots exhibited a large semicircle at high frequency and an inclination in the low-frequency regions before the first charge/discharge cycle. The semicircle in the hPANI/S/PANI composite was divided into two small circles, followed by an inclination after the charge/discharge cycles. As indicated by the EIS results at the 0th, 20th, 50th, 100th and 214th cycles, the size of the semicircle decreased significantly when the cycle number increased to 100 but increased slightly when the cycle number further increased to 214. In accordance with the resistance analysis in a previous work [24], equivalent circuits in Figs. 10b and 10c were used to calculate the resistance of the lithium–sulfur battery before and after the charge/discharge cycles, respectively. R_e is the resistance of electrolyte, R_f is the resistance through the SEI layers, and R_{ct}

is the interface of charge-transfer resistance. R_e , R_f , and R_{ct} at different charge/discharge cycles were obtained from the simulation based on equivalent circuits (Table 1). Although R_e , R_f , and R_{ct} changed with the charge/discharge cycles, various trends were observed. R_e fluctuated slightly with increased charge/discharge cycles, which may be attributed to the polysulfide concentration change in the electrolyte caused by the evolution between sulfur, polysulfide, and lithium sulfide during the charge/discharge cycles. R_f and R_{ct} experienced similar trends; their values decreased with the increased number of cycles from 0 to 100 but slightly increased when the number of cycles further increased from 100 to 214. This improvement was ascribed to the high conductivity during charge transfer from the formed lithium polysulfide intermediaries in the PANI layers [25].

Therefore, the introduction of dual-shell hollow polyaniline/sulfur-core/polyaniline composites significantly improved the electrochemical performance of sulfur (Figs. 7 and 8). Such improvement was first attributed to the self-assembled PANI, S, and PANI, which were successively deposited on the template silica sphere, causing fine sulfur particles to be uniformly distributed inside dual PANI layers (Figs. 3–5). The hollow inner PANI layer exhibited a void sphere and a large void space inside the polymer shell, which acted as a carrier for sulfur deposition and accommodated the volume expansion of sulfur or sulfur diffusion during lithiation. The sulfur diffusion was caused by the heat generated during the charge/discharge process. DSC results showed that the melting temperature of sulfur in the hPANI/S/PANI composite was approximately 10 °C lower than that of pure sulfur

prepared under similar conditions (Fig. 6). The outer PANI layer wrapped hPANI/S, which prevented polysulfide dissolution during lithiation [15] and accommodated the volume expansion of sulfur or sulfur diffusion. In addition, the good conductivity of PANI presented several good electron-conducting paths for the rechargeability of lithium/sulfur battery, as confirmed by EIS results (Fig. 10), and positively affected the transition between S_8 and lithium sulfide (Li_2S_2 or Li_2S) during the charge/discharge cycles. The detailed effects of inner or outer PANI layer will be discussed in the future.

4. Conclusion

A novel hPANI/S/PANI composite was synthesized in situ in this study. Charge and discharge tests indicated that the hPANI/S/PANI composite exhibited a reversible capacity of 572.2 mAh g^{-1} after 214 cycles at 0.1 C and an improved capacity with a Coulombic efficiency higher than 87%. The hPANI/S/PANI composite demonstrated a remarkably higher cycle performance than that of pure sulfur prepared using a similar process. The improved cycle property of the hPANI/S/PANI composite was ascribed to the dual core-shell nanostructure formation of fine sulfur particles homogeneously distributed on the two PANI layers. This behavior was observed as an activation process in the charge and discharge tests. Small particle size, high lithiation/delithiation voltages, and high conductivity were the effects observed from the results of SEM, TEM, CV, and EIS.

Acknowledgments

This work was financially supported by the Scientific Research Foundation for the

Returned Scholars, a postdoctoral support of PR China (2015M581910), a postdoctoral preferential support of Zhejiang province (BSH1502029), the National Science Foundation of China (Project No. 51501175), and the Guangxi Key Laboratory of Information Materials (Guilin University of Electronic Technology, Project No. 1210908-02-K).

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Table and Figure Captions

Table 1 Resistance of electrolyte (R_e), resistance through the SEI layers (R_f), and interface charge-transfer resistance (R_{ct}) of Li/S cells with hPANI/S/PANI composite cathode at different cycles. The results were obtained by modeling EIS data and equivalent circuits in Fig. 10.

Fig. 1 Microstructure evolution of hPANI/S/PANI composite during preparation and charge/discharge cycles

Fig. 2 XRD patterns of PANI, sulfur, and hPANI/S/PANI composite

Fig. 3 Morphology of sulfur, PANI, hPANI/S, and hPANI/S/PANI composite; (a) sulfur; (b) PANI; (c) hPANI/S composite; (d) and (e) hPANI/S/PANI composite

Fig. 4 TEM images of hPANI/S/PANI composite

Fig. 5 Elemental mapping of hPANI/S/PANI composite

Fig. 6 TG-DSC curves of sulfur, PANI, and the hPANI/S/PANI composite

Fig. 7 Cycle performance of (a) sulfur and (b) hPANI/S/PANI composite at 0.1 C

Fig. 8 Rate capacity of hPANI/S/PANI composite from 0.1 to 0.5 C

Fig. 9 CV curves of (a) sulfur and (b) hPANI/S/PANI composite

Fig. 10 EIS data of Li/S cells with hPANI/S/PANI composite cathode. (a) Nyquist plots of hPANI/S/PANI composite at different charge/discharge cycles within a frequency range of 100 kHz to 100 mHz; (b) circuit used to fit experimental data at the 0th cycle; (c) circuit used to fit experimental data at the 20th, 50th, 100th, and 214th cycles.

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426 Table 1

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Cycles	Re	Rf	Rct
0 th	8.7		468.4
20 th	11.5	137.8	129.4
50 th	8.9	79.2	40.4
100 th	20.8	26.3	12.40
214 th	12.9	51.6	19.0

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Fig. 6

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Fig. 9

Fig. 10

(a)

(b)

(c)

Graphical Abstract