The construction of high sulfur content spherical sulfur-carbon nanotube-polyethylene glycol-nickel nitrate hydroxide composites for lithium sulfur battery

Yiyong Zhang a, Kun Li a, He Li a, Yunhui Wang a, Yueying Peng a, Shuangshuang Lin a, Bing Joe Hwang b, Jinbao Zhao a,∗

a State Key Laboratory of Physical Chemistry of Solid Surfaces, State-Provence Joint Engineering Laboratory of Power Source Technology for New Energy Vehicle, Collaborative Innovation Center of Chemistry for Energy Materials, College of Chemistry and Chemical Engineering, Xiamen University, Xiamen 361005, PR China
b NanoElectrochemistry Laboratory, Department of Chemical Engineering, National Taiwan University of Science and Technology, Taipei 106, Taiwan

ARTICLE INFO

Article history:
Received 26 April 2017
Received in revised form 20 July 2017
Accepted 12 September 2017
Available online 14 September 2017

Keywords:
Ball-milling
Lithium sulfur battery
CNT
Polyethylene glycol
Nickel nitrate hydroxide

ABSTRACT

Lithium sulfur batteries have been widely studied because of their high energy density. However, their commercialization has been impeded by several problems, such as the poor conductivity of the active material sulfur and its discharge products, the volume expansion and the shuttle effect caused by the polysulfide intermediates dissolving in organic electrolytes. To address these problems well, we have constructed high sulfur content spherical sulfur-carbon nanotube-polyethylene glycol-nickel nitrate hydroxide (SCNT-PEG-NNH) composite material by using a simple ball-milling method. The conductivity of the composite material gets improvement due to the spherical conductive frame constructed by CNT, while the shuttle effect of polysulfides is well inhibited by the wrapping of the PEG and the fixation of NNH. The results of electrochemical tests have shown that the performance of cathode made by the SCNT-PEG-NNH composite material is greatly improved. Therefore, the SCNT-PEG-NNH composite material can be a promising cathode material for lithium sulfur batteries.

© 2017 Elsevier B.V. All rights reserved.

1. Introduction

Lithium sulfur batteries (LSBs) have been followed with widespread attention and studied earnestly for their high specific capacity. The theoretical mass specific capacity of sulfur is 1675 mAh g⁻¹, and the theoretical energy density of LSB is 2600 Wh kg⁻¹ which is more than six-fold of the LiCoO₂/C battery [1−4]. Therefore, LSBs are the most promising next-generation power supply for electric vehicles or energy storage from renewable energy sources [5]. Unfortunately, the commercialization of LSBs has been impeded by several problems. Primarily, the active material sulfur (S) and its discharge product are insulators with a poor conductivity, for example, the electronic conductivity of S is ~10⁻³⁰ S cm⁻¹, inducing a poor battery kinetic on charge transfer and low S utilization efficiency. Secondly, the discharge intermediates Sₓ²⁻ (x ≥ 3) dissolving in organic electrolytes, together with their ‘shuttle effect’, will lead to low coulombic efficiency, fast capacity decay and poor cycle performance. Besides, the volume change of S cathode can exceed 80% during charge and discharge cycle, which will also decrease the cycle performance of the battery [6].

The long cycle life, high energy density and high sulfur load are the key points for the commercialization of LSBs. To achieve these goals, the above mentioned problems are needed to be solved. Firstly, it is needed to improve the conductivity of S cathode to ensure that the cathode material has a high conductivity which will in turn ensure a high discharge capacity and energy efficiency. Secondly, it is needed to control the deposition and dissolution of discharge product Li₂S, i.e. to prevent the reunion of Li₂S which will make it loss conductivity and become dead active material thus decrease the utilization of active material in the process of discharge. Finally, we need control the dissolution and shuttle of polysulfides to improve the coulombic efficiency and cycle performance of battery, etc. For the above several aspects challenges, scientists have carried out many advanced methods such as designing cathode materials [7], employing new electrolytes [8−12] and perfecting lithium anode [13−15], and have made certain progress. In particular, the strategies for preventing

∗ Corresponding author.
E-mail address: jbzhao@xmu.edu.cn (J. Zhao).

http://dx.doi.org/10.1016/j.jallcom.2017.09.131
0925-8388/© 2017 Elsevier B.V. All rights reserved.
dissolution of polysulfides and trapping polysulfides are well-established for long life LSBs. Many advances have been made in the design of cathode materials, including various porous carbon/S composites [16–18], CNT/S composites [19], graphene/S composites [20,21], various inorganic materials/S composites [22–25] and polymer/S composites [26,27], to form a ‘confined space’ to suppress the dissolution and shuttle of polysulfides and thus to improve the coulomb efficiency and battery performance of LSBs. The CNTs are well known for their unique physicochemical properties, including extremely high tensile strength, high electrical conductivity, high ductility and relative chemical inertness. Therefore, there have been many studies in CNTs/S composites as well. The CNTs were used as effective scaffolds to improve the electrode performance of LSB [28]. By direct thermal treatment of CNTs with S powder, the CNTs/S composites can be prepared with tight adhesion of S on CNTs surfaces [29]. However, the capacity decay is still critical for actual applications of LSBs. The interfacial modifications and porous structure engineering of CNTs as well as rational combination of CNTs with other kinds of nanocarbon have been underway to achieve further improvements of LSBs [30,31]. Yu et al. [32] fabricated highly nitrogen doped CNT-graphene-S composite, which exhibited reversible capacities of 1314 and 922 mAh g\(^{-1}\) at 0.2 C and 1 C, respectively, and a capacity retention of 97% after 200 cycles at a high rate of 2 C. Choi et al. [33] fabricated ordered CNTs/S composites, which showed a capacity retention of 75.8% after 1000 cycles at a high rate of 5 C and reversible capacity of 960 mAh g\(^{-1}\) after 300 cycles at 30 C. Also, Yu et al. [34] reported an applicable way, which used the thin-layered nickel-based hydroxide as a feasible and effective encapsulation material. Such hydroxide thin films could irreversibly react with lithium to generate protective layers that combined good ionic permeability and abundant functional polar/hydrophilic groups, leading to drastic improvements in electrochemical performances. Nazar’s group [16] and Wei’s group [19] reported that the polyethylene glycol (PEG) barrier layer could greatly suppress the shuttle of polysulfides. However, the implementation cost is high and the preparation process of almost all S-based composites is complex. Therefore, it is still necessary to optimize the design of the S-based composites and further promote their practical applications in LSBs.

To obtain homogenous composite, the ball milling technology is an easy handling method and inclines to realize large scale synthesis with many advantages such as reproducible results, economy and simplicity. It has been widely used for large-scale grinding various materials in industrial production [35]. Furthermore, we have previously prepared spherical Si/CNT/C composites by using the ball milling techniques [36]. Accordingly, it is attractive and practicable to realize large-scale synthesis of S/CNT composite by the facile ball-milling techniques.

In this article, we used a simple wet ball-milling method to constructed spherical sulfur-carbon nanotube-polyethylene glycol (SCNT-PEG) composite material, followed by coating with a layer of nickel nitrate hydroxide (NNH) on the SCNT-PEG composite material to obtain the SCNT-PEG-NNH composite material. The inter-twined CNTs can ensure continuous electron transfer and withstand the large volume expansion, while the polar groups of PEG and layered NNH show a good inhibition for the dissolution of polysulfides. As a result, the LSBs using spherical SCNT-PEG-NNH composites as the cathode material have a good coulomb efficiency and cycle performance.

2. Experiment

2.1. Material synthesis

Commercial S powders (≥99.5%) were purchased from Sinopharm Chemical Reagent Corporation. Ni(NO\(_3\))\(_2\)-6H\(_2\)O (≥98.0%) was purchased from Guangdong Guanghua Sci-Tech Co., Ltd. Hexamethylene tetramine (≥99.5%) and PEG were purchased from Aladdin Chemistry Corporation. CNTs was purchased from Chengdu Organic Chemicals Co. Ltd., Chinese Academy of Sciences. All reagents were used without further purification.

Commercial S powders and CNTs were added to zirconia at the ratio of 5:1, then 5 wt% PEG and 10 mL NMP were added as a dispersant, followed by ball-milling at 400 rpm min\(^{-1}\) for 12 h and freeze-drying after ball-milling ended, and the obtained composite material was marked as SCNT-PEG. The 0.6 g SCNT-PEG, 0.5 g hexamethylene tetramine and 0.25 g Ni(NO\(_3\))\(_2\) were added to 50 mL deionized water, then heated in an airtight container for 6 h. After that, the products were filtrated using a suction filter and washed with deionized water, followed by drying at 60 °C in a vacuum oven, and finally the SCNT-PEG-NNH composite material was obtained.

2.2. Characterization

The scanning electron microscopy (SEM) images of as-prepared materials were characterized by using a scanning electron microscope (SEM, HITACHI S-4800). Transmission electron microscopy (TEM) images were tested on JEM-2100 (JEOL, Japan) at 200 kV. The XRD patterns of the composites were recorded by the Philips X’pert Pro Super X-ray diffract meter and Cu K\(\alpha\) radiation.
photoelectron spectroscopy (XPS) was conducted on PHI Quantum 2000 Scanning ESCA Microprobe. Element analyses were performed on a Vario ELIII (Elementar Analysen System GmbH, Germany) elemental analyzer. Thermogravimetric (TG) analysis was performed on a SDTQ600. The dried sample of 5–10 mg was placed in an Al2O3 pan and heated at 10 °C min⁻¹ from 35 °C to 800 °C under a flow of nitrogen atmosphere.

2.3. Electrochemical measurements

The slurry of the composite material, acetylene black and polyvinylidene fluoride (PVDF) at the mass ratio of 7: 2: 1 was covered to an aluminum foil, followed by drying at 60 °C, thus we obtained corresponding cathode. Then a lithium foil was used as the counter electrode, the 1 M lithium bis(trifluoromethanesulfonyl)imide (LiTFSI) dissolved in 1,3-dioxolane (DOL)/1,2-dimethoxyethane

Fig. 2. SEM image: (a) SCNT-PEG and (b) SCNT-PEG-NNH composites, TEM image: (c) and (d) SCNT-PEG-NNH composites.

Fig. 3. XRD patterns of composites.
(DME) with the volume ratio of 1:1 was used as the electrolyte, and the battery was assembled in the glove box filled with argon atmosphere. The battery was then evaluated by the CT2001A cell test instrument (XINWEI Electronic Co.) at different current densities between 1.8 and 2.6 V (vs. Li⁺/Li). In the voltage range between 1.5 V and 3.0 V (vs Li⁺/Li), at the scan rate of 0.1 mV s⁻¹, the cyclic voltammogram (CV) curves were tested on a CHI660e potentiostat. The electrochemical impedance spectroscopy (EIS) was recorded by the autolab PGSTAT 101 cell test instrument in the frequency range of 10 mHz–100 kHz, using two-electrode coin cells with Li metal as the counter electrode. All of the electrochemical tests were performed at room temperature.

3. Results and discussions

This research embarks from the overall structure of composite material as shown in Fig. 1. Firstly, the ball-milling method is used to prepare SCNT-PEG spherical composite material, then NNH is coated on the surface of SCNT-PEG composite material via solution reaction, thus the nearly spherical SCNT-PEG-NNH material which is controlled on the whole structure can be obtained. In this composite material, the CNTs make up of conductive frame, and lots of carboxyls of CNT formed during the ball-milling can react with the hydroxyls of PEG to form ester bond so as to prevent PEG from dissolving into organic electrolyte [37]. The PEG can fix polysulfide and has the certain conductivity for lithium ion [16]. The NNH as a layered hydroxide can serve as a physical barrier to block polysulfide. Most importantly, there are lots of polar groups in NNH, which can provide strong chemical adsorption for polysulfide to prevent it from dissolving into electrolyte. Moreover, forming a mixture of Li-based hydroxide and Ni-based hydroxide during charge and discharge cycle can form some holes which are conducive to improve the electrolyte infiltration and lithium ion conductivity [34].

Fig. 2a shows the SEM image of SCNT-PEG composite material. From this figure we can see that approximately spherical composite

Fig. 4. TG analysis of the SCNT-PEG-NNH composites.

Fig. 5. Electrochemical performance of Li/(SCNT-PEG-NNH) cells at a current density of 200 mA g⁻¹. (a) Discharge-charge profiles, (b) cyclic voltammetry curves, (c) cycling performances, (d) EIS.
material can be obtained by ball-milling method. The spherical composite material has many holes on the surface which is conducive to improve the electrolyte infiltration. In order to fix polysulfides well, the NNH is then chose to coat on the surface of SCNT-PEG composite materials. The SEM image of the SCNT-PEG-NNH composite materials obtained is shown in Fig. 2b. It can be clearly seen that the spherical structure of composite materials is not impaired and the rough surfaces become smooth, which may be caused by the coated layer of NNH. To better demonstrate that the NNH is well coated on the spherical SCNT-PEG particle, TEM characterization is conducted as shown in the Fig. 2c and d. We can see that a layer of NNH is well coated on the spherical particle, which is well agreed with the SEM.

To verify the crystal type of composite material, XRD patterns are characterized and the results are shown in Fig. 3a. As we can see, the crystal type of S does not change during preparation. However, the crystal peak of CNT is not detected. This is due to that the peaks of CNT are weaken because the PEG and S are coated on the surface of CNT and the peaks between S and CNT are overlapped. Similarly, the peaks of NNH in XRD are not found. To further confirm NNH contained in the composite material, we used the same method to synthetize NNH without adding SCNT-PEG composite material. The XRD of obtained material is shown in Fig. 3b. All the diffraction peaks are well indexed to a nickel nitrate hydroxide (JCPDS No. 00-022-0752). It indicates that NNH is indeed synthesized in the experiment by using the method. To detect the content of S in the composite material, the TG analysis was carried out and the result is shown in Fig. 4. According to the TG analysis, the S content in the composite material is about 78.0%. The content of S via the elemental analysis is 76.6%, which is well agreed with the TG analysis.

To evaluate the electrochemical performance of the SCNT-PEG-NNH composites, the as-prepared cells are subjected to the cyclic voltammetry test in the potential window of 1.5—3.0 V at the constant potential scan rate of 0.1 mV s⁻¹ and the long-term cyclic test in a potential window of 1.5—3.0 V at the constant current density of 200 mA g⁻¹. Fig. 5a shows the galvanostatic discharge/charge profiles of the SCNT-PEG-NNH composites at current density of 200 mA g⁻¹. The discharge curve shows two potential plateaus, which is consistent with the transformation mechanism of LSB. At the same time, in contrast to the voltage gap between the charge plateau and the discharge plateau of the discharge/charge profiles, the voltage gap of the second cycle becomes small than the first cycle. This is due to the mixture of Li-based hydroxide and Ni-based hydroxide formed by NNH during charge and discharge cycle. Meanwhile, some holes are formed which are conducive to improve the electrolyte infiltration and lithium ion conductivity. The cyclic voltammetry curves in Fig. 5b show two cathode peaks and one anode peak, which are consistent with the discharge/charge profiles. In the first cycle, there is a weak broad peak between 1.5 V and 1.8 V, however, it fades away in the subsequent cycles. This is ascribed to the irreversible electrochemical reaction which happens between NNH and lithium during the first few cycles, producing Li and Ni mixed hydroxyl. The cyclic performance is as shown in Fig. 5c. We can see that the discharge capacity of the SCNT-PEG-NNH in the first cycle is 974 mAh g⁻¹ but it fades fast in the first five cycles until gradually stabilized in 640 mAh g⁻¹, and the discharge capacity maintains in 575 mAh g⁻¹ after 200 cycles.
However, the discharge capacity of the SCNT-PEG quickly decays to about 300 mAh g\(^{-1}\). This is due to the absence of NNH in the SCNT-PEG, the ability to block polysulfides is relatively poor. It demonstrates that the cyclic performance of the SCNT-PEG-NNH composite gets improved. It can be attributed to the spherical conductive structure constructed by CNT and PEG together with NNH for fixing polysulfides without affecting lithium ion conductivity in the composite material. There are no obvious differences in terms of charge-transfer resistance (R\(_{\textrm{ct}}\)) between original cell and the one after 5 cycles (see Fig. 5d), once again ensuring the good electrochemical stability of the SCNT-PEG-NNH composites. However, after 5 cycles, there is another depressed semicircle in the mid-frequency region, which is due to the forming of solid electrolyte interphase (SEI) film.

To further prove that the PEG can be well fixed on the CNT, we used S and CNT for ball-milling without adding PEG, the SCNT composite material obtained in this way was used for S and CNT for ball-milling without adding PEG, the SCNT composite material obtained in this way was used for XPS. We gratefully acknowledge the financial support of National Natural Science Foundation of China (Grant Nos. 21273185 and 21321062) and National Found for Fostering Talents of Basic Science (J1310024). The authors also wish to thank their thanks to Prof. D. W. Liao for his valuable suggestions.

4. Conclusions

We have constructed high sulfur content spherical SCNT-PEG-NNH composite material by using a simple ball-milling method. The SCNT-PEG-NNH composite material is a preferable host to fix S, resulting in an improved electrochemical performance. It turns out that the cycle performance of cathode made by the SCNT-PEG-NNH composite material is improved. When charged-discharged at the current density of 200 mA g\(^{-1}\), the specific capacity is 974 mAh g\(^{-1}\) at the first discharge and 575 mAh g\(^{-1}\) after 200 cycles with the capacity retention ratio of 59.0% for the Li/(SCNT-PEG-NNH) cells. Owing to the spherical conductive framework constructed by the CNTs, the conductivity of composite material gets improvement. Besides, the PEG and NNH which fix polysulfides well can also contribute to a good performance. Therefore, the SCNT-PEG-NNH composite material can be a promising cathode material for the LSBs.

Acknowledgments

We gratefully acknowledge the financial support of National Natural Science Foundation of China (Grant Nos. 21273185 and 21321062) and National Found for Fostering Talents of Basic Science (J1310024). The authors also wish to thank their thanks to Prof. D. W. Liao for his valuable suggestions.

References


