



Short communication

Improved performance of sulfur cathode by an easy and scale-up coating strategy

Jing Fang, Furong Qin, Jie Li, Kai Zhang^{*}, Wenwen Liu, Mengran Wang, Fan Yu, Liyuan Zhang^{**}

School of Metallurgy and Environment, Central South University, 932#, Lushan South Road, Changsha 410083, China

H I G H L I G H T S

- An improved sulfur cathode is fabricated by coating SP slurry on the surface.
- The proposed two-step coating technique is easy for industrialization.
- The cathode simultaneously realizes high areal and mass sulfur loading/content.
- Sulfur cathode exhibited great cycle performance and rate-performance.

A R T I C L E I N F O

Article history:

Received 5 May 2015

Received in revised form

10 June 2015

Accepted 30 June 2015

Available online xxx

Keywords:

Lithium sulfur battery

Sulfur cathode

Polysulfides

Improved performance

Super P

A B S T R A C T

A new fabricating process for high-performance sulfur cathode is proposed. The fabricating process relies on two-step coating technique: firstly, high sulfur content slurry is coated on the current collector. After drying, the electrode is coated with another slurry composed of Super P and binder. The sulfur electrode with relatively high sulfur content/loading of 60 wt%/2 mg cm⁻² discharges capacity of ~695 mAh g⁻¹ at 0.5 C after 100 cycling. This method is easy for industrialization and well controlled over the areal sulfur loading and mass, therefore it is efficient for fabricating high-performance Li-S batteries with high-energy density.

© 2015 Elsevier B.V. All rights reserved.

1. Introduction

Lithium-sulfur (Li-S) batteries hold immeasurable potential as the next generation of high-energy storage systems [1,2], due to the facts that *i*) sulfur cathode possesses a very high theoretical capacity (1675 mAh g⁻¹) and specific energy density (~2600 Wh kg⁻¹) and *ii*) sulfur is eco-friendly and cheap [3,4]. Li-S batteries can therefore deliver capacity of at least 3 times more than that of the state-of-the-art Li ion batteries [5]. During the running of batteries, however, sulfur reacting with lithium could transform into the soluble polysulfides intermediates (Li₂S_n, 4 ≤ n ≤ 8), which readily dissolve into the electrolyte and shuttle between the

cathode and anode to reduce the stability and coulombic efficiency of batteries [6,7]. Consequently, sulfur cathode suffered from low utilization of active materials and poor cycle life. Moreover, the intercalation of Li into the sulfur inevitably causes the expansion of cathode, which can destroy the unity of the electrode and invalid the batteries [8,9].

To improve the performance of Li-S batteries, much attention has been paid to modify the sulfur cathode. Infiltrating sulfur into conductive matrixes (e.g., porous carbon and conducting polymers) or metal oxides (e.g., TiO₂) is one feasible route [10–18]. Guo et al. [5] have reported the trapping of small sulfur molecules into the microporous carbon shell to build a stable sulfur cathode with superior rate capability. Cui et al. [13] have fabricated a TiO₂-S yolk-shell nanostructure to successfully accommodate the sulfur expansion. However, these carbon-S or metal oxides-S hybrids are still needed to blend with highly conductive carbon black (Super P, acetylene black) to build the cathode, which reduces the actual

* Corresponding author.

** Corresponding author.

E-mail addresses: chinamcsu@163.com (K. Zhang), zhang_livy@csu.edu.cn (L. Zhang).

content/loading of sulfur in the cathode [19]. This inevitably declines the areal and volumetric energy density of sulfur cathode [19]. Some data about sulfur-carbon electrodes were collected in Table S1 (Supplementary Materials) for comparison, many free-standing cathodes included. Although free-standing cathode can be fabricated by graphene, its preparation is really complicated. Moreover, the preparation of the sulfur-carbon hybrids usually requires the infusion of sulfur into pores of those conductive matrixes by heating or dissolving [17,20], which complicated the fabrication of sulfur cathode.

As an alternative approach, inserting a conductive interlayer between the cathode and separator is capable to promote the electrochemical performance of the Li-S batteries. Manthiram et al. have revealed the unexpected potential of microporous carbon film as bifunctional interlayer to increase the utilization efficiency of active materials and cyclability of the batteries [21–23]. Thereafter, abundant researches have been launched to develop superior interlayers. In general, the interlayers can be fabricated by graphene and its derivatives, microporous carbon, carbon nanotubes, activated carbon, carbon cloth, biomass-derived carbon or Ni foam [21,24–28]. The dissolved polysulfides can be effectively stabilized in the cathode zone by conductive interlayer and therefore the batteries display obviously improved capacity and cyclability. Despite the well-known advantages, approach of inserting interlayer still faces many challenges: a) the preparation of the interlayer is relatively complicated, which commonly needs filtration; b) the integration of interlayer and cathode is still difficult in practical continuous production; c) many interlayers lack flexibility to satisfy the requirement of roll-to-roll assembly procedures; d) the interlayer is general too heavy to maintain a relatively high loading of active materials. Most recently, graphene@TiO₂ hybrid was applied to build a flexible and ultralight interlayer to promote the performance of Li-S batteries [29]. However, the cathode was fabricated by infiltrating the melted sulfur into the porous carbon nanotubes prepared by steam activation, which highly increases the cost and complicates the procedures. For the commercialization, sulfur cathode must possess high mass loading, good flexibility and long-lasting capability and should be fabricated as simple as possible. Typically, it is highly desirable to develop a superior cathode without using extra materials to lower the sulfur loading or other procedures to reduce the fabrication efficiency and it is the best choice to just use raw commercialized products. Here we reported an easy method to fabricate a superior sulfur cathode by the mature coating technique. The sulfur loading reaches as high as ~2.0 mg cm⁻² (areal) and 60 wt% (mass), which is much higher than many reported value (Table S1). The cathode is flexible and only the commercialized materials were used without any modification.

2. Results and discussion

The experimental details are provide in the Supporting Materials and the processes of cathode fabrication can be found in Fig. 1. The sulfur and carbon nanospheres (Super P) were purchased and used as received. Figure S1 (in Supplementary Materials) presents the TEM images of Super P. As seen, the spherical particles stack as carbon chains. SEM image revealed that the sulfur is irregular particles with tens of micrometer in size. The sulfur and carbon nanospheres were mixed with Polyvinylidene Fluoride (PVDF) using N-2-methyl pyrrolidone (NMP) as dispersant and the sulfur cathode was first prepared by coating the mixture slurry onto Al foil, as shown in Fig. 1a. The SEM image showed that the raw cathode is highly uneven and mainly the irregular sulfur particles can be found. Onto the raw cathode a slurry composed of PVDF and carbon nanospheres was coated, which built a conductive carbon layer onto the sulfur layer (Fig. 1b). The surface section of the

carbon layer is relatively smooth as comparing to the raw sulfur cathode. Moreover, the carbon nanospheres pile up with each other to develop abundant pores or gaps, which makes the carbon layer very loose and therefore facilitates the electrolyte transportation through the layer. The cross-section SEM image indicated that the carbon layer was ultimately jointed with the raw cathode. The thickness of sulfur cathode and carbon layer is ~30 and ~10 μm, respectively. Actually, after drying no powders departed from the carbon layer and the carbon layer cannot be peeled off from the cathode. This should be due to the partial dissolution of the PVDF binder from the interfacial section of the raw cathode, which integrated together with the PVDF of carbon layer after drying (Fig. 1b). The raw cathode contains 70 wt% sulfur (~2.0 mg cm⁻²) and after coating the carbon layer the sulfur content becomes 60 wt%. The calculation of the weight was based on the mass difference of the electrode before and after coating. In other words, the carbon layer accounts for only ~14 wt% of the total weight. In the comparison to the previous reports, our fabrication displays three important advantages: a) the fabrication is purely relied on the mature industrialized coating technique, which allows the large-scale preparation of the flexible electrode and therefore satisfies the potential commercialization of the S cathode, b) the treatment or modification of the sulfur (e.g., infiltration, coating or melting of the sulfur) is avoided and only the commercial sulfur is used, which simplifies the fabrication procedures and the production costs, c) the sulfur content in the cathode is relatively high as taking the areal and volumetric density together into account, which promises the fabrication of high energy density Li-S batteries. Fig. 1c illustrates the Li-S batteries configuration with coating the carbon layer. The thin carbon layer functioned as the trapping shield to reuse the polysulfides and prevent it from escaping to the anode to break the batteries. The performance will be depicted below.

Fig. 2a gives the cyclic voltammetry (CV) curves of the sulfur cathode with carbon nanospheres coated on the surface. In the cathodic scanning, there are two reductive peaks centered at ~2.25 V and ~1.95 V, respectively, which are related to the multi-step reduction of elemental sulfur. The peak arising at high potential is associated with the reduction of elemental sulfur and the formation of S₈²⁻ and the peak locating at low potential is corresponding to the reduction from soluble intermediates (Li₂S_x, 4 ≤ x ≤ 8) to insoluble Li₂S₂ and Li₂S [3,30,31]. In the anodic scanning only one peak centered at ~2.52 V can be observed which is corresponding to the oxidation from Li₂S₂ and Li₂S to elemental sulfur [32]. After the first cycle, the subsequent CV curves change slightly but overlap very well, which indicates good cycle stability. Moreover, the slight change between the first and second cycles of the CV curves is possibly related to the movement of the sulfur compounds from primary position to the stable location [29,33]. The CV curves of the pristine sulfur cathode is also obtained, as presented in Fig. 2b. Obvious difference can be found when comparing Fig. 2b with Fig. 2a. In the cathodic scanning, the reductive peak centered at low potential shows a relatively lower intensity than that of the reductive peak centered at high potential. The small area of the reductive peak centered at low potential indicates low utilization of active materials. Considerable amount of soluble intermediates cannot be reduced to Li₂S₂ or Li₂S. This is primarily owing to the dissolution of polysulfides into the electrolyte, which lost effective electrochemical contact with the carbon nanospheres in the cathode. In other words, a simply coating of carbon nanospheres onto the pristine sulfur cathode promote the utilization efficiency of the sulfur compounds.

The sulfur cathodes with carbon layer or not are also tested by Galvanostatic charge and discharge. Fig. 2c depicts the Galvanostatic charge-discharge profiles of the sulfur cathode with coating carbon nanospheres at 0.1 C, 0.2 C, 0.5 C, 1 C and 2 C. Two discharge

Download English Version:

<https://daneshyari.com/en/article/7730582>

Download Persian Version:

<https://daneshyari.com/article/7730582>

[Daneshyari.com](https://daneshyari.com)