Materials Letters 228 (2018) 195–198

Contents lists available at ScienceDirect

Materials Letters

journal homepage: www.elsevier.com/locate/mlblue

Confine sulfur in urchin-like nitrogen doped carbon particles for lithium-sulfur batteries

Na Li, Xuan He, Kanghua Chen *, Songyi Chen, Fangyu Gan

Light Alloy Research Institute, Central South University, Changsha 410083, China
Science and Technology on High Strength Structural Materials Laboratory, Central South University, Changsha 410083, China
Collaborative Innovation Center of Advance Nonferrous Structural Materials and Manufacturing, Central South University, Changsha 410083, China

A R T I C L E I N F O

Article history:
Received 28 March 2018
Received in revised form 7 June 2018
Accepted 7 June 2018
Available online 8 June 2018

Keywords:
Energy storage and conversion
Carbon materials
Urchin-like structures
Lithium sulfur battery
Cathode

A B S T R A C T

Melt-diffusion and vapor-phase infusion is widely used to introduce sulfur into the pores of carbon matrix to improve the performance of lithium-sulfur (Li-S) batteries. However, it is limited performance enhancement due to low sulfur content and unavoidable land on the outer surface of host material. Herein, we introduce an effective and facile strategy to prepare an urchin-like S@N-doped carbon composite by in situ oxidizing the N-carbon coated metal sulfide precursor. The prepared urchin-like S@N-doped carbon particle cathode for lithium-sulfur batteries exhibits a high initial capacity of 820 mAh^{-1} and excellent cycling performance of 760 mAh^{-1} after 100 cycles at 0.5 C with a high mass sulfur loading (78.9 wt%, 3.5 mAh cm^{-2}). This work provides an efficient route to prepare sulfur/porous carbons for energy storage application.

1. Introduction

Lithium-sulfur (Li-S) battery has a great potential in electrochemical energy storage systems because of its high theoretical energy density of 2600 Wh kg^{-1} [1,2]. Recent studies discover that the electrochemical property of Li-S batteries can be improved by introducing sulfur into carbon shell via melt-diffusion or vapor-phase infusion [3–7]. However, diffusion or infusion process induces four obviously drawbacks: i) some sulfur inevitably land on the outer surface of shell, resulting in fast diffusion into the electrolyte; ii) little or no sulfur in pores can hardly deliver battery capacity; iii) the limited void cannot accommodate the volume expansion of sulfur upon lithiation; iv) the weak interaction between carbon shell and polar LiPSs.

Considering that all above viewpoints, urchin-like ZnS@nitrogen doped carbon (ZnS@NC) microspheres are prepared through a facile hydrothermal and carbonization process. By soaking ZnS@NC in the aqueous solution of $Fe(NO_3)_3$, ZnS is oxidized to form sulfur particles inside the carbon shells, leaving voids inside which can relieve volumetric expansion. Meanwhile the conductive networks of urchin-like shell can facilitate electron transport and electrolyte infiltration. N-doped carbon shell adsorbs and immobilizes polysulfide via physical adsorption and chemical binding. In this paper, the as-prepared urchin-like S@N-doped carbon cathode exhibits a high initial capacity of 820 mAh g^{-1} and excellent cycling performance of 760 mAh g^{-1} after 100 cycles at 0.5 C with the benefit of structural merits and nitrogen functionalities on carbon shell surface.

2. Experimental section

2.1. Materials synthesis

The ZnS powder is synthesized according to the reference [5]. 0.8 g ZnS powder was added into 1000 ml Tris-buffer aqueous solution (pH = 8.5) and then the solution was stirred for 24 h to form a homogeneous suspension. The obtained black ZnS@PDA was washed by alcohol and dried at 100 °C for 12 h. After it was treated in a thermal environment at 600 °C for 2 h under Ar atmosphere, the black urchin-like ZnS@NC composite was got. The prepared ZnS@NC composite was scattered into an 1 M $Fe(NO_3)_3$ solution, and stirred for 12 h. The obtained S@NC composite was vacuum dried at 60 °C for 12 h to remove the water.

2.2. Electrochemical measurements

When prepared the electrodes, 80 wt% S@NC composites was mixed with carbon black and PVDF in N-methyl-2-pyrrolidone

* Corresponding author at: Light Alloy Research Institute, Central South University, Changsha 410083, China.
E-mail address: csuchenkh@126.com (K. Chen).

https://doi.org/10.1016/j.matlet.2018.06.017
0167-577X/

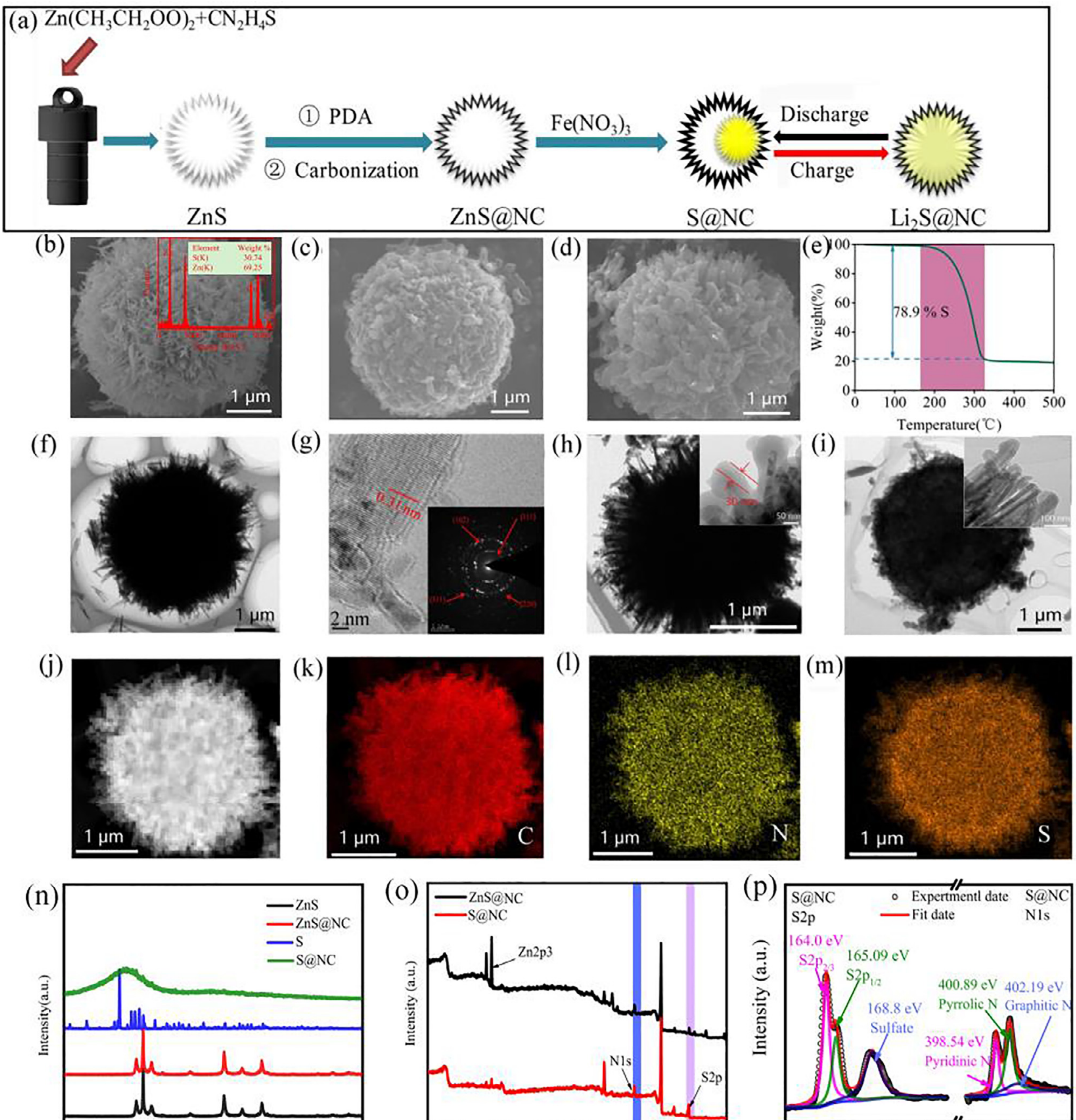

Fig. 1. a) Schematic illustration for the synthesis process of S@NC and the produce of discharge; SEM images of b) ZnS and corresponding EDX spectrum, c) ZnS@NC, d) S@NC; e) TG curve of S@NC; TEM images of f) ZnS, g), HRTEM image of ZnS and the corresponding SADE pattern, h) ZnS@NC (the insert: the thickness of carbon shell is about 30 nm); i, j) S@NC (the inert: the carbon shell of S@NC); k-m) C, N and S elemental mappings of S@NC; n) XRD patterns, o) XPS survey spectrum of ZnS@NC and p) the magnified of N 1s and S 2p of S@NC.

(NMP) under vigorous stirring. The resultant slurry was then spread onto aluminum foils. The sulfur loading density of the cathode is 3.5 mg cm^{-2}. CR2025 cells were assembled in an argon-filled glove box, using lithium metal as the counter electrode and Celgard 2400 as the separator. During the fabrication, 20 μL mg_{sulfur}^{-1} of electrolyte was injected into the coin cell. The electrolyte solution was 1 M lithium bis (trifluoromethane sulfonimide) (LiTFSI) in a solvent mixture of DOL/DME (1:1 by volume) with 1 wt% $LiNO_3$ as an additive.

3. Results and discussion

The efficient fabrication of S@NC particles is depicted in Fig. 1a. For further comparison, N-doped carbon shell (NC) was prepared by scatting ZnS@NC into diluted HNO_3. Sulfur is introduced by melting diffused sulfur in the N-doped carbon shell (MSNC). The SEM and TEM images (Fig. 1b and f) revealed that ZnS has a typical urchin-like structure with diameter about 4 μm. The EDX spectroscopy confirms the present of ZnS. After being annealed at