Journal of Power Sources 327 (2016) 474–480

Contents lists available at ScienceDirect

Journal of Power Sources

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

Highly-flexible 3D Li_2S/graphene cathode for high-performance lithium sulfur batteries

Jiarui He [a], Yuanfu Chen [a, **], Weiqiang Lv [b], Kechun Wen [b], Pingjian Li [a], Fei Qi [a], Zegao Wang [a], Wanli Zhang [a], Yanrong Li [a], Wu Qin [c], Weidong He [a, b, d, *]

[a] State Key Laboratory of Electronic Thin Films and Integrated Devices, University of Electronic Science and Technology of China, Chengdu 610054, PR China
[b] School of Energy Science and Engineering, University of Electronic Science and Technology of China, Chengdu 610054, PR China
[c] National Engineering Laboratory for Biomass Power Generation Equipment, School of Renewable Energy Engineering, North China Electric Power University, Beijing 102206, PR China
[d] College of Chemistry and Molecular Engineering, Peking University, Beijing 100871, PR China

HIGHLIGHTS

- Flexible 3D Li_2S/graphene cathode is synthesized with an infiltration method.
- 3D Graphene increases the surface area and conductivity of the cathode.
- The cathode exhibits a high discharge capacity of 894.7 mAh g^{-1} at 0.1 C.
- The cyclic performance is record-breaking compared to the previous reports.
- The high-rate capacity up to 4 C reaches 598.6 mAh g^{-1}.

ARTICLE INFO

Article history:
Received 26 April 2016
Received in revised form
9 July 2016
Accepted 23 July 2016

Keywords:
Lithium sulfide
3D graphene foam
Free-standing
Flexible
Lithium-sulfur batteries

ABSTRACT

Three-dimensional Li_2S/graphene hierarchical architecture (3DLG) is synthesized with a facile infiltration method. Highly-crystalline Li_2S nanoparticles are deposited homogenously into three-dimensional graphene foam (3DGF) network grown by chemical vapor deposition (CVD), resulting in 3DLG with high surface area, porosity, flexibility and conductivity. The 3DLG is employed as flexible, free-standing and binder-free cathode without metallic current collectors or conducting additives. Due to the unique structure, the 3DLG exhibits a high discharge capacity of 894.7 mAh g^{-1} at 0.1 C, a high capacity retention of 87.7% after 300 cycles at 0.2 C, and the high-rate capacity up to 4 C reaches 598.6 mAh g^{-1}. The cyclic performance is record-breaking compared to the previous reports on free-standing graphene-Li_2S cathodes. Flexible lithium-sulfur batteries based on the high-capacity 3DLG cathode have promising application potentials in flexible electronics, electrical vehicles, *etc*.

1. Introduction

The lithium-sulfur (Li–S) battery is regarded as one of the most promising next-generation rechargeable batteries, owing to its high theoretical specific energy (~2500 Wh kg^{-1}) [1–3]. However, the application of Li–S batteries is frequently challenged by low electrical conductivity of elemental sulfur, large volume expansion of sulfur (80%) during cycling process and high solubility of the intermediates (Li_2S_n, $n > 2$) in the electrolyte leading to active mass loss and shuttle effect [4–7]. In addition, the formation of Li dendrite on the anode surface in operation causes safety problems. Compared to sulfur cathode, fully lithiated lithium sulphide (Li_2S) with a high theoretical specific capacity (1166 mAh g^{-1}) is advantageous due to the lithium metal-free anodes [8]. Similar to sulfur cathode, Li_2S is also hindered by the high potential barrier (during the first charge process), low electronic conductivity (~10^{-13} S cm^{-1}) and polysulfide shuttle phenomenon [9,10].

To alleviate these problems and improve the electrochemical performance of Li_2S, strategies have been proposed. For instance, the potential barrier during the first charge process can be

* Corresponding author. School of Energy Science and Engineering, University of Electronic Science and Technology of China, Chengdu 610054, PR China.
** Corresponding author.
E-mail addresses: yfchen@uestc.edu.cn (Y. Chen), weidong.he@uestc.edu.cn (W. He).

http://dx.doi.org/10.1016/j.jpowsour.2016.07.088
0378-7753/

effectively alleviated by decreasing the particle size of Li_2S [11,12]. Furthermore, the carbonaceous materials such as polypyrrole, microporous carbon, CMK-3, graphite and graphene have been widely used as the conductive matrix to enhance the conductivity of Li_2S composite [9,13–20]. In particular, graphene with high electrical conductivity and excellent flexibility has been considered to be the most promising matrix [11,15]. Polymeric binders, carbon black additives and metallic current collector (aluminium foil) are widely used in most of the reported Li_2S cathodes to ensure mechanical stability and electrical connectivity of the composite [8,9,12–20]. However, the conductive additives, polymer binders and metallic current collectors used in the batteries typically reduce the energy and power density of full batteries and decrease the electrochemical performance [21].

Recently, Zhou et al. reported a new electrode strategy by loading the Li_2S on the doped reduced graphene oxide aerogel and achieved pronounced electrochemical performance [22]. However, the application of boric acid and dicyandiamide leads to experimental complexity and uncontrollability. Compared to the reduced graphene oxide aerogel, chemical vapor deposition (CVD) grown three-dimensional graphene foam (3DGF) has been proposed to be more advantageous as an excellent backbone for fabricating binder-free and self-standing electrodes owing to the high electrical conductivity (1000 S m^{-1}), low density (0.6 mg cm^{-2}), and high flexibility [23,24]. Nevertheless, to the best of the authors' knowledge, the fabrication of integrated three-dimensional Li_2S/graphene cathode by direct growth of Li_2S nanoparticles into 3DGF network has not been reported.

In this study, three-dimensional Li_2S/graphene hierarchical architecture (3DLG) with Li_2S nanoparticles homogenously deposited into 3DGF network was prepared by infiltrating Li_2S dispersion into the 3DGF. The 3DLG exhibits a high energy capacity, a high rate capability, and a low potential barrier, and the study provides insights into the route to realizing high-capacity cathodes for next-generation Li–S batteries.

2. Experimental section

Synthesis of 3D graphene foam: Three-dimensional graphene foam was grown with chemical vapor deposition (CVD). Nickel foam (0.5 mm thick, Alantum Advanced Technology Materials, China) was used as substrate and placed into a quartz tube. It was then heated up to 1000 °C at a heating rate of 50 °C min^{-1} and maintained for 10 min with a gas flow of H_2/Ar (H_2/Ar = 50:100 sccm) to clean the surface of nickel foam. After 20 min graphene growth under $H_2/Ar/CH_4$ flow ($H_2/Ar/CH_4$ = 50:100:50 sccm), the sample was rapidly cooled to the room temperature at a cooling rate of 100 °C min^{-1}. Finally, the nickel template was etched off with $HCl/FeCl_3$ ($HCl/FeCl_3$ = 1:1 M) solution at 80 °C to result in free-standing 3DGF.

Synthesis of 3DLG: Lithium sulfide (Li_2S, 99.98% trace metals basis) and anhydrous ethanol (≥99.5%) were purchased from Sigma-Aldrich. Drop casting method was used for the synthesis of 3DLG in a glove box [11]. In a typical procedure, 75 mg Li_2S was added to 5 mL ethanol to obtain a 15 mg mL^{-1} solution. Although we used the anhydrous ethanol (≥99.5%) purchased from Sigma-Aldrich, a trace amount of water could exist. Water in ethanol reacted with Li_2S to form LiOH, and precipitated in ethanol. The supernatant was pale yellow. The above 3DGF were put on aluminium foil and Li_2S solution was added using a pipette. The 3DGF was then put into an autoclave in glove box and heated to 300 °C for 2 h to *in-situ* form Li_2S nanoparticles in 3DGF network. The obtained 3DLG (Fig. 1d) was used directly as a cathode electrode in coin cells. Since Li_2S is highly sensitive to moisture and oxygen, all the processes were completed in a glove box.

Characterizations: The component ratio of the composite was determined by comparing the weights of the 3DGF before and after loading Li_2S (after heat treatment at 300 °C for 2 h) and the mass ratio of Li_2S and graphene in DLG samples is ~1:1. The crystalline structure of the obtained samples was characterized by x-ray diffraction (XRD Rigaku D/MAX-rA diffractometer) using Cu Kα radiation after the samples were tightly sealed using Kapton tape. The morphology investigations were performed by scanning electron microscope (SEM, JSM-7000F, JEOL) with an energy dispersive X-ray spectrometer (EDS) and transmission electron microscope (TEM, Tecnai F20 at 200 kV).

Electrochemical measurements: 3DLG discs are used as the electrode and the Li_2S mass loading of the cathode is 1 mg cm^{-2}. Coin-type (CR2025) cells were assembled in an argon-filled MBraun glove box with oxygen and water content below 0.5 ppm, using lithium metal as anode. Celgard 2400 was used as separator. 1.0 M lithium bis(trifluoromethanesulfonyl)imide (LiTFSI) in 1,3-dioxolane (DOL) and 1,2-dimethoxyethane (DME) (v/v = 1:1) (Zhangjiagang Guotai-Huarong New Chemical Materials Co., Ltd) with 0.2 M lithium nitrate ($LiNO_3$) as an additive was used as electrolyte. Cyclic voltammetry (CV) and electrochemical impedance spectroscopy (EIS) were conducted by CHI 660D electrochemical workstation (CHI instrument). CV measurements were performed at a scan rate of 0.1 mV s^{-1} in the voltage range from 1.5 V to 3.6 V at the first cycle and 1.5 V–3 V in subsequent cycles.

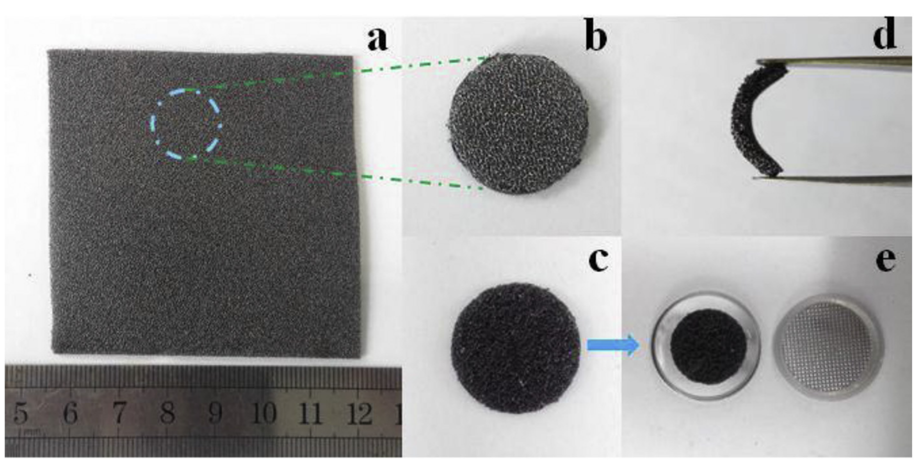

Fig. 1. Photographs of (a) 65 × 65 mm^2 free-standing 3DGF and (b) the disk of 3DGF with a diameter of 14 mm. (c) The 3DLG synthesized by the drop casting method. (d) Bent 3DLG, indicating a good flexibility. (e) The 3DLG used as freestanding cathode.