Materials Research Bulletin 84 (2016) 218–224

Contents lists available at ScienceDirect

Materials Research Bulletin

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

Highly improved electrochemical performance of Li-S batteries with heavily nitrogen-doped three-dimensional porous graphene interlayers

Huihui Deng[a], Libing Yao[a], Qiu-An Huang[a], Qingmei Su[a], Jun Zhang[a,b], Gaohui Du[a,*]

[a] Institute of Physical Chemistry, Zhejiang Normal University, Jinhua 321004, China
[b] College of Materials Science and Engineering, Zhejiang University of Technology, Hangzhou, 310014, China

ARTICLE INFO

Article history:
Received 3 May 2016
Received in revised form 20 July 2016
Accepted 7 August 2016
Available online 8 August 2016

Keywords:
A. Nanostructures
B. Chemical synthesis
B. Microstructure
C. Electron microscopy
D. Energy storage

ABSTRACT

A freestanding nitrogen-doped graphene functional interlayer placed between the sulfur cathode and the separator has been investigated to enhance the electrochemical performance for lithium-sulfur (Li-S) batteries. The interlayer with three-dimensional porous structure and abundant of N-doping active sites, not only can increase electron transport pathway and the storage capacity of liquid electrolyte, but also can physically and chemically adsorb the highly soluble lithium polysulfides to reduce the loss of active material. With a pure sulfur electrode (high sulfur content of 70 wt%), the as-assembled Li-S battery delivers a high initial discharge capacity up to 1481 mAh g^{-1} at a rate of 0.1C, and maintains a reversible capacity of 956 mAh g^{-1} after 50 cycles of charge/discharge. Comparing with conventional cells, we have highly improved the electrochemical performance for Li-S batteries.

1. Introduction

As the attention of environmental issues is on the rise, the development of emerging energy-storage technology is critical for electric vehicles (EV) and advanced portable electronics applications. Rechargeable lithium-ion batteries (LIBs) have successfully authorized the used of EV and electronics devices attributed to the advantages of high open-circuit voltage, low maintenance, long life, and environmental friendliness [1,2]. However, the inherent issues of LIBs are the security risks and low energy density. Lithium-sulfur batteries are based on the electrochemical redox reaction $16Li + S_8 \leftrightarrow 8Li_2S$, which possess extremely high theoretical specific capacity (1675 mAh g^{-1}) and high energy density (2600 Wh kg^{-1}). In combination with the safe operating voltage (2.15 V *vs.* Li/Li^+), nontoxic nature and abundant availability of sulfur, Li-S batteries are regarded as one of the most promising electrochemical energy-storage system [3,4].

Despite these advantages, lithium-sulfur batteries suffer from critical challenges related to the poor active material utilization and rapid capacity fading that hamper their widespread application because of the insulating natures of sulfur ($\sigma = 5 \times 10^{-30}$ S m^{-1}) and lithium sulfide, the shuttle effect and high solubility of intermediate lithium polysulfides (Li_2S_n, $8 > n > 2$) in the liquid electrolyte, and huge volume expansion on the electrode during the electrochemical process [5,6]. Various strategies have been investigated to address the above-mentioned challenges, like encapsulating sulfur in porous carbon matrix [7–9], optimization of the organic electrolyte [10,11], coating conductive polymer to confine active materials [12–14], and optimization of battery structures [15]. Although extensive approaches can suppress the shuttle phenomenon of lithium polysulfides and enhance the conductivity of the cathode, the electrochemical performances for Li-S batteries have been enhanced to some extent. However, the low output, high cost and complex manufacturing processes restrict the feasibility of industrial-scale production. Recently, Manthiram and co-workers [15–18] proposed a novel strategy by inserting a bifunctional interlayer between the cathode and the separator to suppress the shuttle phenomenon of lithium polysulfides and diminish the Li^+ ion transfer resistance. For example, Manthiram's group inserted a free-standing MWCNT interlayer for Li-S battery which delivered a specific capacity of 962 mAh g^{-1} after 50 cycles [17]. Since then a variety of materials, such as porous carbon [18–20], conductive polymer [21], and metal oxides [22] have been employed as the interlayer in high performance Li-S batteries. Huang et al. successfully designed a multi-functional interlayer by coating a graphene-TiO_2 film on the surface of sulfur cathode, which provided rapid electron transfer and absorption to the soluble polysulfides, and showed a high

* Corresponding author.
E-mail address: gaohuidu@zjnu.edu.cn (G. Du).

http://dx.doi.org/10.1016/j.materresbull.2016.08.014
0025-5408/

reversible specific capacity and excellent cycling stability [22]. The benefit of the interlayer configuration is the trapping of active materials within the interlayers and providing effective electrochemical contact between the active material and the conductive network. One of the main advantages by employing interlayers over other methods is the feasible large-scale application in commercial Li-S batteries.

Graphene has become the research spotlight due to its unique properties, like high specific surface area and multidimensional electron transport pathways. Graphene has been investigated as host for sulfur and shows an enhanced electrochemical performance in Li-S batteries [23–25]. Recently, Zhang et al. found that N-doped graphene–S composite cathode could reach the ultralong cycle life of the Li/S cells to 2000 cycles due to N functional groups of graphene which alleviate dissolution of polysulfides and help redisposition of polysulfides in the electrode [26]. The electrochemical performance of the N-doped graphene was compared with pristine graphene as the sulfur matrix by Cao et al.; the S@N-graphene composite electrode delivered a high reversible capacity of 825 mAh g^{-1} after 200 cycles at 2 A g^{-1} while the S@graphene without N-doping delivered only 640 mAh g^{-1} [27]. The N-doped graphene can act not only as an electronic conductive network but also as a Lewis base "catalyst" matrix that promotes the higher Li_2S_n to be further oxidized completely to S_8, which can thus significantly improve the sulfur utilization and cycling stability [27]. Moreover, N-doping in the carbon matrix can effectively increase electrical conductivity and can enhance the absorption energy of Li_2S_n (n = 4–8) to restrain the polysulfides shuttle in Li-S batteries [28].

Herein, we investigate the feasibility of a three-dimensional nitrogen-doped graphene (3D-NG) functional film as the functional interlayer for the first time, which is sandwiched between the cathode and the separator. Due to the three-dimensional porous structure of graphene film with a number of N-doping active sites, the loss of active material and the shuttle phenomenon of lithium polysulfides can be effectively suppressed. The Li-S battery shows a high initial discharge capacity up to 1481 mAh g^{-1} and good capacity retention of 956 mAh g^{-1} after 50 cycles of charge/discharge with the sulfur content of 70 wt%. Comparing with conventional cells, the electrochemical performance for Li-S battery with 3D-NG interlayer has been highly improved.

2. Experimental

2.1. Material preparation

Graphene oxide (GO) was synthesized from flake graphite powder via a modified Hummer's method [29]. 3D-NG was fabricated by one-pot hydrothermal process. In a typical process, 20 mL GO aqueous dispersion (3 mg/mL) was mixed uniformly with 60 μL ethylenediamine and then transferred into an autoclave with a volume of 30 mL, and heated at 180 °C for 12 h. After the autoclave was naturally cooled, the as-prepared hydrogels were taken out and immersed under deionized water for 24 h and then freeze-dried. Eventually, the three-dimensional nitrogen-doped graphene (3D-NG) functional films were obtained from the as-prepared sample by cutting with a blade.

2.2. Material characterization

The morphologies and microstructures of the 3D-NG interlayer were characterization by scanning electron microscopy (SEM, Hitachi S-4800) and transmission electron microscopy (TEM, JEM 2010F). The elemental distribution on 3D-NG interlayer was observed by energy dispersive X-ray spectroscopy linked to transmission electron microscope. The elemental information was examined by X-ray photoelectron spectra (XPS) on an ESCALAB 250Xi Spectrometer (Thermo Scientific).

2.3. Electrochemical measurements

CR2025-type coin cells were assembled in a glove box under argon atmosphere for testing the electrochemical properties. The working electrodes were fabricated by a simple ball milling of sublimed sulfur, acetylene carbon black and polyvinylidenefluoride (PVDF) binder with N-methyl-2-pyrrolidone (NMP) as the solvent to form a homogeneously slurry in a weight ratio of 70: 20: 10. The slurry was coated onto aluminum foil substrates and then dried at 60 °C overnight. Lithium foils were used as the counter electrodes and micro-porous polypropylene membranes (Celgard 2300) were used as the separators. The electrolyte was 1.0 M lithium bis(trifluoromethanesulfonyl)imide in 1,3-dioxolane (DOL) and 1,2-dimethoxyethane (DME) (1:1 by volume) with 1.0 wt%

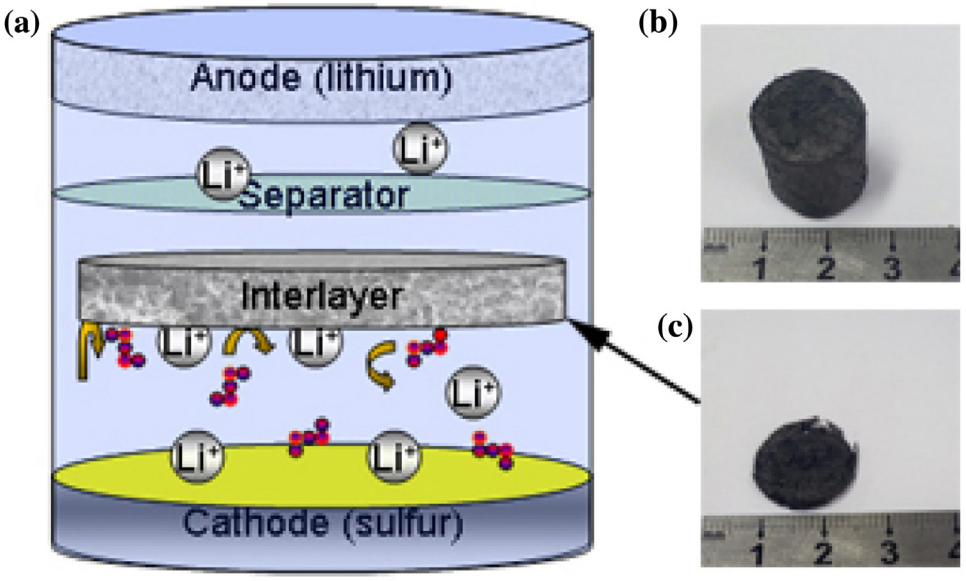

Fig. 1. (a) Schematic of the novel Li-S battery device with a 3D-NG interlayer; (b) photograph of the 3D-NG after freeze-drying; (c) photograph of the 3D-NG interlayer.