



A high-level N-doped porous carbon nanowire modified separator for long-life lithium–sulfur batteries



Xiangyang Zhou^a, Qunchao Liao^a, Jingjing Tang^b, Tao Bai^a, Feng Chen^a, Juan Yang^{a,*}

^a School of Metallurgy and Environment, Central South University, Changsha 410083, China

^b Department of Mechanical and Engineering, The Hong Kong Polytechnic University, Hong Kong, China

ARTICLE INFO

Article history:

Received 20 December 2015

Received in revised form 18 February 2016

Accepted 23 February 2016

Available online 26 February 2016

Keywords:

N-doped

Porous carbon nanowire

Modified separator

Lithium–sulfur batteries

ABSTRACT

Lithium–sulfur (Li–S) batteries are an attractive candidate for the next generation energy storage systems. However, the practical use of Li–S batteries is hindered by poor cycle life and low Coulombic efficiency, which are induced by shuttle effect. Modifying the properties of a separator is an effective way to inhibit the shuttle effect. However, only physical interactions of common carbon materials are not enough to confine lithium polysulfides. In this paper, a porous carbon nanowire (N-PCNW) is designed to modify the separator. The N-PCNW with high N-doped level (7.12 wt%) not only possesses excellent electron conductivity, but also traps the soluble polysulfides effectively with both physical and chemical interactions. With the N-PCNW modified separator, the pure sulfur cathode exhibits enhanced electrochemical performance, showing a high initial discharge capacity of 1430 mA h g⁻¹ at 0.2 C (1 C = 1675 mA h g⁻¹) and good long-term cycling stability at 0.5 C with 0.08% capacity fading per cycle. This design is easy and efficient, providing a great promise for the practical use of Li–S batteries.

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1. Introduction

Lithium–sulfur batteries (Li–S) have been touted as one of the most promising next generation systems, as sulfur offers a high theoretical capacity of 1675 mA h g⁻¹ [1–3]. However, massive implementation of Li–S batteries remains hindered by the poor conductivity of sulfur and the low utilization of the active sulfur material [4,5]. Also, the soluble nature of the polysulfide (S_n²⁻, n ≥ 4) intermediates gives rise to low Coulombic efficiency, unexpected self-discharge, and fast fading of capacity [3,5–9].

Many different strategies such as rational designs of electrode materials [10–15] and new electrolytes [16–19] are being explored in order to address these scientific issues. However, these designs are limited by two main problems: 1) complex manufacturing processes and 2) fast capacity decay, when sulfur percentage in cathode is high [20].

Alternatively, modifying the properties of a separator is another strategy to regulate the polysulfides shuttle. As an essential part in the lithium ion batteries, the separator is a nanoporous polymer membrane. Moreover, it functions as an ion conductor to maintain the pathway and an electron insulator to prevent short circuit [21]. In Li–S batteries, high dissolution of polysulfides can diffuse freely throughout the whole cell, which induces a fast fading of capacity [22]. Therefore, a lot of conductive carbon materials, including conductive carbon black [23,24], multi-walled carbon nanotube [25], graphene [26,27] and their composites

[28] have been proposed to modify the separator or as an interlayer to trap the soluble polysulfides in electrolyte. Undoubtedly, these carbon-coated separators have presented a great success in improving the electrochemical performance of Li–S batteries. However, studies have demonstrated that the interaction between nonpolar carbon and polar lithium polysulfides is not strong enough to prevent the loss of sulfur thoroughly [29]. Therefore, in order to improve the interaction between lithium polysulfides and barrier layers, researchers start to pay attention to the chemical adsorption of polysulfides. Following this concept, nitrogen-doped porous hollow carbon sphere [30], a bifunctional MCNT@PEG [31], and nitrogen/sulfur-codoped graphene sponge [32] have been reported to modify the separator or as an interlayer. In this work, we present a novel modified separator with N-doped porous carbon nanowire (N-PCNW) coating for use with pure sulfur cathodes. The N-PCNW was synthesized by a facile pyrolyzation of polypyrrole followed by KOH activation, exhibiting a one dimensional porous nanostructure, high N-doped level and large specific surface area. Subsequently, N-PCNW was prepared to coat on one side of a commercial Celgard separator, forming a light conductive layer, which functions as another current collector and a polysulfide diffusion barrier region. The N-PCNW coating has the following advantages: 1) providing a fast and short-distance electron transport to get high capacity at a high current density; 2) a large conductive surface area for absorbing the dissolved polysulfides to reactivate them; and 3) a high percentage of N doping promoting the chemical adsorption of polysulfides to restrain the polysulfides shuttle. As a result, the N-PCNW modified separators allow the pure sulfur cathode to exhibit an excellent electrochemical performance.

* Corresponding author.

E-mail address: j-yang@csu.edu.cn (J. Yang).

2. Experimental

2.1. Preparation of N-doped porous carbon nanowire (N-PCNW)

First, we used a simple method to synthesize polypyrrole nanowire (PNW) [33]. The resulting PNW was washed with deionized water to remove residual reactant and dried overnight at 80 °C. The dried PNW was mixed with KOH three times and dried at 80 °C for 48 h. Finally, the mixture was calcined at 700 °C for 2 h under nitrogen atmosphere. The product was dipped in 1 mol L⁻¹ HCl solution for 6 h, then washed with deionized water and dried in oven at 80 °C.

2.2. N-PCNW coated separator preparation

A slurry coating method was used to fabricate the N-PCNW modified separator. The slurry was prepared by mixing N-PCNW and polyvinylidene fluoride (PVDF) (9:1, by mass) with N-methyl-2-pyrrolidinone (NMP). The slurry was then spread on one side of a commercial Celgard separator and dried in a vacuum oven at 50 °C for 12 h. The dried N-PCNW-modified separator was punched into a disk with a diameter of 1.9 cm for assembly of coin cells. The N-PCNW coating is approximately 0.4 mg cm⁻² in weight.

2.3. Characterization

The microstructure of the as-prepared samples was characterized by field emission scanning electron microscopy (SEM, Nova Nano SEM 230) and transmission electron microscopy (TEM, JEM-2100F, Japan). Energy-dispersive X-ray spectroscopy (EDS) was employed to characterize the elements on the surface of a sample. X-ray photoelectron spectra (XPS) was used to inspect the surface and bulk chemical compositions. The Brunauer–Emmett–Teller (BET) method was used to characterize the specific surface area and pore structure of N-PCNW.

2.4. Electrochemical measurements

The S cathode was consisted of 60 wt% S, 30 wt% conductive carbon black and 10 wt% PVDF binder. Then the mixed materials

were dispersed in NMP, coated onto an aluminum foil and dried at 50 °C overnight. The mass loading of sulfur on the electrode was 1.5–1.7 mg cm⁻². The electrolyte was consisted of 1.0 M lithium bis(trifluoromethanesulfonyl)imide (LiTFSI) and 1 wt% LiNO₃ dissolved in dimethoxyethane (DME) and 1,3-dioxolane (DOL) with a volume ratio of 1:1. The coin cells were tested between 2.8 and 1.7 V (vs Li/Li⁺) on a LAND CT2001A instrument at 25 °C. The amount of electrolyte in a coin cell was about 0.1 ml. Electrochemical impedance spectroscopy (EIS) measurements were tested by an impedance analyzer. The frequency ranges between 100 kHz and 10 mHz.

3. Results and discussion

Fig. 1 depicts a schematic of the cell with the N-PCNW-modified separator. The side of the separator coated by N-PCNW towards the sulfur cathode acts as a barrier to astrict lithium polysulfides in the cathode side [34]. On the other side, it also works as another current collector to transport electrons to the absorbed polysulfides to reactivate them during cycling [35].

The morphologies of the original separator, N-PCNW modified separator and N-PCNW were examined by SEM in Fig. 2. As shown in Fig. 2a, a uniformly interconnected submicron pore structure is observed for the Celgard separator, which functions as ions' conductor and electrons' insulator [36]. In contrast to the routine separator, the surface morphology of the N-PCNW-modified separator which composed of N-PCNW and PVDF binder is exhibited in Fig. 2b. A large amount of porous micron-sized nanowire clusters which are consisted of N-PCNW adheres to the Celgard separator and forms a compact coating. As revealed in Fig. 2c, the N-PCNW coating is approximately 9 μm in thickness and only 0.4 mg cm⁻² in weight. However, the thickness and weight of the Celgard separator are about 24 μm and 1.3 mg cm⁻², respectively, which are much thicker and heavier than the N-PCNW coating layer.

To reveal the microstructure of the N-PCNW explicitly, the SEM and TEM of the N-PCNW before mixed with PVDF are shown in Fig. 2d, e and f. Obviously, a homogeneous morphology of cross-linked nanowires is presented. And the diameter of the N-PCNW is about 80–100 nm. As researches demonstrated one-dimensional nanowire nanostructure can

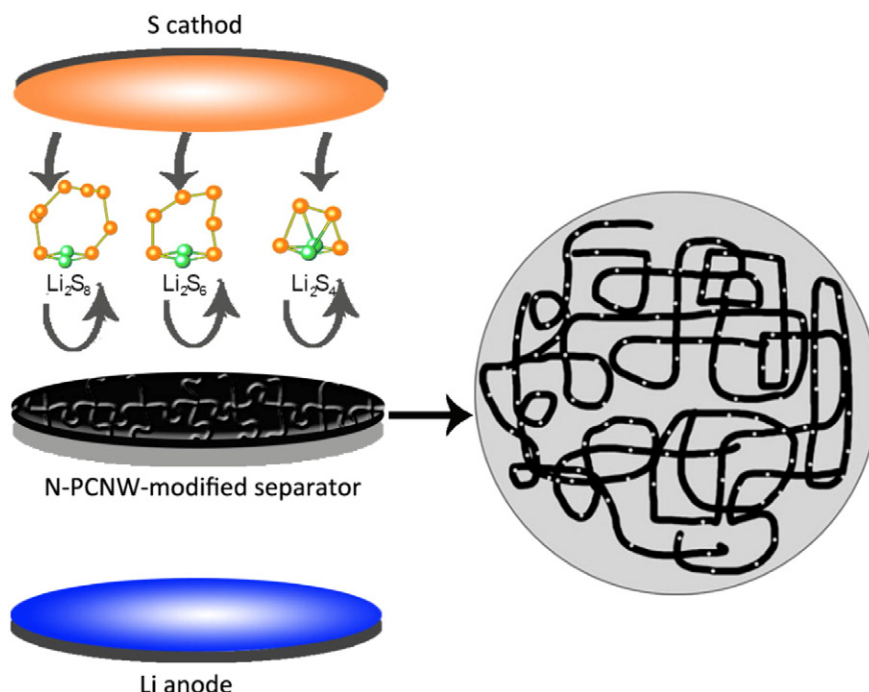


Fig. 1. Schematic of a Li-S cell configuration with the N-PCNW-modified separator.

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