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Porous carbon nanofiber paper as an effective interlayer for high-performance lithium-sulfur batteries

Jiangan Wang [a,*], Ying Yang [b], Feiyu Kang [c]

[a] State key Laboratory of Solidification Processing, Center for Nano Energy Materials, School of Materials Science and Engineering, Northwestern Polytechnical University, Xi'an, 710072, China
[b] Department of Electrical Engineering, Tsinghua University, Beijing 100084, China
[c] Institute of Advanced Materials Research, Graduate School at Shenzhen, Tsinghua University, Shenzhen 518055, China

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A B S T R A C T

Lithium-sulfur (Li-S) battery with new configuration is demonstrated by inserting a flexible activated carbon nanofiber (ACNF) interlayer between the sulfur cathode and the separator. The ACNF with tunable pore structure is fabricated by a combination of electrospinning polyimide and a subsequent activation treatment. The influence of the textual characteristics of ACNFs on the electrochemical performance of Li-S batteries has been studied. The highly porous ACNF not only effectively intercepts/stabilizes the shuttling migration of polysulfides within the cathode region, but also provides reliable ionic/electronic conductivity for fast kinetics. The lightweight ACNF interlayer with higher specific surface area can yield enhanced cell performance at a low mass ratio of ACNF/sulfur (0.4). An initial specific capacity of 1224 mAh g^{-1} along with high Coulombic efficiency, long cycling stability and good rate capability is achieved in the modified Li-S cell.

1. Introduction

Rechargeable Li-ion batteries are considered to be the most promising technology for large-scale applications of consumer electronics, electric vehicles and smart utility grids [1]. Unfortunately, the currently Li-ion batteries suffer from limited energy density. Lithium-sulfur (Li-S) batteries are one of the excellent alternative energy storage systems. Owing to the ultrahigh capacities of sulfur and Li metal (1675 and 3861 mAh g^{-1}, respectively) operated under a safer cell voltage of about 2.15 V, the Li-S cell can deliver a theoretical energy density of 2567 Wh kg^{-1} [2,3]. However, to enable this system to be a viable technology, there are many challenging issues required to be urgently addressed [3–7]. The first obstacle is the insulating nature of sulfur and its Li_2S product, which leads to poor utilization of active materials. The second limitation is the shuttle effect caused by the soluble polysulfides (Li_2S_x, $4 < x \leq 8$), resulting in low Coulombic efficiency and serious capacity fading. The last but not the least problem is the huge volume change (80%) during the electrochemical conversion between sulfur and Li_2S. Such a structural expansion/contraction would give rise to pulverization of active materials, followed by electrical disconnection to the current collector and thus fast capacity degradation.

To solve these critical problems, a great number of studies have devoted significant efforts to develop effective design strategies. The mainstream approach includes inside modification of sulfur cathodes, such as integrating sulfur with various substrates of carbon materials, conducting polymers and metal oxides, *etc* [3,4]. The heterogeneous substrates are expected to increase the electrical conductivity, suppress the shuttling migration and accommodate the volume change. Despite the effectiveness of these sulfur-based composites, this approach involves complex fabricating processes and reduces the actual sulfur loading in the cathode. Recently, Manthiram's group proposed a novel cell configuration based on a carbon interlayer inserting between the cathode and the separator [4,8,9]. The new cell configuration eliminates the complex material processing concerns compared to the sulfur-based composites. The interlayer serves as bifunctional roles of current collector and polysulfide stockroom, which localizes/stabilizes of the redox reactions within the cathode region. Porous carbon particles, carbon nanotubes (CNTs), carbonized leaf/Kimwipes, reduced graphene oxide (rGO) films, carbon microfiber paper and carbon nanofibers have been demonstrated to be appropriate interlayers for Li-S batteries [8–16]. For example,

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* Corresponding author. Tel. and fax:. +86 029 8846 0361
E-mail address: wangjiangan@nwpu.edu.cn (J. Wang).

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the modified Li-S batteries using interlayers of microporous carbon paper [8], carbon microfiber paper [14] and carbon nanofiber fabric [16] can deliver a specific capacity over 1000 mAh g^{-1} after 100 cycles. Although the novel configuration strategy is effective to improve sulfur utilization, it is important to note that the interlayer is electrochemically inactive, which would decrease the overall cell performance when taking all of the components into account. In other words, one should reduce the weight of the interlayer as much as possible. However, decreasing the weight or thickness of interlayer would weaken its unique bifunctional roles [11,16]. Porous structure is demonstrated to be efficacious for localizing/reutilizing active sulfur-based species. Therefore, to maintain the effectiveness of the interlayer at a reduced thickness (weight), it is expected to create a highly porous structure to compensate the weight limitation.

Electrospining technique is a straightforward method to fabricate freestanding carbon nanofiber (CNF) fabrics with tunable porous structure and good electrical conductivity. Recently, Singhal et al. employed polyacrylonitrile (PAN)-based CNF fabrics as interlayers to intercept the migrating polysulfides. However, the best performance is based on a high weight interlayer of 4.2 mg cm^{-2}, which is three times higher than the sulfur loading (1.4 mg cm^{-2}). Owing to the low specific surface area of CNF, the performance is substantially degraded when the weight of the CNF interlayer is decreased to 1.3-1.8 mg cm^{-2}. In order to obtain an improved performance at a lower weight of CNFs, we herein explore a highly porous activated carbon nanofiber (ACNF) fabric as an effective interlayer between the cathode and the separator (Fig. 1(a)). Polyimide (PI) is used as the carbon precursor to produce porous ACNFs, because PI has a high carbon yield of 70 wt.% (*vs.* 40-50 wt.% for PAN) [17]. In addition, the PI-based CNFs show much better mechanical strength than the PAN-based CNFs [18], which may be favorable for cycling stability. The areal weight of ACNF is about 1.0 mg cm^{-2} to couple an areal sulfur loading of 2.5 mg cm^{-2}. ACNFs with different surface area and pore structure have been prepared to study the effect of textual characteristics on the performance of Li-S batteries. The highly porous ACNF is found to offer numerous nano-reservoirs for interception/stabilization of soluble polysulfides and reliable ionic/electronic conductivity for fast kinetics, which results in much improved electrochemical performance of Li-S cells.

2. Experimental

2.1. Material synthesis

The polymer precursor of polyamic acid (PAA) for electrospinning was synthesized according to our previous study [17]. Typically, 2.2 g of pyromellitic dianhydride (PMDA) and 2 g of 4,4-oxydianilline (ODA) were dissolved in 30.8 g of N,N-dimethyacetamide (DMAc) to form a homogeneous polymer solution of PAA, which was used as a precursor for electrospinning. During the electrospinning process, the polymer precursor was loaded into a syringe pump and a high voltage of 25 kV was provided by a high-voltage power supply. A flow rate of 1 ml h^{-1} and a needle-to-collector distance of 25 cm were applied to ensure a stable electrospinning. The as-electrospun nanofiber was collected as a flexible fabric, which was subsequently stepwise-treated by imidization and carbonization (900 °C/2 h under argon atmosphere). Finally, the CNF fabric was activated at 700 °C under

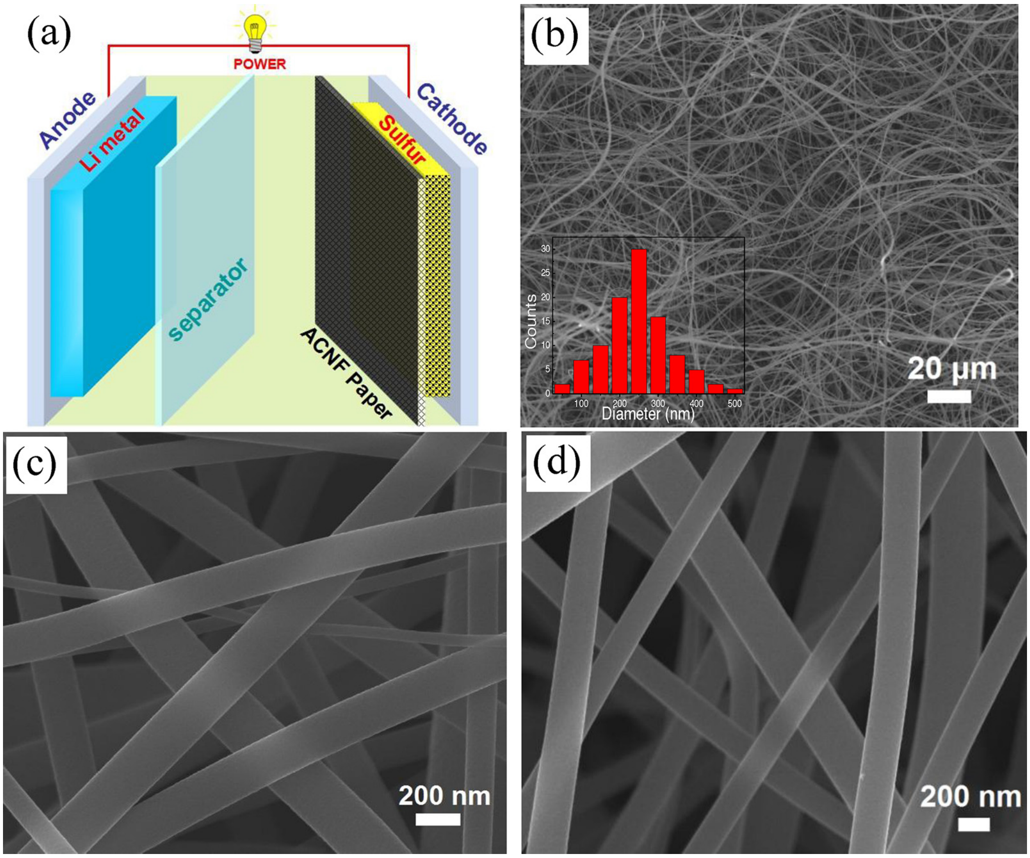

Fig. 1. (a) Schematic illustration of a Li-S cell configuration with an ACNF paper inserting between cathode and separator; (b) A panoramic view of the ACNF paper (inset is the diameter distribution statistic of the nanofibers). (c-d) Magnified SEM images of (c) ACNF3 and (d) ACNF1.