Nano Energy 51 (2018) 425–433

Contents lists available at ScienceDirect

Nano Energy

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

Full paper

All-fiber-based quasi-solid-state lithium-ion battery towards wearable electronic devices with outstanding flexibility and self-healing ability

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ARTICLE INFO

Keywords:
Fiber-shaped device
Lithium ion battery
Self-healing
Flexibility
Wearablity

ABSTRACT

In recent years, high-performance flexible power sources require not only the improvement for high energy density and power density, but also the reliability and flexibility for practical application. However, the energy storage devices often fail to work and even cause safety problems under deformation, so the effective protection is particularly important. Here, we present a flexible and self-healable all-fiber-based quasi-solid-state lithium-ion battery (LIB). The anode is made up of porous reduced graphene oxide (rGO) fiber with SnO_2 quantum dots and the cathode consists of spring-shaped rGO fiber with $LiCoO_2$. The adjustable length of the spring-shaped cathode makes it easy to match the capacity with anode. The fibrous anode and cathode with diameters of 750 μm and 250 μm, respectively, are thick enough to reconnect by visual observation. The LIB can be assembled by the as-prepared cathode, anode and gel polymer together with the self-healing protective shell. The flexible and self-healable LIB has a capacity of 82.6 mAh g^{-1} under a series of deformation and retains 50.1 mAh g^{-1} after the 5^{th} healing process at a current density of 0.1 A g^{-1}. This work gives an essential strategy to design LIB for wearable devices.

1. Introduction

With the advancement of portable and wearable electronic devices, there is an increasing demand on the next-generation power systems, which should simultaneously possess specific features, such as high flexibility, lightweight, high energy density and long cycling life [1–6]. Obviously, conventional power sources cannot satisfy the desire owing to the bulk, rigidness, and inherent unalterable shapes [7–10].

Recently, numerous attempts have been made to exploit the state-of-the-art materials and products to fabricate and design flexible energy storage devices [11–18]. Among those strategies, fiber-shaped devices have advantages of flexibility, adaptability, miniaturization and weavability, attracting public attention to power wearable devices in the future. Especially, they are capable of accommodating extensively to not only the daily deformation like bending and folding, but also to complex and extreme shape changes as rolling and twisting [16,17,19–23]. As one of the most practical and powerful energy supply devices, lithium-ion battery (LIB) has been widely used in our daily life. Unfortunately, the LIB in a fiber shape remains challenging for the difficulty in arranging applicable electrode materials and electrode architectures at the same time. The general battery configuration of fibrous electrodes is usually designed with a parallel or helix structure while it cannot keep up with the trend of developing and utilizing the high-specific-capacity materials as the next-generation anode [23–28]. A major issue to be addressed is the capacity matching between the anode and the low-specific-capacity cathode material. Increasing the mass loading of the cathode seems a good solution, but it may have a negative influence on the flexible performance. From these points of view, it is highly desired and urgent to seek a way to find appropriate electrodes with a suitable design for the all-fiber-based LIB.

In order to ensure the lightweight and flexibility of devices, the general method for device packaging tends to make the protective sealing layer thinner and lighter. However, it may fail to withstand the occasional deformation and cutting, resulting in the damage to devices and even safety accident [29,30]. Lately, the self-healing polymer has been invented, which can recover the mechanical injuries and heal the damage by reconstructing the broken interface with chemical bonds or some other reaction [31,32]. It is believed that the self-healing polymer will be a promising encapsulation material, and many electronic devices with a self-healable layer have been designed [15,33–36]. Peng and his co-worker creatively fabricated a CNT-based planar (two dimensional, 2D) aqueous LIB with a self-healing ability. The self-

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https://doi.org/10.1016/j.nanoen.2018.06.067
Received 3 May 2018; Received in revised form 19 June 2018; Accepted 19 June 2018

healable polymer sufficiently shed the light on the potential for restoring structure fractures and keeping the integrity of devices [33]. Nevertheless, it is still too difficult to accurately reconnect the thin planar cross-section by naked eye, and the energy density of aqueous LIB remains far from satisfactory [15,35].

Taken those factors into consideration, building a 3D structural electrode with a self-healable encapsulation layer is a possible solution. 3D reduced graphene oxide (rGO) composite fiber has been widely applied since the unique features can synergistically enhance interaction with active materials [37,38]. On one hand, the active materials can mitigate the stacking of graphene caused by the intersheet π-π bond, and the activation tactics could control the microstructure of the rGO fiber, the prevalent nanopores, as well as the micropores, turn out to provide reservoirs in solvent/salt electrolyte systems [8,39–42]. On the other hand, the porous rGO substrate simultaneously promotes the flexible, thermal, mechanical and electrochemical performances of the electrode, offering an easy access to reach the higher surface area sites and minimize the ionic resistance [43–46]. In particular, most electrode material with high specific capacity suffer from large volumetric changes, unstable solid electrolyte interphase (SEI), leading to succeeding rapid capacity deterioration and unpleasing Coulombic Efficiency (CE). These disadvantages are originated from the recrystallization and lithiation/delithiation stress during the cyclic electrochemical process, which could also be alleviated by the introduction of grapheme [47–53]. Meanwhile, the nanoscale material (under 50 nm) with a highly conductive carbon support could increase a pseudocapacitive lithium storage ability thus consolidates rate and cycling performance [51,54,55]. More importantly, the self-healing shell could boost the mechanical strength and flexibility of 3D porous rGO fiber, making it possible to be restrained into various shapes and protect fiber electrodes from damages for specific electronic and mechanical devices [33–35].

Herein, we design and fabricate a self-healable all-fiber-based quasi-solid-state LIB by using the annealed spring-like $LiCoO_2$ nanopartiles@rGO (ASLG) fiber as cathode materials, the SnO_2 quantum dots@rGO (ASG) fiber as anode materials, the poly (vinylidenefluoride-co-hexafluoropropylene, PVDF-***co***-HFP) soaked in $LiClO_4$ with EDC/EC as gel electrolyte and a self-healable carboxylated polyurethane (PU) as package layer. The 3D porous ASG displays a good specific capacity of 846 mAh g^{-1}, and a great cyclic stability for a capacity retention up to

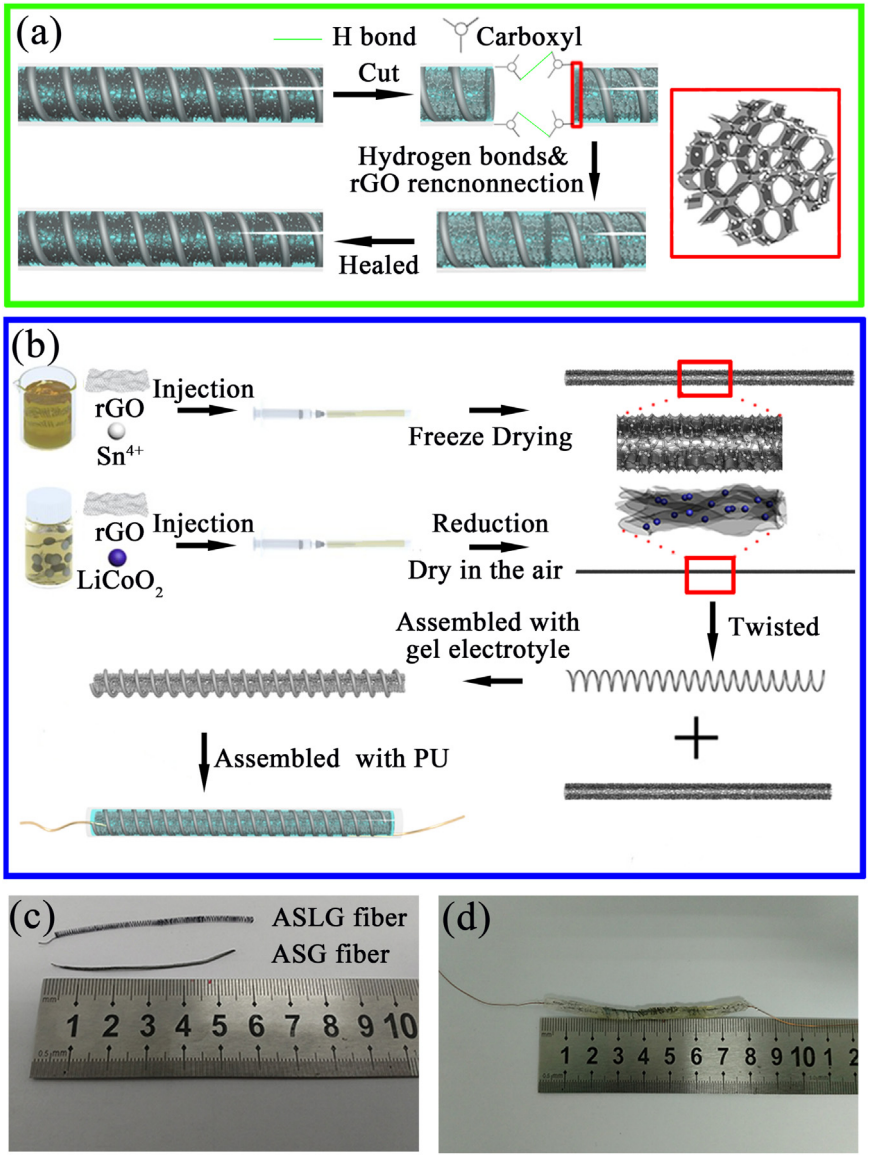

Fig. 1. Schematic illustration of the self-healing mechanism and the fabrication procedure of an all-fiber-based LIB. (a) Schematic diagrams for the self-healable mechanism of the fiber-shaped LIB with the PU packaging layer. (b) Schematic diagrams of the manufacturing steps for fibrous electrodes and assembly process of the LIB. (c) Photographs of ALSG fiber (up) and ASG fiber (down). (d) Optical image of an all-fiber quasi-solid-state LIB.