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Flexible and robust N-doped carbon nanofiber film encapsulating uniformly silica nanoparticles: Free-standing long-life and low-cost electrodes for Li- and Na-Ion batteries

Liye Li[a,b,1], Pengcheng Liu[a,b,*,1], Kongjun Zhu[a,*], Jing Wang[a], Guoan Tai[a], Jinsong Liu[a,b]

[a] State Key Laboratory of Mechanics and Control of Mechanical Structures, Nanjing University of Aeronautics and Astronautics, Nanjing 210016, China
[b] College of Materials Science and Technology, Nanjing University of Aeronautics and Astronautics, Nanjing 210016, China

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ABSTRACT

With the wearable electronics progressing rapidly, the demand for flexible, long-life and low-cost electrodes of Li-ion batteries (LIBs) becomes more and more urgent. Due to the abundant resources and low cost, silica (SiO_2), especially the amorphous one, has attracted a lot of interests on the application of anode materials for LIBs. However, SiO_2 still suffer from the poor cycling performance mainly caused by the huge volume change during cycling like other alloy-type materials. Furthermore, it remains a challenge to fabricate the SiO_2–based flexible electrode. Herein, we propose a facile in situ strategy to fabricate the electrospun robust free-standing SiO_2/carbon nanofibers (denoted as in-SCNFs) film constructed by N-doped carbon nanofibers encapsulating uniformly amorphous SiO_2 nanoparticles. The in situ synthesized finer SiO_2 nanoparticles in the in-SCNFs are uniformly encapsulated in flexible carbon nanofibers, which can effectively buffer the volume change. Furthermore, the robust in-SCNFs film possesses the excellent mechanical flexibility and strength. So, when served as the free-standing anode of LIBs, the in-SCNFs film exhibits superior cycling performance. A discharge specific capacity of 405 mAh/g can be delivered even after a long-term 1000 cycles at a large current density of 500 mA/g, and the retention is up to 115%. It is an exciting finding that the in-SCNFs film is also a long-life anode of Na-ion batteries (NIBs). The 99% of initial capacity can be kept after 250 cycles at 500 mA/g. To our best knowledge, this is the first report on the application of SiO_2/C composite for NIBs. These results suggest that the as-fabricated in-SCNFs film can become one promising free-standing long-life anode for LIBs and NIBs.

1. Introduction

With the wearable electronics, such as Apple Watch, progressing rapidly, the demand for flexible portable power sources is increasing [1–3]. Since Sony commercialized the first product, Li-ion batteries (LIBs), possessing the high energy density and light weight, have become proved to be the most ideal power sources for various portable electronics, and achieved huge development during the past decades [4–7]. Recently, another important storage technology, room-temperature Na-ion batteries (NIBs), has attracted more and more attention because of the abundant resources [8–11]. Currently, one important development tendency for both of LIBs and NIBs is to improve the cycling life of electrode materials, and cut down their cost [12–15]. Furthermore, to fabricate the better flexible energy storage devices, the development of mechanical flexible self-standing electrode is also especially urgent [16–19].

Metal oxides are one kind of promising alloy-type anode materials because of the large discharge specific capacity [20–22]. As a metal oxide, silica (SiO_2), one of the most abundant materials on Earth, has attracted more and more interests due to the quite low cost and availability [23–26]. The initial reports revealed that SiO_2 was inactive to Li due to its stability as an oxide when applied as the anode material for LIBs [23]. In recent studies, it was found that amorphous SiO_2 can possess Li reactivity [24,25]. However, due to the huge volume change during charging/discharging like other alloy-type metal oxides, SiO_2 also suffers from the poor

* Corresponding authors at: State Key Laboratory of Mechanics and Control of Mechanical Structures, Nanjing University of Aeronautics and Astronautics, Nanjing, 210016, China.
E-mail addresses: pch060710111@hotmail.com (P. Liu), kjzhu@nuaa.edu.cn (K. Zhu).
[1] Pengcheng Liu and Liye Li contributed equally to this work.

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cycling performance [22]. Synthesizing nano-scale materials and building the carbon buffering layer are two quite effective methods to reduce the volume change, and thereby improve the cycling life [20,27–29]. For example, Cui et al. [20] synthesized the Si nanowires with enhanced cycling performance. They further developed another yolk-shell nanostructure constructed by Si nanoparticles core and carbon shell, which exhibited better cycling performance [30]. Nevertheless, for SiO_2, it remains a huge challenge to simultaneously realize the uniform nanomaterials synthesis, carbon coating, and flexible electrode fabrication.

Electrospinning technique is a promising method to fabricate the 1D carbon nanofibers and their composites [31–36]. Especially, the metal oxides/carbon composite nanofibers can be easily synthesized by electrospinning [34,37,38]. It is a key point to uniformly distribute the nanomaterials in carbon nanofibers. Kang et al. [32] designed and synthesized bubble-nanorod-structured Fe_2O_3-carbon nanofibers, in which Fe_2O_3 nanomaterials were uniformly distributed in carbon nanofibers so that the cycling performance was highly enhanced. The electrospinning is also an effective method to fabricate the flexible self-standing carbon-based film [39–41]. Such self-standing film can be directly used as electrode without adding inactive binder, carbon black, and metal substrate, so that the electrode can possess the lighter weight, higher conductivity, and better electrochemical performance. For example, Lou et al. [42] obtained the free-standing nitrogen-doped carbon nanofiber films by using PAA as precursor, which possess the ultra-long cycling life for NIBs. Wang et al. [43] synthesized electrospun self-standing Sb/C fibers film, and it exhibited quite stable cycling for NIBs. Furthermore, recently, Pintauro and Self et al. [44–46] reveal that the electrospinning technology is also a quite potential strategy to greatly improve the electrode's areal and volumetric capacities, especially at high C-rates, which are important measures for the applications with a limited battery space and high loading, such as electric vehicle propulsion. The free-standing mats electrodes of TiO_2/PAA, carbon nanoparticles/PVDF and $LiCoO_2$/PVDF fibers have been successfully fabricated respectively, and exhibit high areal and volumetric specific capacities at high C-rates [44–46]. However, to our best of knowledge, the reports on the free-standing SiO_2/carbon anode materials fabricated by electrospinning for LIBs and NIBs are quite limited.

Herein, we propose a facile in situ strategy to fabricate the electrospun robust free-standing silica/carbon nanofibers (denoted as in-SCNFs) film (in situ strategy in Fig. 1), which is constructed by N-doped carbon nanofibers encapsulating uniformly amorphous SiO_2 nanoparticles, by taking TEOS and PAN as resources of SiO_2 and carbon, respectively. For better comparison, another ex situ fabricated silica/carbon nanofibers (denoted as ex-SCNFs) film was synthesized by taking amorphous SiO_2 nanoparticles as the resource (ex situ strategy in Fig. 1). Compared with ex-SCNFs, the finer SiO_2 nanoparticles, which can further reduce the volume change, are in situ synthesized in in-SCNFs. Moreover, these in situ synthesized SiO_2 nanoparticles are more uniformly encapsulated in carbon nanofibers, so that the carbon nanofibers matrix can not only improve the conductivity, but also serve as a buffering layer to release the volume change of SiO_2. Furthermore, the as-synthesized in-SCNFs film possesses excellent mechanical flexibility and intensity. So, the in-SCNFs film exhibits superior cycling performance. When the in-SCNFs film is applied as the anode of LIBs, no capacity fading can be found even after long-term 1000 cycles. Moreover, we also find that the in-SCNFs film is also a promising long-life anode of NIBs, which is the first report on the application of SiO_2/C composite for NIBs.

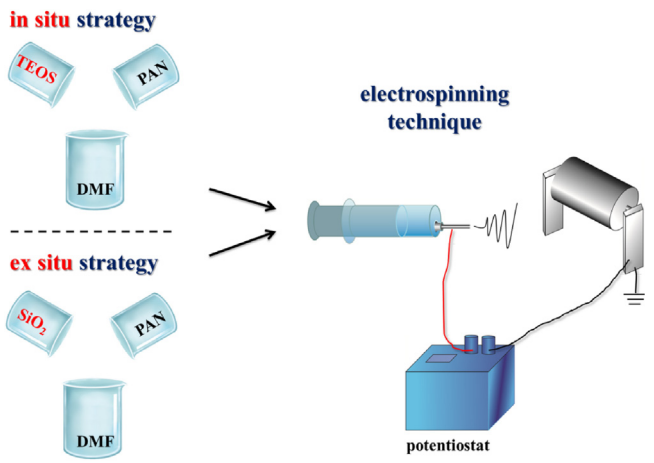

Fig. 1. Schematic illustration of electrospinning synthesis for in-SCNFs and ex-SCNFs films.

2. Experimental

2.1. Materials

SiO_2 nanoparticles (50 nm) and tetraethyl orthosilicate (TEOS) were purchased from Aladdin. Dimethylformamide (DMF) and polyacrylonitrile (PAN) (Mw = 150000 g mol−1) were purchased from Sigma-Aldrich. All chemical reagents are analytical grade and used without further purification.

2.2. Preparation of in-SCNFs film

The in-SCNFs film was fabricated by the in situ strategy in Fig. 1. TEOS and PAN are taken as resources of SiO_2 and carbon. 0.25 g of TEOS was added in 5 g of DMF at 60 °C with intense magnetic stirring for 10 min to obtain homogeneous solutions. After that, 0.5 g PAN was added into the above solutions and continue stirring for 12 h (the mass ratio of PAN and TEOS was 2:1). Electrospinning was conducted at 15 kV using a glass syringe with a flat needle and a feeding speed of 0.5 ml h-1. The distance between the tip of the needle and the collector was 15 cm. The as-spun TEOS/PAN fibrous membranes were then stabilized under 280 °C for 2 h in an air atmosphere at a heating rate of 5 °C/min. Next, the films were carbonized in a tube furnace at 800 °C for 2 h in Ar,H_2 (vol%: vol % = 95: 5) atmosphere at a heating rate of 5 °C/min. Finally, the as-fabricated product was denoted as in-SCNFs film. To investigate the effects of temperature on the morphology and electrochemical properties, different carbonized temperature (500 °C, 1000 °C) were adopted.

2.3. Preparation of ex-SCNFs film

To fabricate the ex-SCNFs film, the TEOS was replaced by SiO_2 nanoparticles with same SiO_2 content and other process unchanged (the ex situ strategy of Fig. 1).

2.4. Preparation of pure carbon nanofibers film

To fabricate the pure carbon nanofibers film, the TEOS was removed with other process same as the fabrication of in-SCNFs film.

2.5. Structural Characterization

The morphology and microstructure of carbonized fibers were observed by field emission scanning electron microscopy (FE-SEM, HITACHI S-4800, Japan) and transmission electron microscopy