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Electrospinning Sn@C nanofibers for high-performance flexible lithium ion battery anodes

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Abstract. Lithium ion batteries are considered as one of the most important energy storage devices in the field of portable electronics and electric vehicles. However, exploring novel and high-performance electrode materials are still urgently needed, as the state-of-the-art lithium ion batteries cannot meet the ever-increasing demand for high energy/power densities. Metal tin and its oxides are promising lithium ion battery anodes, but suffering from drastic volume change and crack issues during lithium intercalation/deintercalation cycling. Here we report a feasible technology to fabricate flexible and free-standing Sn@C nanofiber membrane via electrospinning method, consisting of one dimensional carbon matrix with Sn nanoparticles confined inside. Owing to the superior electron/ion transfer ability and confinement effect from the carbon coating, the as-obtained Sn@C electrode exhibits a capacity of 668 mA h g⁻¹ at 1 A g⁻¹ even after 350 cycles and a reversible capacity of 263 mA h g⁻¹ can be achieved at an ultrahigh current density of 10 A g⁻¹. In all, this work provides a promising anode for practical application on lithium ion batteries.

1. Introduction

Lithium ion batteries (LIBs) have attracted great attention to power portable electronics and electric vehicles due to its high energy and power density, good safety and long cycle life [1, 2]. Conventional graphite anode material has only a theoretical capacity of 372 mAh g⁻¹, which cannot meet the ever-increasing demand of the energy and power densities of lithium ion batteries [3]. In this case, developing new kinds of anode material with higher theoretical capacity is urgently required [4]. Metallic tin has emerged as an alternative anode material in view of its high theoretical capacity (993 mAh g⁻¹ with 4.4 Li per Sn atom), low potential for Li⁺ intercalation, low material cost, nontoxic and abundant element characteristics [5, 6]. However, the poor rate and cycle capabilities and rapid capacity deterioration induced by the large volume change (~300%) and severe pulverization during Li-ion intercalation/deintercalation have hindered its application in LIBs [7, 8]. Various methods have been used to mitigate the problems, including adopting Sn-based alloys [9], nanostructure modification [8, 10], 3D array of Sn nanorods, compositing Sn with conductive matrix [11, 12] and so on. One of the most widely employed approaches to solve this problems is reducing the particle size of Sn [13]. However, particle aggregation occurs during long term cycling. Therefore, confining active materials into carbon matrix is an effective way to solve this aggregation problem. Free-standing electrode films are attractive as they can be directly used without additional slurry coating, and eliminate the use of



current collectors or binders when assembled into cells [14], which can improve the energy density of the LIBs. To fabricate free-standing electrodes and confine the active material inside the carbon matrix, a promising way is to use the electrospinning method, which can be used to fabricate fibrous structures [15] and to coat active materials with carbon by calcination [16]. Owing to the uniform structure, oriented electronic/ionic transport pathway, and strong tolerance to stress change, the fibrous carbon nanostructures show superior electrochemical performance [17, 18]. Here we fabricated a free-standing flexible carbon-coated tin (Sn@C) nanofiber anode for lithium ion batteries using the electrospinning method, followed by heat treatment in Ar atmosphere. We controlled the ratio of tin acetate (SnAc) as the precursor of Sn and polyacrylonitrile (PAN) as the precursor of C. The fibrous structure can effectively reduce the ion diffusion length and improve the rate performance of electrodes [19, 20]. Moreover, the large surface area of the nanofibers can improve the electrode/electrolyte contact area, which is beneficial for enhancing the electrochemically active sites [21]. The carbon coating can accommodate the large volume change during charge and discharge, which can suppress the pulverization of active material and mitigate capacity fading [22-24]. Notably, the as-prepared nanofibers can be directly used as the anode without involving binder or current collector. The Sn@C electrode exhibited a high cycling stability at 1 A g^{-1} for 350 cycles with a final specific capacity of 668 mA h g^{-1} and ultrahigh rate capability at 10 A g^{-1} with a specific capacity of 263 mA h g^{-1} , suggesting promising future for practical application.

2. Experimental

2.1. Synthesis of the polymer fibers

Firstly, polyacrylonitrile (PAN) (6 wt%) was dissolved in N,N-dimethylformamide (DMF) using magnetic stirring at 70°C for 6 hours; then, various amount of tin acetate (SnAc) (4 wt%, 5 wt%, 6 wt%) was dissolved in the above-prepared solution followed by magnetic stirring overnight at 70°C , after which a viscous light yellow precursor solution was obtained. The precursor solution was then loaded into a 10 mL plastic syringe with a 21-gauge needle at a flow rate of 0.5 mL h^{-1} (controlled by a syringe pump). The metallic needle was connected to a high voltage power supply, and a piece of aluminium foil was placed on the collector. The distance between the needle and the aluminium foil was 15 cm. A voltage of 18 kV was applied between the needles and the aluminium foil. The polymer fiber membrane can be directly peeled off from the aluminium foil after electrospinning.

2.2. Carbonization of the polymer fibers

After drying at 60°C for 12h, the as-collected polymer fiber membrane was calcinated in a tube furnace under the argon atmosphere at 250°C for 2 hours with a heating rate of 2°C min^{-1} , then the temperature was increased from 250°C to 700°C with a heating rate of 5°C min^{-1} and the temperature was held at 700°C for 2 hours.

2.3. Fabrication of the battery

The electrochemical measurements were carried out using CR2032 coin cells. The carbonized fiber was cut into free-standing circled electrodes. The electrodes were dried at 110°C overnight before assembly. The coin cells were assembled in an Ar-filled glove box with moisture and oxygen concentrations below 0.1 ppm. Lithium foil was used as the anode, and a solution of LiPF_6 (1 M) in EC/DMC/EMC (1:1:1 vol/vol/vol) with 10.0% FEC was used as the electrolyte. The commercial microporous membrane (Celgard 2500) was used as the separator.

2.4. Materials characterizations and electrochemical measurements

The morphologies of the electrospun fiber and the carbonized fiber were characterized by scanning electron microscopy (SEM, ZEISS SUPRA 55, 5 kV, Germany). The structure of the samples was studied by X-ray diffraction (XRD, RINT2000V/PC, Bruker DS, Germany). Galvanostatic charge-

discharge measurements were carried out on a LAND battery testing working station between 0.01 V and 3 V.

3. Results and discussion

The Sn@C nanofibers were prepared by a single-nozzle electrospinning method. The precursor with different ratio of SnAc (4 wt%, 5 wt%, 6 wt%) and PAN (6 wt%) was fed through a spinneret by a syringe pump, and the precursor droplets were elongated and stretched under high voltage to form nanofibers. The following carbonization process was accomplished in Ar atmosphere at 750°C. The photographic image of the flexible and free-standing electrode after carbonization is shown in fig. 1(a). The crystal structure of the carbonized nanofibers was characterized using X-ray diffraction. As shown in fig. 1(b), the majority of the diffractions were assigned to Sn metal, while some weak peaks can be indexed to SnO.

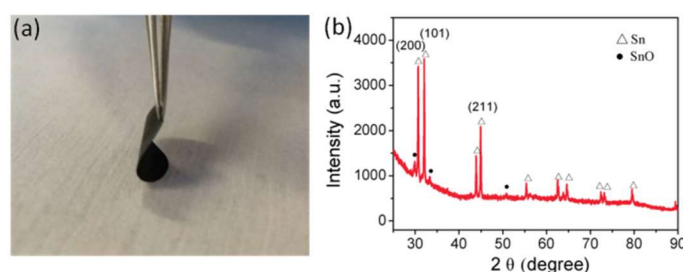


Figure 1. (a) Photographic image of the free-standing, flexible Sn@C electrode, (b) XRD of Sn@C electrode.

The morphology of the electrospun nanofibers was characterized by scanning electron microscopy (SEM). As shown in fig. 2(a-f), the individual and uniform nanofibers presented rough surface, and the diameter of the nanofiber with 4 wt% SnAc was 270 nm (fig. 2(a), (b)), while the diameter for the fiber with 5 wt% SnAc and 6 wt% SnAc as precursor was 200 nm (fig. 2(c), (d)) and 100 nm (fig. 2(e), (f)), respectively. The diameter of the fiber decreased with the increasing amount of SnAc.

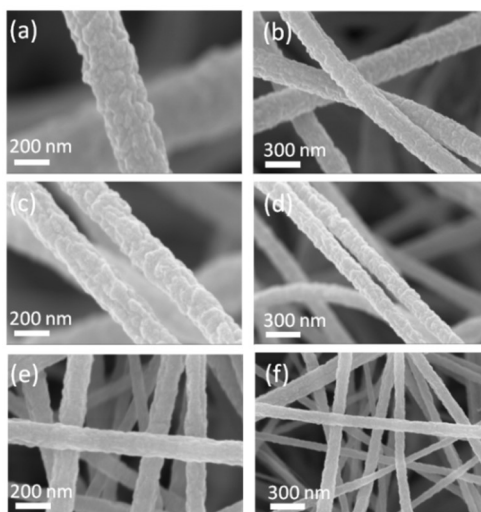


Figure 2. The SEM images of the fibers after electrospinning with different ratio of precursor: (a), (b) 4 wt% SnAc, 6 wt% PAN, (c), (d) 5 wt% SnAc, 6 wt% PAN, (e), (f) 6 wt% SnAc, 6 wt% PAN.

The as-obtained nanofibers were then carbonized in Ar under 750°C to complete the calcinations process. Fig. 3(a-f) shows the morphology of the fibers after carbonization. As can be seen, the surface of the carbonized nanofibers became smooth and with the increasing amount of SnAc, the diameter of the nanofibers decreased and more particles permeated out from the fibers and agglomerated after carbonization. The leakage of the particles can lead to the decrease of the electrochemical performance.

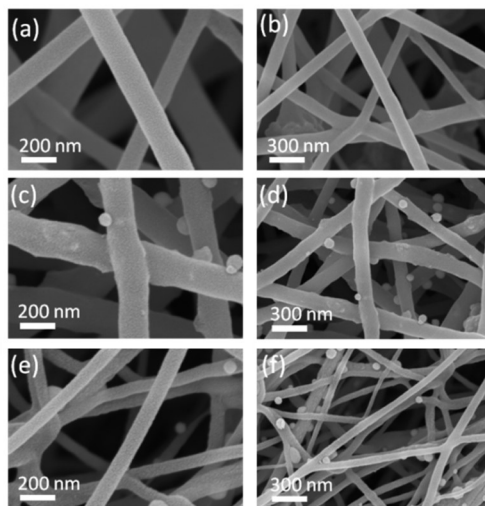


Figure 3. The morphology of the nanofibers with different ratio of precursors after carbonization: (a), (b) 4 wt% SnAc, 6 wt% PAN, (c), (d) 5 wt% SnAc, 6 wt% PAN, (e), (f) 6 wt% SnAc, 6 wt% PAN.

The long-term cycle performance of the Sn@C electrode with different ratio of the SnAc precursor at a current density of 1 A g⁻¹ is shown in fig. 4(a), (c) and (e). The electrode with 4 wt% SnAc precursor showed the highest specific capacity and most stable cycle performance. In the first cycle, the electrode with 4 wt% SnAc precursor displayed a discharge capacity of 1158 mA h g⁻¹ and after 350 cycles, a specific capacity of 668 mA h g⁻¹ was still maintained. The electrode with 5 wt% SnAc precursor displayed a discharge capacity of 1071.7 mA h g⁻¹, but during the cycle, it showed an upward trend and only maintained a discharge capacity of 446 mA h g⁻¹ after 300 cycles. Similarly, the electrode with 6 wt% SnAc precursor only had an initial discharge capacity of 1001 mA h g⁻¹ and after 300 cycles the discharge capacity dropped to 440 mA h g⁻¹.

The rate performance of the Sn@C electrode is shown in fig. 4(b), (d) and (f). When the current densities increased from 0.5 to 1, 1.5, 2, 2.5, 3, 3.5, 5 and 10 A g⁻¹, the electrode with 4wt% SnAc displayed a high reversible capacity from 740 mA h g⁻¹ at 0.5 A g⁻¹, 674 mA h g⁻¹ at 1 A g⁻¹, 637 mA h g⁻¹ at 1.5 A g⁻¹, 441 mA h g⁻¹ at 5 A g⁻¹, 263 mA h g⁻¹ at 10 A g⁻¹, and 710 mA h g⁻¹ after 90 cycles to the initial current density of 0.5 A g⁻¹, maintaining a capacity retention of 96%. By contrast, the electrode with 5 wt% SnAc and 6 wt% SnAc delivered capacity retention of 84% and 88%, respectively, both lower than that of the electrode with 4 wt% SnAc precursor.

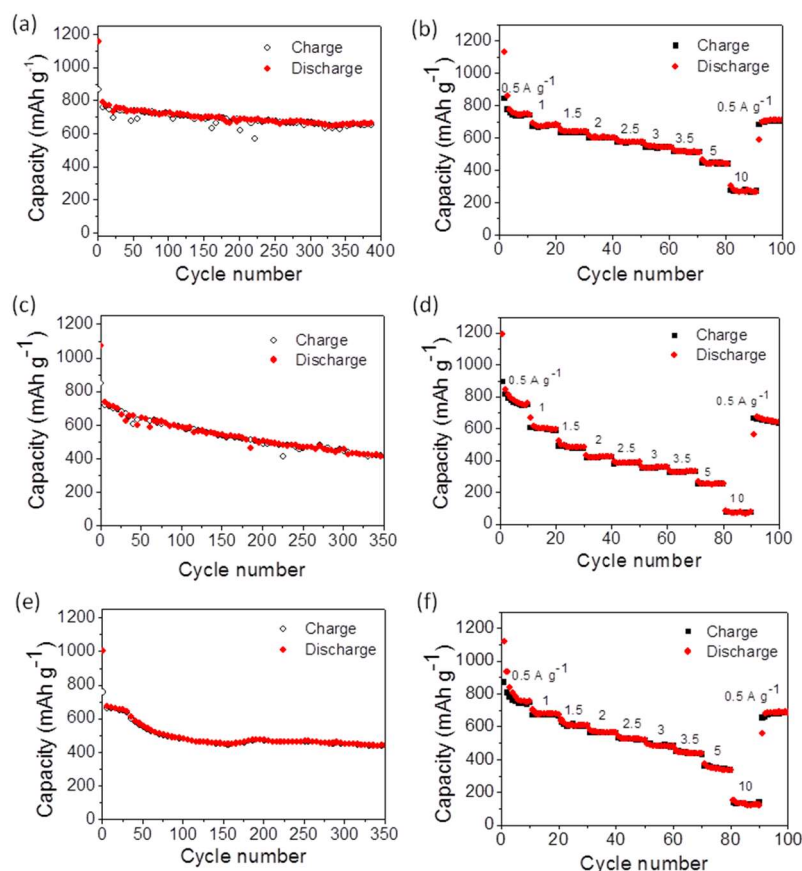


Figure 4. The cycle performance of the electrode at 1 A g⁻¹ with (a) 4 wt% SnAc, (c) 5 wt% SnAc, (e) 6 wt% SnAc as precursor; The rate performance of the electrode with (b) 4 wt% SnAc, (d) 5 wt% SnAc, (f) 6 wt% SnAc as precursor.

The superior performance of the electrode with 4 wt% SnAc as the precursor can be attributed to the uniform carbon fiber matrix without the leakage of active material, which can well accommodate the volume change and release the stress generated during long term cycling to suppress the pulverization and capacity fading. Furthermore, the fibrous structure can effectively decrease the ion diffusion length to increase the rate performance. The large surface area of the nanofibers can also increase the electrode/electrolyte contact area and benefit for the access of ion to active materials.

Hence, high cyclic and rate performance can be achieved from the electrospun Sn@C nanofiber electrode, which provides a promising anode for lithium ion batteries.

4. Conclusion

In conclusion, we have successfully fabricated a high-cycle-stability and high-rate-performance Sn@C anode for lithium ion batteries. The uniform carbon fibers membrane fabricated by electrospinning method with active material confined inside was used directly as the electrode without the involvement of current collectors or additives. The uniform carbon coating can increase the electrode/electrolyte contact area, which is beneficial for the access to electrochemically active surface. Additionally, the fibrous structure can effectively reduce the ion diffusion length and improve the rate performance. The pulverization and capacity fading were largely suppressed due to the uniform carbon coating. We designed three electrospinning conditions to control the electrochemical performance. The free-standing Sn@C electrode with 4 wt% SnAc and 6 wt% PAN precursor exhibited a smooth surface without leakage after carbonization. Notably, the Sn@C electrode displayed a high specific capacity of 668 mA

h g^{-1} after 350 cycles at 1 A g^{-1} and a reversible capacity of 263 mA h g^{-1} can be achieved at an ultrahigh current density of 10 A g^{-1} . This work can provide new insights into fabricating new electrode structures for lithium ion batteries.

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