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The effects of electrospinning parameters on coaxial Sn/C nanofibers: Morphology and lithium storage performance

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ABSTRACT

For tin-based anode materials that suffer from poor cycling stability due to severe volume changes upon lithiation/delithiation processes, the morphology control method might provide a solution. Today, coaxial core-shell structure has attracted wide attention due to its ability to accommodate the volume changes of tin (core), which is well encapsulated in the carbon matrix (shell). Coaxial electrospinning is a simple and effective method to prepare this kind of material. In this work, tin was dispersed in the carbon core and then coated a carbon shell to form Sn@C/C nanofibers by coaxial electrospinning. Flow ratio and tin content were investigated as two main critical factors for controlling the core/shell structure, so as to improve the cycling preference of tin anodes. When tested as a lithium-ion battery anode, the material not only showed higher reversible specific capacity (626 mAh g^{-1}) than pure carbon nanofibers, but also exhibited better cycling performance (50 cycles with 73% capacity retention), indicating that the volume change problem of tin anodes has been well resolved by this morphology control.

1. Introduction

Tin-based materials for lithium-ion batteries have the superiority of high capacity and low cost, which are attractive to the next-generation lithium-ion battery anode [1–3]. However, the large volume changes during lithiation and delithiation processes and the resultant capacity loss seriously restrict their practical application in lithium-ion batteries [4,5]. In order to overcome the significant capacity fade, one effective approach is morphology control [6–8], and core/shell structure is promising to overcome the unstable cycling problem. In this structure, the core is typically the major component, *i.e.*, tin or tin-based materials with functional properties; while the shell surrounding the core acts as a protection layer [9,10]. As for the shell material, carbon is considered an ideal coating candidate due to its high electronic conductivity and considerable flexibility [11–13].

So far, several methods have been developed to fabricate tin/carbon core/shell structure materials, including hydrothermal synthesis [14], solvothermal method [15], chemical vapor deposition [16], self-assembly [17], and coaxial electrospinning[18,19], etc. Among these methods, coaxial electrospinning is a simple and low-cost approach to achieve a core/shell nanofiber structure and has attracted much attention [20,21]. The structure of core/shell nanofibers can be manipulated by selectively adjusting solution properties and operating parameters [22,23]. In general, the diameter of electrospun jet is strongly correlated with the solution flow rate, but has a relatively weaker dependence on the solution properties, as described below [24],

$$D \sim Q_t^{1/2}(k\gamma)^{-1/6} \tag{1}$$

where D is the jet diameter, Q_t the flow rate of the electrospinning solution, γ the solution surface tension, k the solution conductivity. In coaxial electrospinning, the flow rate Q_t can be treated as the sum of the core flow rate (Q_c) and the shell flow rate (Q_s) [25].

This study aims to control the ratio of core and shell flow rates to obtain core/shell nanofibers with controlled fiber diameter and morphology for use as advanced anodes in lithium-ion batteries. The core/shell nanofibers have tindispersed carbon core, wrapped with carbon shell, and they are denoted as Sn@C/C nanofibers, where "@" and "/" symbolize simple mixture and core/shell structure, respectively. The mass flow ratio of core and shell solutions, as well as the ratio of tin and carbon in the core, are carefully controlled to achieve desired electrochemical performance. Results

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demonstrate that the Sn@C/C core/shell nanofiber structure can offer sufficient expansion space, enhanced electronic transport framework, and hence improved cycling stability.

2. Experimental

2.1. Preparation of Sn@C/C nanofibers

Stannic chloride pentahydrate ($SnCl_4{\cdot}5H_2O$, Aldrich) and polyacrylonitrile (PAN, Pfaltz & Bauer Inc., 150,000 g mol^{-1}) were used as Sn and C precursors, respectively. Two core solutions were prepared by adding $SnCl_4{\cdot}5H_2O$ into 8 wt. % PAN in N, N-dimethylformamide (DMF, Aldrich), with different $SnCl_4{\cdot}5H_2O$:PAN weight ratios of 1:1 and 1:2, respectively. The shell solution was prepared by adding 8 wt. % PAN in DMF. All solutions

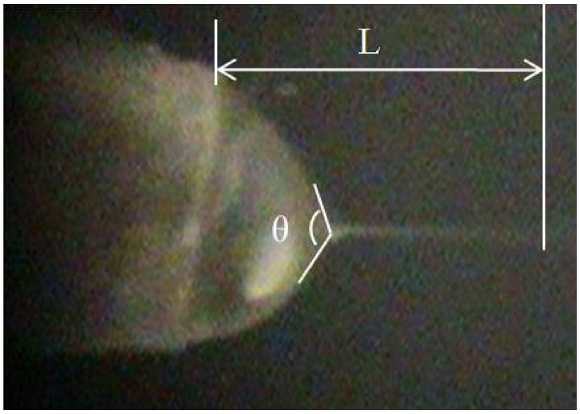

Fig. 1. Photograph of the Taylor cone during coaxial electrospinning.

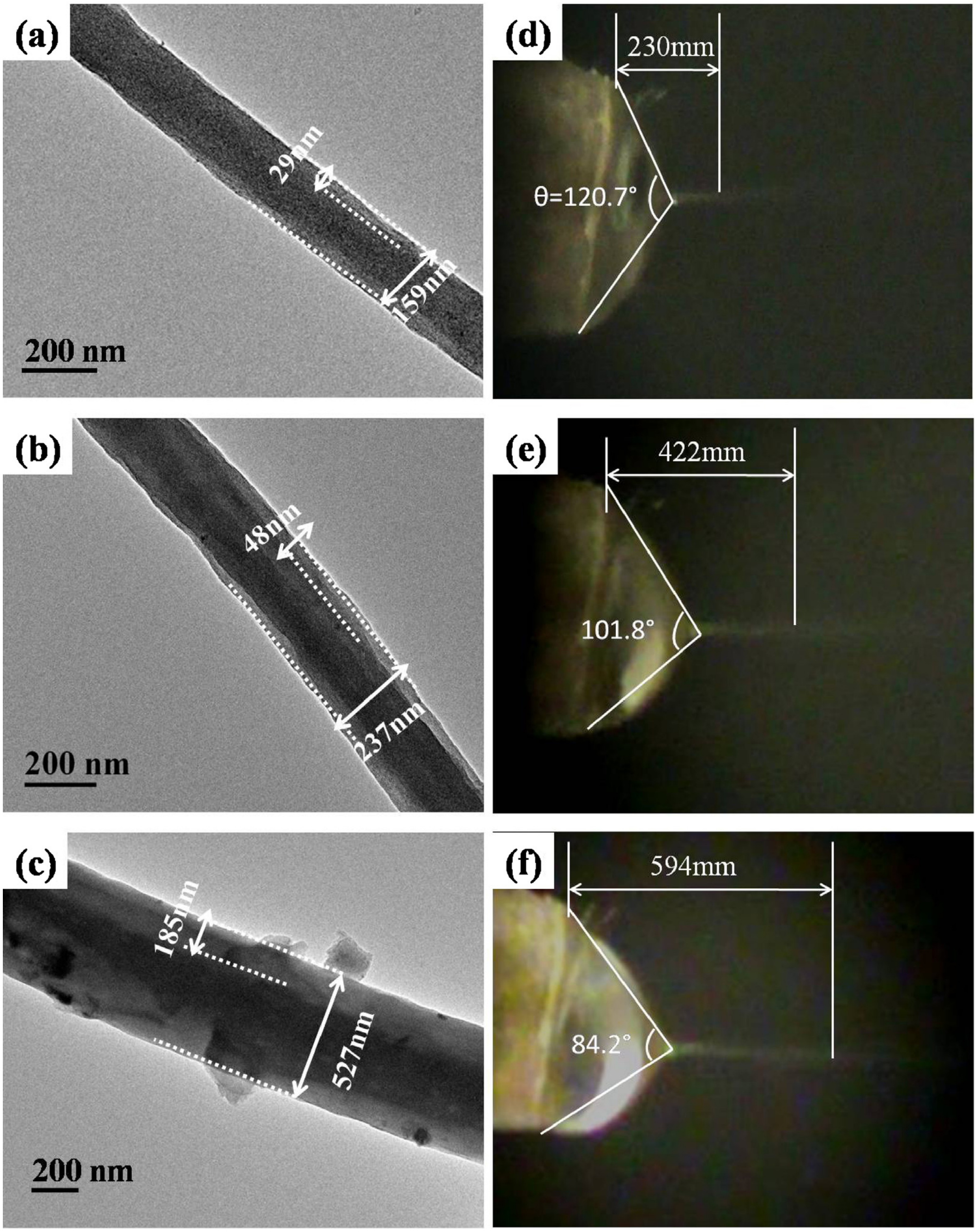

Fig. 2. TEM images and photographs of Sn@C/C (I) nanofibers prepared using different flow ratios of (a,d) 1:1, (b,e) 1:2, and (c,f) 1:3.