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A comparative study on the performance of binary SnO_2/NiO/C and Sn/C composite nanofibers as alternative anode materials for lithium ion batteries

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ABSTRACT

The development of alternative anode materials out of flexible composite nanofibers has seen a growing interest. In this paper, binary carbon nanofiber electrodes of SnO_2/NiO and Sn nanoparticles are produced using a scalable technique, Forcespinning (FS), and subsequent thermal treatment (carbonization). The Sn/C composite nanofibers were porous and flexible, while the SnO_2/NiO composite nanofibers had “hairy-like” particles and pores on the fiber strands. The nanofiber preparation process involved the FS of Sn/PAN and SnO_2/NiO/PAN solution precursors into nanofibers and subsequent stabilization in air at 280 °C and calcination at 800 °C under an inert atmosphere. The flexible composite nanofibers were directly used as working electrodes in lithium-ion batteries without a current collector, conducting additives, or binder. The electrochemical performance of the SnO_2/NiO/C and Sn/C composite fiber anodes showed a comparable cycle performance of about 675 $mAhg^{-1}$ after 100 cycles. However, the SnO_2/NiO/C electrode exhibited a better rate performance than the Sn/C composite anode and was able to recover its capacity after charging with a higher current density. A postmortem analysis of the composite nanofiber electrode after the aging process revealed a heavily passivated electrode from the electrolyte decomposition by-products. The synthesis and processing methods used to produce these composite nanofibers clearly were a factor for the high rate capability and excellent cycle performance of these binary composite electrodes, largely on the account of the unique structure and properties of the composite nanofibers.

1. Introduction

The use of nanostructured materials for energy storage devices has been the trend in recent years. Nanostructured fibers made from metals, metal oxides, ceramics, and composites have been developed for use in various energy storage devices. The popularity of these nanostructured fibrous materials stem from their many attributes: controllable fiber diameter, high surface area- to-volume ratio, low density, and high pore volume [1,2]. These properties make the nanofiber structure advantageous compared to their powder, crystal, nanowire, thin film, etc. counterparts [3,4], when used as electrodes in lithium ion batteries (LIB). These nano fibrous metal/metal oxides and ceramic composite electrodes deliver a comparable electrochemical performance including: a stable cycle performance, enhanced capacity, and superior low temperature performance [5,6]. These improved properties/ performances of composite nanofibers are often attributed to the non-woven structure that gives the nanofibers its high labyrinth-like porous structure, good high surface and interfacial areas resulting in a short-diffusion distance of Li-ions (Li^+) during the charge/discharge cycles. These physical characteristics lead to the creation of more reactive sites while the porous structure provides the buffering effect to accommodate the large volume changes often associated with the alloying/de-alloying of lithium with these metal/metal oxide and ceramic composite compounds [7,8].

Tin (Sn)-based derivatives such as tin oxides, tin sulfides, and stannates have become attractive anode materials for LIBs [9–11].

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The popularity of these Sn-based lithium alloys stem from their properties that include the ability to inhibit solvent co-intercalation and significant improvement in electrochemical performance over the commercial graphite anode in LIBs [12,13]. In addition, these Sn-based/carbon nanofiber composites are easy to process and exhibit a lower potential hysteresis compared to other transition metal oxides [14,15]. The crystal structure of Sn has the ability to host a higher amount of lithium ions, i.e. about four (4) atoms (i.e. Li_xSn, $0 < X \leq 4.4$) compared to carbonaceous anode (i.e. $LixC_6$, $0 < X \leq 1$) thereby giving Sn-based/C composite nanofibers a higher lithium storage capacity. Typically, the Sn-based/C nanofiber composite electrodes show a reversible capacity between 800 $mAhg^{-1}$ and 600 $mAhg^{-1}$ even at a higher current density of 200 mAg^{-1}–1 Ag^{-1} [8,16]. The electrochemical performance has been found to largely depend on the carbonization temperature which tends to have a direct impact on the fiber morphology, structure, and the pore distribution [8].

Ternary composites of Sn/CNFs containing other metals and their oxides have been investigated and shown to further improve the conductivity and the cyclic and rate performance of the composite electrode. Tin-based ternary composites such as SnO_2/ZnO heterogeneous nanofibers [17,18], Nitrogen doped CNFs with Sn quantum dots [19], Co-Sn alloy carbon nanofibers [20], and Fe_3O_4/SnO_2 coaxial nanofibers [21] have been reported to enhance the electrochemical performance when used as anodes in LIBs. For instance, the N-doped Sn/CNF's, provides fast and versatile electrolyte transport and can act as efficient electron transport pathways and stable mechanical supports to keep the structural integrity of the electrodes during cycling [19]. On the other hand, the Cobalt in Sn/CNFs reduces the volume expansion and enhances the electrical conductivity of the electrode [2]. In this paper, we compare the electrochemical performance of Sn-particles/carbon composite nanofibers with that of SnO_2/NiO binary carbon composite nanofibers. These composite nanofibers are considered potential alternative anodes for LIBs. The composite nanofibers were prepared using a facile technique known as Forcespinnning® (FS) that was recently developed at UTPA [22]. Several methods can be used to produce nanofibers such as electrospinning [23], liquid shearing method [24], centrifugal and/or rotary jet-spinning [25,26], electrospray [27], touch-brush spinning [28] and reactive magnetospinning [29]. The FS method is the trade name of the centrifugal spinning method that has been recently used to produce fibers for energy storage [30–34] and biomedical applications [35] .The centrifugal spinning process was originally

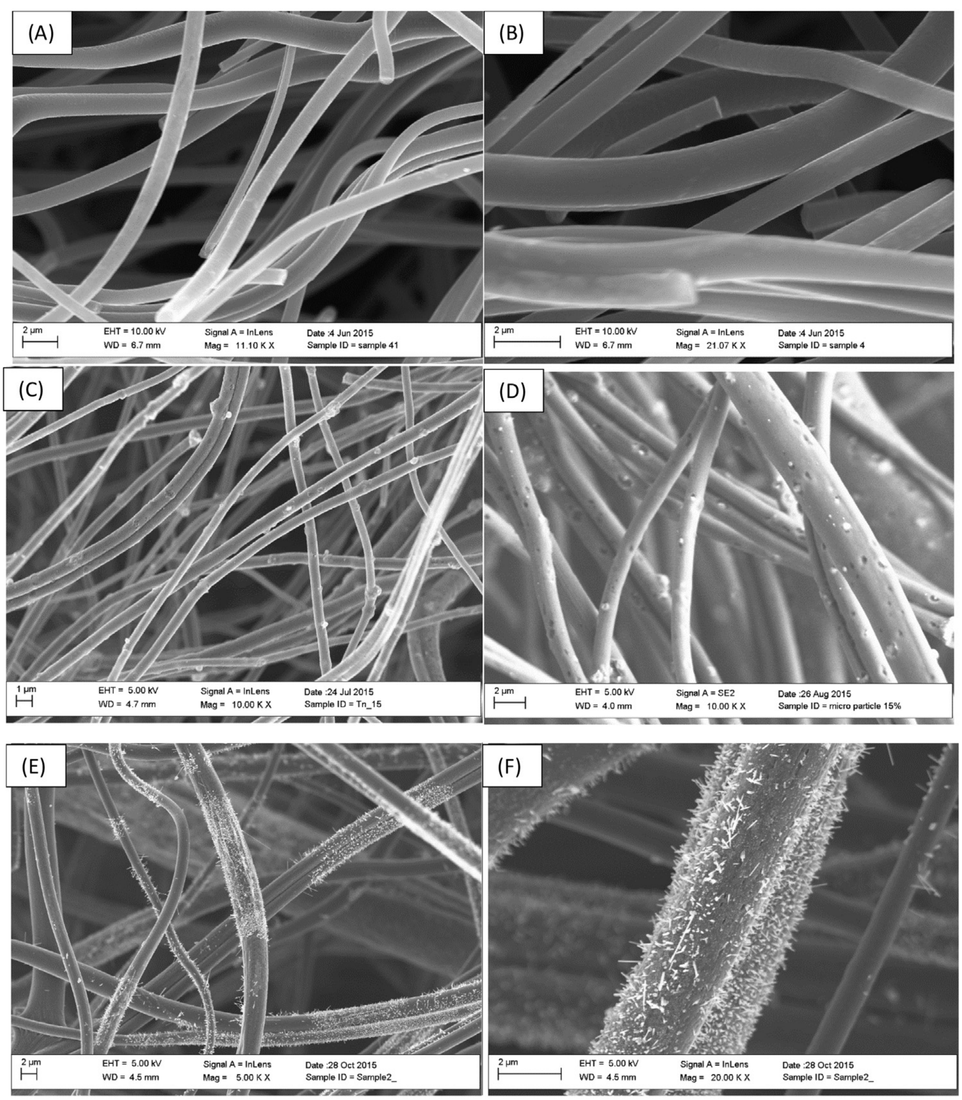

Fig. 1. SEM images of solid carbon fiber (a,b), Sn/CNFs composite fibers (c,d) with nanoparticles of the Sn sttached to the fibers strands and pores distributed evenly. SnO_2/NiO/CNFs composite fibers at different magnification showing unform fiber mat (e.f), and fiber strands with nanoparticles of the SnO_2 and NiO attached to the fibers strands in a hair-like structure with pores distributed evenly.