Short communication

# Tin nanoparticle-loaded porous carbon nanofiber composite anodes for high current lithium-ion batteries

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## HIGHLIGHTS

- Sn nanoparticle-loaded porous and nonporous CNF anodes are introduced.
- A porous structure was formed by the volatilization of mineral oil.
- The morphology exhibits nanosized Sn dispersed in porous CNF uniformly.
- Ultra-disperse Sn and porous CNF led to high capacity in high current.

## ARTICLE INFO

## ABSTRACT

Metallic Sn is a promising high-capacity anode material for use in lithium-ion batteries (LIBs), but its huge volume variation during lithium ion insertion/extraction typically results in poor cycling stability. To address this, we demonstrate the fabrication of Sn nanoparticle-loaded porous carbon nanofiber (Sn-PCNF) composites *via* the electrospinning of Sn(II) acetate/mineral oil/polyacrylonitrile precursors in *N,N*-dimethylformamide solvent and their subsequent carbonization at 700 °C under an argon atmosphere. This is shown to result in an even distribution of pores on the surface of the nanofibers, allowing the Sn-PCNF composite to be used directly as an anode in lithium-ion batteries without the need to add non-active materials such as polymer binders or electrical conductors. With a discharge capacity of around 774 mA h g$^{-1}$ achieved at a high current of 0.8 A g$^{-1}$ over 200 cycles, this material clearly has a high rate capability and excellent cyclic stability, and thanks to its unique structure and properties, is an excellent candidate for use as an anode material in high-current rechargeable lithium-ion batteries.

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## 1. Introduction

Lithium-ion batteries (LIBs) have attracted increasing research interest over recent years due to their superior energy density, operating voltage and cycle life when compared with the majority of other rechargeable battery technologies [1]. However, although the graphite used as an anode material in commercial LIBs offers stable cycling performance and low cost [2], its low theoretical capacity (372 mA h g$^{-1}$) greatly limits its further application in future applications [3,4]. Accordingly, metallic Sn in the form of a Li$_{4.4}$Sn alloy has been proposed as a more suitable anode material based on its much higher theoretical capacity of 992 mA h g$^{-1}$ [5,6]; however, unlike graphite, these anodes suffer from an enormous volume expansion and contraction during Li insertion/extraction [7,8]. The resulting cracking of the Sn particles invariably leads to mechanical failure, loss of electrical contact, and capacity fading [6–9]. This is further exacerbated by the coalescence of Sn particles during the discharge process [10,11], and is the reason why the practical realization of pure-Sn anodes has not been achieved.

Various strategies have been developed to try and overcome the inherent weaknesses of Sn-based anodes, which include using combining a carbon composite with nanocrystallization [12,13]. Indeed, a great deal of research effort has already been directed toward reducing the size of Sn particles [14,15], as well as developing new carbon materials such as carbon nanofibers (CNF),

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carbon nanotubes, graphene, graphene oxide, etc. Of these, CNF prepared by electrospinning has been demonstrated to offer significant advantages in terms of its high flexibility, large surface area and good conductivity [16,17], with the addition of nanostructured Sn reported to improve cycle performance by enhancing conductivity, while limiting the volume change in the Sn particles [18,19]. This electrochemical performance can be further improved by making the smooth fibrous structure of CNF more porous to create an ultrahigh specific surface area that can provide more charge transfer [20–22]. When compared to traditional electrodes, the use of binder-free electrodes in LIBs can provide a high energy density, good electrical conductivity and greater ease of preparation [11,23,24].

Building on these past studies, we fabricated a Sn nanoparticle-loaded porous carbon nanofiber (Sn-PCNF) composite by means of electrospinning a precursor of Sn(II) acetate/mineral oil/polyacrylonitrile nanofibers, which was then stabilized in air and carbonized in an argon atmosphere. This process is shown schematically in Fig. 1, and relies on the volatilization of the mineral oil to create the porous structure needed. The structural morphology of this material is herein discussed, and its electrochemical performance when used as a binder-free anode in a LIB is assessed.

## 2. Experimental

### 2.1. Preparation of samples

The precursor solution for electrospinning was prepared by dissolving 0.40 g polyacrylonitrile (PAN, Mw = 150,000 g mol$^{-1}$, J&K Chemical Inc.) and 0.05 g mineral oil (Acros) in 4.43 g $N,N$-dimethylformamide (DMF, TianJin Yongda Chemical Reagent Co. Ltd) by magnetic stirring for 24 h at around 60 °C. After that, 0.12 g Sn(II) acetate (J&K Chemical Inc.) was added into precursor solution, and then vigorously stirred for 6 h. As for a typical electrospinning process, the spinneret had an inner diameter of 0.43 mm and grounded aluminum foil was used as the collector. A distance of 15 cm and a direct current voltage of 15 kV were maintained between the tip of the spinneret and the collector. The as-collected electrospun nanofibers were stabilized in an air environment at 280 °C for 2 h (heating rate: 5 °C min$^{-1}$) and then carbonized in a tube furnace at 700 °C for 6 h in an argon atmosphere (heating rate: 2 °C min$^{-1}$) to obtain the Sn-PCNF composites. For comparison, Sn nanoparticle-loaded carbon nanofiber composites were designed under the same conditions without mineral oil.

### 2.2. Characterization

The structure of Sn-PCNF composites were investigated by powder X-ray diffraction (XRD, Thermo ARL XTRA) and Raman spectra were recorded using a confocal Renishaw Raman microscope with a 633 nm of He–Ne laser. X-ray photoelectron spectroscopy (XPS, Thermo Fisher Scientific K-Alpha) was conducted to support the composition of Sn-PCNF composites. The morphology of Sn-PCNF composites were examined by scanning electron microscope (SEM, Zeiss vltra55) and transmission electron microscope (TEM, JEOL JEM-2100). EDX mapping has been acquired at K-edge of C and O and L-edge of Sn. Nitrogen adsorption/desorption isotherms were measured on a Micromeritics ASAP 2020. The Brunauer–Emmett–Teller (BET) methods used to analyze the specific surface areas of the samples.

### 2.3. Electrochemical measurements

The electrochemical performance of the Sn-PCNF anode material was evaluated by using it as a working electrode without any binder or conductive filler in CR2032 coin-type cells with lithium foil as the counter electrode and 1 M LiPF$_6$ dissolved in a mixture of ethyl carbonate (EC), dimethyl carbonate (DMC) and diethyl carbonate (DEC) (1:1:1, v/v/v) as the electrolyte. These cells were assembled in a glovebox (Mbraun Labstar 1450/780) filled with highly pure argon gas, with direct contact between the working and counter electrodes prevented by using a Celgard 2400 separator. Once assembled, the cells were aged for 24 h prior to any measurements so as to ensure adequate percolation of the electrolyte to the electrodes.

Charge and discharge measurements were carried out using a LAND-CT2001A battery-testing system at a high current density of 0.8 A g$^{-1}$ and cut-off potentials of 0.01 and 3.00 V. The rate performance was measured at current densities of 0.8, 1.6, 2.4, and 4 A g$^{-1}$. Cyclic voltammogram (CV) experiments were conducted at room temperature on an electrochemical workstation (Metrohm, PGSTAT 302N) at a scan rate of 0.5 mV s$^{-1}$, with the same workstation also used to measure the electrochemical impedance spectroscopy (EIS) at a voltage of 10 mV within a frequency range of 100 kHz to 0.1 Hz after first equilibrated the cells for 1 h.

## 3. Results and discussion

### 3.1. Structure and composition of the Sn-PCNF anode material

In the X-ray diffraction (XRD) patterns of the Sn-PCNF composites and CNF given in Fig. 2a, the main reflections of metallic Sn are indexed according to Miller's notation, while the reflections from SnO$_2$ are marked with an asterisk. From this, we can see that the strong peaks in the 2θ regions of 30–33° and 44–46° correlate to the (200), (101), (220) and (211) peaks of metallic Sn. Reflections from SnO$_2$ are also evident, which may well be because carbonization at 700 °C in an argon atmosphere does not allow for the complete reduction of any SnO$_2$ that may be formed through decomposition and oxidation of Sn(II) acetate during stabilization at 280 °C in air [20]. Nevertheless, the SnO$_2$ content is substantially lower than that of metallic Sn. Also seen in Fig. 2a is a broad and weak diffraction peak at around 2θ = 26°, which is attributed to the (002) planes of the amorphous CNF matrix [25,26]. This is supported by the Raman spectrum of the Sn-PCNF composite (Fig. 2b),
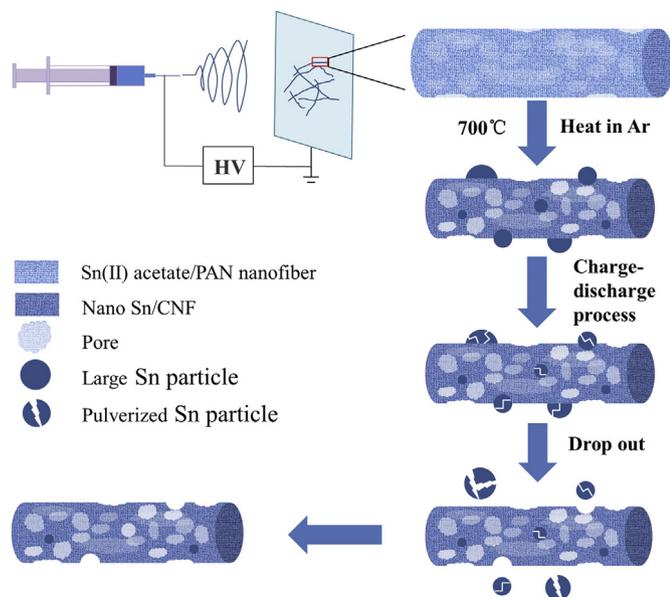


**Fig. 1.** Schematic of Sn-PCNF composite.