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Does carbon coating really improves the electrochemical performance of electrospun SnO_2 anodes?

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ABSTRACT

In this paper, we report the influence of carbon coating on the electrochemical performance of hollow structured SnO_2 electrospun nanofibers. The electrospun nanofibers are subjected to plasma enhanced chemical vapour deposition for a conformal carbon coating of ~6 nm thickness without destroying the one dimensional morphological features of the fiber mats. Li-storage properties are evaluated in half-cell configuration between two different potential windows *i.e.* 0.005-0.8 V and 0.005-2.5 V *vs.* Li. The potential regions tested corresponds to the alloying/de-alloying and alloying/de-alloying & conversion reactions for former and latter cases, respectively. Very high reversibility over 3.6 moles of Li is feasible for both bare and carbon coated SnO_2, without an obvious difference between the electrochemical profiles noted during cycling. In contrary, huge differences in the electrochemical performances are observed for bare and carbon coated SnO_2 when the test cell is cycled for conversion reaction. This result clearly shows the importance of carbon coating for conversion reaction compared to alloying/de-alloying reaction.

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1. Introduction

Li-ion batteries (LIB) are one of the ubiquitous electrochemical energy storage devices in this era for portable and miniature electronic applications [1–3]. Recent research work is devoted to employ them in high power applications such as hybrid electric vehicles (HEV) and electric vehicles (EV)[4]. Unfortunately, commercially available graphitic anodes endure a problem of Li-platting while operating at high current rates, hence inclusion of such anodes for aforementioned HEV and EV application is quite complicated[5]. Therefore, several insertion type electrodes such as TiO_2, $Li_4Ti_5O_{12}$, $LiCrTiO_4$, TiP_2O_7 etc. are proposed as prospective anode material, however said materials exhibits lower theoretical capacity and higher operating potential than graphitic anodes, which results in drastic reduction of net energy density [6–8]. According to Poizot *et al.* [9] nano-sized transition metal oxides will undergo conversion reaction with Li and provide higher reversible capacity than graphitic anodes, nevertheless poor cycleability and higher operating potential than graphitic anodes renders them as showcase anode. Alloy-based anodes such as Ge, Si and Sn based derivatives are found attractive candidates compared to insertion (except graphite) and conversion type anodes due to its higher reversible capacity, lower operating potential and high rate capability[10–12]. On the other hand, meager capacity fading associated with huge volume change during alloying/de-alloying reactions cannot be avoided for such anodes. Therefore, several research efforts likely carbon coating or composites with carbonaceous materials have been made to improve the electrochemical profiles of SnO_2. Further, SnO_2 synthesized with inactive material are also been explored to improve the battery performance of such alloying type anodes [10–12]. Among them, SnO_2 is found noteworthy as it undergoes both alloying/de-alloying and conversion reactions during electrochemical cycling by adjusting the testing windows. In addition to above, lower operating potential (~0.25 V *vs.* Li), higher theoretical specific capacity (for alloying/de-alloying reaction ~782 mAh g^{-1} and for alloying/de-alloying & conversion

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reactions ~1494 mAh g^{-1}), and easy synthesis protocol with various nanostructures makes them attractive for practical applications compared to rest of the anodes [12–15]. It is well known that electrochemical profiles of SnO_2 are strongly influenced by its morphological features [12]. In addition, testing potential is also very crucial to yield high performance anode material along with morphology [6,13]. In this regard, we made an attempt to employ the one-dimensional SnO_2 hollow nanofibers prepared by electrospinning technique. Homogeneous carbon decoration has been carried out for such fibers without affecting the morphological features by plasma enhanced chemical vapour deposition (PECVD)[16]. However few reports are available on the electrochemical properties of electrospun SnO_2 nanofibers, for example Li *et al.* [17] reported the performance of SnO_2 hollow nanofibers and delivered the reversible capacity of ~850 mAh g^{-1} between 0-2 V *vs.* Li at current density of 180 mA g^{-1} with severe capacity fading. Xia *et al.* [18] reported the synthesis and electrochemical profiles of SnO_2 nanofibers with two different polymer backbones *i.e.* polyvinyl acetate (PVA) and polyvinyl pyrrolidone (PVP). The half-cell delivered the reversible capacity of 871 and 847 mAh g^{-1} for PVA and PVP assisted routes, respectively between 0.02-2 V *vs.* Li at current density of 50 mA g^{-1} with severe capacity fading. Electrochemical performance of core-shell-shell structured (C/SnO_2/C) hybrid fibers are suggested by Kong *et al.* [19] and showed the decreasing cycling profile with initial charge capacity of ~961 mAh g^{-1} between 0-3 V *vs.* Li at current density of 52 mA g^{-1}. Yang *et al.* [20,21] reported the performance of bare and carbon encapsulated electrospun SnO_2 nanofibers and observed fading in reversible capacity with first charge capacity of ~781 and ~984 mAh g^{-1} between 0.05-1.5 V *vs.* Li at current density of 100 mA g^{-1} for bare and encapsulated fibers, respectively. Apparent to notice that, unfortunately most of the works reported for the utilization of both allying/de-alloying and conversion reaction, which results severe capacity fading during cycling, although SnO_2 is decorated with carbon. Only a few reports are available for the utilization of such one dimensional structures particularly for the alloying/de-alloying region. According to Dahn *et al.* [13–15], the testing window exceeds 0.8 V *vs.* Li results the oxidation of metallic Sn^0 nanoparticles (SnO) which subsequently leads to the capacity fading during cycling. Such oxidation and severe fading upon cycling was clearly proven by us for atomic layer deposited SnO_2 nanostructures[6].

In this scenario, we would like to study the performance of such one dimensional hollow structures within alloying/de-alloying regime by restricting the upper cut-off potential in to 0.8 V *vs.* Li. Further, influence of carbon coating on the electrochemical performance of such one dimensional SnO_2 hollow fibers (C-SnO_2) decorated by PECVD process during alloying/de-alloying and conversion reaction is evaluated, compared and presented in detail.

2. Experimental

0.4 g of anhydrous Tin (II) chloride was dissolved in a mixture of 12.5 mL of di-methylformamide (DMF) and 4 ml of ethanol and stirred for 2 h. Then, 3.2 g of polyvinylpyrollidone (PVP) was added to the mixture and continually stirred for 4 h to obtain a clear solution. Later, the solution was subjected to electrospinning using a 27 G ½ in. hypodermic needle under an applied voltage of 25 kV and at a flow rate of 1 ml/h with aluminum foil as the collector. The distance between the needle tip and the collector was maintained around 10 cm. The electrospun SnO_2-PVP composite fibers were then collected carefully in the form of a freestanding membrane and calcined at 500 °C for 3 h to induce crystallization and polymer removal. The SnO_2 hollow fibers were coated with amorphous carbon by plasma-enhanced chemical vapor deposition (PECVD) in a procedure similar to the one recently reported by us for carbon coated V_2O_5 nanofibers[16]. PECVD process was performed on a commercial vacuum system (Plasma Electronics, CVD-PECVD DOMINO) working with radio-frequency excitation (13.56 MHz). 50 sccm of C_2H_2 were introduced into the reaction chamber through a mass flow controller (MKS MFC 1179) controlled by a software interface during the reaction and the reactor pressure was kept constant at 10 Pa. C_2H_2 was used as unique precursor source without any additional carrier gas and was decomposed directly onto the nanofibers which were loaded in a copper boat placed on the heatable RF electrode. The temperature was set to 300 °C and the plasma power to 15 W. The nanofibers were coated for duration of 20 min to assure a thin carbon layer.

Bruker AXS, D8 Advance X-ray diffractometer equipped with Cu Kα radiation was used to study the structural properties of electrospun nanofibers. Rietveld refinement was also carried out for the obtained XRD reflections using Topas V3 software. Surface morphological and internal structure of the SnO_2 hollow fibers were studied using field emission scanning electron microscope (FE-SEM, JEOL JSM-7600F) and transmission electron microscope (TEM, JEOL 2100F), respectively. Standard two-electrode coin-cell configuration (CR 2016) was used to study the electrochemical properties of electrospun SnO_2 hollow nanofibers. Composite electrodes were formulated with mixing of accurately weighed 10 mg active material (SnO_2 and C-SnO_2), 1.5 mg of super P, and 1.5 mg of binder (Teflonized acetylene black, TAB-2) using ethanol as solvent. Then the mixture was pressed over 200 mm^2 stainless steel mesh (0.25 mm thickness, Goodfellow, UK) which served as current collector for the half-cell configuration. The electrodes were subsequently dried at 60 °C in vacuum oven for overnight before conducting cell assembly in Ar filled glove box (MBraun, Germany). In the half-cell assembly, test electrodes were separated by glass fiber separator (Whatman, Cat. No. 1825-047, UK) and filled with 1 M $LiPF_6$ in ethylene carbonate (EC)/dimethyl carbonate (DMC) (1:1 wt.%, Merck KGaA, Germany) as electrolyte solution. Cyclic voltammetric (CV) traces were recorded at slow scan rate of 0.1 mV s^{-1} using Solartron, 1470E and SI 1255B Impedance/gain-phase analyzer coupled with a potentiostat in two electrode configuration, in which metallic lithium was used as both counter and reference electrodes. Galvanostatic cycling profiles were recorded at constant current mode between 5-800 mV and 0.005-2.5 V *vs.* Li at current density of 60 mA g^{-1} using Arbin 2000 battery tester in ambient temperature conditions.

3. Results and discussion

FE-SEM studies were used to analyze the morphological features of the electrospun SnO_2 nanofibers. Fig. 1a shows the FE-SEM image of green fibers (as-spun fibers) which assembled in a highly interconnected network with more or less uniform fiber-diameter. As expected, the calcination of green fibers at 500 °C in air resulted in a slight reduction of fiber diameter (Fig. 1b) due to the decomposition of PVP backbone evidenced from Fig. 1b. It seems that during the calcination process, nucleation growth of SnO_2 particles takes place only over outer surface of the polymer backbone. As a result, complete removal of polymer allows the formation of hollow structured one dimensional fibers which are consisting of aggregated nano-sized SnO_2 particulates along with the fiber axis. The presence of hollow structures is further proven by the TEM analysis of calcined fibers (Fig. 1c-d). High resolution-TEM (HR-TEM) images clearly revealed the well-defined lattice fringes with *d* spacing of ~2.6 Å (Fig. 1e) corresponding to the (1 1 0) plane of SnO_2 in cassiterite phase. Selected area electron diffraction (SAED) pattern showed the appearance of concentric rings which indicates the highly crystalline nature of SnO_2 in the synthesized electrospun

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