

Nanoparticles of tin confined in microporous carbon matrices as anode materials for Li batteries

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Abstract

A new approach has been developed for the preparation of anodes for rechargeable Li batteries based on nanoparticles of tin as an alloying medium embedded in microporous (pore diameter, <2 nm) carbon matrices. It is assumed that if tin particles are confined within the carbon micropores, they may exhibit better cyclability upon alloying–dealloying with lithium, since the detrimental effect of the volume expansion of Li_xSn upon alloying can be avoided. A volatile compound of tin, SnCl_4 , was physisorbed to the carbon surface. This was followed by hydrolysis to SnO_2 and by high temperature degassing, which completed the hydrolysis and removed any volatile residue. Using SEM, EDAX and XRD analyses, we could show that we indeed obtained porous carbon, with particles of tin oxide within the microporous system. These matrices were tested as negative electrodes for secondary Li batteries. At this early stage of the study, a reversible capacity as high as 305 mAh g^{-1} was obtained (carbon and Sn), which means that the capacity of the Li–tin alloying was not too far from its theoretical value. The next steps in this study are:

1. Increasing the amount of tin that can be included in the carbon matrices.
2. The development of the preceding reduction process of SnO_2 to Sn, which will reduce pronouncedly the initial irreversible capacity.

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1. Introduction

The rechargeable Li-ion batteries are probably the most important innovation in battery technology achieved during the past decades. The anode in these batteries, an essential component, is usually an intercalation compound of lithium with graphite that can reach (in a staging process) the stoichiometry of LiC_6 , which corresponds to a charge capacity of 372 mAh g^{-1} .

Intensive worldwide attempts are underway to surpass this capacity, using several modifications of carbons and graphites, many of which do exceed the LiC_6 values [1–4]. However, in many cases of high capacity carbons (hard carbons and disordered carbons), the stability upon cycling is limited [5]. We recently described the approach of employing the micropores (<2 nm) of activated carbons as reversible

storage spaces for an inserted Li [6]. For this purpose, activated carbon fibers, containing no mesopores (i.e., pores with sizes ranging from 2 to 50 nm that could insert Li ions) and initially showing no reversible insertion of lithium, were successfully modified to reversibly insert lithium electrochemically, in non-aqueous salt solutions. The modification involved chemical vapor deposition (CVD) of carbon, which partially clogged the micropores' apertures on the surface of the fibers, thus allowing Li-ion insertion and preventing massive reduction of solution species within the pores. Although the capacity of those materials was far below 372 mAh g^{-1} , it was clear that the reversible capacity obtained was due only to the CVD process [6].

Another approach to obtain high capacity anodes for Li batteries (not based on the insertion of lithium into carbons) is based on the reversible alloying of lithium with elements such as Al [7], Sn [8], Si [9], Ge [10] and/or intermetallic compounds that contain these elements. For instance, tin can alloy with lithium up to a stoichiometry

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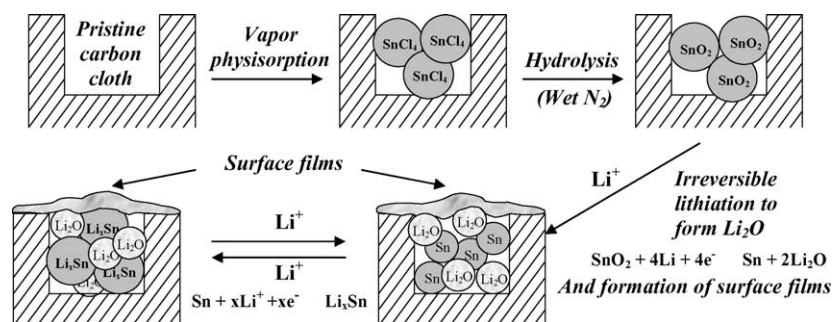


Fig. 1. An illustration of the preparation of the Sn–C electrodes: a pristine porous active carbon undergoes physisorption of SnCl_4 in its pores. The SnCl_4 is hydrolyzed to form nanoparticles, confined in the pores. Cathodic polarization in a Li salt solution forms protective surface films, Sn and Li_2O . The Sn nanoparticles in the pores alloy reversibly with lithium.

of $\text{Li}_{4.4}\text{Sn}$, corresponding to a reversible capacity close to 900 mAh g^{-1} [8]. The problem with most of the reversible alloying processes of the above elements with lithium is the huge volume change involved, which causes unstable morphology that leads to the pronounced and fast capacity fading of anodes based on Li alloys. Li alloys, their capacity fading and solutions to prevent capacity fading, have been given a great deal of attention in recent years [11]. Many hundreds of papers have been published during the past two decades on Li alloy electrodes and related phenomena.

In this paper, we describe an approach to develop stable Li–Sn electrodes by the synthesis of Sn–C matrices, in which nanoparticles of tin are confined in the micropores of activated carbons. The micropores' volume of the porous carbon matrix, if partially filled with tin provides the extra space needed for the alloy expansion upon Li insertion. It is expected that when the tin particles are confined in small pores within the carbon matrix, detrimental reactions between Li–Sn alloy and solution species (that lead to pronounced capacity fading with many types of tin electrodes) may be largely avoided. We assume that the passivating surface films that are formed in these systems should cover the pores on their outer side, thus protecting the Sn/Li–Sn particles inside. The concept of this work is described in Fig. 1.

2. Experimental

The preparation of activated carbons, i.e., the precursors of the electrodes described herein, has already been described [12]. In this paper, we describe studies with carbon cloth from a phenolic resin precursor (type SC2225, distributed by Spectra Corp Inc., USA). The BET surface area of the pristine carbon was $1650 \text{ m}^2 \text{ g}^{-1}$. Impregnation of carbon by a tin compound was carried out in a vacuum line, made of glass, which contained all the necessary compartments, valves, a cooling bath and an oven. Liquid SnCl_4 was cooled down to 77 K and a porous carbon sample, about 100 mg, was heated in parallel to 1000°C . Both compartments were pumped out in order to

remove residual air. The two vessels were then disconnected from the vacuum line, the SnCl_4 reservoir was warmed up to 0°C and the carbon sample compartment was cooled down to 10°C so that the SnCl_4 adsorption into the porous carbon sample took place at a relative pressure (P/P_0) of 0.58 (P and P_0 : vapor pressure of SnCl_4 at 0°C and at 10°C , respectively) during half an hour. The physisorbed SnCl_4 was then hydrolyzed to tin dioxide by purging the sample with a flow of prewetted nitrogen at room temperature during several hours. Finally, the carbon samples were exposed to boiling triply distilled water for several hours in order to complete the hydrolysis. The samples were then evacuated at 500°C for about an hour to remove residual water, tin and hydrogen chlorides. By this method, we could introduce about 30% (by weight) of SnO_2 into the micropores of the carbon fibers. The samples thus prepared were transferred to highly pure, Ar atmosphere (standard glove boxes from M. Braun Inc.). These samples, carbon fibers in the form of cloth, were tested as electrodes in standard electrolyte solutions for Li-ion batteries.

These electrodes were characterized by XRD (Advance D8 system from Bruker Inc.), SEM (ISM 840 JEOL Inc.) and EDAX (Link Inc.). The BET area of the carbons before and after deposition of SnO_2 was measured using a Gemini 2375 surface analyzer (Micromeritics Inc.), with N_2 adsorption at 77 K.

Three-electrode cells (parallel plate configuration, with Li foil reference and counter electrodes) were used for the electrochemical characterization. All the electrochemical measurements were carried out under highly pure argon atmosphere (O_2 and H_2O levels less than 5 ppm) in VAC Inc., glove boxes.

The electrochemical behavior of these materials was measured in a standard 1 M LiPF_6 solution in a 1:1 mixture of ethylene carbonate (EC) and dimethyl carbonate (DMC) from Merck, KGaA (Li battery grade, could be used as received). Cyclic voltammetry was measured using a PGSTAT Autolab system from Ecco Chemie Inc. Galvanostatic cycling was performed using a computerized multichannel Maccor-2000 battery tester. All experiments were carried out at 25°C .

3. Results and discussion

3.1. Insertion of tin nanoparticles into the carbon micropores

The insertion of the gaseous SnCl_4 into the micropores by physisorption of the activated carbon was straightforward. However, the next step of the hydrolysis of SnCl_4 , formation of non-volatile tin oxide particles inside the pores, demanded more careful control and monitoring, since the hydrolysis might remove the adsorbed tin compounds from the micropores, where it can grow into more stable crystallites. Furthermore, reduction of tin dioxide to metallic tin prior to the assembly of the electrochemical cells is of major interest, since it should dramatically decrease the irreversible capacity. For both purposes, the SEM–EDAX system served as a monitor for the chemical treatment processes.

Initially, we tried to use a saturated SnCl_2 /ethanol solution for the impregnation of tin into carbon, as suggested in the literature [13]. The impregnated samples were then dried in air at 200°C and treated under H_2 at 350°C , in order to reduce the impregnated tin oxide into metallic tin. Using this procedure, we obtained carbon fibers covered externally by tin spherules, which were not the desired product.

Fig. 2a presents a SEM micrograph of an active carbon cloth sample that underwent the four steps of treatment described in Section 2, namely SnCl_4 physisorption, hydrolysis

with wet N_2 , further completion of the hydrolysis with boiling water and heating in air at 200°C . The micrograph shows the smooth cylindrical fibers, uninterrupted by any irregularities that could indeed contain the SnO_2 deposits, as was approved by EDAX measurements. Fig. 2b and c shows high-resolution TEM micrographs of part of a cross-section of pristine and SnO_2 -containing carbon fibers, respectively. Well-dispersed nanoparticles of tin oxide (black spots in Fig. 2c) can be seen all over the fiber's cross-section. This demonstrates the successful insertion of this active mass into the pores of the carbon matrix.

We tried to reduce the SnO_2 within the carbon fibers, using a flow of hydrogen gas at 250°C . The SnO_2 was indeed reduced to tin, which accumulated as flakes on the outside surface of the fibers, as seen in the SEM micrograph in Fig. 2d. Developing methods for reducing the tin oxides within the carbon pores, before the electrochemical processes, is in progress.

In order to obtain more information on the location of the tin dioxide particles into the active carbon cloth, EDAX spectra of the fully treated anodes (including all the steps described in Section 2) were taken from fiber surfaces, and from cross-sections of fibers. Fig. 3 shows practically the same element content for both the outer surface (Fig. 3a) and the cross-section (Fig. 3b). This indicates that the tin compounds reside within the micropore systems. The absence of chlorine confirms a completed hydrolysis of the tin precursor and the removal of HCl from the carbon pores.

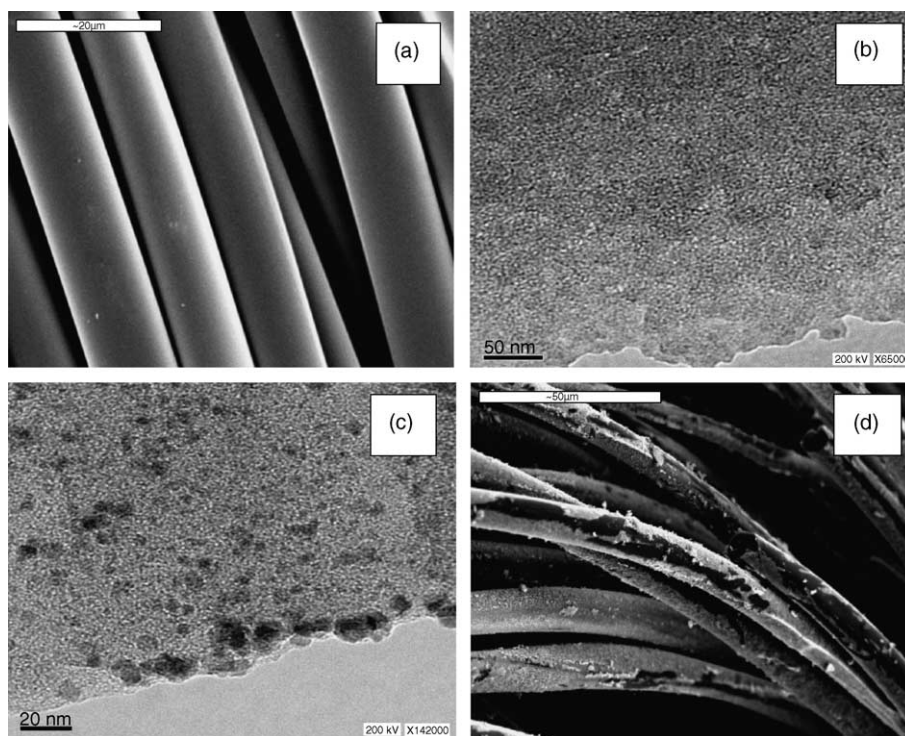


Fig. 2. (a) A SEM micrographs of the active carbon cloth containing the SnO_2 (pristine electrode material). (b) An HRTEM image of the cross-section of a pristine carbon fiber (before SnO_2 deposition). (c) An HRTEM image of a carbon fiber containing SnO_2 nanoparticles (black areas). (d) A SEM micrograph of fibers containing SnO_2 that underwent reduction by H_2 at elevated temperatures.

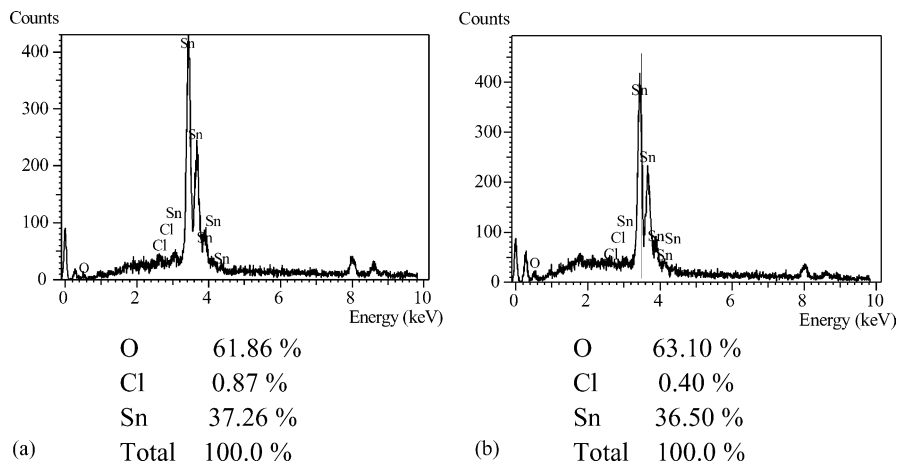


Fig. 3. EDAX spectra of an active carbon fiber containing SnO_2 particles taken from the: (a) fiber surface and (b) fiber cross-section.

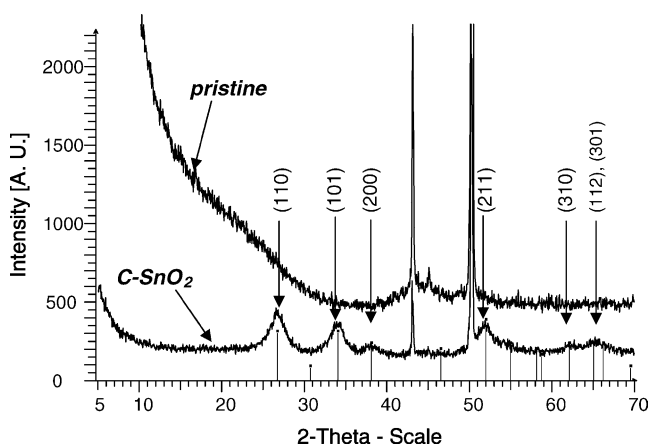


Fig. 4. XRD patterns of activated carbon fibers before and after the insertion of SnO_2 (indicated). Library patterns of SnO_2 are also provided for comparison.

Fig. 4 shows XRD patterns of pristine carbon fibers and carbon fibers containing SnO_2 . The SnO_2 patterns from the literature are also shown for comparison. This figure clearly shows that the tin compound is SnO_2 . The widening of the lines indicates nanometric dimensions, which by means of the Debye–Scherer equation, could be estimated as 40 Å. This is indicative of the nanometric scale of the SnO_2 particles.

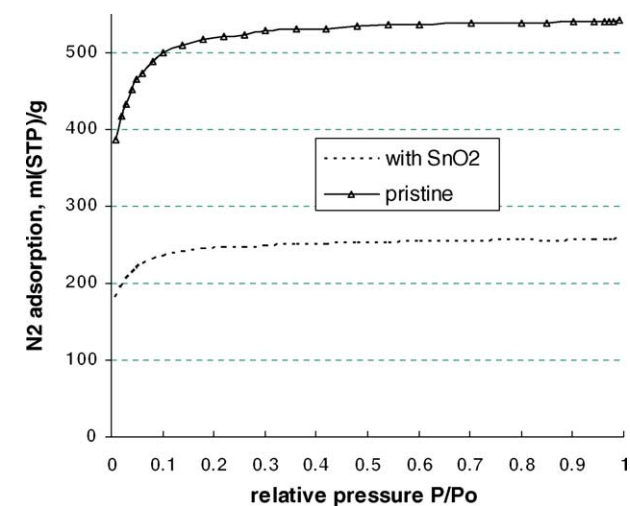


Fig. 5. N_2 adsorption isotherms at 77 K: a pristine active carbon cloth and carbon cloth containing SnO_2 nanoparticles.

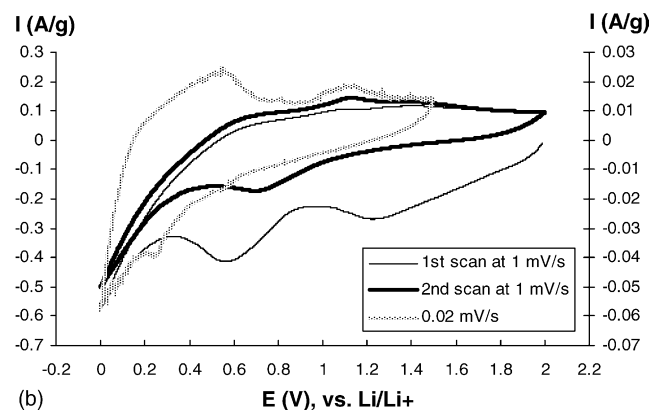
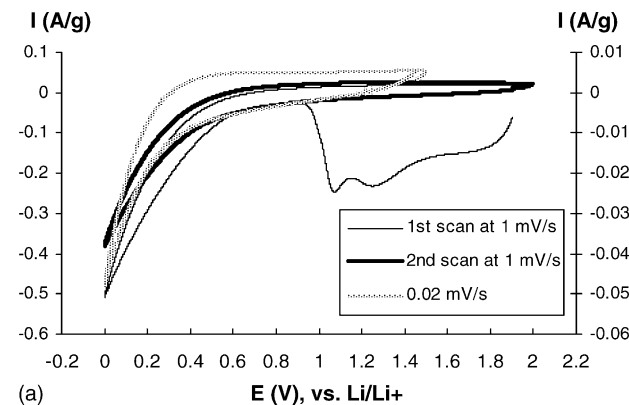


Fig. 6. Cyclic voltammograms of the activated carbon cloth electrodes: (a) pristine carbon cloth with no SnO_2 and (b) carbon cloth containing SnO_2 nanoparticles. Scan rates: 1st and 2nd cycles at 1 mV s^{-1} ; 10th cycle at 0.02 mV s^{-1} . EC-DMC/LiPF₆ 1 M solution.

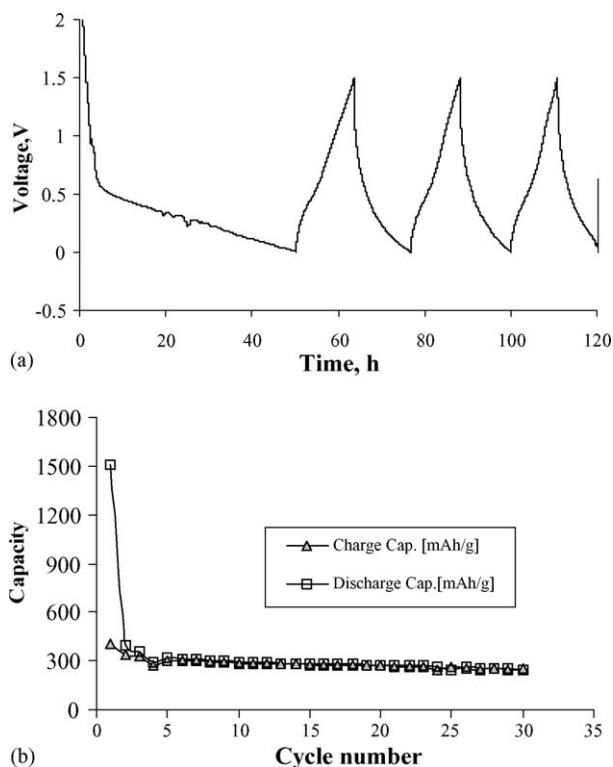


Fig. 7. Galvanostatic cycling of a carbon cloth electrode containing SnO_2 nanoparticles. EC–DMC, 1 M LiPF_6 solution, C/10 rates 25 °C: (a) voltage profile and (b) capacity vs. cycle number.

Fig. 5 shows N_2 adsorption isotherms related to the pristine active carbon cloth, having its full pores system opened for adsorption and to a sample containing SnO_2 nanoparticles. These isotherms indicate the expected drop in the pores' volume due to the insertion of SnO_2 , which can be estimated from the amount adsorbed at the highest pressures according to the Gurvitsch rule (This rule assumes that the adsorption saturation value of an adsorbate close to its vapor pressure, within the micropores, can be considered as related to a process of filling the pore system by a liquid.) [14].

It was possible to overlap the two isotherms in Fig. 5 by multiplying the isotherms related to the C– SnO_2 sample by a factor of 2.11 (the overlap was perfect throughout the entire pressure range). This means that close to half of the opened volume of the carbon fibers is filled with tin oxide, after the treatment developed herein.

Fig. 6a shows cyclic voltammograms (CVs) of a porous carbon cloth electrode before the introduction of SnO_2 treatment (an EC–DMC 1:1/ LiPF_6 1 M solution). There is no uptake of Li^+ into the carbon in this case and the capacity obtained in a steady state CV is that of the electrical double layer (EDL). At a potential lower than 1.5 V, irreversible reduction of solution species on the electrode's surface takes place. With a similar carbon cloth electrode containing the SnO_2 nanoparticles, a reversible process of Li^+ intercalation is ob-

tained, as seen in Fig. 6b, with a capacity of 305 mAh g^{-1} . This reversibility is more apparent in the galvanostatic cycling shown in Fig. 7a, which also exhibits large initial irreversible capacity of 1500 mAh g^{-1} . It is most likely the reduction of SnO_2 to Sn and $2\text{Li}_2\text{O}$, which causes the large irreversible capacity. The cyclability of the Sn–C illustrated in Fig. 7b demonstrates a stable capacity upon cycling. Taking into account that the weight percent of the tin in the matrices is about 30%, this means that the reversible alloying of Li with tin occurs at capacities close to the theoretical value ($\approx 900 \text{ mAh g}^{-1}$).

4. Summary

A route for successful insertion of SnO_2 nanoparticles into the micropores of highly activated carbon cloth was developed herein. Electrodes comprising this SnO_2 -containing carbon, show highly reversible Li alloying with tin. The untreated active carbon shows no reversible capacity of lithium insertion. The high irreversible capacity measured in the first cycle should be attributed mostly to the reduction of SnO_2 to metallic tin and $2\text{Li}_2\text{O}$ and the formation of surface films. Reduction of the tin oxide in the pores before assembly of the electrochemical cells and the better management of the pores being filled up with the tin oxide should improve both the capacity and the reversibility of these materials.

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