

# The use of tin-decorated mesoporous carbon as an anode material for rechargeable lithium batteries†

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A sonochemical process has been developed for the insertion of tin nanoparticles into mesoporous carbon, giving a product which was used as a building block for the anode of a rechargeable Li battery; the electrode could deliver a reversible capacity of 400 mAh  $\text{gr}^{-1}$  (C + Sn) at 100% cycling efficiency, which is higher than that of graphite electrodes.

The insertion of nanoparticles into mesoporous structures has attracted much interest since the discovery of the mesoporous materials.<sup>1</sup> Various methods that have been employed for this goal include impregnation,<sup>2</sup> gas-phase chemical vapor infiltration,<sup>3</sup> an ion exchange method,<sup>4</sup> a sonochemical method,<sup>5</sup> supercritical fluids,<sup>6</sup> covalent grafting,<sup>7</sup> and a recent method<sup>8</sup> in which colloidal gold solution is premixed with the precursors for the preparation of the mesoporous material. The various applications suggested for this product are: catalysts,<sup>9</sup> separations, nanoelectronics, optical devices,<sup>10</sup> and fuel cells.<sup>11</sup> Ryoo and his associates<sup>12</sup> have developed a new strategy for the synthesis of highly ordered, rigid arrays of nanoporous carbon having uniform but tunable diameters. These mesoporous carbon structures were synthesized using mesoporous silica as the template and then removing the template. Ryoo *et al.* were the first to insert nanoparticles into the mesoporous carbons.<sup>13</sup> The inserted 3 nm platinum nanoparticles show electrocatalytical reactivity in the reduction of oxygen.

As stated above, sonochemistry has already been used for the insertion of Mo oxide, and Co/Mo oxides into MCM-41 as well as into the pores of Al-MCM-41,<sup>5</sup> Fe<sub>2</sub>O<sub>3</sub> was anchored to the inner walls of mesoporous titania,<sup>14</sup> and WS<sub>2</sub> and MoS<sub>2</sub> slabs inserted inside SBA-15.<sup>15,16</sup> Zhang and his group have also used sonochemistry to insert nanoparticles of various noble metals into mesoporous silica.<sup>17–19</sup> The insertion mechanism is related to the specific properties of bubbles collapsing near a solid surface creating microjets and shockwaves. These after effects are responsible for the homogenous spreading of the nanoparticles in the mesostructure.

In the current paper we have inserted and decorated mesoporous carbon with tin nanoparticles. The search for a new Li-containing anode has continued for several decades. The use of Li-alloys as an anode material was found to be very advantageous due to its higher gravimetric and volumetric theoretical capacity and extra safety relative to the carbonaceous anodes.<sup>20–23</sup> Recently, it was found that using nanoparticles of these alloys (for example Li<sub>21</sub>Si<sub>5</sub> and Li<sub>17</sub>Sn<sub>4</sub>) could prevent the mechanical

failure of the anode.<sup>24–26</sup> The tin-decorated mesoporous carbon was tested as an anode material for a rechargeable Li battery.

Mesoporous carbon (MSPC) was prepared using SBA-15 material as a template. Synthesis of SBA-15 was carried out according to D. Zhao and coworkers.<sup>27</sup> The as-prepared SBA-15 was calcined at 500 °C for 6 hours and then 1 g of this material was mixed with a solution consisting of water (5 g), sulfuric acid (0.14 g) and sucrose (1.25 g). After sonication in an ultrasonic bath (20 min) the suspension was heated at 100 °C for 6 h and later at 200 °C for 6 h. To improve the filling of the carbon in the SBA-15 pores, the obtained black solid material was treated again with another sucrose solution with 5 g of water, 0.09 g of sulfuric acid with 0.8 g of sucrose, and then annealed at 900 °C for 5 h under argon. The carbon–silica composite obtained was mixed with 1 M solution of sodium hydroxide (50 vol.% ethanol + 50 vol.% water) to remove the silica, and then washed with pure water and dried in vacuum.

For the insertion of Sn into the MSPC, 0.3 g of the MSPC was mixed with a solution of tin chloride, SnCl<sub>2</sub> (0.42 g) in 50 ml of ethanol. The solution was sonicated in an ultrasonic bath for 30 minutes. After the sonication the ethanol was evaporated and the residue was heated at 530 °C for 2 h under argon.

The product underwent the regular characterization process including wide angle XRD, TEM, and BET measurements.

The mesoporous nature of the pristine MSPC is clearly seen from the TEM image (see Fig. S1) and the measured width of pore is 4.0 nm, as compared with 4.2 nm, measured by Ryoo *et al.*<sup>13</sup> After the tin-insertion modification, we can clearly observe that nanoparticles are inserted into the mesopores as well as on the surface (see Fig. 1).

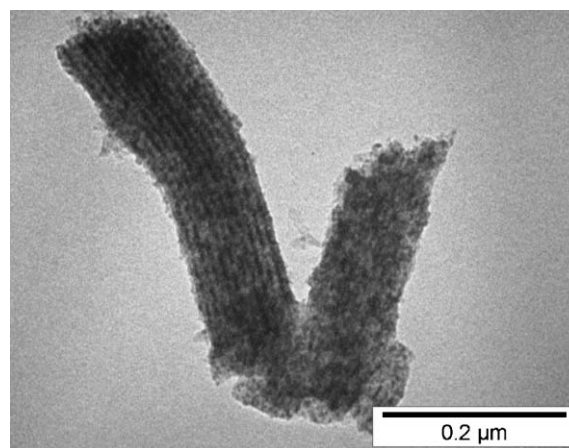


Fig. 1 TEM images of the Sn/MSPC matrix.

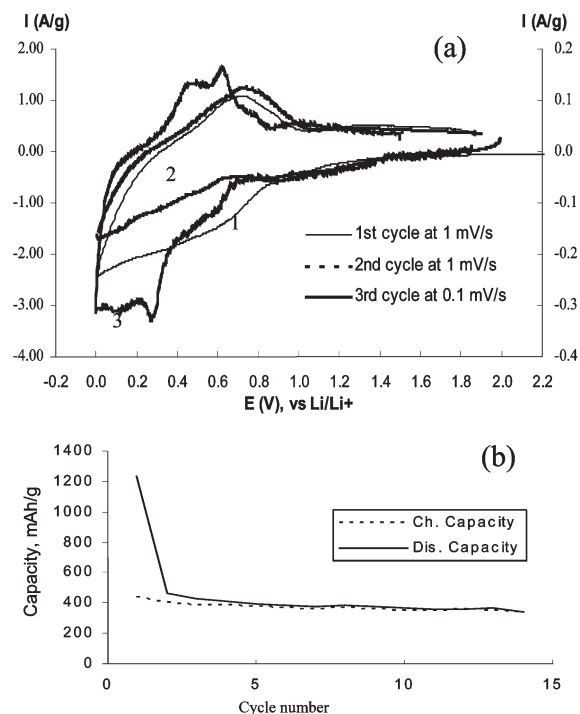
† Electronic supplementary information (ESI) available: Figs. S1–S3. See <http://www.rsc.org/suppdata/cc/b414240c>  
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The composition of the tin-decorated MSPC has been clarified by XRD measurements (see Fig. S2). The main peaks fit the metallic Sn pattern very well, and they can be designated as the (200), (101), (220) and (211) planes of metallic Sn (PDF NO. 4-673). This means that metallic Sn is formed under our reaction conditions, where the carbon and ethanol serve as the reducing element. There are also a few very weak peaks, which are not labeled in the curve, related to SnO<sub>2</sub>. We are not surprised to find these diffraction peaks, since considering the high reactivity of the small sized metallic Sn particles, their oxidation is very reasonable. The mean particle size has been evaluated with the Debye-Scherrer formula and a mean particle size of about 6.4 nm has been obtained for the intense (200) and (101) diffraction peaks.<sup>28</sup> This value is larger than the average pore size of the MC. This difference can be explained as due to the presence of big particles on the outside of the pore and also due to the unlimited possibility of particle growth along the channels.

Composite electrodes comprised 80% active mass (Sn/MSPC), 10% carbonaceous additive (carbon black or graphite KS-6 from Timrex, Inc.), 10% poly(vinylidene difluoride) (PVdF) binder (Solvey, Inc.), and a copper foil current collector. The powder mixtures obtained were then suspended in *N*-methylpyrrolidone to make a slurry that spread uniformly on both sides of a 0.125 mm thick copper foil (GoodFellow, 99.8%) current collector and were dried 2 h at 80 °C and then overnight in a vacuum at room temperature. The active mass of the electrodes was 2–3 mg cm<sup>-2</sup>. Three-electrode cells (parallel plate configuration, with Li foil reference and counter electrodes) were used for the cyclic voltammetry measurements and two-electrode coin type cells were used for galvanostatic cycling. All the electrochemical measurements were carried out under a highly pure argon atmosphere (O<sub>2</sub> and H<sub>2</sub>O level less than 1 ppm) in VAC, Inc., gloveboxes.

The electrochemical behavior of these materials was measured in a standard 1 M LiPF<sub>6</sub> 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.

Fig. 2a shows the first 3 consecutive cyclic voltammograms of a composite electrode with tin containing MSPC particles as the active mass. The first two cycles were measured at a relatively fast scan rate (for Li insertion materials), 1 mV s<sup>-1</sup>. The first cycle reflects irreversible cathodic charge (see the wave with an onset at 0.9 V vs. Li/Li<sup>+</sup>) which relates to reduction of solution species which form passivating surface films on the carbon particles.<sup>29</sup> In the subsequent cycles, a reversible insertion of lithium was obtained, at cycling efficiency close to 100%. The third cycle in Fig. 2a obtained at 0.1 mV s<sup>-1</sup>, reflects reversible alloying of Li with tin.<sup>30</sup> Fig. 2b shows the initial cycling performance of these electrodes in galvanostatic cycling. These electrodes could deliver a reversible capacity of 400 mAh gr<sup>-1</sup> (C + Sn) at 100% cycling efficiency, which is higher than that of graphite electrodes (which are the usual practical anodes in Li ion batteries, 372 mAh gr<sup>-1</sup> theoretical and 350 mAh gr<sup>-1</sup> practical capacity). As was measured separately, electrodes comprising MSPC without tin were nearly inactive as Li insertion electrodes, showing mostly electric double layer charging and irreversible reduction of solution



**Fig. 2** Electrochemical measurements of a composite electrode with tin containing MSPC particles as the active mass: a) cycling voltammograms; b) galvanostatic cycling, C/20 h rate,  $\approx 0.05$  mA cm<sup>-2</sup> of geometric area.

species (in the first cycle, see Fig. S3). Hence, taking into account that the Sn/C ratio (in weight) was around 1/3 in the electrodes' active mass, the specific capacity of the Li alloying with tin in these electrodes is close to the theoretical capacity ( $\approx 900$  mAh gr<sup>-1</sup> for Li<sub>4.4</sub>Sn).

We have demonstrated herein that confining nanoparticles of tin in a mesoporous carbon matrix provides reversible and reproducible Li alloying with tin at 100% cycling efficiency. Hence, these types of materials can be considered as a promising active mass for anodes in rechargeable Li batteries. Further studies aimed at clarifying the nature of the reducing agent are in progress.

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