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Metallic tin-based nanoparticles synthesis by laser pyrolysis: Parametric studies focused on the decreasing of the crystallite size

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ABSTRACT

Due to their characteristic to allow a continuous, one-step nanosize particles production, the laser pyrolysis technique was employed to synthesize metallic Sn-based nanoparticles using tetramethyltin vapors as precursors and ethylene as laser energy transfer agent (sensitizer). Small size of tin particles is a requirement for their use as anodes in lithium ion batteries. In order to decrease the particle size, some experimental parameters were varied, allowing the control of the crystallite size down to 30 nm. The diminishing diameter of the reactive flow injection nozzle as well as the increasing of the tin precursor vapor flow enhance the gas velocity and the decrease the reactive species residence time in the laser beam, resulting smaller tin nanodroplets which forms solid nanoparticles after rapid cooling. XRD, TEM, EDX and SAED analysis point to the formation of nanosize β-Sn particles accompanied by various amount of disordered carbon as coating provided by ethylene decomposition (associated with their polymerization/dehydrogenation) in the presence of methyl radicals from $Sn(CH_3)_4$.

1. Introduction

Lithium-ion batteries are well known as modern chemical sources of electrical power having as advantage their low production costs and high capacity for energy storage (due to the low atomic mass of Li element) [1]. Moreover, they have a low self-discharge rate and also containing fewer environmental pollutants when comparing with order battery types (NiCd, NiMetalHydride, Zn-C, etc.) [2,3]. Generally, when such a battery is charged, the lithium ions travel from cathode to anode, whereas the alkaline ions movement is reversed during the discharge, accompanied by an electron flow that passes through external electrical circuit. The battery will store more energy and will have longer lifetime when the anode will absorb more lithium ions (Li is known as the lightest alkaline element having also the lowest density). In order to improve the performances, the reliability and the lifetime of the Li-ion batteries (LIBs), considerable efforts are made in the fields of nanotechnology and materials science. There is an increasing demand for small mobile electrical sources for portable electronics (mobile phones, laptops, photo/video cameras, toys, etc.) as well as for bigger sources (for electrical vehicles) [4–7]. To answer these needs, new combinations of metals and other substances are experimented for the obtaining of materials with extended lifetime and high specific energy density [1,8].

Many studies undertaken in the last decades proposed that the anode battery to be build from elements like: Sn, Mn, Co or their alloys or from C (graphite) [9–13]. Recently, the use of tin (Sn) as anode for rechargeable batteries has attracted a special attention. The element tin, with a theoretical energy storage capacity of 994 mAh g^{-1} (near three times greater than the 372 mAh g^{-1} which is corresponding value of the graphite) [14] is known for its tendency to dissolve the lithium, resulting thus various Li–Sn intermetallic compounds. The maximum lithium content can be

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found in $Li_{22}Sn_5$ (or more correct $Li_{17}Sn_4$) which have the theoretical storage capacity of 790 mAh g^{-1} [15,16]. Its combination with Li leads to a considerable change in volume (>300%) resulting the advanced fragmentation (pulverization) of the Sn anode [15,17,18] and the loss of electrical contact with the current collector, accompanied with the rapid degradation of the electrode performance [19]. To overcome this problem which results in dramatic reducing of the electrode life-time after only few lithiation/delithiation cycles, the first approach was the replacing bulk material with nanoalloys [15] which can diminish the unwanted cracking due to more facile phase transitions that accompany the alloy formation [20]. Moreover, due to the short distance for Li^+ diffusion within the nanoparticles, the rate of these ions insertion and deinsertion increases significantly [15]. Due to their larger specific surface compared with those of microparticles, the nanoparticles have a higher contact area with the electrolyte resulting an enhanced Li ions flux across the interface [21]. Another possible alternative to alleviate problems with the tin volume changes was its encapsulation inside of carbon hollow spheres [22,23] or insertion into carbonaceous matrices [24–26]. Thus, the resulted materials had high and stable energy storage specific capacity (reaching 500 mAh g^{-1}) [27]. The fibrilar carbon was also used with good result in this kind of composites under the form of carbon nanotubes [28,29], nanofibres [30,31] or even nanocables [32].

Because metallic tin possesses a low melting point (232 °C) it prefers to agglomerate into large particles during high temperature processes required in most cases [33]. This is the main reason for which it is very difficult to obtain small Sn nanoparticles with high productivity. Gas phase methods are well known for their ability to obtain nanoparticles in a continuous mode, having the possibility to be extended to pilot and even industrial scale [34]. There are few reports in the literature concerning the gas phase synthesis of metallic tin-based nanoparticles. For example, Kjeldsen et al. obtained tin nanoparticles embedded in Si or SiO_2 layers using RF magnetron sputtering at very low pressure after heating the samples at the 450 °C [35]. Starting from $Sn(CH_3)_4$, Chen et al. obtained also small tin nanoparticles using RF plasma [36]. Laser pyrolysis technique was recently proved to be a successful method to obtain tin-based metallic alloys nanoparticles (starting from vapor-phase precursors) such as $Ge_{1-x}Sn_x$ (from tetramethyltin and tetramethylgermanium) [37,38], β-Sn/SnSi (from SiH_4 and SnH_4) [39] and Fe–Sn (from $Sn(CH_3)_4$ and $Fe(CO)_5$) [40]. The present study explores the influence of some main experimental parameters of laser pyrolysis technique in order to decrease as low as possible the resulted tin-based nanoparticles.

2. Experimental

The laser pyrolysis technique is based on the absorption of laser radiation by specific molecules called sensitizers (there is an overlapping between a major infrared band of this species and the laser emission wavelength). Laser energy is thus transformed into thermal energy of the excited molecules which also undergoes collisions with the non-absorbing species on the precursors (tetramethyltin in our case), resulting molecular fragments which then condense to form clusters/nanoparticles (metallic tin-based nanoparticles).

The experimental set up, presented in Fig. 1, shows the orthogonal geometry of the intersection of the infrared (λ = 10.6 μm) continuous-wave CO_2 laser beam with the reactive gas flow (injected through inner tubular nozzle) surrounded by an inert annular Ar flow which pass through the external concentric nozzle having a fixed diameter of 14.1 mm (with the exception of Sn12 experiment when a nozzle with 8.8 mm inner diameter was used). The $Sn(CH_3)_4$ are entrained from a bubbler with the aid of the C_2H_4 (mixed in some experiments with Ar) similar with those reported [40]. The Sn nanopowder formed in the reaction zone was than collected on a ceramic microporous filter (located in a collector chamber), whereas the unreacted/dilution gas pass through filter attracted by a vacuum pump. The main experimental parameters are presented in Table 1. Herein, the values presented in columns 2, 3 and 4 show the gas flows for the reactive mixture or its Ar dilution. This gas mixture and the $Sn(CH_3)_4$ vapors were introduced through the central nozzle (inner diameter presented in column 9). In the column 7 the laser power values measured after the reactive chamber both before the experiment in pure Ar atmosphere and during the synthesis process (P_L Ar/abs) are presented and delimited by semicolon. In our experimental set-up the conditions can be maintained stable during hours and rate productions of hundreds milligrams to one gram per hour of an ultrafine grey powder have been achieved.

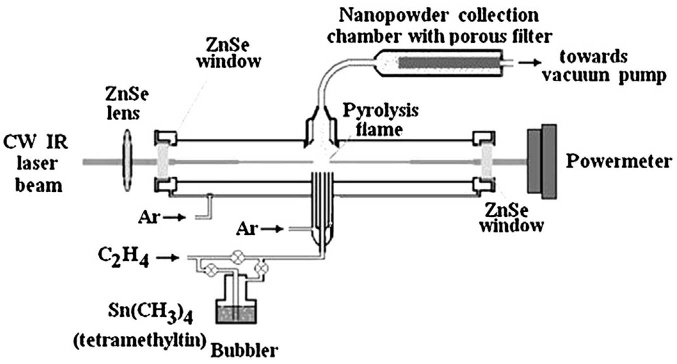

Fig. 1. The laser pyrolysis experimental set-up used for obtaining of tin-based metallic nanoparticles.

For the gas-phase syntheses, we used volatile tetramethyltin (95%) from Merk, as well as gaseous ethylene (99.95%) and argon (99.99%) from Linde Gas. The flame temperature was measured using an optical pyrometer (IR tec P2000) and the Laser power with a Laser powermeter (LM-200 HTD).

The obtained samples have been characterized by X-ray diffraction (XRD), transmission electron microscopy (TEM and HRTEM), energy dispersive X ray analysis (EDX) and Raman Spectroscopy. X-ray diffraction measurements were carried out at room temperature on a PANalytical X'Pert PRO MPD X-ray diffractometer. Incident X-ray radiation was line focused Cu X-ray tube providing a Kα wavelength of 1.5418 Å. A curved graphite monochromator and a variable divergence slit working in the fixed irradiated area mode were placed in the diffracted beam. The X-ray diffractograms were analyzed with the PANalytical X'Pert High-Score Plus software package. Energy-dispersive X-ray spectroscopy (EDX) was performed inside a scanning electron microscope (SEM), FEI Co., model Quanta Inspect S, 0–30 kV accelerating voltage, using an EDAX Co. liquid nitrogen cooled SiLi detector. For the transmission electron microscopy low or high resolution analyses we employed a Tecnai F30 G2 (300 kV) transmission electron microscope (TEM). The Raman spectra were collected using a MicroRaman Spectrometer Jasco NRS 7200 using a 532 nm wavelength laser.

3. Results and discussions

The synthesis of tin-based nanoparticles via laser pyrolysis technique using $SnMe_4$ as tin precursor has two major particularities. Firstly, the organometallic tin precursor decomposition process is one with a thermal threshold (around 500–530 °C) and its value varies slowly with the pressure and the reactive molecules density in the pyrolysis flame. Secondly, at elevated reductive flame

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