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Fabrication of Sn/SnO_2 composite powder for anode of lithium ion battery by aerosol flame deposition

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ABSTRACT

Crystalline SnO_2 and Sn/SnO_2 composite nano-powder were synthesized by aerosol flame deposition (AFD) method employing an oxy-hydrogen flame torch and a heated deposition turn-table. The aqueous precursor solution of the tin (IV) chloride and methyl alcohol was atomized with an ultrasonic nebulizer and subsequently carried into the central tube of the torch by flowing dry Ar gas. SnO_2 were formed by oxy-hydrogen flame and deposited on a substrate placed in a heating stage. To produce Sn metal particles and control the ratio of Sn/SnO_2, as-synthesized SnO_2 were heat-treated under 5% H_2 and 95% Ar mixed gas atmosphere at a temperature of 150 °C for 3 h, and then at 600 °C for 1–4 h. The average particle size of as-synthesized SnO_2 was in the range 5–15 nm and that of Sn/SnO_2 composite powder was slightly grown to 20–90 nm depending on the heat treatment temperature. The analysis on morphology, crystalline phases, and chemical state of Sn revealed that AFD method is one of the favorable approaches to produce nano-sized Sn/SnO_2 composite powder with good morphology, size distribution, and well-controlled Sn/SnO_2 ratio.

1. Introduction

In the lithium ion battery industry, the enormous efforts to respond to ever-increasing demand on the battery capacity have brought remarkable increase in this performance, while it simultaneously raised the safety issues. To increase specific energy density of battery, new electrode materials and sophisticated engineering on the performance of these materials have been developed. On the line of these efforts, recently numbers of researches on SnO_2 have been reported to exploit the potential as the negative electrode of lithium ion batteries because of its high theoretical capacity of 781 mAh/g [1–3]. According to previously reported studies [2], the reaction mechanism of SnO_2 with lithium can be summarized by two steps:

$$SnO_2 + 4Li^+ + 4e^- \rightarrow Sn + 2Li_2O \quad (1)$$

$$Li^+ + xe^- + Sn \leftrightarrow Li_xSn\ (0 \le x \le 4.4) \quad (2)$$

In the first cycle, SnO_2 is irreversibly reduced to form Sn metal and lithia (Li_2O) in the matrix. Further reaction of the newly formed metallic Sn with lithium subsequently leads to the formation of Li–Sn alloys with the composition, $Li_{4.4}Sn$ [4]. However, the large volume change (up to 300%) associated with alloying and de-alloying causes critical mechanical damage to the electrode, resulting in loss of capacity and rechargeability [5]. As a result, these materials have not been applied in practical lithium ion batteries until now.

To overcome this problem, there have been many studies of combining Sn-based material with other materials to form composite electrodes with the intention to increase the dispersion of Sn-based oxide in other oxide matrix and/or surface [6–10]. Using of tin–tin oxide composites could be a solution in realizing increased reversible capacity as well as reduced irreversible capacity and capacity fade upon cycling, as this could increase the $Sn:Li_2O$ ratio in the anode matrix [10]. In this approach, the ratio between metallic Sn and SnO_2 is critical factor for the optimum cycle performance of the fabricated cell [10]. Therefore, to employ this material system for the anode of battery, it is necessary to develop an adequate preparation process enabling nano-sized SnO_2 and Sn/SnO_2 composite powder with precisely controlled Sn/SnO_2 ratio. Many routes have been applied to fabricate nano-sized SnO_2 particles, such as the sol–gel method [11], chemical vapor deposition [12], magnetron sputtering [13], spray pyrolysis [14], aerosol flame deposition [15], etc. Among these methods, the AFD (aerosol flame deposition) process is unique since it offers a route to prepare a nano-porous body composed of nano-sized particles. In this study, SnO_2 and Sn/SnO_2 composite powders have been

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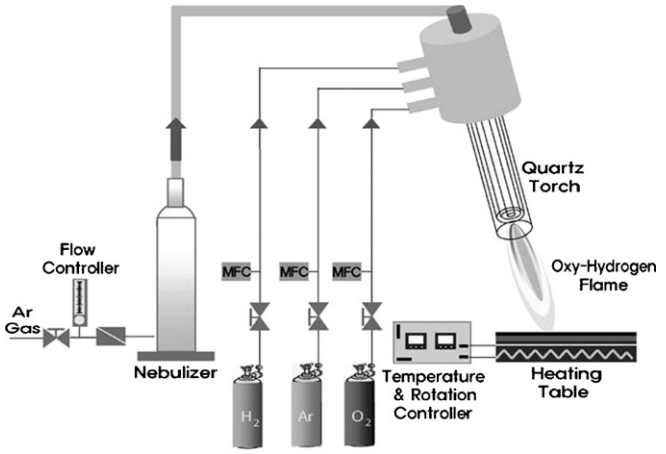

Fig. 1. A schematic diagram of the aerosol flame deposition system for the synthesis of SnO_2 nano-powder.

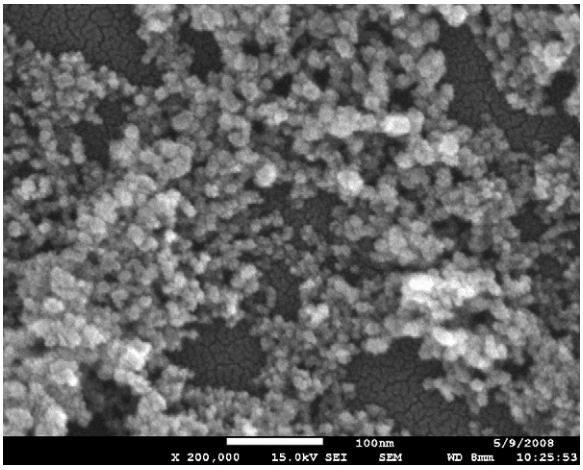

Fig. 3. SEM image of as-prepared nanocrystalline SnO_2 powder synthesized by AFD.

synthesized by AFD techniques and subsequent heat treatment. The microstructure and crystalline structure of the synthesized powder were characterized by scanning electron microscopy (SEM), X-ray diffraction (XRD) and X-ray photoelectron spectroscopy (XPS).

2. Experiments

Nanocrystalline SnO_2 powders have been synthesized by the AFD technique. Schematically shown in Fig. 1 is the AFD system employed in this study. The experimental apparatus consists of an aerosol generator, a deposition chamber, and a gas delivery system. In the AFD process, a liquid precursor solution was prepared by dissolving the desired precursors into a solvent and then atomized into micro-sized droplets by ultrasonic nebulizer. The aerosol generation was performed by an ultrasonic nebulizer employing 1.7 MHz resonator. The precursor solution was prepared by dissolving tin (IV) chloride ($SnCl_4$ 99%, Aldrich) in methanol (CH_3OH, 99.9%) at concentration of 0.1 M. After synthesized SnO_2 powders were heat-treated under 5% H_2 and 95% Ar mixed gas atmosphere at a temperature of 150 °C for 3 h, and then at a temperature 600 °C for 1–4 h.

The crystalline structures and morphology of the products were characterized by an X-ray diffractometer (Rigaku D/max-2500, with Cu Kα X-ray radiation 40 mA 100 mV), and a field-emission scanning electron microscope (JEOL, JSM-7500F). XPS analyses were performed using a VG Multilab ESCA 2000 system for chemical analysis, which was conducted with a focused monochromatic Al Kα radiation of energy 1486.6 eV. The binding energy was calibrated using the C 1s signal (284.6 eV).

3. Results and discussion

The nanocrystalline SnO_2 powder was obtained by the aforesaid AFD technique. The XRD pattern of as-synthesized nanocrystalline SnO_2 powder is presented in Fig. 2. The diffraction peak positions were in good agreement with that of cassiterite SnO_2 (JCPDS No. 41-1445) and no impurity peaks were detected. To investigate the particle sizes, the mean particle sizes (D) of these samples were calculated by using the Scherrer equation to the (1 1 0) plane diffraction peak ($2\theta = 26.6^\circ$),

$$D = \frac{0.9\lambda}{(b\cos\theta)} \tag{3}$$

where λ is the X-ray wavelength, β is the pure full width of the diffraction line at half its maximum intensity, and θ is the Bragg angle. The mean particle size of as-synthesized SnO_2 powder was ~5.4 nm and it was in agreement with the values obtained from the SEM image. Fig. 3 shows the SEM image of the nano-sized SnO_2 powder. It is clear from the image that the powder is composed of nano-sized particles with round morphology and narrow size distribution. The particle size ranges between about 5 nm and 15 nm. Shown in Fig. 4 are the X-ray diffraction patterns of the Sn/

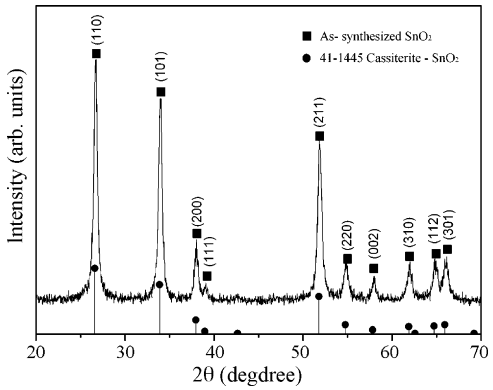

Fig. 2. X-ray diffraction pattern of as-prepared nanocrystalline SnO_2 powder synthesized by AFD.

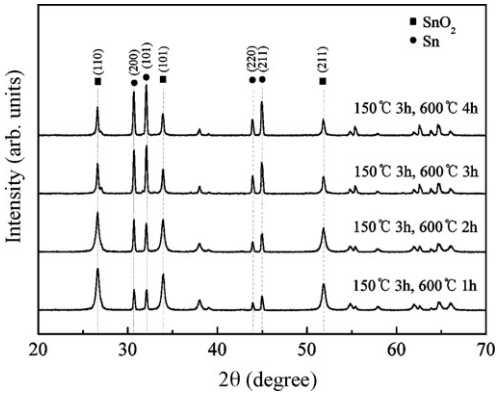

Fig. 4. X-ray diffraction patterns of the Sn/SnO_2 composite powders produced by heat treatment at 150 °C for 3 h and at 600 °C for 1–4 h of SnO_2 powder.