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Facile synthesis and electrochemical properties of porous SnO₂ micro-tubes as anode material for lithium-ion battery

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ABSTRACT

Porous SnO₂ micro-tubes were synthesized by the thermal decomposition of SnC₂O₄ precursor. The morphology of SnC₂O₄ could be preserved after the controlled heat treatment and a lot of mesopores left due to the release of gases. The mesoporous nature with a range of 3–50 nm was characterized by BET method. SEM images showed that the obtained SnO₂ samples were rhombic tube-like with swallow-tailed nozzles. When the porous SnO₂ micro-tubes were used as anode materials for lithium-ion battery, they exhibited high lithium storage capacity and coulomb efficiency. In addition, CV results demonstrated that the formation of Li₂O at high voltage was partially reversible reactions.

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1. Introduction

SnO₂ is an important inorganic compound with novel electrical and chemical properties. It finds wide application in the fields of catalysis, gas-sensing devices [1,2], and is also studied widely as a promising alternative anode for lithium-ion battery [3]. It is well-known that the particle size and morphology have great influence on the properties. The controlled synthesis of SnO₂ with specific morphology and the researches on the shape-depended properties have attracted considerable attention. Up to now, it has been shown that well-defined SnO₂ nanostructures with an abundant variety of morphologies, such as nanotubes, nanowires, zigzag belts, and hollow spheres [4–7], have been achieved through chemical or physical strategies. Some applications may actually benefit from a properly designed nanostructure. In particular, as anode materials for lithium-ion battery, the porous structure shows a promising way to improve the performance of SnO₂ electrodes [8].

In this work, porous SnO₂ micro-tubes are synthesized by temperature-controlled decomposition method [9], which is a facile strategy to synthesize porous structure without any templates or surfactants. Oxalates are the best choices due to their low cost, good stability and low decomposition temperature [10]. During the decomposition process, gases (such as CO₂, H₂O) are released which makes it possible to obtain porous materials easily. Here, stannous oxalates are used as the precursor and the electrochemical properties of porous SnO₂ micro-tubes are also investigated.

2. Experimental

In a typical experiment, 0.28 g H₂C₂O₄·2H₂O was dissolved in deionized water (100 ml). When a pellucid solution was obtained, 0.5 g SnCl₂·2H₂O was added directly without stirring. The white precipitates were separated by centrifugation and dried in vacuum. Then, the obtained precursor was calcined at 350 °C for 2 h. It could be described by the formula as follows:



The heating rate was limited to as low as 1 min^{−1}.

The crystal structures of the produces were characterized by Shimadzu-7000 type X-ray diffraction apparatus with Cu-Kα radiation. The morphology was observed by FESEM (JSM-7000F). Nitrogen adsorption–desorption isotherms were obtained with the surface area and pore size analyzer (Coulter SA 3100). And then, BET and BJH method were introduced to calculate surface area and determine the pore size distribution.

Electrochemical experiments were carried out in two-electrode Swagelok cells. The working electrodes were fabricated as follows: porous SnO₂ micro-tubes, carbon black and binder (polyvinylidene fluoride, PVDF) with a mass ratio of 80:10:10 were dispersed in N-methyl pyrrolidone (NMP). The mixture was then spread uniformly onto a copper foil with a diameter of 10 mm and dried in vacuum at 100 °C. The cells were assembled in an argon filled glove box. Metallic lithium foil was used as counter electrode. The electrolyte was made of 1 M LiPF₆ dissolved in the mixture of ethylene carbonate (EC) and diethylene carbonate (DEC) with the volume ratio of 1:1. Then, galvanostatical charge and discharge were carried out at a current

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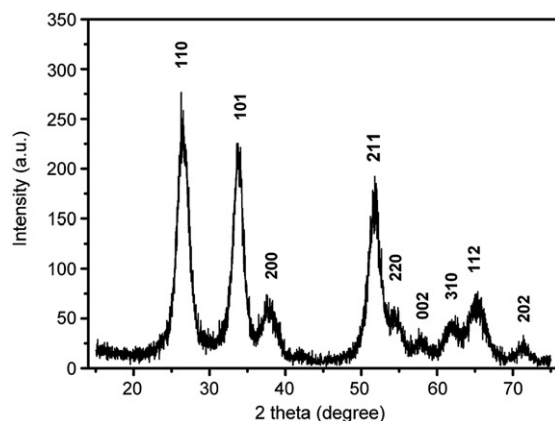


Fig. 1. XRD pattern of porous SnO₂ micro-tubes.

density of 0.2 mA·cm⁻² and cyclic voltammograms (CV) were tested between 3.0 V and 0 V at a scan rate of 0.3 mV s⁻¹.

3. Result and discussion

The crystal structure of the SnO₂ micro-tube is confirmed by X-ray diffraction, as shown in Fig. 1. All the diffraction peaks in XRD pattern can be well indexed to a rutile structure of SnO₂ (JCPDS No. 41-1445), which shows good phase purity.

The morphology of the obtained product is investigated by FESEM. Fig. 2 indicates that the tube-like SnO₂ could be obtained in large scale. The as-synthesized samples are rhombic tube-like with swallow-tailed nozzles (Fig. 2b). The representative length is estimated to be 15 μm and the rhombus side is about several micrometers. Fig. 2c shows the top view of the SnO₂ micro-tubes. The tube-like structure is revealed distinctly. The thickness of the tube wall is about 1 μm. Fig. 2a (inset) is a single particle of SnC₂O₄ precursor. It is found that the rhombic tube-like morphology is preserved after the heat treatment. However, the decomposition process results in a high weight loss up to 27.1% according to formula (1). This implies that there will be a lot of pores left.

The porous nature is determined by nitrogen adsorption–desorption. Fig. 3 shows the nitrogen adsorption–desorption result, which exhibited the typical IV isotherm with a distinct hysteresis loop. Basing on the report of nitrogen adsorption–desorption, the SnO₂ micro-tubes exhibit a BET surface area of 61 m² g⁻¹ and pore volume of 0.0939 mL g⁻¹. The pore size distribution is shown in Fig. 3 (inset), which indicates the presence of mesopores in the size range of 3–50 nm. The peak value of the pore size is 4.3 nm. As a conclusion, the porous crystalline SnO₂ with regular rhombic tube-like morphology could be obtained simply by the controlled decomposition approach.

The anode reaction mechanisms of Li with SnO₂ can be described as follows [11]:

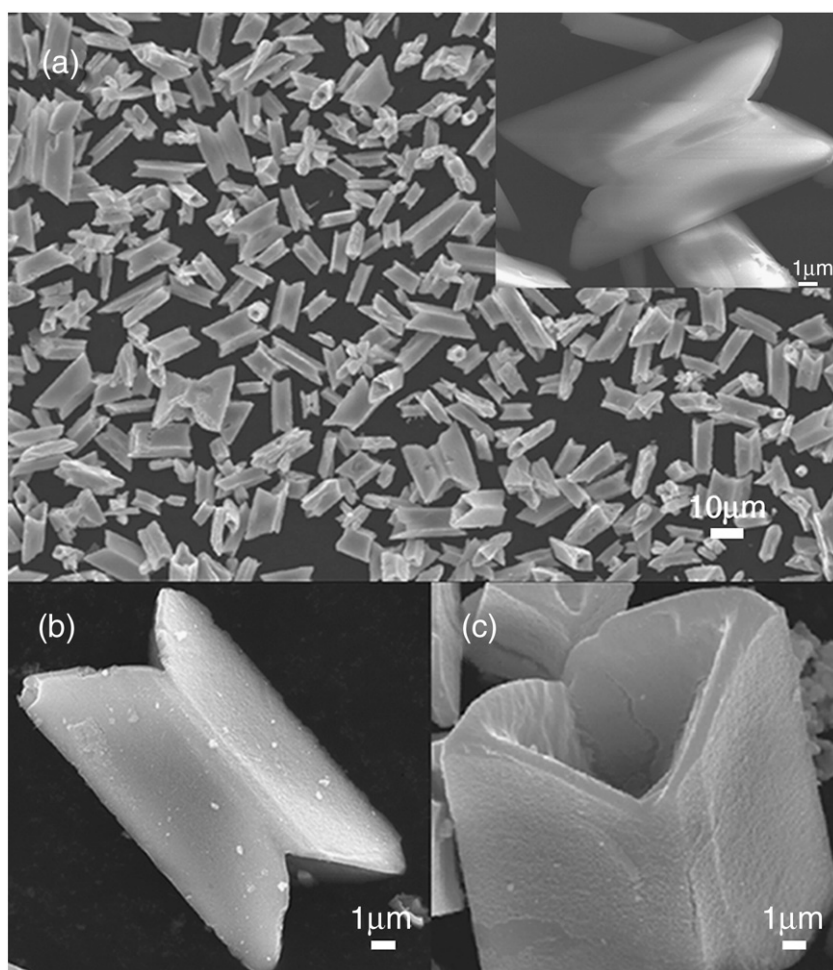
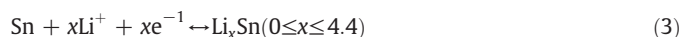


Fig. 2. SEM images of as-synthesized SnO₂ micro-tubes in low (a), high magnification (b), and top view (c). Inset (a) is a single particle of SnC₂O₄ precursor.

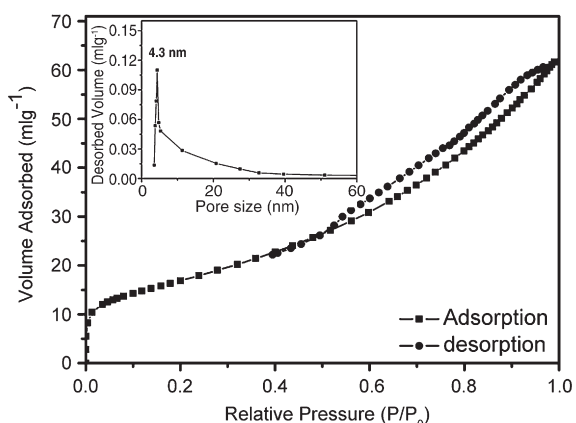


Fig. 3. Nitrogen adsorption and desorption isotherms and pore size distribution curve (inset) of porous SnO₂ micro-tubes.

Here, cyclic voltammograms are performed to study the reaction mechanism of the SnO₂ micro-tubes. As shown in Fig. 4a, during the first cathodic scan, the peak at 0.7 V is ascribed to the reduction of SnO₂ as described in Eq. (2). The broad peak extending to 0 V corresponds to the formation of Li_xSn. Similarly, in the first anodic scan, there are also two peaks that appeared obviously. The first peak near 0.7 V indicates the dealloying reaction of Li_xSn and the relatively weak peak at high voltage should correspond to the deformation of Li₂O. It is generally accepted that the reaction of Eq. (2) is irreversible in SnO₂ electrodes. But in the porous SnO₂ micro-tube electrode, the two peaks at the high voltage (>0.8 V) both in anodic and cathodic scans can be clearly

observed in the following cycles just with the intensity decreased. It means that the first reaction process as described in Eq. (2) is reversible partially, which results in a higher specific capacity. The reversible reaction of the formation/deformation of Li₂O has been demonstrated in nanosized transition metal oxides [12]. In parallel with the transition metal oxides, the existence of nanosized metal Sn particles at enormous surfaces driven by electrochemical reaction in porous SnO₂ micro-tube electrodes is believed to enhance the electrochemical activity towards the formation/deformation of Li₂O, which effectively enhance the Li storage capacity. Furthermore, the partially reversible reaction mechanism of Li₂O in SnO₂ nanocomposites and hollow SnO₂ microspheres is also proposed by Liu et al. and Han et al. recently [13,14]. This interesting point waits further verifying in SnO₂ electrodes with novel nanostructure.

The cycle performance of porous SnO₂ micro-tube electrode is shown in Fig. 4b. From it we can see clearly that the coulomb efficiencies improve rapidly with the cycling and high coulomb efficiency is shown after the 4th cycle. The discharge and charge capacities of the first cycle are approximately 1790 mAh g⁻¹ and 750 mAh g⁻¹, respectively. In detail, it is found that the discharge capacity in the first five cycles is much larger than the theoretical reversible capacity of SnO₂ (790 mAh g⁻¹). The partially reversible reaction of Eq. (2) results in higher lithium storage capacity of SnO₂ electrodes. The subsequent 20 cycles indicate a high specific capacity above 530 mAh g⁻¹. Unfortunately, the cyclability is not so satisfactory since there is a continuous capacity fading during the 30 cycles. The main problem of the capacity fading is the pulverization problem induced by severe volume expansion and contraction during the lithiation/delithiation process, which results in poor electronic contact and leads to deterioration in capacity [15]. The porous SnO₂ micro-tube indicates limited interior hollow spaces to accommodate large volume change and the further works focus on highly porous SnO₂ are on the schedule.

4. Conclusions

A facile method has been developed to prepare porous SnO₂ micro-tubes. As the anode materials for lithium-ion battery, the porous SnO₂ micro-tube electrodes exhibit a high coulomb efficiency and enhanced Li storage capacity. The specific capacity of the porous SnO₂ micro-tube electrodes exceeds 530 mAh g⁻¹ after 20 cycles. The novel porous structure is demonstrated to be a promising way to enhance the electrochemical performance of SnO₂-based anode materials. Also, the partially reversible mechanism of Li₂O is shown directly by CV results in porous SnO₂ micro-tube electrodes.

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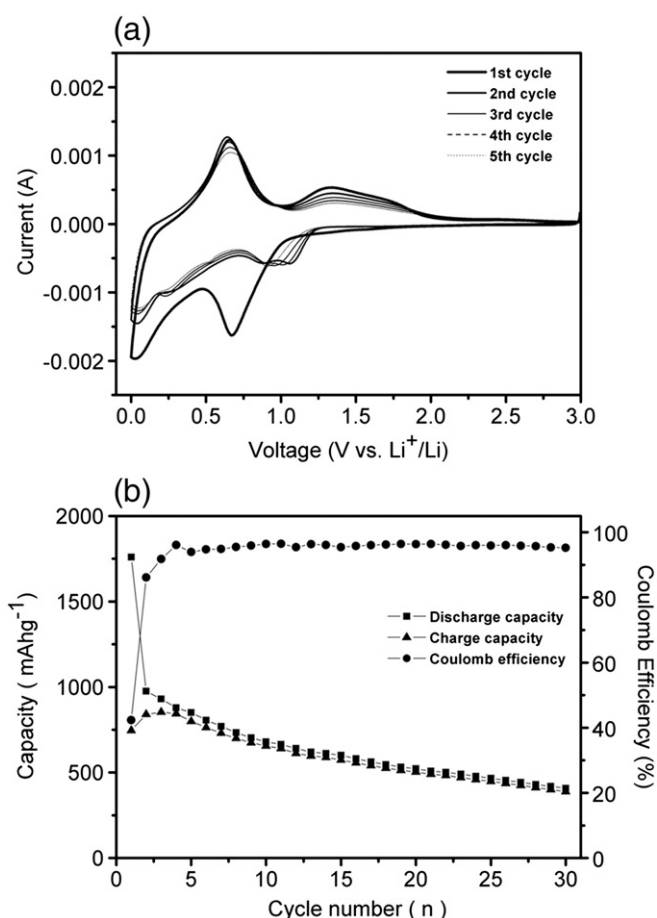


Fig. 4. CV curves (a) and the cycle performance (b) of porous SnO₂ micro-tubes.