Electrodeposition route to synthesize SnO₂ microparticles as an anode material for Li-ion batteries

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Abstract. Tin dioxide (SnO₂) samples were prepared by direct current electrodeposition method and their electrochemical properties as anode materials for Li-ion battery were investigated with Li as counter electrode. The as-prepared SnO₂ powders were characterized by X-ray diffraction (XRD), scanning electron microscopy (SEM) and N₂-adsorption-desorption experiments. It was found that SnO₂ can be synthesized by one-step electrodeposition and the crystallinity improved markedly after annealed. The samples consisted of uniform spherical SnO₂ crystal particles with size in the order of 100~200nm. After dried at 120℃ and annealed at 400, 600, 800℃ respectively, the samples were used as anode materials for Li-ion battery. The results showed that the samples annealed at 600℃ had a high coulombic efficiency and had the best electrochemical performance.

1. Introduction

Although carbonaceous materials are most commonly used as anode materials for commercial Li-ion batteries, new anode materials are needed to improve the safety of Li-ion batteries as well as their capacities and rate capabilities. Tin dioxide is considered to be one of the most promising anode materials for Li-ion battery because it has high energy density (781mAh/g). However, Tin oxides had the drastic volume expansion occurring during the lithiation, which generally resulted in poor cycle performance [1]. Some different approaches have been used to improve the drawback of tin oxides, including introducing nanostructured electrodes [2], doping other elements or compounds [3], and so on. In fact, the preparation method and process also plays an important role in improving the property of many materials. And so, many methods such as sol-gel, co-precipitation etc, were used to prepare SnO₂ as an anode material for Li-ion battery. In this work, we prepared submicron-SnO₂ powders by one-step electrodeposition method and the electrochemical proformance of materials treated in different temperatures was also investigated.

2. Experimental

The traditional electrolytic cell with two electrodes was used in the process. A sheet of copper (99.99%) in 200mm × 500 mm × 1 mm size was used as the working electrode. It was cleaned with acetone, diluted hydrochloric acid and deionized water. The tin tablet (99.99%) was the counter electrode. The distance between the working electrode and the counter electrode was 2cm. Electrolyte
solutions contained SnCl₂ (c=0.02mol/L), NaNO₃ (c=0.1mol/L) and HNO₃ (c=0.075mol/L). All the 
used reagents were AR purity. WYJ-30 DC was used as the power supply. The current density was 
8.0mA/cm², the time of the deposition was 10h, and the electrolyte temperature was controled at 
around 50°C. The product was collected and cleaned with deionized water, and then dried at 120°C. 
The sample was recorded as Dried at 120°C. The parallel samples were treated at 400°C, 600°C, 800°C 
for 2h and recorded as Annealed at 400°C, 600°C, 800°C respectively.

The crystal structure of the as-prepared samples were characterized by XRD (Bruker D8), using 
CuKα (λ =0.15418nm) radiation at 40kV and 60mA in a 2θ range from 20° to 80° at room 
temperature. The morphology and the microstructure were observed by SEM (JEM-5600 scanning 
electron microscopes) with an accelerating voltage of 200kV. N₂-adsorption-desorption experiment 
instrument (3H-2000, Beijing Haihong) was employed to test the specific surface area of samples by 
the Brunauer-Emmett-Teller (BET) method.

Electrochemical performance of samples versus Li metal was also evaluated for possible use in 
lithium-ion batteries. The electrochemical reactions of samples with lithium were investigated using a 
simple two-electrode cell: Li/LiPF₆(EC+DMC)/SnO₂. The working electrode consists of 80wt.% as-
prepared powders, 10wt.% Super P carbon as the conducting agent, 10wt.% polyvinylidene fluoride 
(PVDF) as the binder, and Cu foils as the substrates (current collector). The cells were assembled in an 
Ar-filled glove box using polypropylene (PP) micro-porous film as the separator, a solution of 1M 
LiPF₆ in ethylene carbonate(EC)/dimethyl carbonate(DMC)(1:1, v/v) as the electrolyte and metallic 
lithium foils as counter electrodes. The electrochemical tests were performed on a CT2001A Land 
battery testing systems (Hannuo Electronics Co. Ltd ., China). The cells were charged and discharged 
at a current of 0.2C, and a temperature of 25°C in the voltage range of 0–1.5V.

3. Results and discussion

3.1. Structure and morphology

The XRD pattern of the sample dried at 120°C was given in Figure 1. The diffraction peaks including 
four major peaks (110), (101), (200) and (211) can be indexed to cassiterite phase SnO₂ (JCPDS file 
41-1445), which testified that SnO₂ can be obtained by one-step electrodeposition. The reflections of 
samples annealed at 400, 600 and 800°C are also corresponding well with reflections of cassiterite 
phase (JCPDS file 41-1445). The XRD pattern of the sample treated at 600°C was also given in Fig.1. 
It is seen that the reflections of the annealed sample become sharper, indicating the annealed sample 
has better crystal degree.

![Figure 1. XRD patterns of SnO₂ samples, A: Dried at 120°C, B: Annealed at 600°C.](image)

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A typical SEM image of SnO$_2$ powders is given in Figure 2. It is clearly seen from the image that the powders contains sub-micron sized particles with good morphology and size. The samples consisted of uniform spherical SnO$_2$ crystal particles with the size in the order of 100–200nm and a few are seen to be present as agglomerates. Particles with this size and morphology can get a full contact with electrolyte, reduce the resistance, increase the reaction area and conductivity to the insertion and deinsertion of the lithium ion, so it is suitable to be the anode material of lithium ion battery.

![Figure 2. SEM imagine of SnO$_2$ (annealed at 600°C)](image)

3.2. Electrochemical properties

The first-cycle insertion capacities for SnO$_2$ dried at 120°C, annealed at 400, 600 and 800°C are 1204.4, 1376.8, 1803.2, and 1378.9mAh/g, respectively. The higher insertion capacity for the 600°C sample may be due to the better refined crystallinity of the sample, which can provide easier pathways and necessary rearrangement of the constituent atoms [3]. The first-cycle deinsertion capacities for SnO$_2$ heat-treated at 120, 400, 600 and 800°C are 246.4, 429.3, 723.3, and 426.3mAh/g, respectively. The higher deinsertion capacity obtained with the sample heat treated at 600°C is attributed to the lower irreversible capacity which probably is due to smaller concentrations of surface hydroxyl groups [3]. But we can see the capacity of the sample annealed at 800°C decreased compared with that of the sample annealed at 600°C. The Brunauer-Emmett-Teller (BET) test showed that the SnO$_2$ treated at 600°C has a bigger specific surface area compared with that of samples treated at 800°C. It was speculated that the insertion and deinsertion capacity will increase with the specific surface area sharply increasing.

In the tenth cycle, the deinsertion capacities of the sample dried at 120°C, annealed at 400°C, 600°C, 800°C are 127.4, 206.5, 414.9 and 245.1mAh/g, respectively. The sample treated at 600°C has a relatively high deinsertion capacity and a high capacity retention rate (57.4% at the 10th cycle). For the samples dried at 120°C, annealed at 400°C, 800°C, was not only deinsertion capacity lower than that of the former, but also the capacity retention lower than the former (51.7%, 56%, 48.7% at the 10th cycle, respectively).

Figure 3. shows the coulombic efficiency of the samples dried at 120°C and annealed at 600°C. It is clear that the sample annealed at 600°C has a higher efficiency in the first cycle. This is perhaps due to the perfect crystallinity of the annealed sample. As for samples annealed at 400°C and 800°C, the efficiency in the first cycle was higher than that of sample dried at 120°C but lower than the sample annealed at 600°C. After two cycles, the coulombic efficiency of all samples had reached to above 90%. It can be thought that sample annealed at 600°C has the best electrochemical performance. The result may be related to higher crystal degree and bigger specific surface area.
4. Conclusions
Submicron-SnO₂ was prepared by one-step electrodeposition method, and the samples were characterized by X-ray diffraction (XRD), scanning electron microscopy (SEM) and N₂-adsorption-desorption experiments. The results showed that the samples have uniform spherical shape and particle size was in the order of 100~200nm. After annealed at 600℃, the electrochemical performance of samples was improved and its first discharge specific capacity could reach to 723mAh/g. It had a relatively high cycle efficiency compared with samples heat-treated at other temperatures, remained stable at around 90%. After the second cycle and after 10 cycles its capacity still preserved at 419.2mAh/g. These results showed that sample annealed at 600℃ has the best electrochemical performance. It was thought to be related to its higher crystal degree and bigger specific surface area.

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