Comparison of SnO$_2$-carbon nanotubes composite and the SnO$_2$-carbon black mixture as an anode for Li-ion batteries

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Abstract. This article reports a comparative study on the electrochemical properties between SnO$_2$-carbon nanotubes (CNTs) composite and SnO$_2$-carbon black (CB) mixture. The SnO$_2$-CNTs composite was directly synthesized by a sol-gel method with purified multi-walled carbon nanotubes and tin chloride. The SnO$_2$-CB mixture was obtained by mixing carbon black with the previously prepared SnO$_2$. XRD profiles of SnO$_2$-CNTs and the obtained SnO$_2$ have shown the pure tin dioxide phase for the composite and the mixture. TEM images confirmed that SnO$_2$ nanoparticles with average particle size of 3-20 nm are deposited on the outer surface of carbon nanotubes, while the SnO$_2$ obtained for the mixture indicate larger average particle size than that of in the SnO$_2$-CNTs composite. These samples were used as anode materials for the lithium ion battery. The SnO$_2$-CNTs composite showed an initial charge capacity of 810 mAg$^{-1}$ which slightly reduced to 500 mAg$^{-1}$ after 100 cycles. The SnO$_2$-CB mixture had a smaller capacity, i.e., an initial charge capacity of 350 mAg$^{-1}$, and decreased to 230 mAg$^{-1}$ after 100 cycles. A reversible capacity at 0.2 Ag$^{-1}$ was recovered for both samples after the cycling at different current densities, which implies excellent rate performance of the materials.

1. Introduction

The development of new anode materials for lithium-ion batteries has become one of the focus areas of materials science. In the past decade, tremendous progress has been made due to the significant advances in nanotechnology and materials science, and various nanostructured materials have been applied as the electrode materials for lithium-ion batteries. Among those materials, tin dioxide (SnO$_2$) is regarded as a promising anode candidate material for lithium-ion batteries because of its high theoretical capacity [1]. However, in the electrochemical processes, SnO$_2$ base anode materials exhibit an irreversible reduction process from SnO$_2$ to metallic Sn [2]. They also have some defects on high Li$^+$ voltage, low initial coulomb efficiency, and significant volume change during the charge and discharge process.

Several strategies have been proposed to overcome the above shortcomings, while two methods are widely studied recently [3-10]. Creating unique SnO$_2$ nanostructures, such as 1D and 2D nanostructures [11, 12] is one of the effective ways, while introducing carbonaceous materials to produce SnO$_2$-C composites or mixtures into electrodes is another beneficial approach. The formation of composites or mixtures blend with tin oxide and carbon is facile in execution. The composites or mixtures could also
bring forwards many advantages [13-15], such as carbon acted as supports with elastic properties further provide a buffer effect against volume strain. Carbon-containing materials improved the electrical conductivity of the composites or mixtures as well [1].

The presented work aims to overcome the above problems of SnO$_2$ presented in the lithium battery application, further to explore high-performance SnO$_2$ base anode materials in energy storage filed. Therefore, the composite of tin dioxide with carbon nanotubes (SnO$_2$-CNTs) and a mechanical mixture of tin dioxide with a carbon black (SnO$_2$-CB) were prepared, their electrochemical properties were evaluated.

2. Experimental

2.1. Material fabrication

Synthesis of SnO$_2$: The SnO$_2$ was synthesized by the Sol-gel method according to [16].

Synthesis of multiwalled carbon nanotubes (CNTs): CNTs was obtained by the CVD method over the bimetallic catalyst (NiO/Cr$_2$O$_3$/MgO) from acetylene at 600°C, according to our previous work [17]. The as-prepared CNTs were purified by refluxing in concentrated nitric acid for 1 hour. Then it was cooled down to room temperature naturally. After washing and centrifugation, CNTs were dried at 60°C for 12 h.

Synthesis of SnO$_2$-CNTs composite: In the presented procedure, the initial weight ratio of SnO$_2$ to CNTs was calculated in 50: 50. Typically, 0.8 g of SnCl$_2$·2H$_2$O was added into 50 mL of isopropyl alcohol under magnetic stirring for 2 h. Then 0.5 g purified CNTs obtained in above section was added and ultrasonicated for 1 h. The resulting suspension was evaporated at 120°C overnight and consequently calcined in the air atmosphere at 400°C for 2 h [18].

Synthesis of SnO$_2$-CB mixture: The SnO$_2$-CB mixture was prepared by mechanical grounding method in a mortar with carbon black and SnO$_2$. In this way, the initial weight ratio of SnO$_2$ and CB is 50:50. The SnO$_2$ was prepared in the above procedure, the carbon black (Super-P) was purchased from Bonap Co., Ltd. (Shenzhen, China).

2.2. Structural characterization

Samples (SnO$_2$-CNTs composite and SnO$_2$) for transmission electron microscopy (TEM) were sonicated and dispersed in HPLC ethanol and processed in a FEI Tecnai 12 TEM with accelerating voltage of 120 KV. TG analysis was performed on a NETZSCH TG 209F1. Approximately 5 mg of material was heated from 25 °C to 900 °C at the ramping rate of 10 °C min$^{-1}$ under air atmosphere. X-ray diffraction (XRD) patterns were collected by X-ray powder Diffractometer TTR3 Rigaku, Japan with a Cu $K\alpha$ radiation ($\lambda$=1.5406 Å), 30 mA and 40 V.

2.3. Electrochemical measurements

The working electrode (anode) was prepared by mixing of 80 % (weight ratio) of active materials (SnO$_2$-CNTs composite or SnO$_2$-CB mixture), and 20 % of CMC binder. The electrode was coated on Cu foil. The active mass loading on the electrode was about 0.6 mg/cm$^2$. Lithium foil was used as the counter electrode. 1 M LiPF$_6$ in EC/DMC (1:1 in volume) was used as an electrolyte. Electrochemical experiments of the half-cell were carried out on CR 2025 coin cells, which were assembled in the Ar-filled glove box (Mikrouna, China). The charge and discharge tests were performed on a Land cell test system (Land CT2001A, China) in the potential window of 0.01 to 3.0 V at different current densities (mAg$^{-1}$).

3. Results and Discussion

3.1. Characterization of materials for the anode

The X-ray diffraction (XRD) was carried out to confirm the structures of SnO$_2$-CNTs composite and SnO$_2$ obtained by the sol-gel method. For SnO$_2$-CNTs composite, those peaks were located at 2θ values
of 26.5°, 33.8°, and 51.3° (figure 1a) are attributed to the SnO₂ (110), SnO₂ (101) and SnO₂ (211) face (ICDD 01-088-0287). The diffraction peak in the spectra located at 25.9° (figure 1a) are corresponded to C (002) face [19-21]. The average particle size of SnO₂ in the SnO₂-CNTs composite is about 3 nm which was calculated by Scherer Equation. The result is consistent with the following TEM results (figure 3).

On the other hand, the XRD profile of SnO₂ obtained by the sol-gel method has similar peaks (figure 1b). However, SnO₂ is more crystalline in the SnO₂-CB mixture compared with SnO₂-CNT composite. It indicated that the SnO₂ obtained in SnO₂-CNTs composite process weaker crystallinity and smaller size than that of SnO₂ obtained by the sol-gel method.

![Figure 1. XRD profiles of (a) SnO₂-CNTs composite and (b) SnO₂.](image)

Thermal analysis was performed to further reveal the water content and carbon content within SnO₂-CNTs composite and SnO₂-CB mixture. The measurements were carried out in an air atmosphere, and the temperature was raised at a rate of 10 °C/min to 900 °C. As shown in figure 2, the SnO₂-CNTs composite and the SnO₂-CB mixture showed a weight loss of 45.8% and 54.6% in the procedure, respectively. The weight loss of 1.6% for SnO₂-CNTs composite and 4.7% for SnO₂-carbon black mixture below 200 °C should be attributed to the removal of surface-adsorbed water. Above 200 °C, the CNTs and carbon black should have been removed entirely, which was also consistent with the starting weight ratios of 50:50 for the CNTs to SnO₂ and carbon black to SnO₂ in the synthesis procedurals detailed in section 2.1.

![Figure 2. TG profiles of SnO₂-CNTs composite and SnO₂-CB mixture.](image)

The morphology of the SnO₂-CNTs composite and SnO₂ obtained by sol-gel method are revealed by TEM. TEM-images (figure 3a) show that tin dioxide was deposited uniformly in the SnO₂-CNT composite. The SnO₂ particles are distributed arbitrarily on the surface of CNTs in the form of spherical
particles about 3-20 nm in size (round red dash with the size of about 3 nm, and square yellow dash in size about 20 nm). It is consistent with the XRD results and our previously obtained results [21]. The specific surface area of SnO₂-CNTs is 310 m² g⁻¹. Such high specific surface area is derived from the initial CNTs. The SnO₂-CNTs with such structural adsorption characteristics could have a high potential in the preparation of nanocomposites as anode materials in lithium-ion batteries [16]. Figure 3b displays TEM images of the synthesized sample of SnO₂ in the sol-gel method, in which the individual crystal sizes are in the range of 50-100 nm. The particles showed a pronounced hexagonal shape. These findings are consistent with the XRD results.

![TEM images of (a) SnO₂-CNTs electrode displayed continuous superiority in lithium performance SnO₂-CNTs composite and (b) SnO₂.](image)

3.2. Electrochemical measurements

To determine the rate tolerance of the materials, galvanostatic charge/discharge performance of SnO₂-CNTs and SnO₂-CB was carried out at different current densities. As shown in figure 4, the discharge capacity of SnO₂-CNTs electrode is 810 mAh g⁻¹ which is continuously higher than that of the SnO₂-CB electrode (200 mAh g⁻¹). Furthermore, SnO₂-CNTs electrode displayed superiority in lithium performance when the current densities were increased from 200, 400, 800, 1600 to 2400 mA g⁻¹ respectively, indicating excellent rate capacity. Moreover, a reversible capacity about 700 mAh g⁻¹ for SnO₂-CNTs can be recovered after cycled at high current densities. The capacity is higher than that of SnO₂-CB (350 mAh g⁻¹) which implied better rate performance for SnO₂-CNTs electrode than that of SnO₂-CB.

The 1st, 10th and 60th of the charge/discharge profiles of SnO₂-CNTs and SnO₂-CB anodes are presented on figure 5. The initial capacities for the SnO₂-CNTs (1380 mAh g⁻¹) are almost twofold than that of SnO₂-CB anodes (630 mAh g⁻¹). It should be noted that high initial Coulombic efficiency (ICE), about 65.1% for the SnO₂-CNTs composite and 52.4% for SnO₂-CB can be observed as well. Such ICE could be ascribed to the buffer effect against volume strain produced by the multi-walled carbon nanotubes or carbon black, at the same time, carbon-containing materials increase the electrical conductivity of the composite.
Finally, the cycling performances of samples were carried out at a current density of 200 mA g\(^{-1}\) for 100 cycles (figure 6). The SnO\(_2\)-CNTs anode showed an initial charge capacity of 810 mAh g\(^{-1}\) which slightly reduced to 500 mAh g\(^{-1}\) after 100 cycles. The initial charge capacity for SnO\(_2\)-CB anode corresponds to 350 mAh g\(^{-1}\) and drops to 230 mAh g\(^{-1}\) after 100 cycles. These results indicated the excellent stability of those carbon materials’ samples.

4. Conclusion
In this article, the influences of the formation way of SnO\(_2\), i.e., in a composite with multi-walled carbon nanotubes and a mixture with carbon black, on their electrochemical properties are considered. The
SnO$_2$-CNTs composite was synthesized by the facile sol-gel method. The SnO$_2$-CB mixture was prepared by mechanical mixing of two phases. The formation of SnO$_2$ phase was confirmed by XRD and thermal analysis. The SnO$_2$ particles in the SnO$_2$-CNTs composite had a size of 3-20 nm, the size of SnO$_2$ in the SnO$_2$-CB mixture was 50-100 nm, the smaller size of the SnO$_2$ particles and the presented of CNTs have great contribution of their electrochemical performance for lithium ion batteries, i.e., the SnO$_2$-CNTs composite demonstrates excellent initial capacity (810 mAh g$^{-1}$), it is higher than the theoretical capacity of carbon (370 mAh g$^{-1}$) and tin dioxide (790 mAh g$^{-1}$). Despite the differences in the initial capacity, both anodes exhibit the high initial Coulombic efficiency and excellent cycling stability.

The comparative study on the SnO$_2$-CNTs composite and SnO$_2$-CB mixture reveals that the SnO$_2$ exhibits smaller particle size, more uniform distribution and more abundant in chemical bond with the carbon surface on the SnO$_2$-CNTs composite could be the main contribution on its superior electrochemical properties than that of SnO$_2$-CB mixture. This work created an opportunity and a proper perspective for the development of the high performance of carbon-based electrode materials for lithium-ion batteries.

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