Hydrothermal Synthesis of SnO₂ Nanorod as Anode Materials for Lithium-Ion Battery

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Received 30 April 2019

Accepted 23 July 2019

Published 10 September 2019

In this study, SnO₂ nanorods are successfully prepared by simple template-free hydrothermal method without surfactant. SnO intermediate with lamellar morphology is first formatted by hydrothermal method and SnO₂ nanorods are obtained after calcinations. The results of XRD characterization show that lamellar structured SnO intermediate has preferred orientation in 0 0 1 direction. According to supposed mechanism during formation process of SnO₂ nanorods, tiny crystal nucleus of Sn(OH)₂ and a bit of SnCO₃ are generated from SnCl₂ and urea. Then the crystal nucleus gather together to form a nanorod. With continued reaction, nanorods gather together to form sheets and the sheets grow up to lamellar morphology and the intermediate decomposes into SnO because of the hydrothermal process. The SnO intermediate convert to SnO₂ with sheets breaking to nanorods after calcination. The results of galvanostatic cell cycling show that SnO₂ particle has high specific discharge capacity. This experiment of SnO₂

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nanorod preparation provides us an effective way of easy processing, low cost, and more environmentally synthesis strategy to synthesize SnO_2 nanorods.

Keywords: SnO_2 ; nanoparticles; hydrothermal method; anode materials; lithium-ion battery.

1. Introduction

Tin dioxide (SnO_2) is an important N-type semiconductive material with the advantage of stability, large band gap, low cost and eco-friendliness. SnO_2 has wide applications in many areas such as solar cell, gas sensor and optoelectronic device.^{1–3} Since transition metal oxides (MO , $\text{M}=\text{Cu}$, Co , Fe or Sn) as anode materials of lithium-ion battery were reported in 2000, SnO_2 has been found as a potential anode material due to the high theoretically gravimetric lithium storage capacity of 780 mAh g^{-1} and low potential of lithium ion intercalation.^{4,5}

It is well-known that different morphologies of nanomaterials have great influence on the performance. Now, people make many efforts to fabricate SnO_2 with various nanostructures, such as hollow spheres,⁶ porous SnO_2 nanospheres,⁷ SnO_2 nanosheets,⁸ nanoflowers⁹ and nanorods.¹⁰ For instance, Zhu *et al.*¹¹ prepared SnO_2 nanomaterial with flower morphology, which shows better gas sensing properties due to the large surface area providing more active sites. SnO_2 hollow nanosphere as electrode material of supercapacitor was synthesized by Kang *et al.*¹² This SnO_2 hollow nanosphere exhibited excellent cycling properties and much higher specific capacitance than the pristine SnO_2 particle due to unique structure stability and greatly increased available surface area. One-dimensional (1D) SnO_2 nanostructures such as nanorod and nanowire, have excellent optical and electrical properties and large surface-to-volume ratio. They could provide unique advantages in many fields such as electrode material,¹³ photovoltaic devices,¹⁴ photocatalysis¹⁵ and surface adsorption.¹⁶ For example, the SnO_2 nanorod synthesized by oleic acid-assisted hydrothermal method possesses improved discharge capacity of 694 mAh g^{-1} after 40th cycles when it was used as lithium-ion battery anode materials.¹⁷ Therefore, many efforts have been made to synthesize SnO_2 nanorod by chemical vapor deposition (CVD), vapor liquid solid (VLS) approach, spray pyrolysis method, template-based liquid phase synthetic approaches and so on.^{18–21} However, most of these reported methods usually require high

temperature or other strict experimental conditions. Therefore, the method for simple and effective preparation of SnO_2 nanorods remains to be further explored.

Hydrothermal synthesis of SnO_2 nanorod has been widely adopted in recent years due to its simple operation and low cost. For example, Guo *et al.*²² prepared SnO_2 nanorods by hydrothermal method using CTAB as template. The prepared nanorods are 40–100 nm in diameter and up to $2\text{--}3 \mu\text{m}$ in length. Hydrothermal methods provide us an efficient strategy for preparing the nanorod. However, it often requires the assistance of hard template or molecular template. It also needs a complex processes of cleaning and dispersion for the obtained samples. Therefore, developing more easily processable, low-cost and environmentally friendly hydrothermal strategy is still needed.

In this study, SnO_2 nanorods were synthesized by simple template-free hydrothermal method with no surfactant. The effects of reaction temperature and time on the nanorod morphology evolution were revealed. The formation process of SnO_2 nanorods from SnO nanoflowers was observed. This experiment of SnO_2 nanorod preparation provides us an effective way of easily processable, low-cost and more eco-friendly synthesis strategy to synthesize SnO_2 nanorods. This rod-like nanomaterial not only exhibits high capacity on the electrode material, but it also may find potential applications in many other fields.

2. Experimental Section

2.1. Synthesis and characterization of SnO_2 nanoparticle

All chemicals used in this study were analytical grade and without further purification. To prepare SnO_2 nanoparticle, 0.6769 g (3 mmol) $\text{SnCl}_2 \cdot 2\text{H}_2\text{O}$ and 1.8018 g (30 mmol) urea were dissolved in 20 mL distilled water with stirring for 0.5 h. Then, the suspension solution was transferred into a 50 mL Teflon lined stainless steel autoclave. The autoclave was sealed and heated at 150°C for 24 h. After that, autoclave was naturally cooled to room temperature.

The black precipitate was washed with distilled water and harvested with centrifugation–redispersion cycles for several times. After that, the products were sintered at 700°C for 7 h in air atmosphere to obtain the SnO₂. To investigate the effect of hydrothermal synthesis temperature and time on the morphology of SnO₂ nanomaterials, the SnO₂ was also prepared by hydrothermal reaction at 100°C, 120°C, 150°C and 180°C for 6 h, 12 h, 24 h and 48 h, respectively.

Morphological studies were conducted using a NOVA NANOSEM-450 scanning electron microscope (SEM, America FEI Company). The crystallographic structures of products were determined with X-ray diffraction (XRD, Bruker D8 ADVANCE) utilizing a Cu target at the scanning rate of 12°/min with 2θ ranging from 10° to 80°.

2.2. Electrochemical studies of SnO₂ nanoparticle

Electrochemical performances of samples were measured using CR2025 coin-type cells assembled in a dry argon filled glove box. To fabricate the working electrode, a slurry consisting of 80 wt.% active materials, 10 wt.% acetylene black, 5 wt.% CMC and 5 wt.% SBR was mixed and casted on a copper foil. Then, it was drying at 60°C under vacuum oven overnight prior to coin-cell assembly. Lithium sheets were served as counter and reference electrodes, while a Celgard 2320 membrane was employed as a separator. The electrolyte was a solution of 1 M LiPF₆ in ethylene carbonate (EC)-1,2-dimethyl carbonate (DMC) and methyl ethyl carbonate (EMC) (1:1:1 in volume). The charge–discharge testing was performed with a Land electric test system CT2001A (Wuhan LAND electronics Co., Ltd.) at a current density of 0.2 C between 0.01 V and 3.00 V (versus Li/Li⁺). Cyclic voltammetry (CV) tests were carried out on an electrochemical workstation (CHI660E, Chenhua, Shanghai) from 0.01 V to 3.00 V (versus Li/Li⁺). Electrochemical impedance spectroscopy (EIS) measurements were performed in the frequency range from 0.1 Hz to 100 kHz with an applied AC signal amplitude of 5 mV.

3. Results and Discussion

3.1. Structure and morphologies

The evaluation of morphology features of prepared SnO₂ nanomaterials with different hydrothermal

Fig. 1. SEM images of SnO₂ samples obtained at different temperature for 24 h. (a) 100°C; (b) 120°C; (c) 150°C and (d) 180°C.

reaction temperature was performed at 100°C, 120°C, 150°C and 180°C for 24 h. The SEM image of obtained SnO₂ sample is displayed in Fig. 1. As shown in Fig. 1, the as-prepared SnO₂ nanomaterials have different morphologies at different hydrothermal reaction temperature. When the reaction temperature is 100°C, the prepared SnO₂ nanomaterial exhibits irregular particle shape with approximately 50–60 nm size. The size of the SnO₂ particles has no obvious change but the morphology has slight change as some particles grow to rod-like shape when the temperature rises to 120°C. Two red arrows are used to identify the rod-like shape particles in Fig. 1(b). When the temperature increases to 150°C, the as-prepared SnO₂ nanomaterials grow into a nanorod shape, as shown in Fig. 1(c). The SnO₂ nanorods have average width approximately 44.4 nm and average length of 213.8 nm. The aspect ratio of this SnO₂ nanorod is approximately 4.9. When the temperature increases to 180°C, the SnO₂ material presents a regular nanorod shape with 45–50 nm in width and 150–190 nm in length. The aspect ratio of this SnO₂ nanorod is about 3.5. It suggests that higher hydrothermal reaction temperature has advantage on the growth of anisotropic materials of SnO₂. However, the aspect ratio of nanorods decreases when the hydrothermal reaction temperature is too high.

Fig. 2. SEM images of SnO_2 samples obtained at 150°C with different reaction time. (a) 6 h; (b) 12 h; (c) 24 h and (d) 48 h.

Different hydrothermal reaction times such as 6 h, 12 h, 24 h and 48 h at 150°C and 180°C were used to prepare SnO_2 nanomaterials in order to explore the relationship between SnO_2 nanorod formation and the hydrothermal reaction time. Figure 2 shows the SEM images of SnO_2 prepared at 150°C with different reaction time. As shown in Fig. 2(a), the SnO_2 sample appears as small particles when the hydrothermal reaction time is 6 h. When the reaction time increases to 12 h, the SnO_2 crystal gradually grows into rod shape and the morphology is a mixture of rods and small particles. When the reaction time continues to increase to 24 h, the SnO_2 crystals turn into rod shape. However, when the reaction time continues to increase to 48 h, the SnO_2 crystals are small particles again. The SnO_2 particles prepared at 48 h are round particles compared to Fig. 2(a). The same growth feature can be obtained at 180°C hydrothermal reaction as shown in Fig. 3. At 180°C , when the hydrothermal reaction time is 6 h, the SnO_2 sample is nanorod shape with very low aspect ratio. When the hydrothermal reaction time increases to 12 h, the SnO_2 crystals are rod-shaped with aspect ratio of 3.66. When the hydrothermal reaction time continues to grow to 24 h, the SnO_2 nanorods grow much wider and the aspect ratio decreases to 2.95. When the hydrothermal reaction time continues to grow to

Fig. 3. SEM images of SnO_2 samples obtained at 180°C with different reaction time. (a) 6 h; (b) 12 h; (c) 24 h and (d) 48 h.

48 h, the SnO_2 crystals show egg-like morphology. It suggests that too longer hydrothermal reaction time has disadvantage on the growth of rod-like nanomaterials. In subsequent studies, we studied the lithium-ion battery properties of samples prepared at 150°C and 180°C for 24 h. According to the hydrothermal reaction temperature, we named the obtained SnO_2 nanorods at 150°C and 180°C at 24 h as H150 and H180.

The sample directly obtained was black color after hydrothermal reaction and it turned to grayish color after calcinations during the experiment. Therefore, both samples before and after calcination were characterized by X-ray diffraction. Figure 4 shows the XRD patterns both before and after calcination of the samples H150 and H180. As shown in Fig. 4(a), before calcination, the diffraction peaks of H150 and H180 appearing at $2\theta = 18.3^\circ, 29.9^\circ, 33.3^\circ, 37.2^\circ, 47.8^\circ, 50.7^\circ, 57.4^\circ$ and 62.6° match well with the diffraction peaks of (0 0 1), (1 0 1), (1 1 0), (0 0 2), (2 0 0), (1 1 2), (2 1 1), and (1 0 3) crystal planes of SnO standard data JCPDS card PDF file No. 85-0423. In JCPDS card PDF file No. 85-0423, the ratio of (0 0 1) and (1 0 1) lattice plane is 5.4%. However, the ratio of (0 0 1) and (1 0 1) lattice plane of H150 is 62.1%, and the ratio of (0 0 1) and (1 0 1) lattice plane of H180 is 30.7%. It suggests that the SnO intermediate product prefers orientation

Fig. 4. The XRD patterns for the rod-like samples of prepared at 150°C and 180°C for 24 h. (a) not calcinated. (b) after calcinated.

growth in the 0 0 1 direction. This preferred orientation growth direction indicate that intermediate process is beneficial to the formation of nanorods.

As shown in Fig. 4(b), the diffraction peaks of calcinated samples appeared at $2\theta = 26.6^\circ$, 33.9° , 38° , 51.8° and 54.8° match well with the diffraction peaks of (1 1 0), (1 0 1), (2 0 0), (2 1 1), and (2 2 0) crystal planes of SnO₂ standard date JCPDS card PDF file No. 41-1445 (cassiterite type, tetragonal rutile SnO₂). No impurity phase was detected for both samples. The XRD results indicate that the sample before calcination is SnO with preferred orientation growth direction in the 0 0 1 direction. It converts to SnO₂ after calcination. So, the reaction process of prepared SnO₂ nano materials by

hydrothermal reaction should be

In order to investigate the growth mechanism of SnO₂ nanorods, SEM observations were performed on the SnO intermediate before calcinations when prepared by the hydrothermal method. Figure 5 exhibits the SEM images of SnO intermediate at different hydrothermal reaction times. The SEM images indicate that the SnO intermediate is lamellar morphology. The formation of this lamellar structure is consistent with the XRD patterns, which demonstrate that the intermediate has a preferred orientation in the 0 0 1 direction. When the hydrothermal reaction time is 6 h, the SnO intermediate slice is about 300 nm in thickness and 3–5 μm in width. When the hydrothermal reaction time is 12 h, the size of the SnO intermediate slice is very similar to that at 6 h, but here some tiny nanorods appear. The SnO intermediate slices grow much bigger and some fine structures are slowly presented with hydrothermal reaction time increases. Figure 5(e) is the enlarged picture of the red circle in Fig. 5(d). As it can be seen in Fig. 5(e), the SnO intermediate has very thin-sheet shape. And the sheets gather together to form a peony flower which is the Chinese national flower. These thin sheets look like the petals of the peony flower. Figure 5(f) is a picture of Chinese peony flower. The sheet is about 30 nm thickness and about 350 nm width. Now, it can be seen that the size of the SnO intermediate is close to the size of final SnO₂ nanorods.

Scheme 1 illustrates the possible formation processes for the SnO₂ nanorods. In the first stage, tiny crystal nucleus of Sn(OH)₂ and a small amount of SnCO₃ are generated from SnCl₂ and urea. This is because urea decomposes into ammonia and carbonic acid at high temperature. Then the crystal nuclei gather together to form a line and the lines grow upto nanorods. With the continuous reaction, the nanorods gather together to form sheets and the sheets grow up to lamellar morphology. Therefore, SnO intermediate with peony flower morphology is collected after hydrothermal reaction as Sn(OH)₂ and SnCO₃ decomposes into SnO during the hydrothermal reaction. At the time of calcination, since the participation of oxygen, the SnO converts to SnO₂ and the sheets break to SnO₂ nanorods.

Fig. 5. SEM images of SnO intermediate products obtained at 150°C with different reaction time. (a) 6 h; (b) 12 h; (c) 24 h; (d) 48 h; (e) surface enlargement and (f) Chinese peony flower.

Scheme 1. Schematic illustration of the formation mechanism proposed for SnO₂ nanorods.

3.2. Electrochemical performance

Figure 6 shows the charge/discharge voltage curves of the anodes constructed from SnO₂ nanorod samples at 0.2 C rate in the voltage range of 0.01 ~ 3.00 V versus. Li/Li⁺. As shown in Fig. 6, both the samples have high initial discharge specific capacity nearly to 1600 mAh g⁻¹, which is much higher than the theoretical discharge specific capacity (782 mAh g⁻¹). The high initial discharge capacity might be due to the formation of solid electrolyte interface (SEI) layer during the first discharging process. The capacity of both samples in the second cycle is more than 1000 mAh g⁻¹. The discharge specific capacity falls to about

900 mAh g⁻¹ after five cycles. After 10 cycles, the discharge specific capacity decreased to less than 800 mAh g⁻¹. After 20 cycles, it decreases to about 400 mAh g⁻¹. The mechanism of lithium intercalation process of SnO₂ can be divided into two processes. The first process is the transformation mechanism. In this process, SnO₂ transforms to Sn, and Li⁺ inserted into the anode to format Li₂O. SnO₂ should be first transformed to SnO during this process. Then the SnO is transformed to Sn. The second process is the alloying mechanism. In this process, Sn forms an alloy with Li in the discharge process. The reaction is as follows:

Fig. 6. Charge-discharge curves for selected cycles for the SnO₂ samples in the potential range of 0.01 ~ 3.00 V at 0.2 C. (a) H150 and (b) H180.

In order to have a deep insight into discharge capacity fading, a comparison of H150 and H180 electrodes before and after 50th charge-discharge cycles was analyzed by SEM. The results are shown in Fig. 7. As can be seen in Figs. 7(a), 7(c), 7(e) and 7(g), before charge-discharge cycles, no obvious crack was observed and the active materials attached tightly with the copper foil. However, after 50th charge-discharge cycles, as shown in Figs. 7(b) and 7(f), the obvious cracks were found on the surface of both H150 and H180 electrode films. As shown in Figs. 7(d) and 7(h), gaps of about

Fig. 7. SEM images of H150 and H180 electrodes before and after charge-discharge cycles. (a) and (c) H150 before cycle; (b) and (d) H150 after cycles; (e) and (g) H180 before cycle; (f) and (h) H180 after cycle.

0.99–1.93 μm of H150 and 0.4–1.09 μm of H180 between active materials and copper foil was observed. The occurrence of cracks and gaps was caused by the volume expansion and contraction and the stress release during the progresses of lithium intercalation into active material and the alloying process during the repeated charge and discharge cycling process. During this process, chemomechanical deformation

of SnO_2 materials occurred, and a part of active material fell off from the copper foil, causing serious capacity fading.²³

As can be expected, SnO_2 as lithium-ion battery anode electrode material has a great application prospect if the cycle stability could be further improved. Nowadays, many researchers have already produced series of studies such as shell coating^{24,25} and synthesis of nanocomposite^{26,27} in order to improve the stability of the discharge specific capacity, which can effectively buffer internal stress caused by volume expansion, reduce the irreversible capacity attenuation and improve cycle performance.

To better understand the electrochemical reaction process, the CV of the battery from the initial cycle was characterized in the potential range of 0.01–3.00 V at a scan rate of 0.05 mV/s. As shown in Fig. 8, there are two reduction peaks around 0.169 V and 0.733 V of the sample H180. The reduction peak at 0.733 V corresponds to the reaction (1), and the SnO_2 converted to SnO . Then the reduction peak at 0.169 V corresponds to the reaction (2), and the SnO converted to Sn . This reduction peak at 0.169 V is very wide and the alloying of Sn with Li also occurs at this peak position. Three oxidation peaks appearing at 0.51 V, 1.27 V and 1.74 V can be ascribed to the de-alloying from Li_xSn to Sn , oxidizing Sn to SnO and oxidizing SnO to SnO_2 .

To further understand the electrochemical performance of SnO_2 nanorod, it was tested EIS and the results are shown in Fig. 9. Figure 9 shows the Nyquist plots of H150 and H180 materials at open

Fig. 8. The CV curves of SnO_2 nanorod sample of H150 and H180 at scan rate 0.05 mV/s.

Fig. 9. The Nyquist plot obtained from Li/SnO_2 cell at open circuit voltage. The frequency ranged from 0.1 Hz to 100 KHz with an applied AC signal amplitude of 5 mV.

circuit voltage. As it can be seen in Fig. 9, impedance spectra mainly consist of an oblate semicircle in high-to-medium frequency region and an inclined straight line in low frequency range. Generally, the semicircles in high-to-medium frequency range is related to the Li -ion migration resistance (R_{sf}) through the SEI film and charge transfer resistance (R_{ct}), and the straight line with respect to the diffusion of Li -ion within the electrode. The sum of R_{sf} and R_{ct} value of the H180 is 290 Ω , as shown in Fig. 9. It is slightly lower compared to H150 (340 Ω). In conclusion, the H150 and H180 SnO_2 nanorods have similar electrochemical resistance.

4. Conclusion

In general, SnO_2 nanorods are successfully prepared by simple template-free hydrothermal method without surfactant. The temperature and reaction time have significant effect on crystallization and growth of final products. SnO intermediate with lamellar morphology is first formatted by hydrothermal method and SnO_2 nanorods are obtained after calcinations. We suppose tiny crystal nucleus of $\text{Sn}(\text{OH})_2$ and small amount of SnCO_3 are generated first from SnCl_2 and urea. Then the tiny crystal nuclei gather together to form lamellar morphology and the intermediate decomposes into SnO . The SnO intermediate converts to SnO_2 with the lamellar morphology breaking into nanorods after calcination. The results of galvanostatic cell cycling show that the SnO_2 particle has high specific discharge capacity. This experiment provides us an

effective way of easy processable, low cost, and more eco-friendly synthesis strategy of SnO₂ nanorods.

Acknowledgments

This work was financially supported by National Natural Scientific Fund of China (Nos. 21761035, 21463028, 21565031 and 21665027), Key Project of Higher Education Research Foundation in Hebei Province (grant: ZD2019106), the Doctoral Scientific Research Foundation of North China Institute of Aerospace Engineering (No. BKY-2018-01), Innovative Training Program of Yunnan Minzu University for graduate student (No. 2018YJCXS249).

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