Facile Synthesis of Donut-like TiO$_2$-SnO$_2$ Nanocomposite Microspheres by a Two-step Hydrothermal Reaction and Subsequent Spray Drying Process and Its Electrochemical Lithium Storage Properties

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Abstract: Donut-like TiO$_2$-SnO$_2$ nanocomposite microspheres were successfully synthesized via a facile two-step hydrothermal reaction and subsequent spray drying. The protonated titanate nanowires with H$_2$Ti$_3$O$_7$ phase in the nanocomposite precursor transformed into not anatase TiO$_2$ but TiO$_2$(B) crystal structure even after calcination at 400 ℃. And the substitutional solid solution (Sn, Ti)O$_2$ with the same tetragonal rutile structure as SnO$_2$ was formed. Moreover, the hierarchical donut-like structure in TiO$_2$-SnO$_2$ nanocomposite microspheres constructed by the second-step hydrothermal and spray drying treatment was maintained after calcination at 400 ℃. The electrochemical test showed that the as-obtained TiO$_2$-SnO$_2$ nanocomposite microspheres reached an initial discharge capacity of 640 m Ah g$^{-1}$ at a current density of 40 mA g$^{-1}$, which is much higher than the theoretical capacity of TiO$_2$(B).

Keywords: TiO$_2$-SnO$_2$ nanocomposite; hydrothermal reaction; spray drying; electrochemical performance

1. INTRODUCTION

Recently, there has been considerable interest in metal oxide as a potential anode material for use in lithium ion batteries [1]. Among them, TiO$_2$ especially the one with anatase crystal structure is extensively studied because it is abundant, environmentally benign and delivers a high discharge voltage plateau of about 1.7 V, stable cycling performance, and small volume expansion (∼3%) during lithiation/delithiation [2-5]. Besides anatase TiO$_2$, the other polymorphs like rutile, brookite and TiO$_2$(B) have been demonstrated to possess the lithium storage properties [6-12]. Their theoretical specific capacity of TiO$_2$ is estimated to be less than 335 mAh g$^{-1}$ which is lower than that of the commercial graphite at 372 mAh g$^{-1}$, so low capacity (200 mAh g$^{-1}$) was usually observed. When they were prepared as nanostructure forms (e.g. nanowires, nanotubes, nanowisker or nanosheet), higher capacity from 200 to 300 mAh g$^{-1}$ was achieved [7, 10, 13-15]. However, the high capacity above 200 mAh g$^{-1}$ was hard to maintain after long cycles due to their structural instability, which can be one of the shortcomings of their anode application [16-19].

SnO$_2$ is another extensively investigated anode material with a high theoretical lithium storage capacity (790 mAh g$^{-1}$). However, it experiences a strong volume change (up to 300 vol.%) during its alloying reaction with lithium ion, which leads to mechanical stress and loss of contact to the current collector and thus to strong capacity fading [20-22]. In order to overcome these obstacles, the preparation of nanostructured SnO$_2$ morphologies has been pursued and the capacity is better retained because of their large strain accommodation ability, short diffusion distance and thus rapid Li$^+$ insertion/de-insertion in the small grains [22, 23]. On the other hand, constructing nanocomposite architectures is demonstrated to be able to further improve the Li$^+$ storage capacity and cycle stability of SnO$_2$ materials due to the “buffering” and “mechanical support” functions from the matrix materials during charge–discharge cycling [24, 25]. Up to now, various TiO$_2$-supported-SnO$_2$ materials had been prepared and exhibited favorable electrochemical performances, which enabled the potential application of those materials in lithium ion batteries [26-31]. However, for the sake of their practical application, there still exist many challenges in synthesizing TiO$_2$-SnO$_2$ nanocomposite by facile synthesis routes.

Herein, considering the advantages of the TiO$_2$-B, which shows the largest specific capacity among the different TiO$_2$ polymorphs and can be obtained by a simple hydrothermal method, we first reported a facile synthesis of TiO$_2$-SnO$_2$ nanocomposite by a two-
step hydrothermal reaction and subsequent spray drying process. The characteristics of the as-prepared nanocomposite and the electrochemical performances as a lithium intercalation host were investigated.

2. EXPERIMENTAL

2.1. Synthesis of TiO$_2$-SnO$_2$ nanocomposite

TiO$_2$-SnO$_2$ nanocomposite was prepared via a two-step hydrothermal reaction and subsequent spray drying route. Titinate nanowires were firstly obtained, which was commonly referred in the previous literatures [9, 10, 12]. TiO$_2$ powders (Degussa P25, ca. 80% anatase, 20% rutile) were used as received. All other chemicals were of analytical reagent grade and used without further purification. Deionized water was used throughout. In a typical synthesis process, commercial P25 powders of 1.0 g were added into the aqueous NaOH solution (60 mL, 10 mol.L$^{-1}$). After stirring for 1 h, the resulting suspension was transferred into a Teflon-lined stainless steel autoclave (100 mL). The autoclave was maintained at 180 $^\circ$C for 12 h in oven and then naturally cooled to room temperature. The obtained precipitate was washed with HCl (0.1 mol.L$^{-1}$) solution and then with deionized water until pH≈7.0. Subsequently, the precipitate was dispersed into 40 mL water to form a white suspension by ultrasonication and subsequent stirring, followed by the addition of SnCl$_4$·5H$_2$O with the TiO$_2$/SnO$_2$ weight ratio of 55/45. Then, 20 mL NaOH solution (containing 4.3 g NaOH) was dropped into the above suspension. After stirring for 1 h, the resulting suspension was again treated at 200 $^\circ$C for 12 h in the Teflon-lined stainless steel autoclave. After washing with water for 3 times, the obtained precipitate was dispersed into 120 mL water homogeneously with the assistance of ultrasound, followed by spray drying at the inlet and outlet temperature of 150 and 80 $^\circ$C respectively to obtain the nanocomposite precursor. The spray-dried precursor was finally heated at 400 $^\circ$C for 3 h in air in a covered alumina crucible at a heating rate of 2$^\circ$C.min$^{-1}$, resulting in the TiO$_2$-SnO$_2$ nanocomposite. In comparison, pure TiO$_2$ was obtained by one-step hydrothermal reaction and post-heat treatment. And pure SnO$_2$ was also synthesized by one-step hydrothermal route at the same conditions without calcination.

2.2. Characterizations

The thermogravimetric analysis (TGA) was used to observe the decomposition reaction of the as-prepared precursor and determine the calcination temperature. The experiments were performed using a METTLER TOLEDO TGA/DSC 1LF1600 apparatus with the temperature from 30 to 600$^\circ$C, at a heating rate of 5$^\circ$C.min$^{-1}$ under an air atmosphere. X-ray diffraction (XRD) measurements were carried out on a diffractometer (Bruker D2 PHASE) with Cu Kα radiation in the range from 10$^\circ$ to 90$^\circ$. The morphology of the samples was studied with a scanning electron microscope (SEM, JEOL JEM-5610). The energy dispersive X-ray analysis was conducted using the EDX analyzer equipped with the TEM in point mode.

2.3. Electrochemical measurements

The working electrodes were prepared from the as-synthesized active nanocomposite, carbon black as a conducting agent, and poly(vinylidene difluoride) (PVDF) binder dissolved in n-methyl pyrrolidinone (NMP, 8 wt%) at a weight ratio of 8:1:1. The slurry was mixed overnight to obtain a homogeneous black paste and then spread onto a copper foil current collector, followed by drying at 120$^\circ$C in vacuum for 12 h. Copper-foil pieces with 14mm diameter were then cut off and used as the electrode in homemade cells which were assembled inside Ar filled glove box. The average amount of TiO$_2$-SnO$_2$ nanocomposite in a round piece of electrode is about 5 mg. Each electrode was carefully weighted before use and several electrodes were tested to assume the reproducibility of the electrochemical behavior. The coin cells (CR 2015) also used Li metal as a counter electrode, a Celgard 2500 as a separator and a 1 M LiPF$_6$ dissolved in ethylene carbonate (EC), dimethyl carbonate (DMC), and ethylene methyl carbonate (EMC) (1:1:1, v/v/v) as an electrolyte.

The assembled cells were aged for 12 h before testing and then were galvanostatically charged and discharged over a voltage range of 2.5–0.01V vs. Li$/\text{Li}^+$ at a current density of 40 mA g$^{-1}$ using a LAND cell test (Land-CT 2001A) system. The specific capacity was calculated based on the mass of active materials in the electrode.

3. RESULTS AND DISCUSSION

The TGA profile of the spray-dried precursor for TiO$_2$-SnO$_2$ nanocomposite is shown in Fig. 1, revealing that the dehydration process of the precursor starts at about 60$^\circ$C and is finished at about 400 $^\circ$C. The total weight loss recorded in this range for the nanocomposite precursor is about 8%, which is mainly attributed to the dehydration of the absorbed water, interlayer water and structural water in the resulting protonated titinate nanowires after hydrothermal treatment [32]. No significant weight loss was observed beyond 400$^\circ$C. So the calcination temperature for the TiO$_2$-SnO$_2$ nanocomposite is set at 400$^\circ$C in our experiment.

Fig.2 shows the XRD patterns of the as-prepared samples. The protonated titinate nanowires with H$_2$Ti$_3$O$_7$-phase were obtained and then transformed into TiO$_2$(B) (JCPDS 46-1237) after heating at 350$^\circ$C as clearly shown in the upper right inset, where the diffraction peaks of H$_2$Ti$_3$O$_7$ and TiO$_2$(B) are both broadened greatly due to their 1D structures [9, 32]. When the protonated titinate...

nanowires were heated at 400°C for 3 h, the main phase is assigned as anatase TiO$_2$ (JCPDS 21-1272) with relatively strong diffraction intensities due to the increasing crystallinity (Fig. 2c). Such results show that the pure protonated titanate nanowires transform into not TiO$_2$(B) but more thermodynamic stable anatase TiO$_2$ above 400°C. According to Fig. 2f, pure SnO$_2$ with a tetragonal rutile structure (JCPDS 14-1445) can be prepared by one-step hydrothermal treatment. By a two-step hydrothermal reaction, the protonated titanate nanowires and SnO$_2$ are successively produced and form the nanocomposite precursor (Fig. 2d). The average particle size of the SnO$_2$ in the nanocomposite was about 100 nm calculated from Sherrer equation. After calcination at 400°C, here we find that TiO$_2$ from the nanocomposite maintains the TiO$_2$(B) crystal structure, which will be beneficial for the lithium storage property. On the other hand, no obvious increase in the size of SnO$_2$ is observed (Fig. 2e) as individual SnO$_2$ nanoparticles in the case of the TiO$_2$ nanowire matrix do not interact with each other during heating (shown in the SEM image below), which is very important for the values of capacity components and stability of lithium recharging. Another interesting phenomenon appearing in the TiO$_2$-SnO$_2$ nanocomposite is that all the XRD peaks ascribed to SnO$_2$ move to higher angles, indicating that Ti with smaller atom radius than that of Sn solubilizes in SnO$_2$ and the substitutional solid solution (Sn, Ti)O$_2$ with the slightly smaller lattice parameters is formed.

The morphology of the nanocomposite precursor was observed by field emission scanning electron microscopy in Fig. 3a. The product by a two-step hydrothermal reaction demonstrates a donut-like microsphere morphology with a size ranging from 1 μm to 5 μm. As clearly seen from the higher magnification SEM image inset in Fig. 3a, the donut-like microsphere consists of protonated titanate nanowires and tiny SnO$_2$ nanoparticles. And the hierarchical donut-like microsphere structure is well retained after heat treatment at 400°C (Fig. 3b). Here, SnO$_2$ nanoparticles with a particle size about 100 nm are individually wrapped by the TiO$_2$ nanowires which can serve as the buffering matrix for SnO$_2$ during Li$^+$ intercalation/deintercalation. Another phenomenon shown in the SEM images is that the surface of the donut particle becomes rougher and porous after the heat treatment. This may be ascribed to the TiO$_2$ transformation from TiO$_2$-B to more stable anatase TiO$_2$ phase and gradual collapse of its 1D structure at higher temperature. The porous morphology also may be from the formation of substitutional solid solution (Sn, Ti)O$_2$ with smaller lattice parameter which leads to the volume shrinkage in the nanocomposite.

Furthermore, the composition of this nanocomposite was also confirmed by the EDX spectroscopy experiments (Fig. 3c), which reveals the presence of Ti, Sn, O and Na in the nanocomposite. The amount of sodium residual from the raw NaOH stuff as determined by EDX analysis is only 5.3 wt%. The average Ti/ Sn weight ratio

Figure 2. XRD patterns of samples: (a) pure precursor for TiO$_2$, (b) TiO$_2$ after calcination at 350°C, (c) TiO$_2$ after calcination at 400°C, (d) nanocomposite precursor for TiO$_2$-SnO$_2$, (e) TiO$_2$-SnO$_2$ nanocomposite after calcination at 400°C, and (f) pure SnO$_2$. The upper right inset is the two XRD patterns of a and b for higher definition purpose.
of the nanocomposite is calculated to be 0.75, which is lower than that of the raw layout (≈0.93) due to a certain amount protonated titanate nanowires loss during washing after the first-step hydrothermal treatment.

Spray-drying technique is a way to prepare nanoparticle granules with a good flowability and a size without inducing additional hard agglomerates, as well as exhibiting advantages like low price, high efficiency. Nakahara et al. reported excellent cycling performance of particulate Li4Ti5O12 prepared by spray drying process with LiOH and anatase type TiO2 as precursors, and it was found that granular morphology of the active Li4Ti5O12 was essential to the high rate capacity of the active materials [33]. In our previous work, porous TiO2 nanowire microspheres within a size of 2-10 μm were prepared by one-step hydrothermal reaction and subsequent spray drying process. Thus, the formation of the donut-like microsphere structure in the as-obtained TiO2-SnO2 nanocomposite should be related with both the second-step hydrothermal treatment and spray drying process.

Fig. 4 displays the galvanostatic discharging-charging curves of the as-prepared TiO2-SnO2 nanocomposite at a current rate of 40 mA.g⁻¹ between 0.01 and 2.5 V. The initial discharge capacities is 640 mAh.g⁻¹, which is much higher than the theoretical capacity of TiO2(B) but a little lower than...

SnO2. And the charge capacity (charge capacity less than discharge for the anode materials) is 200 mAh g\(^{-1}\), indicating a large capacity loss during the lithium insertion/extraction in the as-prepared TiO\(_2\)-SnO\(_2\) nanocomposite. This irreversible capacity could be caused by the formation of Li2O, the inevitable formation of solid electrolyte interface and/or the occurrence of some complicated side reactions. The charge specific capacities tend to decrease as cycle number increases, and approximately 11% (70 mAh g\(^{-1}\)) of its initial discharge capacity is retained after 10 cycles, showing unsatisfying cycle stability. In these respects, further work is being carried out to improve the lithium storage performance of the donut-like TiO\(_2\)-SnO\(_2\) microspheres.

4. CONCLUSION

In summary, TiO\(_2\)-SnO\(_2\) nanocomposite was first prepared on a large scale by a two-step hydrothermal reaction followed by spray drying and post-heat treatment. The hierarchical donut-like TiO\(_2\)-SnO\(_2\) microspheres within a size of 1-5 μm were achieved by the second-step hydrothermal treatment and subsequent spray drying. The transformation from TiO\(_2\)(B) into anatase TiO\(_2\) phase at relatively high temperature was hampered because of the high interaction between TiO\(_2\) and SnO\(_2\), which also resulted in the formation of the substitutional solid solution (Sn, Ti)O\(_2\) with the same tetragonal rutile structure as SnO\(_2\). The as-obtained donut-like TiO\(_2\)-SnO\(_2\) nanocomposite microspheres demonstrated a high initial discharge capacity as anode materials for lithium-ion batteries, implying a promising anode candidate for lithium-ion batteries if the coulombic efficiency could be improved.

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