Fabrication of voids-involved SnO₂@C nanofibers electrodes with highly reversible Sn/SnO₂ conversion and much enhanced coulombic efficiency for lithium-ion batteries

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ABSTRACT

Despite their potential application in lithium-ion battery electrodes, one apparent disadvantage for SnO₂-based materials is that the electrodes suffer low coulombic efficiency especially for the initial cycle, which originates from the irreversible conversion of SnO₂ to Sn, the formation of solid electrolyte interphase and the other possible side reactions. Here we design a novel nanofiber structure in which SnO₂ nanoparticles are well separated and confined by inner porous carbon framework and then hooped by outer carbon shell. The resultant SnO₂/voids@C nanofibers electrode displays not only a high reversible capacity of 986 mAh g⁻¹ at 200 mA g⁻¹ after 200 cycles, but also a high initial coulombic efficiency of 73.5%. It has been shown that such a rational design can efficiently reduce the side reactions and promote the reversible conversion of Sn to SnO₂ for both half and full cells.

Keywords: Inner voids, SnO₂@C nanofibers, Reversible Sn/SnO₂ conversion, Lithium-ion batteries, Full cells

1. Introduction

Rechargeable lithium-ion batteries (LIBs) are the most popular electrochemical energy storage device in many current applications including portable electronics and electric vehicles[1-5]. However, it is difficult to increase the energy density and power density of the commercial LIBs. One critical reason is

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that the used anode material of graphite has a low theoretical specific capacity (372 mAh g^{-1}). To satisfy the growing energy storage demand, it is essential to develop anode materials with high specific capacity to support the development of the next-generation LIBs.

Tin oxide, as a typical metal oxide, has gained persistent attention due to its nature abundance, environmental low-toxic and high specific capacity[6-11]. According to the tradition, SnO_2 undergoes irreversible conversion to Sn and Li_2O , and each Sn atom reversibly reacts with 4.4 Li atoms, corresponding to a reversible capacity of 780 mAh g^{-1} [12-14]. Recently, it has been confirmed that SnO_2 with well-designed nanostructures can convert to Sn reversibly[15, 16], making it have the highest theoretical capacity of 1489 mAh g^{-1} among the transition metal oxides. Therefore, it is possible that using nanostructural SnO_2 to substitute for graphite could largely improve the energy density and power density of LIBs.

Despite its possible high specific capacity, SnO_2 has to face several major challenges as an anode material for LIBs. Primarily, SnO_2 suffers huge volume changes ($>300\%$) during lithium insertion/extraction. The repeated volume changes induce great stress that leads to the active SnO_2 material exfoliation from the current collector and eventually destruction of the electrode[17]. Another particularly noteworthy is that, in the initial few cycles, the electrolyte decomposes and forms a solid electrolyte interphase (SEI) layer on surface of the electrode. In general, a stable SEI layer is considered to be beneficial for the cycle performance because it can terminate the further decomposition of the electrolyte and offer convenient channels for the lithium ion motion[18]. However, the huge volume change of SnO_2 can crack the formed SEI layer, which results in the active SnO_2 material being exposed to the electrolyte again, and thus the SEI layer continues to grow and break up until the electrolyte has been completely consumed in the battery[19, 20]. Moreover, SnO_2 has inherently low conductivity, which leads to a poor cyclability especially at large current densities.

Various SnO_2 nanostructures and their carbon-based composites[21-30] have been designed to overcome the above-mentioned drawbacks. However, reducing the size of SnO_2 to nanoscale can only avoid fracture for just dozens of cycles because the nanoscale SnO_2 particles will re-agglomeration in the electrode. Although compositing with carbon materials can buffer the volume change and enhance the conductivity of SnO_2 , the carbon materials will eventually be broken due to the long-term repeated SnO_2 volume changes. Furthermore, the most designs are rather complicated in the literature.

Herein, inspired by the reported yolk-shell structured composite anode[19, 31, 32], in which nanoparticles can freely expand without breaking the carbon shell, we have designed a novel nanofiber structure in which SnO_2 nanoparticles are separated by inner carbon framework with many voids and the whole nanofiber is well hooped by outer carbon shell. With such a design, the direct contact of SnO_2 nanoparticles to electrolyte is effectively blocked and the formation of the SEI layer is largely suppressed[33], which greatly reduce the irreversible reactions. The SnO_2 nanoparticles in the resultant $\text{SnO}_2/\text{voids}@C$ nanofibers electrode can freely expand and hardly aggregate, showing a much improved electrochemical performance.

2. Experimental

2.1. Preparation of $\text{SnO}_2/\text{Fe}_2\text{O}_3$ nanofibers

First, 1 mM $\text{SnCl}_2 \cdot 2\text{H}_2\text{O}$, 1 mM $\text{FeCl}_2 \cdot 4\text{H}_2\text{O}$ and 300 mg PVP (Polyvinylpyrrolidone, $M_w=150000$) were added into 2.4 g DMF (N,N-dimethylformamide) under vigorous magnetic stirring until the two chlorides were completely dissolved in the viscous solution. Then the prepared solution was electrospun under a voltage of 15 kV. The controlled solution feed rate is 0.15 mL h^{-1} and the collected distance is 17 cm. Finally, by annealing the obtained nanofibers in air at 500°C for 4 h, the involved PVP decomposed and the chlorides turned to metal oxides.

2.2. Fabrication of $\text{SnO}_2/\text{voids}@C$ nanofibers

The prepared $\text{SnO}_2/\text{Fe}_2\text{O}_3$ nanofibers were coated by polydopamine in a tris-buffer solution as reported previously[34-36]. After carbonization in an argon atmosphere at 500°C for 4 h, the sample was put into 3 M HCl solution at least for 72 h to etch off the iron oxides. The $\text{SnO}_2/\text{void}@C$ nanofibers have been fabricated as a result of that SnO_2 and carbon do not react with HCl and the voids are remained after the iron oxides being etched off. The SnO_2 nanofibers and carbon coated SnO_2 ($\text{SnO}_2@C$) nanofibers without voids were prepared as a contrast. The details have been described in the supporting information.

2.3. Materials characterization

The structure and morphology of the samples were characterized by X-ray diffraction (XRD, Rigaku D/Max-2400 diffractometer, $\text{Cu K}\alpha$ radiation), field-emission scanning electron microscopy (FE-SEM, S-4800, Hitachi) and transmission electron microscopy (TEM, FEI, Tecnai G² F30). The chemical properties on the sample surface were determined by X-ray photoelectron spectroscopy (XPS, Kratos AXIS Ultra DLD, Al $\text{K}\alpha$ probe beam).

2.4. Cell assembling and electrochemical analysis

For fabrication of the working electrode, the prepared active material was simply sandwiched between two pieces of nickel foam (380 gm^{-2} surface density, 100 PPI pore size, 1.5 mm thick), followed by a pressing at 10 MPa. The active mass loading for both the $\text{SnO}_2/\text{voids}@C$ and SnO_2/C nanofibers electrodes was more than 1 mg cm^{-2} including the masses of SnO_2 and carbon material. Lithium foil served as the counter and reference electrode for the half-cells. For the full cells, the LiCoO_2 electrodes, which were prepared by casting the slurry of 80 wt.% commercial LiCoO_2 power, 10 wt.% carbon black, and 10 wt.% polyvinylidene difluoride (PVDF) in N-Methyl-2-pyrrolidone solvent on aluminum foil and then drying in a vacuum oven at 120°C for 12 h, were used as cathode. CR-2032 coin cells were assembled in an argon-filled glovebox (H_2O , $\text{O}_2 < 0.5\text{ ppm}$, MBraun). Celgard 2320 microporous polypropylene film was used as the separator membrane. The electrolyte was 1 M LiPF_6 dissolved in a mixture of ethylene carbonate (EC) and diethyl carbonate (DEC) in a volume ratio of 1:1. The electrochemical properties of

the assembled cells were tested on a multichannel battery tester (Neware BTS-610) and an electrochemical workstation (CHI-660C).

3. Results and discussion

XRD patterns shown in Fig. 1 demonstrate the crystallographic structures of the prepared nanofibers. All peaks of SnO_2 and SnO_2/C nanofibers can be well indexed to rutile SnO_2 (JCPDS card No. 41-1445). The strong peaks located at 26.6° , 33.9° and 51.8° can be identified for all the three samples, which correspond to the (110), (101) and (211) planes of SnO_2 [29], respectively. Compared with the two samples without voids space, the $\text{SnO}_2/\text{voids@C}$ nanofibers show much broad full width peaks and slight peak shifts (less than 0.2°), which can be attributed to the low density and small size of the SnO_2 grains in the voids-involved nanofibers. No obvious peaks from the impurities such as C, FeO_x , Sn and SnO can be observed for the $\text{SnO}_2/\text{voids@C}$ nanofibers. Such a result has also been confirmed by XPS measurement, as shown in Fig. S1 of the supporting information.

Fig. 1. XRD patterns of $\text{SnO}_2/\text{voids@C}$, SnO_2/C and SnO_2 nanofibers.

SEM images shown in Fig. 2a present the overall morphology of the $\text{SnO}_2/\text{voids@C}$ nanofibers. Evidently, the nanofibers are randomly distributed with diameters ranging from 100 to 200 nm. From TEM image of a single nanofiber shown in Fig. 2b, it can be seen that a large number of SnO_2 nanoparticles are

conformally anchored inside the nanofiber. The outer carbon with a thickness of about 8 nm is perfectly covered on the nanofiber. Such a carbon shell can prevent the inner nanofiber from directly soaking into the electrolyte, which can effectively reduce the excessive decomposition of the electrolyte and avoid the possible side reactions. The carbon framework can be clearly observed in Fig. S2. Also, as can be seen from the image of a fracture point shown in Fig. 2c, the size of the most SnO_2 particles ranges from 5 to 10 nm. When we observe high-resolution TEM image of an as-synthesized nanofiber shown in Fig. 2d, two lattice spaces of 0.33 and 0.26 nm can be identified, which perfectly correspond with the (110) and (101) planes of SnO_2 , respectively. No lattice space can be observed in the carbon shell, indicating that the structure of the formed carbon is amorphous. Fig. 2e-h demonstrate elemental mapping of energy dispersive X-ray spectroscopy (EDX) for a single $\text{SnO}_2/\text{voids}@C$ nanofiber. Apparently, C and N elements from the carbonized polydopamine are uniform distribution in the whole framework. Sn and O elements from SnO_2 particles are stayed in the inner nanofiber, while there is small amount of O from carbonized polydopamine in the outer carbon coating. The morphologies of the SnO_2 and SnO_2/C nanofibers are shown in Fig. S3.

Fig. 2. (a) SEM image of the prepared $\text{SnO}_2/\text{voids}@C$ nanofibers. (b-c) TEM and (d) high-resolution TEM images of a single $\text{SnO}_2/\text{voids}@C$ nanofiber. (e-h) EDX elemental mapping of a single $\text{SnO}_2/\text{voids}@C$ nanofiber.

The existence of the voids in the $\text{SnO}_2/\text{voids}@C$ nanofibers has been confirmed by the nitrogen adsorption-desorption measurement. For comparison the same measurement was performed on the $\text{SnO}_2@C$ nanofibers. As shown in Fig. 3, after the Fe_2O_3 nanoparticles being etched off, the voids-involved $\text{SnO}_2/\text{voids}@C$ nanofibers show a high specific surface area of $167.5 \text{ m}^2 \text{ g}^{-1}$ and large total pore volume of $0.217 \text{ cm}^3 \text{ g}^{-1}$. On the other hand, the SnO_2/C nanofibers show a low specific surface area of $40.6 \text{ m}^2 \text{ g}^{-1}$ and small total pore volume of $0.098 \text{ cm}^3 \text{ g}^{-1}$. The inner voids created in the

SnO₂/voids@Cnanofibers can effectively accommodate the volume changes of the SnO₂ nanoparticles during the lithiated and delithiated processes.

Fig. 3. (a) Nitrogen adsorption-desorption isotherms of the SnO₂/voids@C and SnO₂/C nanofibers. (b) The corresponding pore size distribution.

To verify the feasibility of the above design that the SnO₂ nanoparticles are encapsulated in carbon nanofibers with numerous buffering voids for effectively improving the electrochemical characteristics, a series of electrochemical tests have been performed on the SnO₂/voids@C nanofibers as an anode material of half cells. The electrochemical performances of the SnO₂ and SnO₂@C nanofibers without buffering voids were also tested for comparison. Fig. 4a shows cyclic voltammograms (CVs) for the initial 5 cycles at a scan rate of 0.2 mV s⁻¹ in a voltage window of 0.02–3 V. In the first cathodic scan a broad peak was recorded at about 0.7 V, which is caused by the conversion of SnO₂ to Sn and the formation of SEI layer. The peak shifts to 0.95 V in the subsequent cathodic scans, and the corresponding oxidation peak of Sn to SnO₂ is clearly observed at 1.3 V, indicating that the conversion of SnO₂ to Sn is reversible [24, 37–39]. Two pronounced peaks located at 0.2 V in cathodic scans and 0.6 V in anodic scans reflect the alloying and dealloying reactions of the metallic Sn, respectively. Moreover, except the first cathodic scan, the CV curves are highly overlapped, indicating that the two reactions are highly reversible. Thus, the electrochemical reactions in the present anode are in good accordance with those reported previously [16, 25, 39–42].

The galvanostatic discharge-charge profiles of the $\text{SnO}_2/\text{voids}@C$ nanofibers electrode were measured at a current density of 200 mA g^{-1} . Fig. 4b presents the discharge-charge profiles in the 1st, 2nd, 3rd, 100th, and 200th cycles. It is clear that the first discharge curve is obviously different from the others, which is induced by the formation of SEI layer. The discharge-charge profiles almost overlap in the subsequent few cycles. Two charge plateaus located at about 0.6 and 1.3 V can be observed, which correspond to the dealloying of Li_xSn and the formation of SnO_2 . The result confirms that the generation of SnO_2 is reversible, which is consistent with the CV analysis. Therefore, it is not surprising that, in the initial cycle, the electrode can deliver high discharge and reversible charge capacities of 1695 and 1246 mAh g^{-1} , respectively. As a contrast, the discharge-charge profiles of the SnO_2 and $\text{SnO}_2@C$ nanofiber electrodes are shown in Fig. S4.

Fig. 4. (a) CV curves of the $\text{SnO}_2/\text{voids}@C$ nanofibers electrode for the initial 5 cycles. (b) Galvanostatic discharge-charge profiles of the $\text{SnO}_2/\text{voids}@C$ nanofibers electrode in the 1st, 2nd, 3rd, 100th, and 200th cycles. (c) Cycling performance and (d) coulombic efficiency of the $\text{SnO}_2/\text{voids}@C$, SnO_2 and $\text{SnO}_2@C$ nanofibers electrodes tested at 200 mA g^{-1} . (e) Rate performance for the three electrodes.

Fig. 4c compares the cycling performances of the $\text{SnO}_2/\text{voids}@C$, SnO_2 and $\text{SnO}_2@C$ nanofibers electrodes tested at a constant current density of 200 mA g^{-1} . It can be seen that, after a slight decaying in the initial 50 cycles, the $\text{SnO}_2/\text{voids}@C$ nanofibers electrode exhibits a reversible charge capacity of 986 mAh g^{-1} and a discharge capacity of 1004 mAh g^{-1} after 200 cycles. As a contrast, although the SnO_2 and $\text{SnO}_2@C$ nanofibers electrodes show high initial discharge capacities of 1816 and 1636 mAh g^{-1} , their corresponding charge capacities are only 958 and 926 mAh g^{-1} , and the reversible charge capacities decay

to 98 and 60 mAh g⁻¹ in the 100th cycle, respectively. These results demonstrate that the SnO₂ and SnO₂@C nanofibers have poor lithium storage capability and capacity retention. The conclusion has also been confirmed by the coulombic efficiency curves as shown in Fig. 4d. It is found that the initial coulombic efficiencies are 73.5%, 52.7% and 56.6% for the SnO₂/voids@C, SnO₂ and SnO₂@C nanofibers electrodes, respectively. The coulombic efficiency is higher than 98% since the 3rd cycle for the SnO₂/voids@C nanofibers electrode, while it experiences some complex changes with cycling for the SnO₂ and SnO₂@C nanofibers electrodes, indicating the occurrence of some irreversible lithium storage or side reactions in the latter two electrodes. It can be seen that the carbon coating can improve the coulombic efficiency in the initial 30 cycles, however, the coulombic efficiency falls down with cycling after the 60th cycle, which may be attributed to the carbon shell being destroyed by the repeated volume changes.

Furtherly we evaluated the rate performance of the three electrodes, as shown in Fig. 4e. Apparently the more superior capacity retention has been obtained for the SnO₂/voids@C nanofibers electrode, showing rather high reversible capacities of 1233, 1028, 798 and 519 mAh g⁻¹ at current densities of 0.2, 0.4, 0.8 and 1.6 A g⁻¹, respectively. Notably, even enhanced the current density to 3.2 A g⁻¹, it can still deliver a high capacity of 284 mAh g⁻¹. Considering that there is no binder or conductive agent added in the electrode, the active material conducts only through its one-dimensional nanostructures, the result is impressive. As a contrast, at the current density of 3.2 A g⁻¹, the SnO₂ and SnO₂@C nanofibers electrodes deliver almost ignorable capacities of 43 and 68 mA h g⁻¹, respectively. Finally, when we reset the tested current density at 0.2 A g⁻¹, the SnO₂ and SnO₂@C nanofibers electrodes show faded capacities of 590 and 471 mAh g⁻¹, respectively, while the SnO₂/voids@C nanofiber electrode can recover a high reversible capacity of 986 mAh g⁻¹ and keep perfect stability in the following cycles. The result supports the conclusion that the SnO₂/voids@C nanofibers electrode is characteristic of excellent rate performance.

Fig. 5. High-resolution XPS spectra of Sn 3d in the as-prepared and cycled $\text{SnO}_2/\text{voids}@C$ nanofibers.

The superior lithium storage capability of the $\text{SnO}_2/\text{voids}@C$ nanofiber electrode can be summarized as follows. First, the conversion of SnO_2 to Sn is highly reversible, which has been identified by CV curves and charge-discharge profiles shown in Fig. 4. To further support this view, we performed XPS measurement on the cycled nanofibers. As shown in Fig. 5, two obvious peaks located at 486.8 and 495.3 eV are detected, which correspond to the binding energies of $\text{Sn}3d_{5/2}$ and $\text{Sn}3d_{3/2}$ in SnO_2 , confirming that SnO_2 still exist in the nanofibers cycled even 200 times. A small shift can be seen for the peaks of Sn 3d after the electrochemical cycles, implying a change of the chemical environment mainly induced by high electronegative elements like O or F from the electrolyte decomposition in the initial cycles. The other important point is the rationally designed nanostructure with numerous voids, which are well preserved in the cycled $\text{SnO}_2/\text{voids}@C$ nanofibers as shown in Fig. 6a. It can be seen that, due to the formation of SEI layer, the surface of the cycled nanofiber becomes rough. To further observe the carbon framework and inner SnO_2 nanoparticles in the cycled nanofibers, we removed the SEI layer by soaking the cycled nanofibers into 1 M HCl solution for several hours, the TEM image for such a treated nanofiber is shown in Fig. 6b. The thickness of the outer carbon shell was found to be slightly increased to 9 nm, and the thickness of the formed SEI layer is only several nanometers. Fig. S5 shows lithiated $\text{SnO}_2/\text{voids}@C$ nanofibers at different magnifications, it can be seen that the overall structure has been perfectly maintained.

even at a maximum volume expansion. In addition, the inner carbon walls separate the SnO_2 nanoparticles and the voids can accommodate the volume changes of SnO_2 during electrochemical cycles. Thus, the SnO_2 nanoparticles in the $\text{SnO}_2/\text{voids}@C$ nanofibers can freely expand and hardly aggregate. Finally, the carbon framework serves as a superior conductive network can promote the electrochemical reactions.

Fig.6. TEM images of a single nanofiber after 200 cycles. (a) As-cycled and (b) SEI-removed samples.

Finally, to investigate the lithium storage performance of the prepared $\text{SnO}_2/\text{voids}@C$ nanofibers electrode for practical application, we assembled full cells by using the commercial LiCoO_2 as the cathode. The full cells were preliminarily tested at a constant current density of 0.2 A g^{-1} (based on the mass of the $\text{SnO}_2/\text{voids}@C$ nanofibers) with a voltage range of 1.2-4.2 V. Fig. 7a shows the charge and discharge curves in the 2nd cycle. Two discharge plateaus located at 3.5 and 2.6 V can be observed, as confirmed by the corresponding differential curves shown in Fig. 7b. To further analyze these two discharge plateaus, we measured the discharge curve of a LiCoO_2 electrode half cell and the charge curve of the $\text{SnO}_2/\text{voids}@C$ electrode half cell in the 2nd cycle. As shown in Fig. 7c, the plateaus in the charge curve at 0.6 and 1.3 V represent the formation of Sn and SnO_2 , respectively, and the two calculated discharge plateaus are located at 3.4 and 2.6 V, which are highly consistent with the measured discharge plateaus in the full cell. Such a result once again demonstrates that the conversion of SnO_2 to Sn is reversible when the $\text{SnO}_2/\text{voids}@C$ nanofibers electrode is used in the full cell. After 30 cycles, the full

cell delivers a reversible discharge capacity of 623 mA h g⁻¹ as shown in Fig. 7d. The cycle performance of the full cell tested at 0.5 mA g⁻¹ is shown in Fig. S6, the reversible discharge capacity is 391 mA h g⁻¹ after 30 cycles. The insert in Fig. 7d is a digital image of a light-emitting-diode powered by the present SnO₂/voids@C and LiCoO₂ based full cell.

Fig.7.(a) The 2nd discharge-charge profiles of the SnO₂/voids@C and LiCoO₂ based full cell. (b) The corresponding differential capacity plot of the 2nd discharge profile. (c) Discharge (LiCoO₂ electrode in halfcell, upper) and charge (SnO₂/voids@C nanofibers electrode in halfcell, lower) curves. (d) Cycle performance of the SnO₂/voids@C and LiCoO₂ based full cell, the insert is a digital image of a light-emitting-diode powered by the full cell.

4. Conclusions

In summary, we designed and fabricated a novel nanofiber structure of SnO₂/voids@C in which SnO₂ nanoparticles are separated and confined by inner carbon framework with many voids. It was found that the conversion of SnO₂ to Sn is highly reversible when the nanofibers were used as an anode material for

LIBs. The initial coulombic efficiency of the electrode in a half cell is as high as 73.5%. After 200 cycles, the electrode delivers a high reversible charge capacity of 986 mAh g⁻¹ at 200 mA g⁻¹. The SnO₂/voids@C nanofibers electrode in the full cell delivers a high reversible capacity too. It has been shown (Table 1) that the prepared SnO₂/voids@C nanofibers electrode displays more superior lithium storage performance compared with those previously obtained on SnO₂ and its carbon composites. Thus, the present design may advance the practical use of SnO₂ based anode materials because having high capacity and high coulombic efficiency are equally important for the electrodes in the next-generation LIBs.

Table 1. A Comparison table for the electrochemical properties of SnO₂ and carbon composites published in the recent literature.

Carbon based SnO ₂ composition	Current density (mA g ⁻¹)	Initial coulombic efficiency	Cycle number	Capacity (mAh g ⁻¹)	Reference	Year
SnO ₂ /voids@C nanofibers	200	73.5	200	986	present	2016
Bowl-like SnO ₂ @Carbon hollow particles	400	68.4	100	963	[25]	2014
SWNTs@SnO ₂ @PPy coaxial nanocable	150	64.4	100	823	[16]	2012
rGO/SnO ₂	200	67.2	200	892	[24]	2014
Graphene-based mesoporous SnO ₂	78.2	69.4	50	847	[43]	2013
SnO ₂ /C nanotube networks	400	68	50	653	[44]	2015
CNT@void@SnO ₂ @C	200	60.7	300	704.1	[45]	2015
Worm-like SnO ₂ @C	100	50.2	60	533.6	[46]	2014
SnO ₂ @C yolk– shell nanoparticles	100	56	100	630	[47]	2014
SnO ₂ @carbon nanofibers	80	60.6	100	410.5	[48]	2014
Hollow SnO ₂ @C nanoparticles	3910	65	573	370	[49]	2015

Carbon coated SnO ₂ /graphene-sheet	100	60	80	703	[50]	2013
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