Three-dimensionally ordered macroporous SnO₂ as anode materials for lithium ion batteries

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Abstract: This paper describes a modified colloidal crystal templating method to prepare three-dimensionally ordered macroporous (3DOM) SnO₂ as anode materials for lithium ion batteries. The as-prepared 3DOM-SnO₂ delivered a higher reversible lithium storage capacity (653 mAh g⁻¹) than non-templated SnO₂ nanoparticles (327 mAh g⁻¹). In addition, 3DOM-SnO₂ electrode exhibited an excellent rate capacity of 326 mAh g⁻¹ at a high current density of 2 C (1.56 A g⁻¹). Good capacity retention performance was also observed in the 3DOM-SnO₂ electrode after 50 cycles at the current density of 0.2 C, maintaining the specific capacity of 338 mAh g⁻¹. The improved electrochemical performance of the 3DOM-SnO₂ electrode benefits from the 3DOM architecture, which can not only shorten the Li⁺ ions diffusion paths within the macropore walls, but also buffer the volume changes during the charge and discharge processes. More importantly, the continuous void space of the 3DOM structure can be readily filled with electrolyte solution, resulting in the improved ionic and electric conductivity. These merits combined with the synergistic effects of smaller particle size should be responsible for the good electrochemical performance. The excellent electrochemical performance of 3DOM-SnO₂ shows its promising applications as an anode material for lithium ion batteries.

Keywords: Lithium-ion battery; 3DOM-SnO₂; Colloidal crystal templating;

1. Introduction

As a consequence of global climate change and the decline in fossil fuels, we are facing a challenge to improve the utilization and management of energy, especially electrical energy. Lithium-ion batteries (LIBs), as electrochemical storage conversion and storage devices, have stimulated great attentions due to their unmatched energy density and longer shelf life relative to other secondary battery technologies [1-3]. However, the low power density and poor rate performance of LIBs limit their practical applications in the emerging field of new applications, such as electric vehicles (EVs) and hybrid electric vehicles. Therefore, much research efforts related to LIBs have been focused on achieving higher power densities, where the development and fabrication of novel materials is of paramount importance.

Numerous studies have been devoted to develop different types of electrode materials with high reversible capacity, long cycle life, and low cost [4, 5]. So far, many nanomaterials of metal oxides, such as NiO, Fe₂O₃, Co₃O₄, and SnO₂, have been explored as alternative anode materials for LIBs [6-10]. Among them, SnO₂ has attracted a considerable attention over the past decades owing to its low lithium alloying potential combined with high theoretical specific capacity (782 mAh g⁻¹, verses 372 mAh g⁻¹ for graphite) [11, 12]. However, SnO₂ electrodes suffer from drastic volume changes during the alloying and dealloying processes, resulting in mechanical cracks, pulverization and fast capacity degradation [13, 14]. To overcome the above deficiencies, great attention has been paid to nanostructured SnO₂, because the nano-sized particles can better accommodate the absolute volume change [15]. Other approaches of modification to improve the electrochemical performance of SnO₂ have also been reported, such as carbon coating on SnO₂ grains or doping of Al to prevent agglomeration of tin particles [13, 14]. Although capacity fading can be

improved by using these modified methods to prepare SnO_2 , the high carbon content resulted in significant dilution of the specific capacity.

Three-dimensional ordered macro-porous (3DOM) architectures can serve as a promising strategy to improve the electrochemical performance of SnO_2 , because the macropores can act as a buffer layer to alleviate volume changes during charge and discharge processes [16]. The structural stability and cyclability of SnO_2 particles can be improved. In addition, the unique 3DOM architecture can provide interconnectivity among the porous network, which not only reduces the diffusion resistance of electrolytes but also enhances the facility of ion transportation. Therefore, better cycling stability and higher current rates can be achieved with three-dimensionally (3D) structure. A wide range of synthetic techniques, including colloidal crystal templating, polymerization, salt-precipitation, chemical conversion, and chemical vapor deposition, have been employed to fabricate 3DOM materials [17]. Generally, solutions containing metal salts are infiltrated into the void of polymethyl methacrylate (PMMA, or other polymer latex colloidal crystal templates) spheres and then metal hydroxides/alkoxides were obtained [14, 18-20]. Subsequently, further heating treatments are carried out to convert this precursor precipitate to metal oxide and remove the PMMA template to form 3DOM materials.

Different from the above traditional synthetic methods, in the present work, nano-sized SnO_2 was initially synthesized by a facile sol-gel method, and then further transformed into 3DOM- SnO_2 nanoparticles by using PMMA colloidal crystals as the template to form the 3DOM structure (as shown in Scheme 1). Herein, we report on the specific preparation methods and electrochemical performance of non-templated SnO_2 and 3DOM- SnO_2 nanoparticles to determine if they offer potential advantages to current electrodes for LIBs. Considering the simple synthetic process and improved

electrochemical performance, the **synthetic** method could be extended for producing other metal oxides with 3DOM structure as anode electrode materials for LIBs.

2. Experimental section

2.1. Synthesis of non-templated SnO₂ (N-SnO₂)

Tin (II) chloride dihydrate (SnCl₂·2H₂O, 98 %, **6 mmol**) was dissolved in **10 mL** of N,N-dimethyl-formamide (DMF) to form a transparent solution of **0.6 mol·L⁻¹** and sealed in an 25 ml Teflon-lined autoclave. The autoclave was heated at 363 K for 16 h and a faint yellow colloform was obtained. Subsequently, 5 drops of hydrogen peroxide (H₂O₂) were added dropwise to the above colloform under stirring for 1 h. The coloration of the precipitate transformed gradually from faint yellow to yellow. The resulting precipitate (**1.2 g**) was collected by centrifugation after washing with ethanol for five times (**5 mL for each time**), and subsequent drying under vacuum at 80 °C for 12 h. The as-prepared sample was denoted as non-templated SnO₂ (N-SnO₂).

2.2 Synthesis of 3DOM-SnO₂

Firstly, polymethyl methacrylate (PMMA) colloidal crystals was heated at 90 °C for 24 h. The above **nano-sized** SnO₂ **precipitate** was separated by centrifugation and washed with ethanol for five times (**5 mL for each time**). The as-obtained **nano-sized** SnO₂ (**1.2 g**) was dispersed **into 4 mL of** ethanol to form liquid suspension. Then, the obtained liquid was mixed with the treated PMMA colloidal crystals (0.8 g) and stirred for 2 h. Subsequently, the resulting mixture was centrifuged **under** 1000 rpm for 4 h to help the **nano-sized** SnO₂ particles to **penetrate** into the template. The mixture was dried under vacuum at 60 °C to remove methanol, and further

heat-treated at 350 °C for 6 h in a tube furnace with a heating rate of 1 °C min⁻¹ and an air flow of 100 mL min⁻¹. Scheme 1 shows the synthetic route of 3DOM-SnO₂.

2.3. Characterization

The XRD of all samples was performed on a diffractometer (Bruker D2 Phaser X-Ray Diffractometer) with Cu K α radiation (λ = 1.54056 Å). Scanning electron microscopy (SEM) analysis (HITACHI S-3400N) was utilized to capture and further determine the morphologies and the particle size of nano-SnO₂ and 3DOM-SnO₂. Transmission electron micrographs (TEM) were taken on a JEOL JEM-2010F microscope at an accelerating voltage of 200 kV. N₂ adsorption–desorption isotherms of the ordered MCNAs were measured on a Micromeritics ASAP 2460 analyzer. The samples were degassed in N₂ at 200°C for 16 h prior to the measurements. The specific surface area was calculated with the Brunauer-Emmett-Teller (BET) equation, and the pore size distributions were calculated from the adsorption curve by the Barrett-Joyner-Halenda (BJH) method.

2.4. Electrochemical measurements

The electrodes were prepared by mixing the SnO₂-based material with carbon black and a polyvinylidene fluoride (PVDF) binder using a weight ratio of 80:10:10, respectively, in N-methyl-2-pyrrolidinone (NMP) solvent and then spreading onto copper foil. The electrochemical measurements were carried out in CR2032 coin-type cells assembled in an argon-filled glove box (MBraun, Unilab, Germany) with lithium foil as the counter electrode and 1 M LiPF₆ in 1:1:1 ethylene carbonate (EC), dimethyl carbonate (DMC), and diethyl carbonate (DEC) (provided by MTI Corp.) as the electrolyte; Celgard 3501 was used as the separator.

The charge and discharge measurements were conducted with an Arbin Instruments BT-2000 equipment in the voltage range of 0.01 to 3.00 V vs. Li/Li⁺. Cells for cycling remained in the dry room during data collection. The C rate was set so that 1 C = 782 mA g⁻¹ of active material in the electrode, which corresponds to the theoretical capacity of SnO₂. Cyclic voltammetry (CV) and electrochemical impedance spectroscopy (EIS) measurements were carried out on an electrochemical workstation (Shanghai Chen Hua CHI660D).

3. Results and discussion

In this work, 3DOM-SnO₂ was fabricated by a modified colloidal crystal templating route based on nano-sized SnO₂ slurry. Fig. 1a shows X-ray diffraction (XRD) patterns of N-SnO₂ and 3DOM-SnO₂ powders. All the diffraction peaks can be indexed to the tetragonal rutile structure of SnO₂ (JCPDS: 41-1445). In particular, the three strong diffraction peaks at $2\theta = 26.60^\circ$, 33.90° and 51.80° can be attributed to the (110), (101) and (211) planes of tetragonal SnO₂. No diffraction peaks originated from the impurities are observed. The XRD patterns in Fig. 1a, confirmed that the N-SnO₂ and 3DOM-SnO₂ nanoparticles are successfully prepared. It should be mentioned that although the characteristic peaks' positions of both samples were in good agreement with the standard XRD pattern, we can see that there were some differences in the intensity of characteristic peaks between non-templated SnO₂ and 3DOM-SnO₂ samples, which may be originated from the diverse crystallinity introduced by the thermal treatment during the calcination process.

The nitrogen adsorption-desorption isotherms and Barrett-Joyner-Halenda (BJH) pore size distributions of N-SnO₂ and 3DOM-SnO₂ are shown as in Fig. 1b. Note that the BET specific surface area of the 3DOM-SnO₂ is 116 m² g⁻¹, which is much higher than that of N-SnO₂ (40 m² g⁻¹). Compared with N-SnO₂, a new intense peak of the

pore distribution centered at 16 nm appeared in the 3DOM-SnO₂. This peak suggests the presence of smaller mesopores in 3DOM-SnO₂ and is responsible for the increased specific surface area. This is deemed favorable for the electrochemical performance due to the fact that the enlarged surface area could ensure locally lower current densities and provide more active sites for Li ions to insert into the whole material [21].

The structure of the as-prepared samples was further investigated by high-magnification transmission electron microscopy (TEM) and scanning electron microscopy (SEM) at different magnification. TEM images (Fig. 2a and 2b) demonstrated that homogeneous SnO₂ nanoparticles were obtained and the diameter of the nano-sized SnO₂ was around 3 to 5 nm. Fig. 2c is a low-magnification view of the 3DOM-SnO₂ sample, which shows that the 3DOM-SnO₂ products are arranged in an orderly fashion. The magnified image in Fig. 2d indicated that the 3DOM-SnO₂ products exhibited the uniform macroporous structure with well-interconnected networks of periodically-distributed spherical voids.

To better understand the electrochemical behavior of the as-prepared electrode, the initial three Cyclic voltammograms (CV) of the 3DOM-SnO₂ anode were obtained at a scan rate of 0.1 mV s⁻¹ in the potential window of 0.01 to 3 V (as depicted in Fig. 3a). The detailed reactions for 3DOM-SnO₂ electrodes in assembled half-cells during the charge and discharge processes could possibly be explained with the following equations [22]:

In the first cathodic sweep, two small reduction peaks at around 1.20 and 0.76 V were observed, which corresponded to the reduction of SnO_2 to Sn and the formation of a solid electrolyte interface (SEI). The reduction of SnO_2 to Sn and formation of SEI are widely believed to be irreversible and these two peaks disappeared after two charge and discharge cycles, resulting in the large initial capacity loss (ICL) (Equation 1). The obvious reduction peak at around 0.25 V could be assigned to the formation of Li-Sn alloys (Equation 2), which is often thought to be reversible and contributing to a high theoretical capacity of $782 \text{ mAh g}^{-1}(\text{Li}_{4.4}\text{Sn})$ [23]. In the anodic sweeps, the strong oxidation peak occurred at about 0.50 V, which can be attributed to the de-alloying process. The broad oxidation peak at around 1.10 V can be attributed to the partial recovery of some tin oxides [24]. But this oxidation peak also disappeared after the first cycle, suggesting that this recovery reaction was irreversible. In addition, the XRD pattern of the 3DOM- SnO_2 electrodes at different cycled state (Fig. 3b) also showed the electrochemical behavior during the charge and discharge processes. As can be seen, the as-prepared electrode showed well-defined diffraction peaks that were in good agreement with standard XRD patterns of SnO_2 (JCPDF: 46-1088). The cubic Cu pattern (JCPDF: 01-085-1326) was originated from the Cu foil that was used as a current collector. The presence of Sn (JCPDF: 04-0673 and 05-0390) and cubic Li_2O (JCPDF: 01-077-2144) in the cycled electrode supports our above interpretation of the electrochemical behavior of the 3DOM- SnO_2 electrode on the basis of the CV curves.

Fig. 3c and 3d depicted the charge and discharge curves of the N- SnO_2 and 3DOM- SnO_2 for the initial four cycles at a current rate of 0.2 C and cycled between 3.00 and 0.01V. During the first cathodic sweep, N- SnO_2 and 3DOM SnO_2 anodes exhibited two similar discharge plateaus. These two discharge plateaus emerged at

around 1.50 V and 1.00 V, respectively, corresponding to the reduction of SnO_2 to amorphous Li_2O and metallic tin. These discharge plateaus disappeared in the following cycles, implying this reduction was irreversible. The main discharge plateaus for the N- SnO_2 and 3DOM- SnO_2 anodes were both at around 0.37 V, which corresponds to the formation of Li-Sn alloy. The 1st, 2nd, 3rd and 4th discharge capacities of the N- SnO_2 electrode were 1792, 829, 826 and 721 mAh g^{-1} , respectively. For the 3DOM- SnO_2 electrode, the discharge capacities of 1st, 2nd, 3rd and 4th were as high as 1864, 1015, 967 and 940 mAh g^{-1} , respectively. It was noteworthy that although there was a sharp ICL after the first discharge, the subsequent three discharge and charge capacities of the 3DOM- SnO_2 anode were also both higher than of the non-templated counterpart. The following three discharge and charge curves of the 3DOM- SnO_2 electrode overlapped well with one another, indicating better cycling stability and capacity retention than the non-templated counterpart. The enhanced electrochemical performance of the 3DOM- SnO_2 anode might be related to the enlarged surface area. On the one hand, the enlarged surface area can provide more active sites and defects for Li^+ ions to insert into the whole active materials [25]. On the other hand, the increased surface area ensures locally lower current densities, which alleviates the capacity loss during charge and discharge processes [21]. The porous nano-sized thick walls of the 3DOM structure also acted as an advantage for the improved performance, which could shorten diffusion length for Li^+ insertion, thus enhancing the electrochemical performance [25]. It should be mentioned that the first discharge capacities of 3DOM- SnO_2 and N- SnO_2 electrodes were both much higher than that of the theoretical capacity of SnO_2 (782 mAh g^{-1}). The large excess initial capacity could be ascribed to the decomposition of organic electrolytes and the amorphization of the nanocrystalline SnO_2 when the cell voltage reaches 0.01 V [26].

Similar phenomena have also been observed in the discharge process of other transition metal oxides [23, 26]. The possibility of interfacial storage in nanocrystals could also contribute to the large excess capacity observed in this material [27, 28]. The large ICL may be mainly attributed to the decomposition of organic electrolytes and formation of the SEI layer.

To fully estimate the electrochemical performance of the samples, the results of cycling performance at various current densities (0.2, 0.5, 1, 2, and 0.2 C) are shown in Fig. 3e. Here 1 C is defined as 782 mA g^{-1} . In the rate performance test, the sample **N-SnO₂** delivers discharge capacities of 640, 253, 44, and 16 mAh g^{-1} when the rates are 0.2, 0.5, 1 and 2 C, respectively. When the current density returned to 0.2 C, the discharge capacity recovered to 327 mAh g^{-1} . In comparison, the **3DOM-SnO₂** electrode exhibited much higher reversible capacities both at low and high rates. The corresponding average discharge capacities of the **3DOM-SnO₂** electrode reach 1141, 757, 547 and 326 mAh g^{-1} at densities of 0.2, 0.5, 1 and 2 C, respectively, and the discharge capacity recovered to 653 mAh g^{-1} when the rate went back to 0.2 C, which indicated good cycling stability of the electrode. These results demonstrated the importance and validity of the 3D structure on stabilizing the cyclic performance and improving electrode capacity. Electrochemical impedance spectroscopy (EIS) was employed to further analyze the charge transfer behavior of these samples using LIR2032 coin-type half-cells, as shown in Fig. 3f. For **3DOM-SnO₂**, the diameter of the semicircle was smaller than that of the **N-SnO₂** electrode, manifesting it had lower charge transfer resistance, which suggested that the 3D architecture of the **3DOM-SnO₂** architecture improved the electronic conductivity of the active material. This fact could be attributed to the unique property of the 3DOM structure, which is

readily filled with electrolyte solution resulting in the improved ionic and electric conductivity [29].

In order to study the effect of the crystallinity on electrochemical performance, non-templated SnO₂ was treated at 350 °C for 6 h in a tube furnace with a heating rate of 1 °C min⁻¹ and an air flow of 100 mL min⁻¹. The as-obtained product was referred as N-SnO₂-350. The XRD pattern and initial charge and discharge curves of the N-SnO₂-350 were presented in Fig 4a and b, respectively. It can be found that N-SnO₂-350 and 3DOM-SnO₂ powders have the extremely similar XRD pattern shape, suggesting the similar crystallinity of both materials (as shown in Fig. 4a). The initial five discharge specific capacities for N-SnO₂-350 were 1618, 851, 783, 701 and 657 mAh g⁻¹, respectively, which were comparable with the specific capacities of the N-SnO₂ (as shown in Fig. 4b). The initial five specific capacities of the N-SnO₂-350 electrode were much lower than that of the 3DOM-SnO₂. These results indicated that the effect of the crystallinity on electrochemical performance was negligible.

To demonstrate the promising application in LIBs, the result of cycling performance of the 3DOM-SnO₂ electrodes in the potential range of 0.01-3.00 V is shown in Fig. 5 (capacity retention vs. cycle number) at a current density of 0.2 C. As expected, the 3DOM-SnO₂ structure manifests exceptional capacity retention. A capacity around 653 mA h g⁻¹ is observed in the first cycle. The reversible capacity is about 336 mAh g⁻¹ after 50 cycles. The corresponding Coulombic efficiency (CE) of the 3DOM-SnO₂ electrode was also shown in Fig. 4. The average CE of the initial five cycles for the 3DOM-SnO₂ anode was about 96.8%, which was a little lower than that of the subsequent cycles. The lower CE of the initial five cycles for the 3DOM-SnO₂ anode was likely due to the enlarged surface area, resulting in the formation of plenty SEI, which grew continuously during cycling and was slowly

established over considerable cycles [30, 31]. Some undecomposed Li_2O phase should be also responsible for the low initial CE [32]. From the fifth cycle onwards, the CE of the 3DOM- SnO_2 anode increased steadily and was greater than 98%. The reduction of the formation of excessive SEI film in the next forty-five cycles improved the CE of the battery. In comparison, the N-SnO_2 electrode exhibited poor cycling performance with a capacity retention of 125 mAh g^{-1} at the same current density.

4. Conclusions

In summary, the 3DOM- SnO_2 nanoparticles were synthesized using a modified colloidal crystal templating method. The electrochemical results showed that the sample 3DOM- SnO_2 exhibited high capacity, good rate capability and excellent cycling ability. The enhanced electrochemical performance of the 3DOM- SnO_2 electrode can be attributed to the 3D morphological features that can improve the electronic conductivity, provide more reaction sites on the surface and shorten the diffusion length for Li^+ insertion. Our results open a way for preparing other metal oxides with 3DOM structure as anode electrode materials for LIBs.

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Scheme 1 Schematic diagram of the preparation route of 3DOM-SnO₂

Fig. 1 XRD patterns (a) and nitrogen adsorption–desorption isotherm (b) of **N-SnO₂** and **3DOM-SnO₂**. Insert: pore size distribution.

Fig. 2 TEM images of **N-SnO₂** (a and b), SEM images of **3DOM-SnO₂** (c and d).

Fig. 3 (a) CV curves of the 3DOM-SnO₂ electrodes from the first cycle to the third cycle; (b) XRD pattern of the 3DOM-SnO₂ at different cycled state; The discharge-charge profiles of the N-SnO₂ (c) and 3DOM-SnO₂ (d) electrodes at a current rate of 0.2C; (e) Multirate tests of the N-SnO₂ and 3DOM-SnO₂ electrodes with 5 cycles for each step; (f) EIS of the N-SnO₂ and 3DOM-SnO₂ electrodes.

Fig.4 XRD pattern (a) and the initial five charge-discharge cycles tested at 0.2 C (b) of the N-SnO₂-350 sample.

Fig. 5 Charge-discharge specific capacity of 3DOM-SnO₂ and N-SnO₂ cycled at 0.2 C.