Design and synthesis of porous nano-sized Sn@C/graphene electrode material with 3D carbon network for high-performance lithium-ion batteries

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1. Introduction

Lithium-ion batteries are the most widely used rechargeable batteries because of their superior energy density, no memory effect. However, the energy density of lithium-ion batteries still lies behind the demands of consumers. To improve the energy density of lithium-ion batteries, many high-capacity anode materials have been exploited, such as metal oxides, silicon and tin [1–11]. Among the reported anode materials, metallic tin (Sn) is one of the most promising anode materials for high performance lithium-ion batteries because of its high theoretical specific capacity (952 mA h g\textsuperscript{-1}), and environmentally benign nature [11–13]. However, the lithiation and delithiation reactions (Sn + 4.4Li\textsuperscript{+} + 4.4e\textsuperscript{-} \rightarrow Li\textsubscript{4.4}Sn) are accompanied by a large volume change [10–13], which lead to the pulverization of the particles and the electrical disconnection of the electrode [14,15]. This is the major reason for the poor cycle performance of metallic Sn, which hampers its application in lithium-ion batteries. Reducing the size of the Sn particles to nanoscale can mitigate the absolute strain induced by the large volume change during lithiation–delithiation process, and retard particle pulverization [16–18]. Nevertheless, the nanoparticles tend to aggregate into large particles, especially during the charge–discharge process [18,19].

Many efforts have been devoted to improving the electrochemical performance of metallic Sn, such as carbon-coating, nanocomposite and porous structure [10–15,20]. Among the reported approaches, the cycle performance of metallic Sn can be considerably improved by dispersing nano-sized Sn into a carbon matrix which acts as both a structural buffer and an electroactive material [10,17,21]. Graphene, a new two-dimensional carbon material, exhibits a number of intriguing unique properties, such as ultrathin thickness, superior electronic conductivity, good mechanical properties, large reversible specific capacity [22–26]. Therefore, graphene is an ideal carbon nanostructure which can be used to
design high performance electrode materials. In the past four years, Sn/graphene nanocomposites with various structures and morphologies have been explored as anode materials for lithium-ion batteries, such as Sn/graphene [27–30], carbon coated Sn/graphene and Sn@CNT/graphene nanocomposites [12,31–33]. Although the graphene sheets in these reported Sn/graphene nanocomposites can act as a barrier to prevent the aggregation of nanoparticles to a certain extent, the nanoparticles on the same piece of graphene still tend to aggregate into large particles [18,19]. In addition, the pulverized Sn particles fall off the graphene sheets during the charge–discharge process [12]. Therefore, the cycle performances of these reported Sn/graphene nanocomposites are not satisfactory [27–30]. Carbon coated Sn/graphene and Sn@CNT/graphene nanocomposites can avoid the exfoliation of the pulverized Sn particles from current collector to a certain extent [12,31–33]. However, most of these reported carbon coated Sn/graphene and Sn@CNT/graphene nanocomposites were prepared using SnX2/graphene oxide (X = O or S) nanocomposites as raw material [12,31–33] (Fig. 1a). The aggregated SnX2 particles still exist in the raw material (SnX2/graphene nanocomposite), which would be reduced to large Sn particles during thermal treatment process, leading to the heterogeneous distribution of tin in the carbon matrix. In addition, the carbon was not only deposited on the surfaces of Sn particles but also those of graphene sheets during the carbon coating process, which is adverse to the electrochemical properties of the graphene component.

In this study, porous nano-sized Sn@C/graphene electrode material with three-dimensional (3D) carbon network was designed and prepared (Fig. 1b). The tin particles were fixed on the graphene sheets with carbon shells, which can not only suppress the aggregation of nanoparticles but also avoid the exfoliation of the pulverized Sn particles from graphene sheets during the charge–discharge process. The porous Sn@C/graphene nanocomposite can provide a void space, which helps to accommodate the volume changes of Sn nanoparticles during the lithium uptake-release process. Most importantly, the preparation method of the

![Diagram](image_url)
porous nano-sized Sn@C/graphene nanocomposite presented here can avoid the agglomeration of nanoparticles, leading to the uniform distribution of tin in the carbon matrix. Therefore, it is very possible that the prepared Sn@C/graphene nanocomposite possesses excellent cycle stability for lithium storage.

2. Experimental

2.1. Preparation of SnO2 nanoparticles

SnO2 nanoparticles were prepared by using a facile gas-liquid interfacial synthesis approach, as reported in our previous paper [19,34]. Briefly, in a 15-mL beaker, 0.3647 g of SnCl2·H2O (Tianjin Kemel Chemical Reagent Co., Ltd., China) was dissolved in 10 mL of ethylene glycol (EG) (Beijing Chemical Reagent Co., Ltd., China). Then the beaker was placed into a 100-mL Teflon-lined autoclave that contained 14 mL of ammonia solution (Guangzhou Chemical Reagent Factory, China). Then the autoclave was sealed and placed in a drying oven preheated to 180 °C and held at this temperature for 12 h. After cooling and centrifugation, washing with ethanol (Beijing Chemical Reagent Co., Ltd., China) for three times, the collected solid product (SnO2 nanoparticles) was dispersed in 25 mL of ethanol by ultrasonication. The obtained suspension is named SnO2-EG.

2.2. Synthesis of graphene oxide

Graphene oxide (GO) was prepared by a modified Hummers method [19]. In a typical reaction, 2 g of graphite powder with the average particle size 30 μm, 2 g of sodium nitrate (Tianjin Jin Chen Chemical Reagent Factory, China) and 100 mL of concentrated sulfuric acid (Beijing Chemical Reagent Co., Ltd., China) were mixed and stirred for 15 min in a 3000 mL reaction flask immersed in an ice bath. Then 12 g of potassium permanganate (Guangzhou Chemical Reagent Factory, China) was slowly added to the above solution and cooled for 30 min in the ice bath. After removing the ice bath and continuously stirring the suspension for 48 h, 184 mL of pure water was slowly added to the suspension in 15 min. Subsequently, the suspension was further treated with 560 mL of warm water and 40 mL of H2O2 (30%, Guangzhou Chemical Reagent Factory, China) to reduce the residual permanganate and manganese dioxide to colorless soluble manganese sulfate. The mixture was centrifuged at 8000 rpm and washed with a mixed aqueous solution of 5% H2SO4/1 wt% H2O2, then washed with water. Finally, the residual impurity ions were removed through dialysis. The prepared graphene oxide was dispersed in deionized water by ultrasonic treatment for 1 h to obtain 1000 mL GO dispersion.

2.3. Synthesis of Sn@C/graphene nanocomposite

The fabrication process of the porous Sn@C/graphene nanocomposite with 3D carbon network is demonstrated in Fig. 1. First, SnO2 nanoparticles were coated with glucose-derived carbon-rich polysaccharide (GCP) by a simple hydrothermal approach. Briefly, 1 g of glucose was dissolved in 40 mL of deionized water, and 20 mL of SnO2/EG was added to the glucose aqueous solution under gentle stir, then the resulting suspension was transferred to a 100-mL Teflon-lined autoclave. The autoclave was sealed and placed into a drying oven preheated to 180 °C and held at this temperature for 12 h. After cooling and centrifugation, washing with deionized water for three times, the collected product (GCP coated SnO2 nanoparticles) was added to 100 mL of GO dispersion and sonicated for 6 h to yield a homogenous suspension. Subsequently, the suspension was transferred to a 100-mL Teflon-lined autoclave. Then the autoclave was sealed and placed into a drying oven preheated to 185 °C and held at this temperature for 12 h. Finally, the as-obtained product was freeze-dried overnight (after hydrothermal self-assembly and freeze-drying, the obtained product was named SnO2@GCP/GO nanocomposite), followed by thermal treatment at 850 °C for 4 h under argon atmosphere to obtain the porous nano-sized Sn@C/graphene electrode material with 3D carbon network.

2.4. Materials characterization

The structure and morphology of the as-prepared SnO2 nanoparticles, GCP coated SnO2 nanoparticles, SnO2@GCP/GO and Sn@C/graphene nanocomposites were characterized by X-ray diffraction (XRD, Bruker D8 Advance), Fourier transform infrared spectroscopy (FTIR, Bruker Vector 33), scanning electron microscopy (SEM, Quanta 200F), and transmission electron microscopy (TEM, FEI, Tecnai G2 F30 S-Twin). N2 adsorption/desorption isotherms were measured using a Micromeritics ASAP 2010 (USA) analyzer at liquid nitrogen temperature. Elemental analysis was carried out on Vario EL III Elementar (Germany) by burning the Sn@C/graphene nanocomposite to form carbon dioxide. The content of carbon in Sn@C/graphene nanocomposite was calculated according to the mass of carbon dioxide. The elemental analysis indicates that the carbon content of the Sn@C/graphene nanocomposite is about 54.3%.

2.5. Electrochemical measurements

The electrochemical experiments were carried out using the coin-type cells. The working electrode was prepared by mixing active material (Sn@C/graphene nanocomposite) with poly(vinylidene fluoride) (PVDF) and Super P carbon at a weight ratio of 75:10:15 in N-methyl-2-pyrrolidone (NMP) to form slurry. Then, the resultant slurry was uniformly pasted on Cu foil with a blade, dried at 120 °C in a vacuum oven and pressed under a pressure of 20 MPa. The active material loading density of the electrode is ca. 1.5 mg cm-2. The Celgard 2325 microporous membrane was used as separator. The electrolyte was 1 mol L-1 LiPF6 dissolved in a mixture of ethylene carbonate (EC) and dimethyl carbonate (DMC) (1:1 by volume). The lithium sheet was used as both counter and reference electrode. CR2025-type coin cells were assembled in an argon-filled glove box and galvanostatically discharged and charged in a voltage range from 3.0 to 0.01 V using a Battery Testing System (Neware Electronic Co., China). The specific capacity was calculated based on the total mass of the active material.

3. Results and discussion

3.1. Microstructural characterization

Fig. 1b shows the schematic illustration of the synthesis route for the porous Sn@C/graphene nanocomposite. First, SnO2 nanoparticles were prepared by using a facile gas–liquid interfacial synthesis approach [19,34]. The XRD pattern of the as-prepared SnO2 nanoparticles is shown in Fig. 2a. The diffraction peaks of SnO2 nanoparticles are clearly distinguishable. All strong diffraction peaks can be indexed to the standard tetragonal SnO2 phase, indicating crystalline SnO2 nanoparticles were formed during the gas-liquid interfacial reaction process. The broad diffraction peaks suggest that the SnO2 nanoparticles are very small in size, which can be further confirmed by the TEM image. As shown in Fig. 3a and b, the TEM images clearly revealed that the particle size of SnO2 nanoparticles is less than 6 nm. However, the bare SnO2 nanoparticles aggregated into large particles as shown in Fig. 3c. Both the structure and morphology are in agreement with those reported in the literature [19,34].

Secondly, the as-prepared SnO2 nanoparticles were coated with glucose-derived carbon-rich polysaccharide (GCP) by a simple hydrothermal approach [35]. Fig. 2b shows the XRD pattern of the GCP coated SnO2 nanoparticles. The diffraction peaks of GCP coated SnO2 nanoparticles are clearly distinguishable. All strong diffraction peaks can be indexed to the standard tetragonal SnO2 phase, and no characteristic peaks of impurities, such as elemental Sn or other tin oxides, were observed. The XRD result clearly indicates that SnO2 cannot be reduced by glucose under

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Fig. 3. TEM images of (a and b) SnO$_2$ nanoparticles, (d and e) GCP coated SnO$_2$ nanoparticles, (g and h) SnO$_2$@GCP/GO nanocomposite, (j and k) Sn@C/graphene nanocomposite, and SEM images of (c) SnO$_2$ nanoparticles, (f) GCP coated SnO$_2$ nanoparticles, (i) SnO$_2$@GCP/GO nanocomposite, (l) Sn@C/graphene nanocomposite.
hydrothermal condition [19]. Fig. 3d–f shows the typical TEM and SEM images of the GCP coated SnO2 nanoparticles, which clearly indicates that the SnO2 nanoparticles were coated successfully. The FTIR spectra of the GCP coated SnO2 nanoparticles is shown in Fig. 4a. A broad absorption band between 3000 and 3700 cm\(^{-1}\) corresponds to O–H (hydroxyl or carboxyl) stretching vibration [36,37]. The band at approximately 1624 cm\(^{-1}\) can be attributed to C=\(\equiv\)C stretching vibration, whereas the weak bands in the 1000–1450 cm\(^{-1}\) region correspond to C\(-\)O (hydroxyl, ester, or ether) stretching and O–H bending vibrations [19,36,37]. The weak band at 893 cm\(^{-1}\) is attributed to aromatic C–H out-of-plane bending vibration, and the band at 571 cm\(^{-1}\) is associated with the vibration of the Sn–OH terminal bonds [36,37]. Obviously, the GCP coated SnO2 nanoparticles should be hydrophilic due to the carbon precursor coating layer with oxygen-containing groups including hydroxyl. Therefore, the GCP coated SnO2 nanoparticles could be easily dispersed in GO dispersion to form homogeneous suspension [19]. This is very important to realize the hydrothermal self-assembly of GCP coated SnO2 and GO sheets in the following step.

Thirdly, the GCP coated SnO2 nanoparticles were dispersed in GO dispersion by sonication to yield a homogeneous suspension. Then GCP coated SnO2 and GO sheets were hydrothermally assembled at 185 °C for 12 h to form 3D carbon precursor network [38,39]. It should be pointed out that both GO sheets and the carbon precursor coating layer of the GCP coated SnO2 nanoparticles have oxygen-containing functional groups, which can react with each other to form a 3D carbon precursor network under hydrothermal condition. After hydrothermal self-assembly and freeze-drying, the obtained product was named SnO2@GCP/GO nanocomposite. The XRD pattern of the SnO2@GCP/GO nanocomposite is shown in Fig. 2c. All strong diffraction peaks can be indexed to the standard tetragonal SnO2 phase, and no characteristic peaks of elemental Sn or other tin oxides were observed. The XRD result clearly indicates that SnO2 had not been reduced during the hydrothermal self-assembly process. Fig. 3g–i shows the typical TEM and SEM images of the SnO2@GCP/GO nanocomposite, respectively. The SEM and TEM images clearly indicate that the 3D carbon precursor network can be formed by hydrothermal self-assembly of the GCP coated SnO2 and GO sheets. It should be noted that the SnO2 nanoparticles were uniformly distributed in the 3D carbon precursor network without agglomeration, which is very important to realize the uniform distribution of tin in the carbon...
nanoparticles can react with lithium but also the 3D carbon network is formed during the heat-treatment. The shape of the discharge/charge curves is generally consistent with those reported previously for carbon coated Sn/graphene nanocomposites [12,32], indicating the same electrochemical reaction pathway. The first discharge and charge specific capacities of the Sn@C/graphene nanocomposite are 1896 and 928 mAh g\(^{-1}\), respectively. The initial coulombic efficiency calculated based on the first discharge/charge specific capacities is 49%. The large irreversible capacity during the first cycle can be attributed to the irreversible lithium loss due to the formation of solid-electrolyte interface (SEI) layer on the electrode surface [12,27]. It should be noted that specific surface area of the Sn@C/graphene nanocomposite is as high as 538.1 m\(^2\) g\(^{-1}\), which may lead to the low initial coulombic efficiency. After five cycles, the coulombic efficiency of the Sn@C/graphene nanocomposite increases to over 95% in the subsequent cycles, revealing an excellent reversibility. The high initial reversible specific capacity should be related to the high reactivity of the nano-sized Sn@C/graphene composite. It should be pointed out that not only Sn nanoparticles in the Sn@C/graphene nanocomposite can react with lithium but also the 3D carbon network consists of graphene sheets and carbon shell is an active material for additional Li\(^+\) extraction from Li\(_2\)Sn alloys [12]. The electrochemical properties of the porous Sn@C/graphene nanocomposite with 3D carbon network were investigated using coin-type cells. The first 50 discharge/charge cycles were tested at a specific current of 100 mA g\(^{-1}\), and the corresponding discharge/charge curves are shown in Fig. 6a. The initial discharge curve exhibits a long slope starting from around 0.95 V to 0 V, which can be attributed to the alloying of lithium with tin and intercalation of lithium into the 3D carbon network. The first charge curve shows three voltage plateaus at 0.58, 0.70 and 0.79 V, corresponding to the Li\(^+\) extraction from Li\(_2\)Sn alloys [12].

3.2. Electrochemical properties of the porous Sn@C/graphene nanocomposite with 3D carbon network

The cycling performance of the porous Sn@C/graphene nanocomposite with 3D carbon network is shown in Fig. 6b. The porous nano-sized Sn@C/graphene electrode material delivered a reversible specific capacity of 693 mAh g\(^{-1}\) in the second cycle. After 50 cycles, the reversible specific capacity still maintained at...
602 mA h g⁻¹, which is comparable or even superior to the previously reported Sn@hollow carbon spheres (550 mA h g⁻¹ after 100 cycles) [15], Sn/graphene nanocomposite (508 mA h g⁻¹ after 100 cycles) [27], and carbon coated Sn/graphene nanocomposites (662 mA h g⁻¹ after 100 cycles [12], 566 mA h g⁻¹ after 100 cycles [32]). It should be pointed out that the active material loading density of the electrode reported here (ca. 1.5 mg cm⁻²) is larger than that of carbon coated Sn/graphene nanocomposite we previously reported (ca. 1.0 mg cm⁻²) [12]. Most importantly, the reversible specific capacity is almost constant from the tenth cycle to the fifteenth cycle, exhibiting excellent cycling stability. The outstanding cycling performance of the porous Sn@C/graphene nanocomposite can be attributed to the following two factors. Firstly, the tin particles were fixed on the graphene sheets with carbon shells, which can not only suppress the aggregation of nanoparticles but also avoid the exfoliation of the pulverized Sn particles from graphene sheets during the charge–discharge process. Secondly, the porous Sn@C/graphene nanocomposite can provide a void space, which helps to accommodate the volume changes of Sn nanoparticles during Li⁺ insertion/extraction process.

After 50 cycles, the same cell was further evaluated for rate capability as shown in Fig. 7. When the same cell was tested at various specific currents from 100 to 1000 mA g⁻¹, the porous SnO₂@C/graphene nanocomposite with 3D carbon network exhibits good rate capability. At the high specific currents of 300, 500 and 1000 mA g⁻¹, the SnO₂@C/graphene nanocomposite can still exhibit high reversible specific capacities of 498, 440 and 344 mA h g⁻¹, respectively. All of these values can be comparable to the theoretical specific capacity of the commonly used graphite anode material (372 mA h g⁻¹). The good rate capability of the porous Sn@C/graphene nanocomposite with 3D carbon network can be related to its unique structure. The 3D carbon network could increase the electronic conductivity of the nanocomposite and the porous structure can facilitate the liquid electrolyte diffusion into the bulk materials [19]. In addition, the nano-sized particles can shorten the path length for electronic and Li⁺ transport [16,17], which also favors the high rate capability. After 90 cycles at various specific currents from 100 to 1000 mA g⁻¹, when the specific current returns to initial 100 mA g⁻¹, a high reversible specific capacity of 649 mA h g⁻¹ can be obtained in the 100th cycle, that is, about 94% retention of the reversible specific capacity in the second cycle.

4. Conclusions

In summary, porous nano-sized Sn@C/graphene electrode material with 3D carbon network was designed and prepared. The as-prepared Sn@C/graphene nanocomposite as an anode material for lithium-ion batteries exhibits high reversible specific capacity, outstanding cyclability and good rate capability. The excellent electrochemical performances can be attributed to the following reasons: (1) Nanometer-sized materials have high reactivity, short path lengths for electronic and Li⁺ transport. (2) The tin particles were fixed on the graphene sheets with carbon shells, which can not only suppress the aggregation of nanoparticles but also avoid the exfoliation of the pulverized Sn particles from graphene sheets during the charge–discharge process. (3) The porous Sn@C/graphene nanocomposite can provide a void space, which helps to accommodate the volume changes of Sn nanoparticles during the
lithium uptake-release process. (4) The porous structure can facilitate the liquid electrolyte diffusion into the bulk materials. The result indicates that the electrochemical performance of tin-based electrode materials can be improved by designing proper structure. We believe that the strategy presented in this work will pave the way for the practical application of high-capacity electrode materials with large volume variations during charge–discharge processes. The preparation approach of porous Sn@C/graphene nanocomposite reported here may also be applied to fabricate porous Si@C/graphene electrode material for high performance lithium-ion batteries.

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