High reversible capacity of SnO$_2$/graphene nanocomposite as an anode material for lithium-ion batteries

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1. Introduction

Lithium-ion batteries are currently the dominant power source for portable electronic devices and viewed as the promising power source of electrical/hybrid vehicles. Graphite is the widely commercial anode material, but its theoretical specific capacity is only 372 mAh g$^{-1}$ (by forming intercalation compounds (LiC$_6$)), which cannot fulfill the increasing demand for high performance lithium-ion batteries [1]. SnO$_2$ is concerned as a promising anode material for lithium-ion batteries due to the following two reasons [2,3]. Firstly, based on an alloying mechanism, SnO$_2$ + 4Li$^+$ + 4e$^-$ $\rightarrow$ 2Li$_2$O + Sn and Sn + xLi$^+$ + xe$^-$ $\rightarrow$ Li$_x$Sn (0 $\leq$ x $\leq$ 4.4), its maximal theoretical capacity is 782 mAh g$^{-1}$ [4,5], which is more than twice that of the already-commercialized graphite (372 mAh g$^{-1}$) [6–8]. Secondly, the potential of the Sn$_2$O$_3$ anode is higher than that of graphite, which reduces the potential safety problems with metallic lithium deposition on the host anode during rapid charge [1,3]. However, its application in practical lithium-ion batteries is still hampered by the poor cycling performance arising from the severe agglomeration and huge volume changes of SnO$_2$ particles during Li insertion/extraction process [6–27]. The large volume changes of SnO$_2$ particles during lithium ions insertion/extraction process causes cracking and crumbling, which will result in electrical disconnection of active material with current collector and consequently limit the cycling capability of electrodes [6–8,17–20]. The agglomeration of primitive particles drastically reduces the total entrance/exit sites available for Li$^+$ ions and creates even more severe mechanical stresses in the surface region of a particulate aggregate, leading to poor electrochemical performance [13,23,25]. In order to alleviate the volume changes and agglomeration, two common strategies have been pursued. One strategy is to design hollow or porous structure SnO$_2$ anode materials [6–8,13,15,20,27]. Another one is to prepare SnO$_2$/C composites by loading SnO$_2$ nanoparticles into a ductile carbon matrix [9–12,17,18,21,25,26]. The second strategy is very effective to improve the electrochemical performance of SnO$_2$ material. The carbon in SnO$_2$/C composites can not only buffer the volume changes of SnO$_2$ nanoparticles and prevent them from aggregating to large particles but also increase electronic conductivity of composites due to its good electronic conductivity [5,9,10,12,16,23,25], which favors high rate performance.

Graphene, a monolayer of graphite, exhibits a number of intriguing unique properties [28,29], such as superior electronic conductivity, high surface area (theoretical value 2620 m$^2$ g$^{-1}$), large surface-to-volume ratio, good mechanical properties. Therefore, graphene is an ideal carbon nanostructure which can be used to design high performance SnO$_2$/carbon nanocomposite electrodes. So far, there have been a few reports about the preparation of SnO$_2$/graphene nanocomposite [30–36]. For example, Paek
et al. [30] synthesized SnO\textsubscript{2}/graphene nanocomposite with three-dimensionally delaminated flexible structure by mechanically mixing SnO\textsubscript{2} nanoparticles with graphene dispersions. The as-prepared SnO\textsubscript{2}/graphene electrode material exhibited an enhanced cycle performance and lithium storage capacity. As claimed, the reversible capacity could remain 570 mAh g\textsuperscript{−1} after 30 cycles that is about 70\% retention of the original reversible capacity at a current density of 50 mA g\textsuperscript{−1}. Yao et al. [31] reported the in situ chemical synthesis of the SnO\textsubscript{2}/graphene nanocomposite. The obtained SnO\textsubscript{2}/graphene nanocomposite exhibits a reversible capacity of 765 mAh g\textsuperscript{−1} in the first cycle and remains 520 mAh g\textsuperscript{−1} after 100 cycles. Besides, some groups [32–35] prepared the SnO\textsubscript{2}/graphene nanocomposite via in situ chemical synthesis route based on an oxidation-reduction reaction. The prepared SnO\textsubscript{2}/graphene nanocomposite also shows enhanced electrochemical performance. However, the mechanically mixing method limits the homogeneous dispersion of SnO\textsubscript{2} nanoparticles and the separation of graphene sheets [31], and all those in situ chemical synthesis methods need extra thermal treatment, which makes the synthesis process complicated and time-consuming. Furthermore, these SnO\textsubscript{2}/graphene nanocomposites only show relatively low reversible capacity. Therefore, it is still necessary to explore facile synthesis techniques for the preparation of SnO\textsubscript{2}/graphene nanocomposite.

Recently, Cui et al. [37] prepared Fe\textsubscript{3}O\textsubscript{4} nanoparticles by a facile gas-liquid interfacial reaction. Lian et al. [38] developed the gas-liquid interfacial synthesis approach and prepared Fe\textsubscript{3}O\textsubscript{4}/graphene nanocomposite. The Fe\textsubscript{3}O\textsubscript{4}/graphene nanocomposite prepared by the gas-liquid interfacial synthesis approach exhibited a very high reversible capacity. In this study, the facile gas-liquid interfacial synthesis approach was firstly used to prepare SnO\textsubscript{2}/graphene nanocomposite. The as-prepared nanocomposite as an anode material for lithium-ion batteries exhibits an unprecedented high reversible specific capacity of 1304 mAh g\textsuperscript{−1} after 150 cycles. Such excellent performance could be attributed to its porous structure and the enhanced surface electrochemical reactivity due to the large surface-to-volume ratio of SnO\textsubscript{2} nanoparticles [30].

2. Experimental

2.1. Materials preparation

All chemicals were of analytical grade and used as received, without further purification. Graphene sheets were prepared via a thermal exfoliation route involving graphite oxidation, following by rapid thermal expansion under nitrogen atmosphere. Detailed preparation procedure can be found in our previous paper [39]. SnO\textsubscript{2}/graphene nanocomposite and SnO\textsubscript{2} nanoparticles were prepared by a gas-liquid interfacial reaction, as shown in Fig. 1. Briefly, in a 20-mL beaker, 0.3647 g of SnCl\textsubscript{4}·5H\textsubscript{2}O (Tianjin Kermel Chemical Reagent Co., Ltd., China) was dissolved in 10 mL of ethylene glycol (EG) (Beijing Chemical Reagent Co., Ltd., China), and then 0.0476 g of graphene sheets were added and sonicated for 6 h to yield a homogeneous suspension. 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 several times, the collected black solid product was dried at 100 °C in vacuum to obtain the desired SnO\textsubscript{2}/graphene nanocomposite. The bare SnO\textsubscript{2} nanoparticles were synthesized under the same condition without the addition of graphene sheets for comparison.

2.2. Materials characterization

The structure and morphology of the as-prepared SnO\textsubscript{2}/graphene nanocomposite and SnO\textsubscript{2} nanoparticles were characterized by X-ray diffraction (XRD, Bruker D8 Advance), scanning electron microscopy (SEM, Quanta 200F) and high-resolution transmission electron microscopy (HRTEM, FEI, Tecnai G\textsuperscript{2} F30 S-Twin). N\textsubscript{2} 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 SnO\textsubscript{2}/graphene nanocom-
posite to form carbon dioxide. The content of carbon (i.e., graphene sheets) in SnO$_2$/graphene nanocomposite was calculated according to the mass of carbon dioxide. The content of graphene in SnO$_2$/graphene nanocomposite was determined to be 22.76 wt.%. To reveal the reaction mechanism of SnO$_2$/graphene nanocomposite with Li, both of the fresh SnO$_2$/graphene electrode sheet and fully charged (3.0 V) one after 150 cycles were characterized by X-ray diffraction. The bare SnO$_2$ nanoparticles electrode sheets were also characterized for comparison.

2.3. Electrochemical measurement

The electrochemical measurements were carried out using the coin-type cells. The working electrode was prepared by mixing active material (SnO$_2$ nanoparticles or SnO$_2$/graphene nanocomposite) with poly(vinylidene fluoride) (P(VDF; Kureha, Japan) and Super P carbon at a weight ratio of 75:10:15 in N-methyl-2-pyrrolidone (NMP, Tianjin Kernel Chemical Reagent Co., Ltd., China) to form a slurry. Then, the resultant slurry was uniformly pasted on Cu foil with a blade, dried at 120 °C in a vacuum oven (DZF-6020, Shanghai Qixin Scientific Instrument Co., Ltd., China) and pressed under a pressure of 20 MPa. The active material loading density of the electrode is ca. 1.0 mg cm$^{-2}$. The Celgard 2325 microporous membrane was used as separator. The electrolyte was 1 mol L$^{-1}$ LiPF$_6$ dissolved in a mixture of ethylene carbonate (EC) and dimethyl carbonate (DMC) (1:1 by volume) (Beijing Institute of Chemical Reagents, China). The lithium-ion battery was 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). Cyclic voltammetry (CV) measurements were carried out on an electrochemical workstation (Zahner IM6ex) over the potential range 0.01–3.0 V vs. Li/Li$^+$ at a scanning rate of 0.2 mV s$^{-1}$.

3. Results and discussion

3.1. Microstructural characterization

As illustrated in Fig. 1, the beaker-in-autoclave setup is designed to confine the synthesis at the gas/liquid interface inside a sealed space [37,38]. SnCl$_4$ (Sn$^{4+}$ species) and graphene sheets in EG solution were stored in the beaker, while aqueous ammonia solution (NH$_3$·H$_2$O) was placed in the autoclave liner outside the beaker. At room temperature, the beaker separates the two solutions. During the reaction, the system was heated to 180 °C quickly and then kept at that temperature for 12 h. Such a temperature increase results in the evaporation of ammonia, which reacts with Sn$^{4+}$ at the gas/liquid interface to produce Sn(OH)$_4$ in situ deposited onto the graphene sheets [8,30]. The produced Sn(OH)$_4$ could be quickly decomposed to SnO$_2$ at 180 °C, and the SnO$_2$/graphene nanocomposite was formed in the beaker. Because all of the NH$_3$, Sn$^{4+}$ and graphene sheets are homogeneously distributed at the gas/liquid interface, the formation of SnO$_2$/graphene nanocomposite is uniform and simultaneous at the interface. Furthermore, the reaction is limited at the interface, so that the particle growth is localized, which is important for synthesizing monodispersed nanoparticles with a narrow size distribution [37]. During the reaction, the convection inside the beaker will cause the graphene sheets to become immersed in the liquid and return back to the interface along the convection flow [37], which helps to achieve a homogeneous loading of SnO$_2$ nanoparticles on all the graphene sheets. It is very important to choose EG as the solvent in the beaker-in-autoclave setup. Firstly, EG is a good dispersant for graphene sheets, which is necessary for forming a homogeneous suspension. Secondly, EG is not a good solvent for NH$_3$, the reaction between NH$_3$ and Sn$^{4+}$ was limited at the gas/liquid interface [37].

Fig. 2a and b shows XRD patterns of as-prepared SnO$_2$/graphene nanocomposite, SnO$_2$ nanoparticles. The diffraction peaks of crystalline SnO$_2$ nanoparticles are clearly distinguishable. All strong diffraction peaks can be indexed to the standard tetragonal SnO$_2$ phase (JCPDS card no. 72-1147), indicating crystalline SnO$_2$ nanoparticles could be formed by the gas/liquid interfacial reaction. All peaks in the XRD pattern of SnO$_2$ nanoparticles are also in good agreement with those reported in the literature [30,31]. The broad diffraction peaks of the bare SnO$_2$ and SnO$_2$/graphene nanocomposite suggest that the nanoparticles are very small in size. There is a weak (002) diffraction peak in the XRD pattern of graphene sheets as shown in Fig. 2c. This result indicates that graphene sheets stacked into multilayers, leading to loss of their high surface area and intrinsic chemical and physical properties [31,33,34]. However, no obvious diffraction peak attributed to graphite in the XRD pattern of SnO$_2$/graphene nanocomposite was observed. This result indicates that the SnO$_2$ nanoparticles deposited on graphene sheets can prevent them from stacking into multilayers, favoring the maintenance of high surface area and intrinsic chemical and physical properties of graphene sheets [31,33,34]. The average crystal size of SnO$_2$ nanoparticles in the SnO$_2$/graphene nanocomposite is around 3.7 nm calculated by Scherrer’s formula based on the (1 1 0) peak.

The SEM and TEM micrographs of SnO$_2$ nanoparticles, graphene sheets and SnO$_2$/graphene nanocomposite are shown in Fig. 3. As shown in Fig. 3a and e, the SnO$_2$ nanoparticles prepared by the gas–liquid interfacial reaction aggregated into large particles. The resulting large particles could be easily pulverized owing to an asymmetrical volume change during Li$^+$ insertion/extraction process, resulting in capacity decay as an anode material for lithium-ion batteries [13,23,25]. Fig. 3b presents the representative SEM image of graphene sheets from the top view, showing the layered platelets composed of curled nanosheets, which is accordant to the weak (002) diffraction peak in the XRD pattern of the bare graphene sheets. Fig. 3c shows the SEM image of SnO$_2$/graphene nanocomposite prepared by the facile gas–liquid interfacial synthesis approach. Obviously, the deposition of SnO$_2$ nanoparticles onto the surfaces of graphene sheets is homogeneous. The SnO$_2$ nanoparticles are uniformly distributed on 2D
Fig. 3. SEM and TEM observation of SnO<sub>2</sub> nanoparticles, graphene sheets and SnO<sub>2</sub>/graphene nanocomposite: SEM micrographs of (a) SnO<sub>2</sub> nanoparticles, (b) graphene sheets (inset shows the edge-side of graphene sheets) and (c) SnO<sub>2</sub>/graphene nanocomposite. Low-magnification TEM images of (d) SnO<sub>2</sub>/graphene nanocomposite. High-magnification TEM images of (e) SnO<sub>2</sub> nanoparticles, (f) SnO<sub>2</sub>/graphene nanocomposite.

graphene sheets in as-prepared SnO<sub>2</sub>/graphene nanocomposite, as shown in Fig. 3d. From Fig. 3c and d, it can be observed that the graphene sheets are distributed between the SnO<sub>2</sub> nanoparticles and the nanoporous composite with large amount of void spaces was formed [30]. Such porous nanocomposite can possess excellent cycle performance as an anode material for lithium-ion batteries due to the large amount of void spaces which could buffer large volume changes of SnO<sub>2</sub> nanoparticles during lithium ions insertion/extraction process [7,8,12,16,18,30,38]. Moreover, the graphene sheets distributed between the SnO<sub>2</sub> nanoparticles can prevent the aggregation of these nanoparticles to a certain extent [9,14,25,32,38], which can be of great benefit to cycle life. The nanoparticles deposited on graphene sheets can also prevent them from stacking into multilayers [31,33,34], matching well with the result that no obvious diffraction peak attributed to graphite in the XRD pattern of SnO<sub>2</sub>/graphene nanocomposite was observed. It should be pointed out that the random hybridization between SnO<sub>2</sub> nanoparticles and ultrathin graphene sheets can form highly conducting 3D graphene electronic conductive network and porous structure of the SnO<sub>2</sub>/graphene nanocomposite [38]. The formed highly conducting 3D graphene electronic conductive network could increase electronic conductivity of the nanocomposite and the porous structure can facilitate liquid electrolyte diffusion into the bulk materials, which is beneficial for achieving high rate performance [7,8,30,31,34]. The HRTEM images (Fig. 3e and f) revealed that the average particle size of SnO<sub>2</sub> nanoparticles in the SnO<sub>2</sub>/graphene nanocomposite is comparable to that of bare SnO<sub>2</sub> nanoparticles. Both of them are less than 6 nm. The average particle size of SnO<sub>2</sub> nanoparticles (ca. 4 nm) in the SnO<sub>2</sub>/graphene nanocomposite observed from the HRTEM image is also well consistent with that estimated by the Scherrer equation. The small SnO<sub>2</sub> nanoparticles can provide short diffusion length for lithium ions insertion, resulting in good rate capability [7,38]. More importantly, even after a long time of sonication
Nanostructured materials

3.2. Electrochemical properties of SnO$_2$/graphene nanocomposite and SnO$_2$ nanoparticles

The electrochemical properties of the SnO$_2$/graphene nanocomposite and the bare SnO$_2$ nanoparticles were investigated using coin-type cells. The first 100 discharge/charge cycles were tested at a current density of 100 mA g$^{-1}$, and the corresponding discharge/charge curves are shown in Fig. 5a. The initial small plateaus and long slope profiles of SnO$_2$/graphene nanocomposite is similar to that of bare SnO$_2$ nanoparticles. Their first discharge voltage profiles both show classic plateaus in the potential ranging from 0.8 to 1.5 V, which was mainly due to the conversion reaction between SnO$_2$ and Li, SnO$_2$ + 4Li$^+$ + 4e$^-$ → 2Li$_2$O + Sn, leading to in situ formation of Sn–Li$_2$O nanocomposites [13,33,41,42].

As shown in Fig. 5b, the initial reversible specific capacity of the SnO$_2$ nanoparticles is 603.4 mAh g$^{-1}$. After the first cycle, the charge specific capacity increases to 639.9 mAh g$^{-1}$ in the 3rd cycle, indicating an activation process in the material [9]. The activation process is due to the aggregation of SnO$_2$ nanoparticles, which result in that only part of active material is involved in the initial reaction. During the first Li insertion/extraction process, the aggregated SnO$_2$ particles were pulverized into small particles due to their large volume changes [13,30,31], resulting in more active materials are involved in the 2nd and 3rd cycles. However, the pulverization of in situ formed Sn nanoparticles during the first three cycles destroyed the electronic conducting network between the active material and current collector [5,7,33], resulting in the reversible capacity decay from the 4th cycle. The reversible capacity of bare SnO$_2$ nanoparticles remains only 198.2 mAh g$^{-1}$ after 100 cycles. As shown in Fig. 3c and d, SnO$_2$ nanoparticles are tightly attached to the graphene sheets and spatially separated by the graphene sheets in the SnO$_2$/graphene nanocomposite, which are favorable for improving the cycling performance [9,31,33]. In addition, the nanosized SnO$_2$ particles and the elastic graphene sheets in the porous SnO$_2$/graphene nanocomposite also help to accommodate the volume changes and prevent the pulverization of SnO$_2$ to a certain extent during discharge/charge cycles [13,30–34], which would lead to excellent cycle capability. As shown in Fig. 5b, the SnO$_2$/graphene nanocomposite indeed shows enhanced electrochemical performances as expected. The charge capacity of the nanocomposite is as high as 936.4 mAh g$^{-1}$ in the first cycle and decreases to 732.2 mAh g$^{-1}$ in the 20th cycle. Nevertheless, the reversible capacity begins increasing from 21st cycle and increases to 1,156 mAh g$^{-1}$ in the 100th cycle. The phenomenon, the reversible specific capacity decreases to a low value then gradually increases, has never been reported for SnO$_2$/C composites. But the similar phenomenon has been reported for Fe$_3$O$_4$/C composites [43]. The decay of reversible capacity of the SnO$_2$/graphene during the first 20 cycles could be due to the pulverization of original SnO$_2$ and in situ formed Sn nanoparticles during Li insertion/extraction process, which lead to loss of electrical connectivity between neighboring particles [17]. During discharge/charge cycles, the in situ formed Sn nanoparticles became smaller and smaller due to electrochemical milling effect [44] and attached on the graphene sheets tightly. It is reported that activation energies for solid-state double decomposition reactions decreased with decreasing reagent particle size [45]. Thus, the conversion reaction, SnO$_2$ + 4Li$^+$ + 4e$^-$ → 2Li$_2$O + Sn, which is usually reported to be irreversible [9,41], can become reversible in the SnO$_2$/graphene nanocomposite due to the very small Sn nanoparticle sizes [5,27,46–49]. It has been reported that the Sn–Li alloying and dealloying reactions only occur below 1.0 V (vs. (Li/Li$^+$)) [4,10,50] and the Li–O bonds are not stable when the charge potential is above 1.3 V [50]. As shown in Fig. 5a, there is a plateau at around 1.3 V at the charge curves of SnO$_2$/graphene nanocomposite, indicating the reaction SnO$_2$ + 4Li$^+$ + 4e$^-$ → 2Li$_2$O + Sn indeed...
became partially reversible in the SnO2/graphene nanocomposite. The plateau above 1.0 V in the 100th charge curve is longer than that at the 20th charge curve, suggesting that the electrochemical reactivity increased due to the reduced Sn and Li2O nanoparticles with increasing cycle number. It is very possible that the increasing electrochemical reactivity results in the increase of reversible capacity of SnO2/graphene nanocomposite after 20 cycles. It should be pointed out that although a plateau above 1.0 V was observed in both the first and third charge curves of bare SnO2 nanoparticles, it completely disappeared in the 20th cycle. This result indicates that the reaction between bare SnO2 nanoparticles and Li, SnO2 + 4Li+ + 4e− → 2Li2O + Sn, is partially reversible during the first several cycles, but the reversibility decrease with increasing cycle number due to the decreasing electrochemical reactivity because of the aggregation of in situ formed Sn nanoparticles [5,13,24,25]. In contrast, a charge plateau above 1.0 V constantly existed during all the charge/discharge cycles of the SnO2/graphene nanocomposite, indicating that the reaction between SnO2 and Li, SnO2 + 4Li+ + 4e− → 2Li2O + Sn, is constantly reversible. The possible reason is that the graphene sheets in the SnO2/graphene nanocomposite can prevent the aggregation of in situ formed Sn nanoparticles [10,22]. The initial coulombic efficiency of the SnO2/graphene is 59%, but it is above 94% after 5 cycles. The large irreversible capacity during the first cycle can be attributed to irreversible lithium loss due to the formation of thick solid-electrolyte interface (SEI) layer on the electrode surface [5,17,35], and the fact that some Sn(0) cannot be re-oxidized back to Sn(IV) [9,19].

Table 1 shows a comparison of the reversible specific capacity at a low current density between the SnO2/graphene nanocomposites reported before and in this work. Obviously, the SnO2/graphene nanocomposite prepared by the facile gas–liquid interfacial synthesis approach possesses higher reversible specific capacity and better cycle performance than those reported previously.

After 100 cycles, the same cell was further evaluated for rate capability as shown in Fig. 5c. When the same cell was tested at various current densities from 100 to 1000 mA g\(^{-1}\), the SnO2/graphene nanocomposite exhibits an excellent rate capability. At the high current densities of 300, 500 and 1000 mA g\(^{-1}\), the SnO2/graphene nanocomposite can still exhibit high reversible capacities of 1072, 976 and 748 mAh g\(^{-1}\), respectively. All of these values are more than twice the theoretical specific capacity of the commonly used graphite anode material (372 mAh g\(^{-1}\)). Such excellent rate capability should be attributed to the highly conducting 3D graphene electronic conductive network and porous structure of the SnO2/graphene nanocomposite. The highly conducting 3D graphene electronic conductive network could increase electronic conductivity of the nanocomposite and the porous structure can facilitate liquid electrolyte diffusion into the bulk materials [7,30,34,35,41]. In addition, the short path length for Li\(^+\) transport due to nanosized SnO2 particles in as-prepared SnO2/graphene nanocomposite can also favor the high rate capability [7,41]. Remarkably, when the current density returns to the initial 100 mA g\(^{-1}\) after more than 140 cycles, a high reversible specific capacity of 1304 mAh g\(^{-1}\) can be obtained in the 150th cycle. The reversible capacity of 1304 mAh g\(^{-1}\) is much higher than the theoretical specific capacity of the SnO2/graphene nanocomposite (858 mAh g\(^{-1}\)) calculated according to the theoretical specific capacity of SnO2 (782 mAh g\(^{-1}\) based on the conventional alloying mechanism) and graphene sheets (1116 mAh g\(^{-1}\)) [38,39]. This result gives assistant information that the conversion reaction of SnO2 in the SnO2/graphene nanocomposite, SnO2 + 4Li+ + 4e− → 2Li2O + Sn, should be reversible to a certain extent. Such a result can be related to the enhanced surface electrochemical reactivity due to its large BET specific surface area and nanocrystalline nature [30,40,41,48]. Based on the novel conversion and alloying mechanism, SnO2 + 4Li+ + 4e− → 2Li2O + Sn and Sn + xLi\(^+\) + xe\(^−\) = Li\(_x\)Sn (0 < x < 4.4) [25], the maximum theoretical specific capacity of SnO2 is 1493 mAh g\(^{-1}\), and the theoretical specific capacity of SnO2/graphene nanocomposite should be as high as 1407 mAh g\(^{-1}\). This theoretical value is quite close to the experimental one of 1304 mAh g\(^{-1}\).

The cyclic voltammetry of the as-prepared SnO2/graphene nanocomposite is shown in Fig. 6a. In the cathodic polarization and anodic polarization processes, the redox peaks of the SnO2/graphene nanocomposite are observed at around 1.2 V and 0.1 V, respectively, which correspond to the redox reactions SnO2 + 4Li+ + 4e− → 2Li2O + Sn and Sn + 2Li\(^+\) + 2e\(^−\) = Li2Sn. The result indicates that the as-prepared SnO2/graphene nanocomposite can be used as an effective anode material for LIBs.
Table 1
Reversible specific capacities of SnO2/graphene nanocomposites reported before and in this work.

<table>
<thead>
<tr>
<th>Current density/mA g(^{-1})</th>
<th>Initial capacity/mAh g(^{-1})</th>
<th>Cycle number</th>
<th>Remaining capacity/mAh g(^{-1})</th>
<th>Ref.</th>
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<tr>
<td>50</td>
<td>810</td>
<td>30</td>
<td>570</td>
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<td>55</td>
<td>765</td>
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<td>264</td>
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<td>50</td>
<td>862</td>
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<td>200</td>
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<td>377</td>
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<td>100</td>
<td>936</td>
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Meanwhile, in the anodic polarization process, two peaks were recorded at about 0.60 and 1.26 V. The peak at 0.60 V represents the de-alloying process of Li\(^+\) ions [48] as described in Eq. (4):

\[
\text{Li}_x\text{Sn} \rightleftharpoons \text{Sn} + x\text{Li}^+ + xe^- (0 \leq x \leq 4.4)
\] (4)

The following peak at 1.26 V could be ascribed to in part reversible reaction of the Eq. (1) [31]. After the first cycle, the peak intensity of CV curve in the 4th cycle becomes lower than that in the 2nd cycle. However, the peak intensity of the CV curve in the 150th is still very high, and the integral area is also very big, revealing the good cycling stability. Note that a peak at 1.32 V at the 150th CV curve of SnO2/graphene nanocomposite is observed, which indicates that the Eq. (1) is at least partially reversible in the SnO2/graphene nanocomposite [5,17,27]. This result is in good agreement with that of galvanostatically discharged and charged tests. For the bare SnO2 nanoparticles in Fig. 6b, there are still characteristic peaks at 0.91 and 0.10 V, corresponding to SEI layer formation and the alloying process, which also correspond to the reaction of lithium with SnO2 during the first discharge process [5,9]. Although the CV curves of the bare SnO2 nanoparticles in the 4th and 2nd cycles almost overlap, the peak intensity and integral area of the CV curve in the 100th cycle are obviously decreased, implying poor capacity retention. This result matches well with that of the discharge/charge tests.

To further confirm that the conversion reaction of SnO\(_2\) in the SnO\(_2\)/graphene nanocomposite is partially reversible, the XRD patterns of electrode sheets before and after being cycled are shown in Fig. 7. As shown in Fig. 7c, the diffraction peaks of fully charged bare SnO\(_2\) nanoparticles electrode sheets after 100 cycles, which are indicated by an asterisk, are almost the same as those observed before cycling. This result is in good agreement with that of the galvanostatically discharged and charged tests.

Fig. 6. Cyclic voltamograms (CV) of (a) SnO\(_2\)/graphene nanocomposite and (b) SnO\(_2\) nanoparticles at a scanning rate of 0.2 mV s\(^{-1}\).

Fig. 7. XRD patterns of electrode sheets for (a) SnO\(_2\) nanoparticles before being cycled, (b) SnO\(_2\)/graphene nanocomposite before being cycled, (c) SnO\(_2\) nanoparticles after 100 cycles, and (d) SnO\(_2\)/graphene nanocomposite after 150 cycles.
cycles match well with characteristic peaks of Sn (JCPDS file card no. 04-0673), indicating that reaction mechanism of bare SnO2 nanoparticles with Li is the usually reported alloying mechanism. In comparison, a diffraction peak at around 30.05° was indexed to Sn (JCPDS file card no. 04-0673), indicating that reaction mechanism of bare SnO2 nanoparticles during discharge/charge cycling process, resulting in high rate capability. Even at a high current density of 1000 mA g⁻¹, the as-prepared SnO2/graphene nanocomposite exhibits an unprecedented high reversible specific capacity of 1304 mAh g⁻¹ in the 150th cycle. This nanocomposite also exhibits excellent rate capability. Even at a high current density of 1000 mA g⁻¹, the reversible capacity is still as high as 748 mAh g⁻¹, more than twice the theoretical reversible capacity of graphite. The excellent electrochemical performances can be attributed to the following reasons: (1) the conversion reaction of SnO2 in the SnO2/graphene nanocomposite, SnO2 + 4Li⁺ + 4e⁻ → 2Li2O + Sn, is partially reversible.

4. Conclusions

In summary, SnO2/graphene nanocomposite was prepared via a facile gas–liquid interfacial synthesis approach successfully. The preparation approach of SnO2/graphene nanocomposite reported here is facile and inexpensive. We believe that the synthesis technique is promising for scaling up and technical implementation.

References