Boron oxide–tin oxide/graphene composite as anode materials for lithium ion batteries

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ABSTRACT

B_2O_3–SnO_2/graphene (B_2O_3–SnO_2/G) composite is fabricated via a chemical heat solvent method and utilized as anode material for lithium ion batteries. The added B_2O_3 dramatically improves the electrochemical performance of lithium ion batteries compared to the SnO_2/G composite. The B_2O_3–SnO_2/G composites as anode show an outstanding discharge capacity of 1404.9 mAh g^{-1} at 500 mA g^{-1} after 200 cycles and an excellent rate capacity, which apparently outperforms the previously reported SnO_2-based anode material. These improved electrochemical performance characteristics are due to the B_2O_3 played a buffering role, which are easily beneficial for accommodating the volume change during the lithium ions insertion/extraction processes. Furthermore, boron atoms can accept electrons for its electron-deficient nature and boron ions could release electrons, which lead to electrons' increased density and conductivity are increased. The results indicate that the B_2O_3–SnO_2/G composite is a promising anode material for lithium ion batteries.

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1. Introduction

Lithium ion batteries (LIBs), as the most prominent energy storage system, have attracted worldwide attention due to their advantages such as high working voltage, high energy density, excellent cycle life, no memory effect, convenience, and environment-friendly [1–3]. However, a considerable lower theoretical capacity of graphite (372 mAh g^{-1}) as an anode material has limited the development of LIBs and cannot meet the increasing energy storage demand. Therefore, it is urgent to explore new selectable anode materials to promote the electrochemical performances.

In recent years, many efforts have been made in researching hybrid structural nanomaterials as lithium ion anode materials. These anode materials have been studied contain core-shell structured NiO@SiO$_2$ [4], carbon doped materials [5] and graphene composites and so on. For the material of NiO@SiO$_2$, the capacity is only 700 mAh g^{-1} after 150 cycles, which is far less than the demand for energy in modern society. For MoO$_2$/N-doped carbon heteronanowires, although the cycle life is up to 500 cycles, the capacity is too low that is only 800 mAh g^{-1}. With the development of science materials, graphene is found to be a material

with excellent performance. Graphene, as a two-dimensional sheet of sp^2-bonded carbon, had been widely investigated as an anode material for application in LIBs and exhibited increased capacity, including other allotropic substances such as one-dimensional nanotubes and zero-dimensional fullerenes. However, LIBs capacity improvement of these carbon materials is limited [6,7]. Besides, metal oxides or sulfides usually have a higher specific capacity, but the structure is not stable. If they are combined with graphene, it is very possible to produce more excellent materials. And there are already many graphene composites including Fe$_3$O$_4$/graphene, CoO/graphene, V$_2$O$_3$/graphene, Cu$_2$O/graphene, TiO$_2$/graphene, SnO$_2$/graphene, MoS$_2$–RGO, etc [8–15]. Among the above composite materials, tin dioxide (SnO$_2$) has been considered to be an excellent candidate as anode material for LIBs for its high theoretical capacity of 782 mAh g^{-1}, which is much higher than that of graphite [16]. Importantly, SnO$_2$ possesses several advantages as a LIB anode material, such as low cost, safety, environmental benignity, high abundance, and lower charge–discharge plateau, which are not contained in other metal oxide anodes [17,18]. SnO$_2$/graphene (SnO$_2$/G) anode composites utilize both advantages of graphene and SnO$_2$ to significantly improve the electrochemical performance. However, SnO$_2$ anodes suffer the disadvantage that they exhibit a large volume change of about 300% during the lithiation and delithiation processes, which results in severe election materials pulverization and rapid capacity fading during the

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charge/discharge processes [16]. In addition, there is a poor initial Coulombic efficiency during the first cycle, which contributes to Li_2O formation in the irreversible conversion reaction.

In order to offset the defects of SnO_2, many efforts by doping with other substances have been made to increase life cycle. For example, Xia et al. [19] reported a novel core-shell nanocomposite structure of SnO_2–B_2O_3 produced by a modified molten-salt decomposition method. The electrochemical performances of the prepared materials were greatly improved because B_2O_3 limited the SnO_2 volume change. Liu and his co-workers prepared composite anode materials of hollow SnO_2 microspheres covered by B_2O_3 layers, which exhibited improved cycling performance and rate capacity compared to that of pristine hollow SnO_2 [20]. There are also many other ternary nanocomposites such as SnO_2–PANI–rGO, graphene–SnO_2–carbon and SnO_2·TiO2/graphene [21–23]. Among those methods, doping boron is deemed as a promising one, for its excellent improving characteristics and simple operation.

In this paper, a one-step chemical heat solvent method was developed to obtain a nanocomposite of B_2O_3–SnO_2/graphene (B_2O_3–SnO_2/G). B_2O_3, distributed on the SnO_2/G surface, resulted in the B_2O_3–SnO_2/G ternary nanocomposites formation. On one hand, as anode for lithium ion batteries, B_2O_3 works as a mechanical support in B_2O_3–SnO_2/G to buffer the volume change of SnO_2 during the lithium ions insertion/extraction processes as well as protects the SnO_2 crystal from agglomeration. On the other hand, electrons density and conductivity was increased owing to that boron atoms can accept electrons for its electron-deficient nature, and boron ions could release electrons, thus facilitate the insertion/de-insertion of Li in SnO_2. Notably, B_2O_3 made a great contribution to the enhanced electrochemical performance, and the specific improvement was systematically researched.

2. Experimental

2.1. Sample preparation

The ternary nanocomposites B_2O_3–SnO_2/G were synthesized using a one-step chemical heat solvent method. All raw chemical materials were of analytical grade and utilized without any further purification. Graphene oxide (GO) was prepared from natural graphite powder by a modified Hummers' method reported previously [24,25].

In a typical synthesis, 100 mg of dried GO was dispersed in 100 mL of deionized water. The obtained solution was ultrasonicated for 30 min in the ultrasonic cell crusher to separate the graphene oxide layer from the layer, followed by centrifugation of 5 min to remove impurities and produce the supernatant for the next reaction. In addition, 5 mL of concentrated hydrochloric acid was added dropwise onto 100 mg of $SnCl_2 \cdot 2H_2O$ to dissolve the $SnCl_2$, followed by adding 100 mL of deionized water to make a transparent solution. Then, the transparent solution and the above supernatant were mixed and stirred for 10 min. After that, 50 mg of boric acid was added to the suspension and stirred for another 20 min to get a homogeneous suspension. The final suspension was transferred to a three distillation flask of 250 mL. Then, the suspension was refluxed and stirred at 85 °C for 12 h. After the reaction was completed and the reaction mixture cooling down to room temperature, the precipitate were rinsed with deionized water until the pH value of the system reached nearly to 7 and dried at 55 °C for 24 h. Then the product was sintered in a tubular furnace at 500 °C with a flow of argon for 1 h. Finally, the B_2O_3–SnO_2/G composite was obtained after annealing. Another sample SnO_2/G was also produced in accordance with the above steps in the absence of boric acid.

2.2. Sample characterization

The as-prepared material of B_2O_3–SnO_2/G was investigated by X-ray diffraction (XRD, D/MAX-2500), Raman spectroscopy (RS, In Via Rflex), thermogravimetric analysis (TGA, STA 409 PC Luxx®), transmission electron microscopy (TEM, Tecnai G2 F20), and Brunauer–Emmett–Teller (BET) specific surface (NOVA2200e; Quantachrome).

2.3. Electrochemical measurements

The electrochemical performances of the as-prepared material were investigated as the anode in the coin-type cell (CR 2032). The as-prepared material, lithium tablets, and 1 M LiPF6 in a mixture of ethylene carbonate and dimethyl carbonate in a volume ratio of 1:1 were used as the working electrode, counter electrode, and electrolyte, respectively, and assembled in an argon-filled glove box. The cells were galvanostatically charged/discharged in the voltage range of 0.01 to 3.0 V versus Li/Li$^+$ by a battery testing system (LAND CT-2001A). Cycle voltammetry (CV) curves were carried out using a Zahner Ennium electrochemical workstation. Electrochemical impedance spectra of the electrodes were recorded from 100 kHz to 100 mHz at 5 mV of the amplitude of the perturbation.

3. Results and discussion

Fig. 1a shows the XRD patterns of the as-prepared SnO_2/G and B_2O_3–SnO_2/G composites. For the SnO_2/G sample, the main peaks for SnO_2 can be clearly observed according to the tetragonal rutile structure of SnO_2 (JCPDS No. 41-1445). More obvious diffraction peaks including $2\theta = 26.5°$, 33.8°, 37.8°, 51.8°, 54.6°, 57.8°, 61.7°, 65.1°, 71.3° and 78.7° can be assigned to the (110), (101), (200), (211), (220), (002), (310), (112), (202), and (321) planes of SnO_2 phase. There are also another two wide diffraction peaks at 22.5° and 41.5° for the B_2O_3–SnO_2/G structure, which are attributed to the presence of single crystalline structure B_2O_3 [20]. The wider peak width of B_2O_3 is due to the particles are relatively small. Moreover, no other redundant peaks are observed, suggesting the reduction of graphene oxide (GO) and no other crystalline borne phase formed in the reaction.

Boric acid can be divided into H_2O and B_2O_3 at 500 °C under a heated condition, so B_2O_3 can adhere to the SnO_2 and graphene. Furthermore, the crystal SnO_2 can be more solid in the surface of graphene. As is known to all, boron atoms can accept electrons for its electron-deficient nature and boron ions can release electrons, which increases the electrons' density and conductivity. Thus, B_2O_3 can be an important additive for the processes of charge and discharge. So, the B_2O_3–SnO_2/G is expected to be a material that performs excellent electrochemical properties.

Fig. 1b shows the Raman spectroscopy of B_2O_3–SnO_2/G and SnO_2/G. For the two kinds of composites, the peaks around 1588 and 1344 cm^{-1} correspond to the G and D bands of graphene, respectively. The G band results from the in-plane vibration of sp^{2}C bonded pairs, while the D band originates from the defect sites or disordered carbon. Also, the peaks at 2675 and 2930 cm^{-1} are assigned to the high reduction of GO and the formation of graphene. In addition, the intensity ratio of D to G band (I_D/I_G) is used for estimating the disorder degree of graphene [26]. The D/G intensity ratio of B_2O_3–SnO_2/G sample ($I_D/I_G = 1.18$) is larger than that of the SnO_2/G nanocomposite ($I_D/I_G = 0.97$), suggesting increased structural disorder of graphene, and simultaneously that the SnO_2 and B_2O_3 nanocomposites have been loaded in the graphene sheets.

The TG curves in Fig. 1c can clearly quantify the concentration of SnO_2 and B_2O_3. The two samples were heated from room temperature to 800 °C at a rate of 5 °C min^{-1}. For both nanocomposites, there