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Antimony (IV) Oxide Nanorods/Reduced Graphene Oxide as the Anode Material of Sodium-ion Batteries with Excellent Electrochemical Performance

Gui-Zhi Wang, Jian-Min Feng*, Lei Dong, Xi-Fei Li, De-Jun Li*

Energy and Materials Engineering Center, Institute of Physics and Materials Science, Tianjin Normal University, Extension of Bin Shui West Road 393, Xi Qing District, Tianjin 300387, PR China

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ABSTRACT

Sodium-ion batteries (SIBs) have attracted lots of significant interests, arising from in regard to the development of developing a low-cost energy storage system for renewable energy. Antimony-based materials with that have high theoretical storage capacities of Na^+ have become one of the most focused SIB anode materials. Among of which, Sb_2O_4 has a higher and thus superior Na^+ storage capacity of 1227 $mAh\,g^{-1}$ compared to other antimony-based materials. In this work, one simple solvothermal process has been developed to prepare Sb_2O_4/reduced graphene oxide (Sb_2O_4/RGO) composites with a nanostructure of Sb_2O_4 nanorods anchored on RGO. Sb_2O_4/RGO shows an obviously enhanced electrochemical performance with an initial Na^+ storage capacity of $842 \pm 5\,mAh\,g^{-1}$, a rechargeable capacity of $551 \pm 5\,mAh\,g^{-1}$ at $50\,mA\,g^{-1}$ after 100 cycles and an excellent rate performance of $401 \pm 5\,mAh\,g^{-1}$ at $1\,A\,g^{-1}$.

1. Introduction

The sodium-ion battery (SIB) has attracted lots of significant interests driven by the increasing demand for renewable energy storage systems [1–4]. The energy storage mechanism of the SIB is the same as that of the lithium-ion battery (LIB), both of which depend on an ion rocking-chair process between the anode and cathode [5–10]. However, Na^+ has a larger ionic size than lithium, which will lead to an intercalation/deintercalation difficulty [11–13] and a larger volume change [14,15]. It means that well-developed LIB electrode materials can not be used in a SIB directly [14]. To bridge this gap, the development of electrode materials for SIBs has become a hot topic [16,17]. Inspired by LIB development, different types of electrode materials have been explored for SIBs, including carbon-based materials [18], such as hard carbon [19], carbon nanowires [20], carbon nanofibers [21], hollow carbon [22] and carbon spheres [23], as well as titanium-based compounds [24], such as sodium titanate [25] and titanium oxide [18], alloys of tin/tin oxide [20,26], antimony/antimony oxide [27,28], phosphorus [29,30], organic compounds [31], among others.

Among of these, antimony-based materials have attracted more interests due to their stable Na^+ anode storage reaction and high Na^+ storage capability ability [32,33]. Like a high capacity LIB anode, the large volume change resulting from the process of amounts of Na^+ intercalation/deintercalation is still an obstacle to the development of high-performance antimony-based SIB anode materials [34,35]. To address this problem, a compositing strategy has been adopted and proven to be effective [36,37]. Nanocomposites of Sb/carbon fibers [38], Sb/carbon black [22], Sb/porous carbon [19], Sb/carbon microspheres [23], Sb/carbon/graphene [1], Sb/reduced graphene oxide (RGO) [39] and others have been developed and have shown enhanced performances. In addition, some non-crystallized antimony-based materials have also been fabricated for SIB anodes, including Sb_2O_3/Sb nanoparticles prepared by microwave plasma irradiation [28], Sb_2O_4 thin films prepared by a magnetron sputtering method [40], and so on. Antimony-based SIB anode materials strongly depend on their composite phase and microstructures [41]. Optimized exploration of the composite phase and antimony-based material morphology is an effective means of further developing high-performance antimony-based SIB anodes.

The carbon composite phase could not only buffer the volume change, but also enhance the electrode's electrical conductivity [42,43]. According to the above analysis, a combining strategy of combining nanocrystallization and compositing should be helpful

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* Corresponding authors.
E-mail addresses: fjmtjun@gmail.com (J.-M. Feng), dli1961@163.com (D.-J. Li).

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for the development of high-performance SIB anodes. In an early study, Zhou et al. [9] applied Sb_2O_4 for use in LIBs. They used Sb_2O_3 and graphene oxide to synthesize Sb_2O_4/rGO by a simple solvothermal method. The composite had a steady structure of Sb_2O_4 nanoparticles that was uniformly anchored on rGO sheets. When applied as the LIB anode, it delivered much a better cyclability of 798 mAh g^{-1} at a current density of 100 mA g^{-1} after 200 cycles. Based on the superb performance of LIBs, we could foresee that Sb_2O_4 could meet the requirements of SIBs. Herein, Sb_2O_4 is explored for use in SIB anodes, and reduced graphene oxide is used as the composite phase [37,44]. Sb_2O_4 has a higher theoretical capacity of 1227 mAh g^{-1}, which is almost twice as that of pure Sb metal (660 mAh g^{-1}) [45–47]. Moreover, graphene has shown beneficial properties for the composite [33,48,49]. The combination of Sb_2O_4 and graphene should be feasible for fabricating SIB anodes with enhanced electrochemical performance.

A two-step controllable process consisting of nanocrystallization and compositing was developed to prepare Sb_2O_4/RGO composites. First, nanocrystallized Sb_2O_4 exhibiting nanorod morphology was prepared by a hydrothermal process. The nanorod morphology should contribute to the enhancement of the electrochemical Na^+ storage manifestation and should also avoid the large volume change during the long-repeating cycling process [50]. Then, Sb_2O_4/RGO with a hybrid nanostructure of Sb_2O_4 nanorods anchored on RGO was prepared by a simple liquid compositing process. Electrochemical tests showed that there was an impressive composite synergistic effect of the Sb_2O_4 nanorods anchored on the surface of RGO. The Sb_2O_4/RGO anode had an excellent electrochemical performance, showing a stable Na^+ storage capacity of 551 ± 5 mAh g^{-1} after 100 cycles and a rate capability of 401 ± 5 mAh g^{-1} at 1 A g^{-1}. In comparison, the Na^+ storage capacity of bare Sb_2O_4 was under 100 mAh g^{-1} after 100 cycles.

2. Experimental

2.1. Synthesis of Sb_2O_4/RGO

GO was first synthesized by a modified Hummers' method [51]. The Sb_2O_4/RGO nanocomposite was synthesized by a simple solvothermal method. First, 0.004 mol of $SbCl_3$ and 0.02 mol of I_2 were dissolved in 40 mL of deionized water. After ultrasonic processing for nearly 20 minutes, the mixing solution was placed in an autoclave and heated to 180 °C for 20 h. Sb_2O_4 nanorods were prepared by filtration, washed with distilled water several times and dry processed at 80 °C overnight. Second, 50 mg of GO was added into 40 mL of deionized water and then ultrasonically treated for 0.5 h. As-prepared Sb_2O_4 (0, 50, 100 and 200 mg) was mixed with the GO solution, separately (labelled as RGO, Sb_2O_4/RGO-I, Sb_2O_4/RGO-II and Sb_2O_4/RGO-III). Then the-obtained solution was placed in an autoclave and heated to 180 °C for 24 h. The final products were collected by filtration, washed with deionized water and dried at 80 °C for 12 h.

2.2. Materials characterizations

The phase of the final products was characterized by X-ray diffraction (XRD, DX-2700), with Cu/Ka radiation in the range from 10° to 80° and Raman spectroscopy (Raman, LabRAM HR800) from 100–2000 cm^{-1}. Energy dispersive electron microscopy (EDS) measurements were recorded under 20 KV. The morphology of the products was checked by using scanning electron microscopy (SEM, SU8010, Hitachi) and transmission electron microscopy (TEM, JEOL JEM-3000F). Thermogravimetric analysis (TGA, METTLER-TOLEDO TGA/DSC1) of the Sb_2O_4/RGO composites was also conducted from room temperature to 1000 °C at a heating rate of 10 °C per minute in 50 sccm of flowing air.

2.3. Electrochemical Measurements

The electrochemical properties of the Sb_2O_4/RGO composites were evaluated by assembling 2032 coin cells in a glove box filled with argon (oxygen and moisture < 0.1 ppm). Sodium metal foil was used as the counter electrode, and 1 mol/L $NaClO_4$ was dissolved in ethylene carbonate and dimethyl carbonate (3:7 by volume) with 5% fluoroethylene carbonate as the electrolyte. The working electrode contained 75 wt.% active materials, 15 wt.% carbon black and 10 wt.% polyvinylidene fluoride (PVDF); N - methyl pyrrolidone (NMP) was then used to form a slurry. The electrode was prepared by casting the slurry onto copper foil and drying at 80 °C overnight under vacuum. Next, electrode slices were cut at 12-mm diameter per disks. The weights of the active materials used from both the bare and composite samples were 1.0 mg cm^{-2} for every disk. The galvanostatic charge/discharge test was conducted on a LAND cycle (LANHE CT2001A) between 0.01 to 3 V vs Na^+/Na at room temperature. Cyclic Voltammogram (CV) and Electrochemical Impedance Spectroscopy (EIS) measurements were performed via a Princeton Applied Research VersaSTAT4. The CV measurement was recorded at a scan rate of 0.1 mV s^{-1} in the range of 0.01–3.0 V vs Na^+/Na and the EIS was conducted in the range from 100 kHz to 0.01 Hz with an amplitude of 5 mV.

3. Results and discussion

Sb_2O_4/RGO nanocomposites were synthesized by a simple solvothermal process from $SbCl_3$, I_2 and GO in an aqueous solution. The XRD patterns of Sb_2O_4/RGO-I, Sb_2O_4/RGO-II, and Sb_2O_4/RGO-III, which had patterns of bare Sb_2O_4, RGO and GO within the theta range between 10° and 80° for comparison, are shown in Fig. 1a. The Sb_2O_4 peaks (PDF#78-2066) can be clearly observed in the XRD patterns of the Sb_2O_4/RGO composites and the bare Sb_2O_4. The characteristic diffraction peaks were at approximately 25.5, 29.0, 33.2, 37.0, 45.6, 48.7, 53.4 and 62.6 degrees, belonging to the (011), (100), (112), (120), (024), (310), (026) and (230) reflections of Sb_2O_4, respectively. These characteristic diffraction peaks indicated that the Sb_2O_4 crystalline phase had been obtained. One wide peak at 2theta = 25° of RGO, overlaps with reflection of Sb_2O_4 in the Sb_2O_4/RGO composites. In addition, a sharp and intense peak for GO was observed at 2theta = 10.4°, which disappeared on the pattern of the Sb_2O_4/RGO composites. The disappearance of the peak at 2theta = 10.4° showed that GO had been reduced during the Sb_2O_4/RGO solvothermal preparation process.

Laser Raman scattering is a sensitive and effective method to analyze graphite- and graphene-based materials [21,27]. In Fig. 1b, two major D and G bands appear in the Raman spectra of Sb_2O_4/RGO-I, Sb_2O_4/RGO-II, Sb_2O_4/RGO-III, RGO and GO. The D and G bands were at approximately 1440 cm^{-1} and 1591 cm^{-1}, respectively. The D band represents the defective graphitic structure of sp^3-bond carbon atoms, while the G band corresponds to the in-place stretching motion of the sp^2-bond carbon atoms. The relative intensity ratio (I_D/I_G) manifested the degree of disorder and defects. The corresponding I_D/I_G values of Sb_2O_4/RGO-I, Sb_2O_4/RGO-II, Sb_2O_4/RGO-III, RGO and GO were 1.12, 1.18, 1.07, 1.01 and 0.99, respectively. We found that the I_D/I_G values of these samples was smaller than Zhou's [9] results. It, possibly because using ethylene glycol and intense magnetic stirring for over 3.5 h to form homogeneous suspensions and somewhat promoted the degree of reduction of the GO and composite. Moreover, disparate systems lead to slight changes. The lowest I_D/I_G value of GO illustrated the highest level of oxidation and regularity. After the solvothermal reaction, the I_D/I_G value increased. Within a certain range,