Electrochimica Acta 214 (2016) 1–10

Contents lists available at ScienceDirect

Electrochimica Acta

journal homepage: www.elsevier.com/locate/electacta

Hollow Amorphous $MnSnO_3$ Nanohybrid with Nitrogen-Doped Graphene for High-Performance Lithium Storage

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ARTICLE INFO

Article history:
Received 21 June 2016
Received in revised form 20 July 2016
Accepted 6 August 2016
Available online 6 August 2016

Keywords:
amorphous
hollow
$MnSnO_3$
nitrogen-doped graphene
long-term life

ABSTRACT

Tin-based metal oxides usually suffer from severe capacity fading resulting from aggregation and considerable volume variation during the charge/discharge process in lithium ion batteries. In this work, a novel nanocomposite (MTO/N-RGO) of hollow amorphous $MnSnO_3$ (MTO) nanoparticles and nitrogen-doped reduced graphene oxide (N-RGO) has been designed and synthesized by a two-step method. Firstly, the nitrogen-doped graphene nanocomposite (MTO/N-RGO-P) with $MnSn(OH)_6$ crystal nanoparticles was synthesized by a facile solvothermal method. Subsequently, the MTO/N-RGO nanocomposite was obtained through the post heat treatment of MTO/N-RGO-P. The designed heterostructure and well-combination of the hollow amorphous MTO and N-RGO matrix can accelerate the ionic and electronic transport, and simultaneously accommodate the aggregation and volume variation of MTO nanoparticles during the lithiation–delithiation cycles. The as-prepared hybrid of MTO and N-RGO (MTO/N-RGO) exhibits a high reversible capacity of 707 mAh g^{-1} after 110 cycles at 200 mA g^{-1}, superior rate capability, and long-term cyclic life with high capacity of 610 mAh g^{-1} over 1000 cycles at 400 mA g^{-1}. Superior capacity retention of 97.3% over 1000 cycles was obtained. This work opens new opportunities to fabricate the high-performance electrode materials with heterostructure for lithium storage systems, especially for novel multi-metal oxide based nanocomposites with high cycling stability.

1. Introduction

In recent two decades, lithium ion batteries (LIBs) have been widely applied as the power source of various portable electronic devices and electric vehicles because of their high energy density, eco-friendly and no memory effect [1–4]. Although graphite is very popular in the current LIBs field as a commercial anode material, its low theoretical specific capacity of 372 mAh g^{-1} cannot meet the increasing demand of rapidly developing LIBs market in modern society [5]. Therefore, it is an urgent task to develop new electrode materials with higher energy density, power density, capacity retentions and excellent cycle life. On this point, large numbers of scientists have devoted efforts on the development of novel electrode materials with the enhanced performance [1,2,4,6–8].

Tin-based oxides such as SnO_2 [9], Zn_2SnO_4 [10], Mn_3O_4/Zn_2SnO_4 [11], and $BSnO_3$ (B = Ca, Zn, and Co) [12–14] are particularly promising alternatives to traditional graphite anode in the next-generation LIBs, owing to their abundance and high theoretical capacities [15]. Unfortunately, this kind of materials experiences considerable volume variation, which results from alloying-dealloying and/or conversion reaction during the charge–discharge process, leading to electrode pulverization, capacity deteriorating and poor cyclic life [9,14]. To overcome these intractable problems, two general strategies have been developed. One approach is the self-adaption of the tin-based oxides materials with elaborately designed structures, such as porous structure, nanotube, nanosheets, and nanoboxes [9,13,14,16]. It is expected that the nanostructures can shorten the transport path of the lithium ions and electrons, contributing to good conductivity and charge/discharge rate. Additionally, the void space in the special structures (porous structure, nanotube and nanoboxes) can accommodate the volume expansion during lithium ion insertion/extraction process. However, there are still some disadvantages including the aggregation of nanomaterials and the collapse of the designed architectures after a long cycling, resulting in poor performance. The other strategy is to introduce carbonaceous materials as the buffer matrices to absorb the volume variation, which can strengthen the structural stability and further enhance the cycle performance [10,12,14,17–19]. Although several studies about tin-based multi-metal oxides showed excellent lithium

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http://dx.doi.org/10.1016/j.electacta.2016.08.022
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storage property with high specfic capacity, their performances are far away from satisfaction, especially for the long-term cyclic life [10–13].

Graphene, a novel 2D carbon material, has been a promising matrix for energy storage and conversion, owing to its large surface area, superior electrical conductivity and mechanical robustness [20–22]. Furthermore, the conductivity and electrochemical property of graphene can be further enhanced by doping nitrogen [23,24]. In addition, the nitrogen atoms in the graphene can not only provide more active adsorption sites for Li^+ but also anchor nanoparticles to alleviate their aggregation, resulting in superior cyclic stability [23,25]. In these regards, many researchers have designed nitrogen-doped graphene composites to obtain the improved lithium storage property. For instance, Sun's group reported a MoS_2/nitrogen-doped graphene composite with a high capacity of 1285.3 mAh g^{-1} compared to 413.8 mAh g^{-1} of pure MoS_2 after 50 cycles [26]. The 3D nitrogen-doped graphene/Fe_3O_4 composite exhibited superior cycling performance with a capacity of 1130 mAh g^{-1} after 200 cycles [27].

Recent studies indicated that metal oxides with the amorphous structure have an advantage over the crystal ones in accommodating the volume strain, resulting from the inherent isotropic nature and the high mobility of atom/ion in the amorphous structures [14,28,29]. Consequently, the amorphous structure of metal oxides can enhance the corresponding electrochemical performance.

Herein, we fabricated a novel hybrid (MTO/N-RGO) with the hollow amorphous $MnSnO_3$ (MTO) nanoparticles decorating on the nitrogen-doped reduced graphene oxide (N-RGO) by a facile solvothermal method and a post heat treatment. The nanocomposite MTO/N-RGO as an anode material of lithium ion batteries can integrate the above three merits. The hollow nanostructure of MTO may facilitate the lithium ion transportation and enhance the rate performance in the nanocomposite. Moreover, the amorphous hollow structure of MTO and the outstanding properties of graphene matrix can further accelerate electron transport and alleviate the aggregation and volume expansion of metal oxide nanoparticles, leading to excellent cycling stability, high reversible capacity and good rate performance of the hybrid of MTO/N-RGO. As a result, the elaborately designed nanostructure and well-combination of both components can be responsible for the greatly improved lithium storage performance. It shows a high reversible capacity and rate capacity, as well as an ultra-long lifetime with high capacity of 610 mAh g^{-1} over 1000 cycles at 400 mA g^{-1}. Moreover, due to the synergistic effect between MTO and N-RGO, the MTO/N-RGO nanocomposite possesses superior lithium storage performance than that of individual MTO and N-RGO. The current work provides new opportunities to design and fabricate the high-performance electrode materials with heterostructure for lithium storage system, especially for long-term cycling lifetime and high reversible capacity of tin-based multi-metal oxide hybrids.

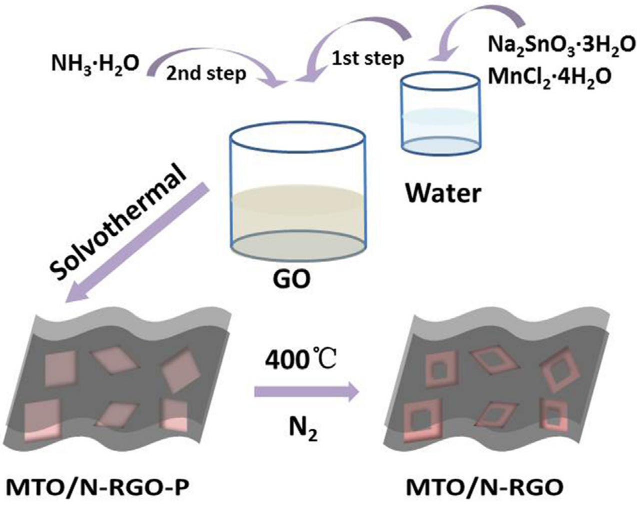
2. Experimental Section

2.1. Synthesis

All the chemicals were analytical grade and used as received without further purification. Graphene oxide (GO) was synthesized from natural graphite flakes as previous reports [30]. The 60 mL GO (2.0 mg mL^{-1}) water–ethanol (1:1 in v/v) dispersion was obtained with the aid of ultrasonication. Meanwhile 0.45 mmol $Na_2SnO_3 \cdot 3H_2O$ and 0.45 mmol $MnCl_2 \cdot 4H_2O$ were simultaneously dissolved into 10 mL of water under stirring. Subsequently, the resulting suspension solution was dropwise added into the above GO dispersion. The mixture was stirred for 1 h at room temperature. Then, 10 mL of concentrated aqueous ammonia (25–28 wt%) was added dropwise into the mixture and kept at room temperature under stirring for 0.5 h. After that, the as-obtained suspension was transferred into a Teflon-lined stainless autoclave (100 mL), sealed and maintained at 180 °C for 24 h. After cooling to room temperature, the product was collected by centrifugation and rinsed with ethanol and deionized water several times, and then freeze-dried overnight. Finally, the as-prepared sample was thermally treated at 400 °C with a heating rate of 2 °C min^{-1} under N_2 flow for 200 min, and the obtained product was named as MTO/N-RGO nanocomposite. Its schematic illustration is shown in Scheme 1. The N-RGO was synthesized by the same method of MTO/N-RGO nanocomposite, just without the addition of the metal salts. The MTO was synthesized as follows: the suspension of $Na_2SnO_3 \cdot 3H_2O$ and $MnCl_2 \cdot 4H_2O$ with the same amount of 0.45 mmol in 10 mL water was collected by centrifugation and rinsed with de-ionized water several times, and then dried at 55 °C in an oven overnight. At last, the as-prepared sample was thermally treated at 400 °C with a heating rate of 2 °C min^{-1} under N_2 flow for 200 min.

2.2. Characterization

The crystal structures were studied by X-ray diffraction (XRD) (Bruker D8 Advance diffractometer) with a scan rate of 2° min^{-1}. Fourier transform infrared (FT-IR) spectra of the synthesized samples were recorded on a MB154S-FTIR spectrometer by pressed KBr pellets. Thermogravimetric analysis (TGA) was conducted on TGA/SDTA851e under air or N_2 flow with a heat rate of 10 °C min^{-1}. The morphology of samples was investigated by the transmission electron microscopy (TEM, JEOL JEM-2100). The high angle annular dark field scanning transmission electron microscopy (HAADF-STEM) was conducted on a Titan G2 60-300 microscope. Scanning electron microscope with an energy-dispersive X-ray was recorded on FEI Quanta 250F. For the specific surface area determination, the nitrogen adsorption–desorption test was measured at 77 K using an ASAP-2020 system. Raman spectra were collected on a LabRam Aramis (HORIBA JobinYvon) using a 532 nm laser. X-ray photoelectron spectroscopy (XPS) was conducted on a Scanning X-ray Microprobe PHI Quantera II (Ulvac-PHI, INC.) with C60 gun.



Scheme 1. Schematic diagrams illustration of the synthesis of the MTO/N-RGO nanocomposite.