Journal of Alloys and Compounds 604 (2014) 188–195

Contents lists available at ScienceDirect

Journal of Alloys and Compounds

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

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

Peichao Lian [a,*], Jingyi Wang [a], Dandan Cai [b], Guoxue Liu [b], Yingying Wang [a], Haihui Wang [b,*]

[a] *Faculty of Chemical Engineering, Kunming University of Science and Technology, Kunming 650500, China*
[b] *School of Chemistry & Chemical Engineering, South China University of Technology, Guangzhou 510640, China*

ARTICLE INFO

Article history:
Received 13 December 2013
Received in revised form 20 March 2014
Accepted 21 March 2014
Available online 1 April 2014

Keywords:
Graphene sheets
Sn
Carbon shell
Nanocomposite
Lithium-ion batteries

ABSTRACT

Tin is a promising high-capacity anode material for lithium-ion batteries, but it usually suffers from the problem of poor cycling stability due to the large volume change during the charge–discharge process. In this article, porous nano-sized Sn@C/graphene electrode material with three-dimensional carbon network was designed and prepared. 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. The porous structure can provide a void space, which helps to accommodate the volume changes of the Sn nanoparticles during the lithium uptake-release process. The carbon shell can avoid the aggregation of the Sn nanoparticles on the same piece of graphene and detachment of the pulverized Sn particles during the charge–discharge process. The 3D carbon network consisted of graphene sheets and carbon shells can not only play a structural buffering role in minimizing the mechanical stress caused by the volume change of Sn, but also keep the overall electrode highly conductive during the lithium uptake-release process. As a result, the as-prepared Sn@C/graphene nanocomposite as an anode material for lithium-ion batteries exhibited outstanding cyclability. The reversible specific capacity is almost constant from the tenth cycle to the fiftieth cycle, which is about 600 mA h g^{-1}. The strategy presented in this work may be extended to improve the cycle performances of other high-capacity electrode materials with large volume variations during charge–discharge processes.

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 (992 mA h g^{-1}), and environmentally benign nature [11–13]. However, the lithiation and delithiation reactions ($Sn + 4.4Li^+ + 4.4e^- \leftrightarrow Li_{4.4}Sn$) 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

---

* Corresponding authors. Tel.: +86 871 65920242 (P. Lian). Tel.: +86 20 87110131 (H. Wang).

E-mail addresses: lianpeichao@126.com (P. Lian), hhwang@scut.edu.cn (H. Wang).

http://dx.doi.org/10.1016/j.jallcom.2014.03.116

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 SnX_2/graphene oxide (X = O or S) nanocomposites as raw material [12,31–33] (Fig. 1a). The aggregated SnX_2 particles still exist in the raw material (SnX_2/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

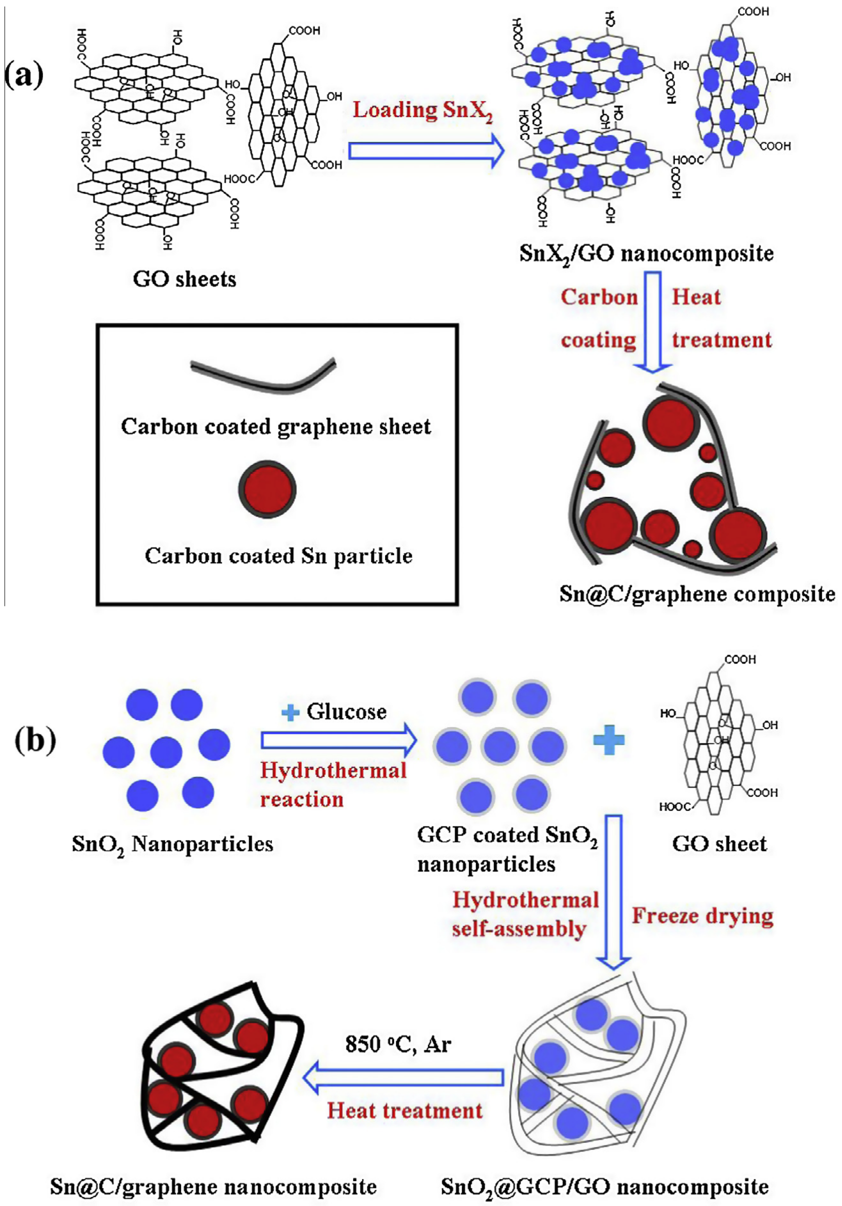

Fig. 1. Schematic illustrations of the synthesis route for (a) the traditional Sn@C/graphene composite, and (b) the porous Sn@C/graphene nanocomposite with 3D carbon network.