



# Sn@SnO<sub>x</sub>/C nanocomposites prepared by oxygen plasma-assisted milling as cyclic durable anodes for lithium ion batteries



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## HIGHLIGHTS

- Sn@SnO<sub>x</sub>/C anodes by oxygen plasma-assisted milling (O<sub>2</sub>-P-milling).
- One-step, environmentally friendly and high-efficiency synthesis.
- Sn nanoparticles coated by amorphous-nanocrystalline SnO<sub>x</sub> embedded in graphite.
- Superior electrochemical performance with high capacity and stable cyclability.

## ARTICLE INFO

### Article history:

Received 19 March 2013

Received in revised form

28 April 2013

Accepted 20 May 2013

Available online 28 May 2013

### Keywords:

Anode  
Lithium ion batteries  
Milling  
Oxygen plasma  
Tin oxides

## ABSTRACT

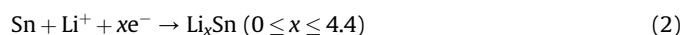
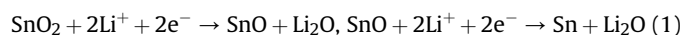
An advanced tin oxide-coated tin in graphite (Sn@SnO<sub>x</sub>/C) nanocomposite is synthesized with a one-step method of dielectric barrier discharge oxygen plasma-assisted milling (O<sub>2</sub>-P-milling). Synergetic effects of rapid plasma heating and impact stress act on the tin/graphite powder during O<sub>2</sub>-P-milling, and SnO<sub>x</sub> (1 ≤ x ≤ 2) is generated *in situ* on the Sn surface from the reaction between Sn and oxygen. The resulting composite possesses a unique microstructure, where Sn nanoparticles coated by an ultrathin amorphous/nanocrystalline SnO<sub>x</sub> layer are homogeneously embedded within a graphite matrix. As lithium ion anodes, the Sn@SnO<sub>x</sub>/C nanocomposites display superior electrochemical performance to Sn–C and Sn–SnO<sub>2</sub>–C nanocomposites milled under argon plasma. The SnO<sub>x</sub>/C nanocomposite obtained after O<sub>2</sub>-P-milling for 25 h that contains a high content of amorphous/nanocrystalline SnO<sub>x</sub> exhibits a high capacity retention of 500 mA h g<sup>-1</sup> at 250 mA g<sup>-1</sup> after 70 cycles, indicating that O<sub>2</sub>-P-milling is a promising method to prepare Sn-based multiphase nanocomposite anode materials.

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## 1. Introduction

Lithium ion batteries are important power sources in portable electronics and electric vehicles. Graphite materials are widely used as anodes in commercial lithium ion batteries because of their stable cycling performance and low cost. However, the limited capacity of graphite (372 mA h g<sup>-1</sup>) cannot meet the ever-growing requirements for high-performance lithium ion batteries. Accordingly, Sn-based materials, are promising anode candidates to replace graphite because Sn can react with Li to form Li<sub>22</sub>Sn<sub>5</sub> alloy, showing a high theoretical capacity (Sn, 992 mA h g<sup>-1</sup>) [1]. However, the large volume changes generated during Sn alloying/dealloying with Li can lead to pulverization of the electrode and rapid capacity decay, which is a major disadvantage of Sn-based

anodes. Tin oxides can also be used as lithium storage materials. The reaction mechanism involves the following processes [2,3]:



The theoretical capacities of SnO and SnO<sub>2</sub> can be as high as 875 mA h g<sup>-1</sup> and 782 mA h g<sup>-1</sup>, respectively. Although their capacities are lower than that of Sn, the Li<sub>2</sub>O formed in reaction (1) can serve as a matrix to accommodate the volume change of the active Sn phase and prevents Sn from aggregating. Therefore, it is obvious to consider the strategy of combining Sn with SnO<sub>x</sub> (1 ≤ x ≤ 2) in an anode to maintain the reversible capacity and improve the cyclability [4–6].

Extensive research has indicated that dispersing an amorphous/nanostructured Sn-based material in a carbon matrix is an effective way to accommodate the large volume change of Sn [7–10].

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Amorphous or nanostructured Sn-based materials tolerate significant expansion instead of cracking and pulverizing like crystalline materials, while carbon matrix prevents aggregation of the Sn-based material and maintains conductive network for the active phases. Therefore, Sn-based carbon composites show enhanced electrochemical performance [11–13]. It has been reported that amorphous/nanostructure Sn–M–C (M = Co, Mn, Fe) alloys were prepared by mechanical attriting, and amorphous Sn–Co–C exhibited good electrochemical property with a capacity of about  $400 \text{ mA h g}^{-1}$  after 100 cycles [14–16]. Composites of hollow or porous Sn/C, SnO/C, SnO<sub>2</sub>/C and Sn/SnO<sub>x</sub>/C have been extensively fabricated by chemical deposition assisted with template synthesis [17–23], hydrothermal method [24,25], electrospinning [26–28] and so forth to improve the cyclic stability. However, these composites possess low tap density because of the insufficient filling, which would reduce the energy density for the application of lithium ion battery. Furthermore, these synthesis processes often include complicated steps (such as template removing, temperature controlling, solution concentration adjusting), and offer limited throughput.

Mechanical alloying (MA) is a simple, effective and eco-friendly method for mass production. In our previous study, we prepared Sn–C nanocomposites on a large scale by dielectric barrier discharge argon plasma-assisted milling (P-milling) [29]. Multi-scale Sn particles embedded in the highly crystalline graphite and the composite exhibited a high capacity of  $400 \text{ mA h g}^{-1}$  for 40 cycles. In this work, we developed a new MA method based on P-milling, namely oxygen plasma-assisted milling (O<sub>2</sub>-P-milling). The synthetic procedure is schematically illustrated in Fig. 1. During O<sub>2</sub>-P-milling, significant synergy between the effects of rapid heating by the plasma and milling impact stress is exerted on the Sn/graphite powders, and amorphous/nanostructured SnO<sub>x</sub> ( $1 \leq x \leq 2$ ) are formed *in situ* due to the reaction of Sn with oxygen. Besides, *in situ* formed SnO<sub>x</sub> particles can serve as a grinding aid to refine and disperse Sn particles. Hence, an Sn@SnO<sub>x</sub>/C composite with an amorphous/nanostructured Sn core coated by a thin, rigid SnO<sub>x</sub> shell embedded in a carbon matrix would be synthesized in one-step by O<sub>2</sub>-P-milling. During charge–discharge cycles, SnO<sub>x</sub> shell would transform into Li<sub>2</sub>O (Eq. (1)) *in situ* on the surface of Sn core, which can restrict swelling of Sn effectively. Therefore, the continual breakdown and reformation of the solid–electrolyte–interface (SEI) is suppressed, and the electric contact between the electrode and matrix is maintained [30,31], which would enable the Sn@SnO<sub>x</sub>/C composite to exhibit high capacity and good cyclability.

## 2. Experimental

### 2.1. Preparation of Sn@SnO<sub>x</sub>/C composites

Details of P-milling are reported in our previous papers [29,32,33]. In this work, oxygen plasma, instead of argon plasma, was generated in the milling cylinder during O<sub>2</sub>-P-milling. The raw materials were graphite with a particle size of 400 mesh and Sn powder with a particle size of 100 mesh. Powder mixtures with an Sn:C ratio of 1:1 (w:w) were treated by O<sub>2</sub>-P-milling for 2, 5, or 10 h, yielding samples denoted as Sn@SnO<sub>x</sub>/C-2 h, Sn@SnO<sub>x</sub>/C-5 h, and Sn@SnO<sub>x</sub>/C-10 h, respectively. The weight ratio of ball to powder was 50:1. Additional oxygen (0.08 mol) was supplied to the system every 2.5 h to compensate for the continuous consumption of oxygen during the milling process. To further study the influence of SnO<sub>x</sub>, the powder mixture was treated by O<sub>2</sub>-P-milling for 25 h with an addition of oxygen (0.08 mol) every 5 h, to form the SnO<sub>x</sub>/C composite. For comparison, an Sn–50 wt%C composite studied previously [29] and a powder mixture with an SnO<sub>2</sub> (particle size:

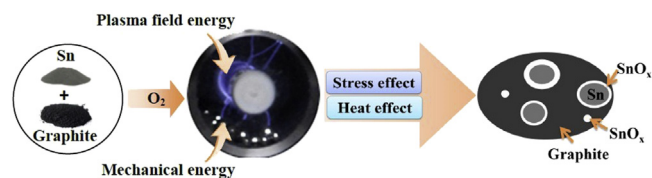


Fig. 1. Synthetic procedure used to prepare Sn@SnO<sub>x</sub>/C composites.

50 nm):Sn:C ratio of 5:45:50 (w:w:w) were treated by P-milling for 10 h; these samples are denoted Sn–C and Sn–SnO<sub>2</sub>–C, respectively.

### 2.2. Microstructure characterization

The microstructures of samples were characterized by X-ray diffraction (XRD, Philips X'pert MPD) with Cu-K<sub>α</sub> radiation, field-emission scanning electron microscopy (FE-SEM, Carl Zeiss Supra 40), and transmission electron microscopy (TEM, JEOL-2100) at 200 kV. The electronic states of Sn in the composite were determined by X-ray photoelectron spectrometry (XPS, AXIS Ultra DLD) using Al-K<sub>α</sub> radiation. The tap density of the powders was tested according to the Chinese standard GB/T 5162-2006/ISO 3953:1993. The contents of Sn, C and O were measured by electron probe X-ray microanalysis (EPMA, EPMA-1600). The degree of graphitization of the carbon after milling was measured by a LabRam Aramis

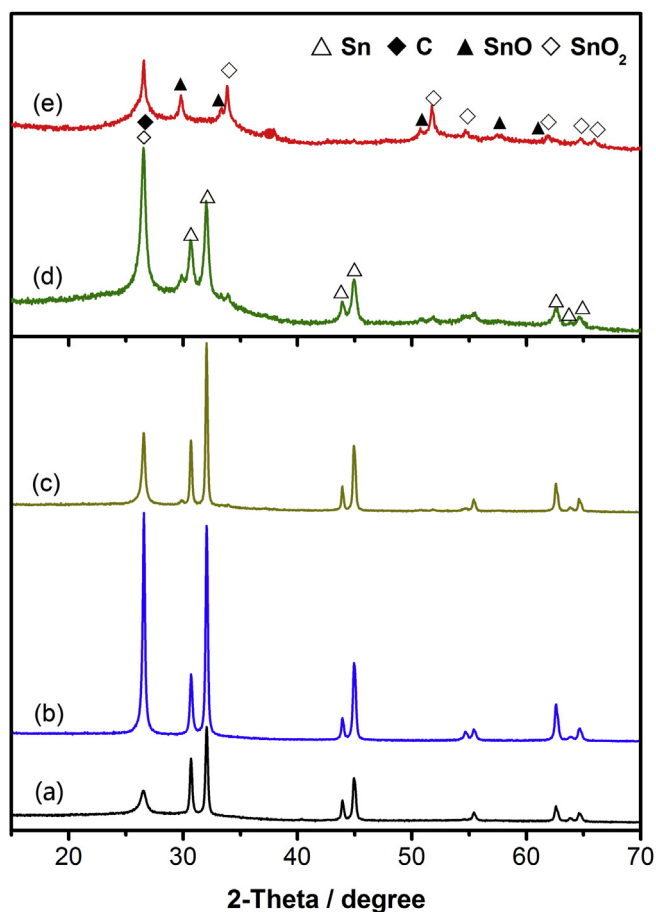


Fig. 2. XRD patterns of (a) Sn–C composite obtained by P-milling, and Sn@SnO<sub>x</sub>/C composites prepared by O<sub>2</sub>-P-milling: (b) Sn@SnO<sub>x</sub>/C-2 h, (c) Sn@SnO<sub>x</sub>/C-5 h, (d) Sn@SnO<sub>x</sub>/C-10 h, and (e) SnO<sub>x</sub>/C.

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