



Full length article

Inhibiting Sn coarsening to enhance the reversibility of conversion reaction in lithiated SnO₂ anodes by application of super-elastic NiTi films



Renzong Hu^{a, b}, Yunpeng Ouyang^a, Dongchang Chen^b, Hui Wang^a, Yu Chen^b,
Min Zhu^{a, *}, Meilin Liu^{b, **}

^a Guangdong Provincial Key Laboratory of Advanced Energy Storage Materials, School of Materials Science and Engineering, South China University of Technology, Guangzhou, 510640, China

^b School of Materials Science and Engineering, Georgia Institute of Technology, Atlanta, GA 30332-0245, USA

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ABSTRACT

The large capacity loss and low initial Coulombic efficiency (ICE) of a conventional SnO₂-based anode for Li ion batteries are originated largely from the limited reversibility of the conversion reaction associated with the anode. Often, the reversibility of the lithiation/delithiation of SnO₂ (with a high ICE value of ~82%) declines with Sn coarsening in the Sn/Li₂O mixture during cycling, leading to gradual capacity decay. Here we demonstrate that the application of super-elastic films of NiTi alloy could accommodate the internal stress and volume change of lithiated nano-SnO₂ layer in a tri-layer NiTi/SnO₂/NiTi sandwich anode, effectively suppressing Sn coarsening. This unique electrode configuration has helped to retain the high reversibility of the SnO₂ layer with reversible capacity more than 800 mAh/g (based on SnO₂) for over 300 cycles, demonstrating stable charge capacities of ~400 mAh/g in the potential ranges of 0.01–1.0 V and 1.0–2.0 V (vs. Li/Li⁺), respectively. *In situ* spectroscopic and *ex situ* diffraction analyses corroborate the highly reversible electrochemical cycling, confirming that the reversibility and cyclability of SnO₂ anodes can be dramatically enhanced by preserving the nanostructure of Sn/Li₂O mixture, which facilitates the reversible conversion reaction.

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1. Introduction

To meet the ever-increasing power demands for emerging applications such as portable electronics and electric vehicles, tremendous efforts have been devoted to design of novel materials and structures for a new generation of lithium ion batteries (LIBs) with dramatically enhanced energy and power densities as well as prolonged operational life. For example, one promising strategy is to replace the commercial graphite anodes of limited specific capacity (372 mAh/g) by other materials of higher Li-storage capacity [1]. Among those alternative anode materials, tin dioxide (SnO₂) has attracted much attention due to its high gravimetric, volumetric capacities, and moderate operating potential in comparison

to graphite and other transition metal oxide anodes [2–6]. It has been accepted that SnO₂ stores Li⁺ ions by a two-step process, a conversion reaction (SnO₂ + Li⁺ → Sn + Li₂O) followed by an alloying reaction (Sn + xLi⁺ → Li_xSn), corresponding to a capacity of 711 and 783 mAh/g, respectively [7–9], offering a theoretical capacity of 1494 mAh/g. However, the realization of the full capacity of SnO₂ in LIBs has been hindered mainly by the following two major issues during cycling. One issue is the severe capacity fading due to disintegration of the electrode structure resulted from large volume change and serious aggregation of Sn particles during the alloying reactions [10–13]. Another issue is the large initial irreversible capacity loss in SnO₂-based anodes due primarily to the poor reversibility of the conversion reaction, as well as other Li-consuming irreversible reactions on new surfaces of the active particles [2,8,14,15].

Significant efforts have been focused on improving structural stability of SnO₂ [6]. Tailoring the nanostructures of SnO₂ [3–5,16,17] and dispersing nano-sized particles of SnO₂ in various types of conductive carbon buffer matrix [18–23] have significantly

* Corresponding author.

** Corresponding author.

E-mail addresses: memzhu@scut.edu.cn (M. Zhu), meilin.liu@mse.gatech.edu (M. Liu).

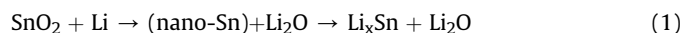
enhanced the cyclability of SnO₂-based nanocomposites. However, very large initial capacity loss and low initial Coulombic efficiency (ICE, defined as the ratio of the 1st charge capacity to the 1st discharge capacity) are still universal in these SnO₂ based anodes [6,20,24]. The formation of irreversible Li₂O from the conversion reaction during the 1st discharge has been believed the main cause of the large capacity loss and low ICE [8,25,26]. However, compared to more efforts focused on enhancing the cyclability, fewer works were devoted to understanding the fundamental reason why the reversibility of conversion reaction in SnO₂ anode is much inferior to those in the transition metal oxide anodes [9,13].

Since Sn and Li₂O are the two immiscible phases in a lithiated SnO₂ electrode, the oxidation of Sn to SnO₂ requires diffusion between Sn and Li₂O phases during Li⁺ extraction. The diffusion length of Sn and O in the interface layers, i.e. the grain size of Sn and Li₂O, would determine the amount of regenerated SnO₂. It had been found that the coarsening of Sn in the Sn/Li₂O mixture could be responsible for the poor reversibility of conversion reaction in lithiated SnO₂ [7,12,13]. In our previous work, we have demonstrated that Li₂O could be highly reversible in a pure SnO₂ film, in which the high-density grain boundaries among nano-sized SnO₂ suppressed the Sn coarsening and enabled the reversible conversion between Li₂O and Sn within the first several cycles [27]. However, as the cycles increased, the reversible capacity within the conversion region (1.2–2.0 V vs. Li/Li⁺, corresponding to Sn + Li₂O → SnO₂) was decreased, accompanying with the coarsening of Sn phases due to the gradual collapse of grain boundaries. The coarsening of Sn grains would reduce the amount of the Sn/Li₂O interfaces, which not only impede the kinetics of the conversion reaction but also prevent a fraction of Sn within the large particles from transforming to oxide (they remain in elemental state). Accordingly, maintaining the nanostructure of Sn/Li₂O mixture and the high dispersion state of Sn in Li₂O matrix, as well as intimate contact between Sn and Li₂O could help to produce large amount of SnO₂ at very short period of time during the reversing conversion reaction.

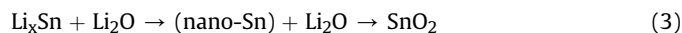
However, as illustrated in Fig. 1a, the nano-sized Sn grains/clusters formed in the lithiated SnO₂ tend to coarsen to larger size due to their extremely low recrystallization temperature ($T_R \sim -50$ °C) and the cyclic electrochemical stress (σ) imposed on the electrode [13,28], as well as the tendency to minimize the interface energy between the immiscible Sn and Li₂O. In addition,

the SEI film formed on the changeable surfaces of Sn particles could also isolate the Sn and Li₂O and reduce their contact [15], resulting in less inter-diffusion and thus low reversibility for conversion reaction. It is challenging to eliminate the thermal-induced coarsening of Sn because it is unpractical to reduce the environmental temperature during cell operations. However, in this work, we demonstrate a method to minimize the stress-induced Sn coarsening by controlling the volume stress of electrode using a super-elastic NiTi shape memory alloy (SMA). It is well known that the super-elasticity of NiTi SMA is based on their stress-induced martensitic transformation (SIMT) from the B2-NiTi phase (*Pm3m*) to B19'-NiTi phase (*P2₁/m*), during which very large strain in NiTi can be achieved and recovered by loading and unloading of stress [29]. Therefore, SIMT and the resultant super-elasticity of NiTi could be employed to accommodate the volume change and stress induced by the SnO₂-based anodes, in which a SnO₂ layer is sandwiched between two NiTi layers to form a SnO₂/NiTi hybrid electrode, as schematically illustrated in Fig. 1b. In our previous work, it has been demonstrated that the large volume change of Li-Sn anodes could be effectively accommodated by the SIMT and super-elasticity of the NiTi matrix, leading to a decrease in the internal stress and closing of cracks in Sn anodes [30].

Discharge:



Charge:



In this work, we focused on SnO₂/NiTi hybrid electrodes. It is anticipated that, as indicated in Fig. 1b, during the Li insertion processes (Eq. (1)), the B2 → B19' phase transformation in the NiTi layers (Eq. (2)) can be induced by the stress from the volume expansion of SnO₂. In the subsequent Li extraction (Eq. (3)), the B19' phase will transform back to the B2 phase as the stress is released (Eq. (4)), with recovery of the deformation in NiTi alloy. In such a manner, the large volume change and internal stress in SnO₂ will be

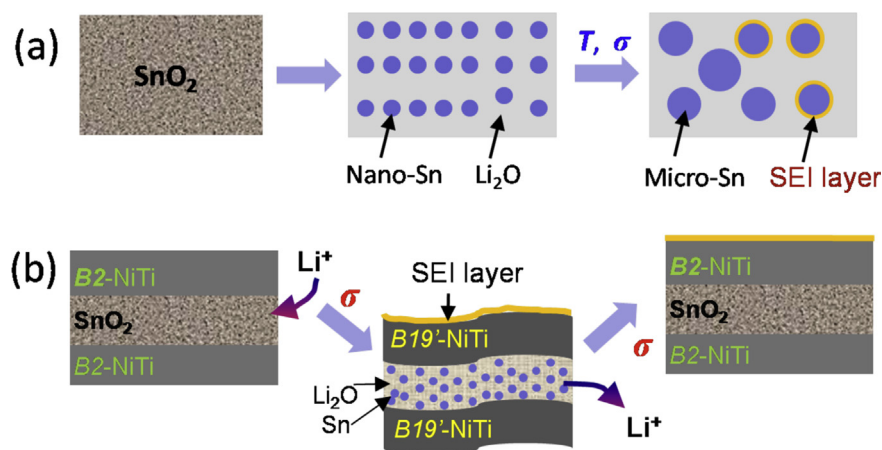


Fig. 1. (a) Schematic drawing shows the structure and phase evolution of a SnO₂ electrode during initial discharge and charge, featuring the formation of nano-Sn and Li₂O during discharge. Due to the thermal-induced recrystallization and the driving force from repeated electrochemical stress, the nanosized Sn phases tend to coarsen to larger grains. The SEI film formed on the changeable surfaces of Sn particles could also isolate the Sn and Li₂O. (b) Schematic drawing shows the interactions between NiTi shape memory alloy and SnO₂ during discharge and charge. The large volume change of SnO₂ layer could be effectively accommodated by the stress-induced martensitic transformation and super-elasticity of the NiTi layers, which lead to a decrease in the internal stress and thus less Sn coarsening in the SnO₂/NiTi electrode.

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