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

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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 800mAh/g (based on SnO₂) for over 300 cycles, demonstrating stable charge capacities of ~400mAh/g in the potential ranges of 0.01-1.0V and 1.0-2.0V(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.

Keywords: Tin dioxide; Conversion reaction; Sn coarsening; Super-elasticity; NiTi alloys

Graphical Abstract

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 (372mAh/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 1,494 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 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 (1.2-2.0V 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 **Figure 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 ($T_R \sim -50^\circ\text{C}$) 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 ($P2_1/m$), 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 SnO_2 -based anodes, in which a SnO_2 layer is sandwiched between two NiTi layers to form a SnO_2/NiTi hybrid electrode, as schematically illustrated in **Figure 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].

Figure 1 (a) Schematic drawing shows the structure and phase evolution of a SnO_2 electrode during initial discharge and charge, featuring the formation of nano-Sn and Li_2O 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 Li_2O . (b) Schematic drawing shows the interactions between NiTi shape memory alloy and SnO_2 during discharge and charge. The large volume change of SnO_2 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 SnO_2/NiTi electrode.

In this work, we focused on SnO_2/NiTi hybrid electrodes. It is anticipated that, as indicated in **Figure 1b**, during the Li insertion processes (Eqn. (1)), the $B2 \rightarrow B19'$ phase transformation in the NiTi layers (Eqn. (2))

can be induced by the stress from the volume expansion of SnO_2 . In the subsequent Li extraction (Eqn. (3)), the $B19'$ phase will transform back to the $B2$ phase as the stress is released (Eqn. (4)), with recovery of the deformation in NiTi alloy. In such a manner, the large volume change and internal stress in SnO_2 will be accommodated and constrained during the Li insertion/extraction cycling, which eventually avoids the aggregation or coarsening of Sn phase. Furthermore, the inert NiTi alloy films on the SnO_2 layer prevent SEI layer formation on Sn surfaces, resulting in stable SEI layers on the surface of NiTi coatings during cycle. Owing to the interactions between the NiTi and the active SnO_2 mentioned above, the reversibility and cyclability of the conversion reactions in the SnO_2 anode have been significantly enhanced in a proof of concept NiTi/ SnO_2 /NiTi film electrode, offering a new approach to enhancing the reversibility of SnO_2 -based electrode.

2. Results and Discussions

As illustrated in **Figure 2a**, a pure SnO_2 film and a sandwich-like NiTi/ SnO_2 /NiTi (SnO_2 /NiTi-B) film were sputtered on Cu foils (see the Experimental section), in which the as-sputtered NiTi layers were amorphous. Since amorphous NiTi material does not exhibit the shape memory effect nor super-elasticity in general[31], the as-sputtered SnO_2 /NiTi-B film was annealed at 600°C for 4h to ensure the amorphous NiTi was transformed into $B2$ -NiTi phase, resulting in a SnO_2 /NiTi-A electrode with expected configuration of a SnO_2 layer sandwiched between two $B2$ -NiTi layers. The comparison in performances of the SnO_2 , SnO_2 /NiTi-B, and SnO_2 /NiTi-A films will demonstrate the super-elasticity effects of amorphous NiTi and $B2$ -NiTi on the electrochemical performance of SnO_2 electrodes.

Figure 2 (a) Schematic drawing for the SnO₂, SnO₂/NiTi-B, and SnO₂/NiTi-A, respectively; (b) cross-section (left), EDS element line-scan (middle) of Sn, Ni, and Ti, and top view (right) of the as-sputtered SnO₂ film. The element scanning of oxygen was excluded to make the spectraclearer; (c) Cross-section (left), EDS element line-scan (middle) of Sn, Ni and Ti, and top view (right) of as-prepared SnO₂/NiTi-B film; (d) Cross-section (left), EDS element line-scan (middle) of Sn, Ni and Ti, and top view (right) of the as-prepared SnO₂/NiTi-A film. The regions where the line scans performed were marked in Fig.S1 (Supporting Information).

Figure 2b, c, and d show some typical cross-sectional and surface morphology of the SnO₂, SnO₂/NiTi-B, and SnO₂/NiTi-A film, respectively. The sandwich-like structure of the SnO₂/NiTi-B and SnO₂/NiTi-A could be clearly revealed by their cross-section SEM images (**Fig. S1, Supporting Information**) and the EDS element line-scanning spectra, which consist of two NiTi layers and a SnO₂ layer in between. However, due to the rough surface of the Cu substrates(**Fig. S2(a), Supporting Information**), the interfaces between the Cu and SnO₂ layer, Cu and NiTi layers, as well as NiTi and SnO₂ layers are not flat but fluctuated. Nevertheless, the thickness of each SnO₂ and NiTi layer in these three samples was ~1 μm. The cross-sectional view and top-view of the SnO₂ film (**Figure 2b, and Fig. S2(b)**) indicate that the SnO₂ layer was not completely dense. The SnO₂ layer was composed of nano- and micro-columns, together with a large amount of nano-, and micro-sized pores or voids. As shown in **Figure 2c** and **Fig. S2(c)**, the NiTi layer covered on top of SnO₂ did not lead to obvious change in the surface morphology of the SnO₂/NiTi-B film, where the as-sputtered NiTi also presented similar voids among the grains to the as-sputtered SnO₂ layer despite their different phases. However, as revealed by the top-view SEM image shown in **Figure 2d** and **Fig.S2(d)**, after annealing the SnO₂/NiTi-A film become denser accompanying with some Cu grains raised to the surface of the NiTi layer. The Cu grains and the migration of SnO₂ in the voids were inspected using EDS (**Fig.S2 and S3, Supporting Information**). These should be resulted from the volume change of the crystallizing NiTi layer, and the Cu diffusion from the substrate to the film surface during the relative high temperature annealing. Nevertheless, as clearly revealed in the cross-sectional SEM image, the voids and boundaries were remained among the SnO₂ columnar structure in the SnO₂/NiTi-A film.

Figure 3a is a set of typical XRD patterns taken from the SnO₂, SnO₂/NiTi-B, and SnO₂/NiTi-A films, confirming the presence of SnO₂ in all three films. The broad and weak peaks corresponding to SnO₂ diffractions revealed their amorphous or nano-crystalline nature in these three films. There is not obvious diffraction peaks corresponding to NiTi in the SnO₂/NiTi-B film, indicating that the as-sputtered NiTi layers were amorphous. In contrast, in the SnO₂/NiTi-A film, the diffraction peaks of cubic *B2*-NiTi phase ($2\theta=42.8, 62.0^\circ$) together with those of Ni₄Ti₃ and NiTi₂ intermetallic appeared in addition to those of the SnO₂. This suggests that the NiTi layers had been crystallized in the SnO₂/NiTi-A film, forming a hybrid electrode composed of SnO₂ with *B2*-

NiTi phase, which agree well with the expected structure illustrated in **Figure 2a**. The microstructure changes of the SnO₂ in these three films were also revealed by Raman spectra as shown in **Figure 3b**. Generally, the micro-sized SnO₂ powders have spectral features with three main peaks, e.g. E_g at 479cm⁻¹, A_{1g} at 635cm⁻¹ and B_{2g} at 774 cm⁻¹, in addition to several peaks usually appeared between 400 and 100cm⁻¹. For the as-sputtered SnO₂ film, the E_g shifted to about 540cm⁻¹ while the B_{2g} shifted to about 730cm⁻¹, due likely to local lattice distortion and preferred (101) orientation of the SnO₂ nanocrystals (**Figure 3a**). **Figure 3c** shows a small bundle of SnO₂ scarped off the Cu substrate in the SnO₂ film, revealing its nano-columnar structure and the homogeneous distribution of SnO₂ nanocrystals inside the SnO₂ bundle. High density grain boundaries existed among the SnO₂ nanocrystallites(~10nm) were also clearly revealed by the high-resolution TEM image (**Figure 3d**). In the SnO₂/NiTi-B film, these Raman peaks of SnO₂ were not detectable because the SnO₂ was completely covered by the Raman-inactive NiTi layer (with thickness ~1μm), as revealed by the EDS analysis. However, in the SnO₂/NiTi-A, two weak peaks (E_g and A_{1g}) of SnO₂ appeared in the Raman spectrum while the E_g shifted to ~450cm⁻¹. These could be due to some diffusion of SnO₂ into the pores in the NiTi grains during annealing at 600°C for 4h and reached the near-surface layer of the film examined by Raman and EDS. Furthermore, during annealing the stress was released while the microstructure of SnO₂ layer would change, leading to reorganization of lattice strain of SnO₂ in the annealed hybrid film. The different configurations of these three films could result in distinguishing different Li storage behaviors in the active SnO₂ layers.

Figure 3(a) XRD patterns, **(b)** Raman spectra of the SnO₂, SnO₂/NiTi-B, and SnO₂/NiTi-A films; the Raman spectrum of pure SnO₂ powders was also included for comparison. **(c)** and **(d)** TEM and high-resolution TEM images of SnO₂ scrapped off the Cu substrate in the SnO₂ film. Inset in **(c)** is a selected area electron diffraction of the nanocrystalline SnO₂.

Figure 4a shows the capacity as a function of voltage for the first cycle of the SnO₂, SnO₂/NiTi-B, and SnO₂/NiTi-A film electrodes. It is clearly revealed that these three electrodes have quite different discharge behaviors in the first cycle. For the SnO₂ film, during discharge a potential plateau was observed around 1.2V (vs. Li/Li⁺) which involved the conversion reaction and Li₂O formation, following with stepped plateaus for Li-Sn alloying within 0.6-0.01V. These experimental observations are consistent with the previous reports for pure SnO₂ electrodes [7-9, 26]. However, the initial lithiation reactions drop to low potentials significantly, which is about 0.5 V for SnO₂/NiTi-A film and even just ~0.1V for the SnO₂/NiTi-B electrode. Subsequently, the lithiation voltage of the SnO₂/NiTi-A mainly took place at ~0.6V, while those of the SnO₂/NiTi-B were around 0.3V. These lithiation potentials of the two SnO₂/NiTi hybrids were much lower than those of the pure SnO₂ film, attributed to the NiTi coating. The inactive NiTi layers could block the fast transport of electrolyte into the SnO₂ layers, leading to the polarization and thus potential drop during the early lithiation stage. Most

importantly, the NiTi layers could suppress the relaxation of lithiation-induced expansion stress from the SnO₂ layers, and thus lowered the lithiation potentials.

Figure 4 (a) The discharge-charge curves of the first cycle for the SnO₂, SnO₂/NiTi-B, and SnO₂/NiTi-A films; (b) Schematic of stress and microstructure change in the SnO₂ and NiTi layers in the three electrodes after lithium insertion and extraction; (c)-(e) SEM images of the three electrodes after the first cycle. The lower magnification images which show larger field of view could be seen in Fig. S4 (Supporting Information); (f)-(h) The cross-sectional view SEM images of the three electrodes after the first cycle. Insets are the EDS line scans for Sn (green), Ti (red), and Ni(aqua) elements.

It had been revealed that the elastic-strain associated with Li_xSn formation accompanying with large volume change affected the Sn electrode potential, making it radically different from the one expected from chemical thermodynamics[31]. In a lithiated Sn plate-shape electrode with thickness of ~250μm, where the stress could not relax through cracking, the electrode potential (~0.2V vs. Li/Li⁺) is much lower than the thermodynamically expected value(0.777V vs. Li/Li⁺). As illustrated in **Figure 4b**, when the SnO₂ film (~1μm thick) was lithiated, most of the elastic-strain energy could be effectively relaxed through the freesurface of SnO₂ layer and generation of some small cracks as shown in **Figure 4c** and **Fig.S4(a)** (**Supporting Information**). Thus, its lithiation potential (~1.2V) was close to the theoretical value. However, with respect to the SnO₂/NiTi-B electrode, the expansion stress could not be relaxed, but accumulated inside the SnO₂ layer due to the restriction of the amorphous NiTi layers, leading to a large potential drop (from 1.2 to 0.1V) in the early lithiation stage of the electrode. At the later lithiation stage, the increasing expansion stress ultimately induced cracks in the SnO₂

layer and the amorphous NiTi layers, leading to many cracks observed in the SnO₂/NiTi-B film after one cycle as shown in **Figure 4d** and **Fig.S4 (b)**. Similarly, in the SnO₂/NiTi-A, the expansion stress of SnO₂ was also restricted by the B2-NiTi layers. However, the SIMT and super-elastically strain in the B2-NiTi layer consumed a large amount of the elastic-strain energy in the SnO₂ layer, resulting in higher lithiation potential (~0.5V) in the SnO₂/NiTi-A, as well as better structural stability with less cracks generated in the NiTi layers, as revealed in **Figure 4e** and **Fig.S4(c)**. As shown in **Fig.S5 (Supporting Information)**, the SnO₂/NiTi-A electrode after the first discharge also shows similar morphology. However, there are large amount of polymer-like films covered on the surface of the SnO₂ electrode after initial discharge. By contrast, there is less SEI film observed on the surface of the SnO₂/NiTi-A electrode, suggesting that the B2-NiTi layer also help to prevent the SEI formation. Thus the SnO₂/NiTi-A presented the smallest resistance of surface film (SEI) and charge transfer resistance after the first cycle, while much higher resistance was observed in the SnO₂/NiTi-B electrode (**Fig.S6, Supporting Information**).

Figure 4f-h show the cross-sectional view SEM images of the SnO₂, SnO₂/NiTi-A, SnO₂/NiTi-B electrodes after the first cycle. It can be found that the thickness of the film layers in both the pure SnO₂ and the SnO₂/NiTi hybrid electrodes have increased after the first cycles. In particular in the SnO₂/NiTi-B electrode (**Figure 4g**), there are many cracks and large voids generated in the film layer, leading to the collapsing of the sandwich structure. In stark contrast, as revealed in **Figure 4h**, the film layer in the SnO₂/NiTi-A electrode remains good structure integrity, with well defined sandwich structure as revealed by the EDS line-scan. These experimental observations demonstrated that combining with B2-NiTi alloys indeed helps accommodating the internal stress and large volume change of the lithiated SnO₂, which was expected to yield enhanced reversibility and cyclability for the SnO₂/NiTi-A anode.

As shown in **Figure 4a**, the first discharge capacity of the SnO₂ film is ~1,271mAh/g, about 85.2% of the theoretical capacity of SnO₂, with an ICE of 81.7%. In contrast, the initial discharge capacity of the SnO₂/NiTi-B and the SnO₂/NiTi-A film electrode is ~1,519 and ~1,590mAh/g, with ICE of 68.4 and 77.1%, respectively. These numbers suggested that both the coating of NiTi layers and the annealing have affected the electrochemical behaviors of the SnO₂. The higher initial discharge capacities in these two SnO₂/NiTi hybrid electrodes could be attributed to the fact that the NiTi layers had also accommodated quite a large amount of Li⁺ ions during the first discharge. However, these Li⁺ ions could not be completely released during charge and thus resulting in lower ICEs in these two SnO₂/NiTi hybrids. In particular, much lower ICE of the SnO₂/NiTi-B film could be related to the serious electrolyte decomposition and SEI formation on the new surface of large cracks in the NiTi and SnO₂ layers as shown in **Figure 4b** and **d**, resulting in large resistance of SEI film as revealed by

the impedance spectrum (**Fig.S5**). Nevertheless, the ICEs of these three electrodes, especially the SnO_2 and $\text{SnO}_2/\text{NiTi-A}$ (81.7% and 77.1%), are much higher than the theoretical value of 52.4% assuming the conversion reactions is completely irreversible. Furthermore, in the first charge curves in **Figure 4a**, in addition to the potential range of 0.01-1.0V for de-alloying of Li_xSn , all these three electrodes yielded quite large amount of reversible capacity between the potential range of 1.0-3.0V, which could be attributed to the regeneration of SnO_2 by the reaction between Sn and Li_2O [22, 32, 33].

Figure 5 The discharge-charge curves of (a) the second and (b) the fifth cycle for the SnO_2 , $\text{SnO}_2/\text{NiTi-B}$, and $\text{SnO}_2/\text{NiTi-A}$ film electrodes. (c) The charge capacities vs. cycle number of the the SnO_2 , $\text{SnO}_2/\text{NiTi-B}$, and $\text{SnO}_2/\text{NiTi-A}$ films cycled between 0.01 and 3V (vs. Li/Li^+) with a current density of $0.2\text{mA}/\text{cm}^2$.

Figure 5a and **b** show the discharge-charge curves of the second and the fifth cycle, for the SnO_2 , $\text{SnO}_2/\text{NiTi-B}$, and $\text{SnO}_2/\text{NiTi-A}$ film electrodes. It could be seen that, since from the second cycle, the potentials for early lithiation stages in the SnO_2/NiTi hybrids have shifted above 1.0V. Furthermore, the potential plateaus with in potential zone of 1.0-3.0V in the charge curves, which could be related to the reversed conversion of $\text{Sn}/\text{Li}_2\text{O}$ to SnO_2 , repeatedly appeared at the first and the subsequent cycles. These suggest that the reversibility of the conversion reaction could be maintained in these SnO_2 -based film electrodes, delivering high reversible capacities. As shown in **Figure 5c**, the SnO_2 film has an initial reversible capacity of $\sim 1,038\text{mAh/g}$, but dropped to $\sim 676\text{mAh/g}$ after 50cycles and then gradually degraded to 430mAh/g at the 300th cycle. The $\text{SnO}_2/\text{NiTi-B}$

1 presents much inferior capacity retention. The reversible capacity of the first cycle ($\sim 1,039 \text{ mAh/g}$) was
2 dramatically reduced to 52 mAh/g after 300 cycles, due primarily to the poor structural stability of the
3 $\text{SnO}_2/\text{NiTi-B}$ film, as revealed in **Figure 4d** and **Fig.S4 (b)**. In contrast, the $\text{SnO}_2/\text{NiTi-A}$ has superior cycling
4 performance. The initial charge capacity of $\sim 1,226 \text{ mAh/g}$ remained stable during the first 50 cycles and slowly
5 decreased to $\sim 874 \text{ mAh/g}$ at the 150th cycle. Subsequently, however, the reversible capacities of the $\text{SnO}_2/\text{NiTi-}$
6 A gradually increased to $1,451 \text{ mAh/g}$ after 300 cycles. The enhancement in capacity retention of the $\text{SnO}_2/\text{NiTi-}$
7 A should be attributed to the $B2\text{-NiTi}$ layers rather than the annealing of the SnO_2 layer, because the $\text{SnO}_2\text{-A}$
8 film yielded very similar reversible capacities and cyclability to the SnO_2 film. Furthermore, comparing to the
9 $\text{SnO}_2/\text{NiTi-B}$, which has similar sandwich-like structure but lacks SIMT features in the amorphous NiTi layers,
10 we could conclude that the SIMT and super-elasticity of the $B2\text{-NiTi}$ layers indeed dramatically enhanced the
11 reversibility and cyclability of SnO_2 layer in the $\text{SnO}_2/\text{NiTi-A}$ electrode.

12 In order to demonstrate that the high ICEs in these SnO_2 anodes were resulted from the reversible
13 conversion reaction of Sn and Li_2O to SnO_2 , we collected *ex-situ* XRD data for the pure SnO_2 film at six different
14 discharge/charge states during the first cycle which were marked in **Figure 6a**. As shown in **Figure 6b**, during
15 discharge the initial SnO_2 phase was slowly transformed to metallic Sn and the transformation was completed at
16 a discharge potential of $\sim 0.3 \text{ V}$ (vs. Li/Li^+) [34]. The formation of Li_xSn phase was then observed at the end of
17 discharge (0.01 V), consistent with the previous studies [8]. In stark contrast, the diffraction peaks corresponding
18 to the Li_xSn and Sn phases disappeared as the recharge proceeded to the cutoff potential at 3.0 V . Instead, a broad
19 hump (2θ range of $20\sim 35^\circ$) in the diffraction pattern appeared, suggesting that the fully-charged SnO_2 electrode
20 was amorphous or in ultrafine nanostructure. Since metallic Sn phase generally can not be amorphous at room
21 temperature, it must be composed of amorphous or ultrafine nanostructural Sn -based oxides in the recharged
22 film.

Figure 6(a) Initial capacity vs. voltage curve of the Li/SnO₂ half cell marked with six lithiated states for microstructure examinations, namely OCP, discharged to 0.8, 0.3, and 0.01V, recharged to 1.2 and 3.0V vs. Li/Li⁺; (b) *Ex situ* XRD patterns, and (c) *In situ* surface enhanced Raman spectrum (SERS) for the SnO₂ film electrode at six different states for the first cycle. Raman data of Li₂O and electrolyte as references could be seen in Fig.S5 (Supporting Information).

To further corroborate the reversible conversion between Sn/Li₂O and SnO₂, we performed *in-situ* SERS on the SnO₂ film. **Figure 5c** shows the SERS data recorded at the six desired potentials (**Figure 5a**), which clearly demonstrated the disappearance and regeneration of the SnO₂ and Li₂O phase during cycling. Specifically, the characteristic peak for Li₂O at ~520cm⁻¹ was observed during discharge, but most of them was absent from the spectra at the end of charge. In contrast, the peaks for SnO₂, in addition to some peaks arising from the electrolyte-related products (**Fig.S7, Supporting Information**), were apparent when charged from 1.2 to 3.0V, remaining a weak signal of Li₂O. It should be pointed out that the broad Raman peak of Li₂O is found to be more similar to that of the Li₂O formed on the surface of a lithium foil (**Fig.S6**), rather than that of a micro-sized Li₂O powder, due most likely to its fine nanostructure or amorphous nature of the lithiated SnO₂ electrode [11, 35, 36]. Nevertheless, these provide the strongest evidence to support that the conversion between Sn/Li₂O and SnO₂ was reversible, which mainly happens among the potential range of 1.2-3.0V during charge. Since the *ex-situ* XRD data (**Figure 9**) collected for the lithiated SnO₂/NiTi-B and SnO₂/NiTi-A films also revealed that all the Sn reflections disappeared when charged to ~3.0V, these experimental facts suggest that the reversed conversion reaction of Sn/Li₂O also happened in these two SnO₂/NiTi hybrid films.

However, it has been found in **Figure 5c** that the reversible capacities of the SnO₂ film was decreased, while those of the SnO₂/NiTi-A film increased with the cycles, suggesting that different process may be responsible for the capacity variation in these two different films. Generally, the reversible capacity fading of

SnO₂ electrodes could result from the structural collapse of the electrode, and the declining reversibility of conversion reaction ($\text{Li}_2\text{O} + \text{Sn} \longleftrightarrow \text{SnO}_2$) and alloying/de-alloying ($\text{Li}_x\text{Sn} \longleftrightarrow \text{Sn}$). In order to clarify these differences, the differential charge capacity plots (DCPs) at different cycles for the SnO₂ and SnO₂/NiTi-A were compared in **Figure 7**.

Figure 7 Differential charge-capacity plots of (a) the pure SnO₂ film, and (b) the SnO₂/NiTi-A film electrode at the 1st, 2nd, 5th, 20th, 50th, 100th, and 300th cycle.

As shown in **Figure 7a**, in the DCPs for the first five cycles of SnO₂ electrode, there are obvious two group of peaks, including sharp peaks at around 0.5V, and broad peaks in the potential region of 1.0-2.0V, respectively. These lower-potential peaks should be responsible for the decomposition of Li_xSn, while the subsequent higher-potential peaks could be attributed to the regeneration of SnO₂[9, 22, 32-34]. The large integral intensity of the DCP peaks between 1.0 V and 2.0V revealed the high activity of the reversed conversion of Sn/Li₂O to SnO₂, which resulted in good reversibility and thus high ICE in SnO₂ film as demonstrated in **Figure 4a**. However, as the cycle number increase, the DCP peaks within 1.0-2.0V almost completely disappeared, suggesting that the activity of the reversed conversion reaction declined dramatically. In addition, the DCP peaks round 0.5V in **Figure 7a** remained strong but gradually shifted to higher potentials, suggesting the increasing polarization in the Li_xSn dealloying due to the coarsening of Sn and Li_xSn phases in the lithiated SnO₂ film,[13] as to be discussed later (**Figure 9**). In contrast, as indicated in **Figure 7b**, the DCPs of the SnO₂/NiTi-A reveal quite different reaction processes during delithiation of the electrode. In the first several cycles, there were also sharp peaks for the Li_xSn dealloying within potential range of 0.01-1.0V, and broad peaks appeared between 1.0 and

2.0V for the reversed conversion reactions. However, after the fifth cycle, a broad peak emerged at ~2.5V, and gradually grew after 100 cycles, which would contribute to increasing capacities among this potential region. However, the DCP peaks in potential ranges of 0.01-1.0V and 1.0-2.0V remained stable among several hundred cycles in terms of potential positions and the integral intensities of peaks, indicating the good reversibility and cyclability of the alloying and conversion reactions in the SnO₂/NiTi-A electrode. And specifically, within the 300 cycles, the DCP peak for Li_xSn dealloying in the SnO₂/NiTi-A was located at the same potential of ~0.5V, suggesting that there was less polarization because the grain size of the Sn/Li_xSn remained very small and unchanged during the repeated cycling.

Since the DCPs indicated that the delithiation of the SnO₂/NiTi-A would involve different reaction processes at different potential regions, its reversible capacities (charge capacities in **Figure 5c**) in each cycle were separated to three parts according to three potential ranges and presented in **Figure 8a**. The three potential regions, namely 0.01-1.0V, 1.0-2.0V, and 2.0-3.0V, were determined from the DCP curves labeled in **Figure 7b**. The capacity between 0.01V and 1.0V comes from the Li_xSn dealloying, while the capacity range of 1.1V-2.0V is attributed mainly to the reversed conversion between Sn and Li₂O to form SnO₂. Accordingly, it can be seen that almost equal capacity of ~400mAh/g were obtained in both potential regions of 0.01-1.0V and the subsequent range of 1.0-2.0V. This suggests that almost all of the Sn formed during dealloying could be transferred to SnO₂ by the subsequent reversed conversion reaction between Sn and Li₂O, demonstrating the high reversibility of conversion reaction in the SnO₂ layer in the SnO₂/NiTi-A electrode. However, as shown in **Figure 8b**, the reversible capacities between 0.01 V-1.0V slowly decreased in the pure SnO₂ electrode, while the capacity in the 1.0-3.0V range (mainly 1.0-2.0V as revealed by **Figure 5a** and **b**) declined most rapidly during the initial 20 cycles and the variation of capacity in this region during cycling is quite similar to the total capacity of SnO₂ shown in **Figure 5c**. These indicated that the capacity fading of the SnO₂ electrode occurred mainly in the potential range of 1.0-3.0V, due to the reversible fading for conversion of Sn/Li₂O to SnO₂.

Figure 8 Reversible capacities vs. cycle number of (a) the SnO₂/NiTi-A electrode separated into potential ranges of 0.01-1.0V, 1.0-2.0V, and 2.0-3.0V; and (b) the pure SnO₂ film separated into potential ranges of 0.01-1.0V, and 1.0-3.0V. (c) Reversible capacity vs. cycle number of the SnO₂/NiTi-A electrode cycled at voltage region of 0.01-1.0V with a current density of 0.2 mA/cm². Insert shows the discharge-charge curves at the 2nd, 100th, and 300th cycle.

In stark contrast, with respect to the SnO₂/NiTi-A, as shown in **Figure 8c**, the cell cycled between 0.01V and 1.0V also yielded very stable reversible capacity of ~450mAh/g over 300cycles, which is close to the capacity at potential region of 0.01-1.0V separated from the cell cycled between 0.01-3.0V, indicating the excellent structural integrity of the SnO₂ layer inside the two B2-NiTi layers during cycling. More importantly, the capacities contributed by the reversed conversion of Sn/Li₂O to SnO₂ among 1.0-2.0V remained stable among the first 200 cycles and gradually increase afterward, suggesting that the reversibility of the conversion reaction in SnO₂ layer was effectively enhanced by the supporting of the superelastics B2-NiTi layers. By further inspecting the **Figure 8a**, it has been found that the increasing capacities of the SnO₂/NiTi-A shown in **Figure 5c** should mainly originate from the potential region of 2.0-3.0V of which capacity of ~200mAh/g at the first cycle dramatically grew to more than 550mAh/g after 300cycles. It has been reported that the charging capacities yielded above 2.0V could be due to the reversible decomposition of polymeric gel-like film and

pseudocapacitive storage on the surface of electrode[37, 38]. In particular, the continuous increase of capacities has been a common phenomenon in transition metal oxide anodes as they are cycled within wide potential window (0 to 3 V vs. Li/Li⁺ or higher), which was now attributed to the catalytic activity of transition-metal oxides on the electrolyte decomposition during delithiation[39, 40]. On this basis, the fast drop of the reversible capacities after ~380 cycles (Figure 5c) could be resulted from the seriously consumption of the electrolyte and collapsing of the NiTi layers. Nevertheless, through the comparative studies on these SnO₂-based electrodes, it has demonstrated that the B2-NiTi layers dramatically enhanced the lithiation/delithiation reversibility and cycleability of the SnO₂. The most important contribution from the B2-NiTi layers should be the successful suppression of Sn coarsening during cycling, which resulted from the stress-induced martensitic transformation in the NiTi layers.

Figure 9 (a) Evolution of the XRD patterns of SnO₂/NiTi-A at different lithiated states, namely the fresh electrode before cycling, 1st discharge to 0.01V, 1st charge to 3.0V, and 20th charge to 3.0V; **(b)** XRD patterns the SnO₂ film at state of charging to 3.0V after the 1st cycle and the 20th cycle; **(c)** XRD patterns the SnO₂/NiTi-B film at state of charging to 3.0V after the 1st cycle and the 20th cycle.

The phase variations of the B2-NiTi and SnO₂ layers in the SnO₂/NiTi-A at different lithiation states were further investigated by *ex situ* XRD. As shown in Figure 9a, the initial SnO₂ phase was transformed to metallic Sn and Li_xSn phase when the electrode was discharged to 0.01V, which was similar to that of the pure SnO₂ electrode shown in Figure 6b. In addition, besides the main diffraction peaks ((110), 2θ at 42.8°) of B2-NiTi were disappeared, instead, several new peaks emerged at 39.1, 43.9, 45.0°, which were very close to the (002), (020), and (012) reflections of martensite B19'-NiTi. However, the three peaks almost completely disappeared when Li⁺ extracted from the electrode and recharged to ~3.0V. These experimental observations confirmed that there were reversible martensitic transformation in the NiTi layers of the SnO₂/NiTi-A film, which were induced by the stress of volume change in SnO₂ layer due to Li⁺ insertion and extraction. The SIMT and super-elasticity of

the NiTi matrix could in turn effectively accommodate the internal stress and volume change of the lithiated SnO₂ layer. And thus, even after 20 cycles, there was no obvious diffraction peaks corresponding to Sn in the fully charged SnO₂/NiTi-A electrode (at ~3.0V vs. Li/Li⁺). In stark contrast, as shown in **Figure 9b** and **c**, in both pure SnO₂ and SnO₂/NiTi-B films, several sharp diffraction peaks of Sn appeared in the fully charged state within 20 cycles, resulted from the dramatically stress-induced coarsening of Sn phase in these two electrodes. These in turn corroborated that the architecture of the SnO₂/NiTi-A film and the B2-NiTi layers have effectively suppressed the Sn coarsening in the lithiated SnO₂ during cycling, which maintained fast inter-diffusion kinetics among nanoscale Sn/Li₂O interfaces, resulting in excellent reversibility and cyclability of conversion reaction in the SnO₂ anode.

3. Conclusions

By applying the stress-induced martensitic transformation and super-elasticity of NiTi alloys, the internal stress and volume change in the lithiated SnO₂ layer could be accommodated, suppressing effectively the coarsening of Sn phase in a sandwich-like NiTi/SnO₂/NiTi film electrode. This unique structure has helped to retain the reversibility of the alloying and conversion reactions of SnO₂ for over 300 cycles, achieving stable charge capacities of ~400mAh/g in the potential ranges of 0.01-1.0V and 1.0-2.0V, respectively. The results demonstrate that the reversibility and cyclability of conversion reaction in SnO₂ anodes can be enhanced by using a shape memory alloy to maintain the structure integrity of the electrode, especially the nanostructure of the Sn/Li₂O mixture in the lithiation products.

4. Experimental

Preparation of SnO₂ and NiTi/SnO₂/NiTi thin film electrodes: Both the pure SnO₂ films and the NiTi/SnO₂/NiTi sandwich tri-layers were deposited on Cu foil substrates (6×6cm²) using a KYKY JGB-560 magnetron sputtering system with a radio frequency magnetron (power 120W, 30 minutes) for the SnO₂ films and a direct current magnetron (power 100W, 10 minutes) for the NiTi (atomic ratio 1:1) alloy films. In a typical deposition, 1.0Pa Ar was used as the working gas during deposition after a base pressure of 2.0×10⁻⁴ Pa was achieved. The preparation steps for a NiTi/SnO₂/NiTi sandwich structure (SnO₂/NiTi-B, B means before annealing) were as follows: first, a NiTi layer was deposited on a Cu foil, and a SnO₂ layer and then another NiTi layer were sequentially deposited. The amount of deposited SnO₂ layers was determined by weighing the film before and after sputtering deposition of SnO₂ using an FA1104N balance. Accordingly, the mass loading of the active SnO₂ phase in the film electrodes was calculated as ~0.5 mg/cm². Halves of the SnO₂/NiTi-B film and

the pure SnO₂ film were annealed at 600°C for 4h in a tube furnace with protection of flowing Ar, to obtain a SnO₂/NiTi-A and a SnO₂-A film (A means after annealing), respectively. These four films, SnO₂, SnO₂-A, SnO₂/NiTi-B, and SnO₂/NiTi-A, were comparatively studied as anodes for LIBs.

In order to prepare the sample for *in situ* surface enhanced Raman spectroscopy (SERS) measurement, ultrafine Ag nanoparticles were deposited on the surface of the pure SnO₂ film by direct current magnetron sputtering (8W, 2min, Ar 2Pa).

Materials Characterization: X-ray Diffraction (XRD) was performed on a PANalytical X'Pert PRO Alpha-1 diffractometer equipped with Cu-K α radiation operating at 45kV and 40mA. The surface and cross-sectional morphologies of the film electrodes were examined using an LEO 1530 scanning electron microscope (SEM). The compositions of the samples were determined by an INCA energy dispersive spectroscope (EDS) attached to the SEM. Transmission electron microscope (TEM) observations were conducted in a FEI TecnaiF30 microscope operating at 300kV. For TEM analysis, the SnO₂ fragments were scraped from the substrate and directly dispersed on carbon-coated Cu grids. Raman spectra were obtained using a Renishaw RM 1000 spectromicroscopy system with a 633 nm wavelength laser. For the *ex situ* XRD/SEM measurement of electrochemically tested electrodes, the samples were carefully stored and transferred to minimize air exposure. The reacted SnO₂-based film electrodes were sealed inside Kapton tape to minimize air exposure during the XRD measurement. The electrodes at different lithiated states were prepared by discharging/charging to a controlled cutoff voltage. These electrodes were then removed from the electrochemical cells, rinsed with DMC and absolute ethanol, and dried under vacuum in the ante-chamber of an argon filled glove box. The *in situ* Raman cell was tested galvanostatically using a Solatron Analytical 1470E potentiostat. At the same time, an *in-situ* time-resolved study was conducted by illuminate the laser spot on the same location, with the laser slightly out of focus to cover a larger area of about 5 μ m in diameter.

Electrochemical measurements: The electrochemical performance of the obtained film electrodes was investigated with half-cells assembled in argon-filled glove boxes. The thin films were directly used as working electrodes. Lithium ribbon and polyethylene membrane (Celgard 2325) were used as the counter electrode and separator, respectively. The electrolyte (Tinci Corporation) was 1M LiPF₆ in mixture of ethylene carbonate and dimethyl carbonate (EC: DEC=1:2 by weight) with an additional 10wt% of Fluoroethylene carbonate (FEC). Most of testing cells were CR2016 coin-type cell configuration, which were galvanostatic charge-discharge cycled on multi-channel battery tester (LAND-CT2001A) with a current density of 0.2mA /cm² over a voltage

range of 0.01–3V. Impedance spectra were acquired at AC voltage of 5 mV in the frequency range of 1MHz to 0.05 Hz using a Gamry Interface 1000 Electrochemical System. The specific charge/discharge capacities of the SnO₂/NiTi hybrid electrodes were calculated by using the overall capacity divided by the mass of the active SnO₂ layer rather than by the total mass of the deposited film layers.

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