**Toward cyclic durable core/shell nanostructure of Sn-C composite anodes
for stable lithium storage by simulating its lithiation-induced internal strain**

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Abstract: To explore the capacity fading mechanism during long-term cycling of the milled Sn-C lithium storage anodes, the structural stability of the cycled Sn-C electrodes has been investigated using internal strain distribution as indicator by simulation with different two-dimensional core/shell nanostructure models solved by Lagrangian description, combining with experimental results. It is revealed that the Sn-C composite of a double-coating structure with the smaller Sn coated by a stiff layer Li_2O and embedding in graphite sustains less deformation, and has higher structural stability than the single-coating one. Due to the lithiation-induced stress and strain effect, Sn particles aggregate and the Sn whiskers grow in the cycled Sn-C electrodes that observed by SEM and TEM, which is closely related to the Sn transportation. This strain induced structural damage causes the capacity fading of Sn anodes. Based on the simulation of strain distribution induced by lithiation, the nanostructure has been designed for Sn-C electrodes of smaller Sn particles embedded in matrix with large elastic modulus and proper thickness to obtain optimized combination of capacity and cycleability. It would provide a guideline for designing material and microstructure of anodes for lithium ion batteries.

1. Introduction

Tin (Sn) is a promising alternative anode material for new generation high-energy lithium ion battery, because it possesses a moderate average voltage of ~ 0.5 V (vs. Li/Li^+), and can host more Li ions to form Li_xSn ($0 \leq x \leq 4.4$), reaching a maximum theoretical volumetric capacity of 2111 mAh/cm^3 [1-3]. However, the pure Sn anode experiences significant volumetric change during alloying/de-alloying of lithium, which creates very large internal stress and serious deformation [4-6]. This results in disintegration of electrode structure, in which Sn particles loss lithiation activity due to the loss of electrical contact with the surrounding Sn phase, Cu current collector or conductive matrix. In addition, the volume expansion would also induce breaking of solid-electrolyte-interphase (SEI) film, and then SEI film would continuously grow on the fresh surface of cracks during cycling, following with continuous irreversible consumption of electrolyte and leading to electrolyte-degradation. Thus, the Sn based anodes suffer structural fracture and fast capacity degradation.

In order to improve the cycling performance of Sn based anodes, the most effective approach is to embed nanostructured Sn-based materials in various carbon materials [7, 8] or elastic alloy matrix [9-13]. Thus, the volume change of Sn can be homogenized and diluted, and become reversible. In addition, the carbon matrix provides conductive networks for the whole electrodes [14, 15], and prevents Sn from aggregation. Therefore, nanostructured Sn-C composites have better structure stability, yielding much enhanced capacity retention compared with pure Sn micro-sized particles [16-18]. Recently, we have developed a high-efficiency method of dielectric barrier discharge plasma assisted milling (P-milling), and used it to synthesize Sn-C and $\text{Sn@SnO}_x/\text{C}$ hybrid anode materials [19, 20]. Those hybrids have a nanocomposite structure of nanosized Sn particles embedded in graphite matrix, which show higher capacity and better capacity retention than those Sn-C composites prepared by conventional

1 milling(C-milling) without the assistance of plasma, demonstrating the positive effective of plasma on the
2 fast refining of Sn. However, there is no clear guidance suggesting that which Sn particle size and
3 distribution would have better electrochemical performance, leading to a great blindness on microstructure
4 tuning of the Sn based carbonaceous composite anodes.

5 Recently, it has been observed by *in-situ* TEM that Sn aggregates and then Sn whiskers grow
6 presumably due to large internal stress in Sn thin film and SnO₂ nanowire during lithiation/delithiation[21,
7 22], but the Sn precipitation can be suppressed by carbon coating on SnO₂ nanowires[21]. With respect to
8 the P-milled Sn-C composites, we noted that the capacity degradation of Sn becomes more serious at a
9 certain cycling stage. This might be related to a sudden activity loss of aggregated Sn, which is probably
10 due to the formation of Sn whisker owing to the stress effect in case that graphite matrix is broken down
11 and could not suppress Sn aggregation after a certain period of cycling. Obviously, the Sn particle size and
12 distribution determine the stress and strain distribution during the lithiation/delithiation, and thus the
13 stability of carbon matrix, as well as the aggregation and growth tendency of Sn. In addition, the practical
14 capacity of the anode is also dependent on the size and distribution of the Sn phase. Thus, it is of great
15 significance to explore the quantitative relationship between the particle size and distribution of Sn and
16 structural structure stability of the Sn-C composite anodes, which could give a design guidance for Sn-C
17 and other metal-carbon composite anodes for Li-ion battery.

18 In this work, two-dimension geometric models are designed to predict the structural stability of active
19 Sn particles in our previous reported Sn-C composites. ANSYS Workbench interface is used to solve these
20 models. The growth mechanism of Sn whiskers in cycled Sn-C is revealed. Combining the simulated strain
21 distribution and experimental results of the electrochemical performance, the criterion of structural stability
22 of Sn and carbon matrix upon lithiation /de-lithiation cycling is proposed for Sn-C based nanocomposites

with core-shell configurations.

2. Experimental methods

Two kinds of Sn-C nanocomposites, as prepared by milling a Sn/C mixture (1:1 of mass ratio) using a discharge plasma assisted milling method (Plasma-BM-L) for 10 hours in Ar and O₂ atmosphere respectively, are denoted as P-milled Sn-C and O-P-milled Sn@SnO_x-C, respectively. The details of P-milling have been reported in our previous works [19, 20]. A Sn-C composite, denoted as C-milled Sn-C, is fabricated by a conventional milling for 10 hours with the same milling parameters but without the assistance of discharge plasma. The distributions of Sn particle size were evaluated from powder X-ray diffraction (XRD), and small-angle X-ray scattering (SAXS) data. The microstructures of samples were characterized by field-emission scanning electron microscopy (FE-SEM, Carl Zeiss Supra 40), and transmission electron microscopy (TEM, JEOL-2100) at 200 kV. Cycled electrodes were washed in diethyl carbonate and absolute ethanol to remove the electrolyte before microstructure analysis.

The electrochemical properties of the as-prepared composites were evaluated using coin-type half-cells (CR2016) constructed in an argon-filled glove box with lithium ribbon serving as the counter and reference electrodes. The electrode slurries were prepared by mixing 80wt% active powder, 10wt% Super-P, and 10wt% PVdF. The slurries were coated on Cu foil and dried at 120°C for 10 h. The loading of active materials on working electrode was 1–1.5 mg/cm². The electrolyte was 1M LiPF₆ in a mixture of ethylene carbonate /diethyl carbonate /ethyl methyl carbonate (1:1:1, v:v:v, Shanshan Tech Co., Ltd.). Galvanostatic charge–discharge measurements were performed with battery testers (CT2001A, Land, China) at a current density of 100 mA/g in the range of 0.01–1.5 V vs. Li/Li⁺. All the electrochemical tests were carried out at ambient temperature.

The internal strain and its variation in the above three Sn based anodes during lithium inserting was

simulated by using ANSYS Workbench interface. **Table. 1** lists the parameters of materials used for simulation. The elastic constant of Li_2O are performed with the Vienna *ab initio* simulation package (VASP) within the projector-augmented plane wave (PAW) method of density functional theory (DFT), and the details of the calculation is given in the **Supplement Information**. The tangent modulus (G) is calculated by the formulation of $G = E / (1 + 2\mu)$. The designed geometry models are solved by Lagrangian description using ANSYS WORKBENCH from the following boundary conditions: assumed the deformation of origin as zero, and expanding freely of the graphite outer edge.

Tab. 1 The mechanical parameters of materials used in simulation.

Material	Young's modulus (E , GPa)	Poisson's ratio(μ)	Yield strength (σ_s , MPa)	Tangent Modulus (G , GPa)
Sn[23]	49.90	0.357	14[24]	29.1
Graphite[23]	10.0	0.25	29.1	6.7
Li_2O	160	0.18	41[25]	121.1

3. Results and discussions

3.1 Microstructure and geometry models of the Sn-C composites

Fig. 1 shows the microstructures of C-milled Sn-C, P-milled Sn-C and O-P-milled $\text{Sn}@\text{SnO}_x\text{-C}$ observed by TEM. As discussed previously [19, 20], a single-coating structure of Sn particles dispersing in graphite is obtained for C-milled and P-milled Sn-C composites. However, as shown in **Fig.1 (a) and (b)**, the particle size of Sn (dark zones) in the P-milled Sn-C composite is much smaller than that of the C-milled Sn-C hybrid. In contrast, as the Sn-C mixture was milled with the assistance of O_2 plasma, there are 6~10 nm SnO_x layers coated on the surfaces of the ultrafine Sn particles, to form a $\text{Sn}@\text{SnO}_x/\text{C}$ with a unique double-coating nanostructure. As shown in **Fig.1(c)**, the corresponding ring-like selected-area

electron diffraction (SAED) patterns demonstrate the amorphous/nanocrystalline nature of the *in-situ* formed SnO_x during O-P milling of the Sn-C mixture. The dark field TEM image shown in **Fig. 1(d)**, taken from the (101) diffraction spot of Sn, reveals that most of the Sn nanoparticles are less than 20nm in size.

Fig.1 Microstructures observed by TEM for: (a) C-milled Sn-C, (b) P-milled Sn-C, (c) and (d) $\text{Sn@SnO}_x/\text{C}$. Inset in (c) is the corresponding selected area electron diffraction pattern (SAED).

Fig.2 (a) XRD patterns of the as-prepared C-milled Sn-C, P-milled Sn-C, and $\text{Sn@SnO}_x/\text{C}$ composites. Histogram of Sn particles size distribution in (b) C-milled Sn-C, (c) P-milled Sn-C, and (d) $\text{Sn@SnO}_x/\text{C}$ composite calculated from SAXS data. The relative frequency and cumulative distribution are indicated on the left vertical axis and right vertical axis, respectively.

XRD patterns shown in **Fig.2(a)** reveal the dramatically refinement of the Sn (JSCD: 00-001-0926) particles during P-milling, as well as the existence of the *in-situ* formed SnO (JSCD: 00-001-0891) and SnO₂ (JSCD: 00-001-0625) phase after P-milling in O₂ atmosphere. In order to evaluate the distributions of Sn particle size, SAXS was performed on the three Sn-C composite powders. **Fig. 2(b), (c), and (d)** show the relative frequency, cumulative distribution and mean particle size (D_m) of Sn particle for C-milled Sn-C, P-milled Sn-C, and O-P-milled Sn@SnO_x/C composites, respectively. Consistent with the statistics results of Sn size from TEM images [19], the majority of Sn particles have sizes between 40-200 nm, with a D_m of 70 nm in the C-milled Sn-C, while most Sn particles are less than 100 nm and the D_m is only 40 nm in the P-milled Sn-C. Not surprisingly, the Sn@SnO_x/C shows the smallest D_m of 21 nm, and the size of most Sn particles is less than 40 nm. Accordingly, as illustrated in **Fig.3**, even with the same milling duration (10 h), the P-milled/C-milled Sn-C composites (**Fig.3(a)**) and the O-P-milled Sn@SnO_x/C (**Fig.3(b)**) have quite different particle size and distribution of Sn phase in the carbon matrix, forming two different kinds of core/shell structures both with dispersive Sn cores and continuous carbon shells.

According to those, as shown in **Fig. 3(c)**, a simple 2D core-shell geometric model with Sn nanoparticles coating by graphite matrix is established for C-milled and P-milled Sn-C compositions by ANSYS Workbench interface. But for the Sn@SnO_x/C, actually after discharging in the first cycle, all the SnO_x (**Fig.3(b)**) would be transferred to form Sn/Li₂O mixtures by an irreversible conversion reaction, during which the more finer Sn particles were surrounded by inactive Li₂O[20]. And thus to simplify the model, as shown in **Fig. 3(d)**, a double-coating geometric model, namely Sn@Li₂O dispersing in graphite matrix, is designed for the O-P-milled Sn@SnO_x/C. In these core/shell structure models, the radius of Sn cores was set as 35, 20, and 10.5 nm for C-milled Sn-C, P-milled Sn-C, and Sn@SnO_x/C based on the SAXS results, respectively, while the radius of all the whole structure units was set to be 50 nm. According

to these models, the internal strain in these Sn-C based anodes during lithium inserting was simulated (Fig.5). In addition, simulation have also been made for the models with different size of Sn cores and carbon shells for microstructural design (Fig.10).

Fig.3 (a) Schematic drawing for the distributions of Sn phases in (a) C-milled Sn-C and P-milled Sn-C, and (b) O-P-milled Sn@SnO_x/C nanocomposites. (c) Single-coating model for unit structure of Sn-C composite, and (d) double-coating model for Sn@SnO_x/C designed by ANASYS WORKBENCH.

3.2 Capacity fading of Sn in Sn-C compositions

The method of differential capacity, namely dQ/dV analysis as a function of cell voltage, is used to investigate the delithiated activity of Li_xSn which affected by the structural change of Sn phase [26, 27]. **Fig. 4** shows the delithiation differential capacity of Sn versus voltage curves (dQ/dV(V_{Sn}), delithiation from Li_xSn) for C-milled Sn-C, P-milled Sn-C, and Sn@SnO_x/C at a small current density of 100 mA/g to ensure full lithiation and delithiation in each cycle. It can be seen in **Fig. 4(a) and (b)** that, the first dQ/dV (V_{Sn}) curves of both C-milled Sn-C and P-milled Sn-C display a broad peak from 0.4 to 0.55 V and three sharp peaks at 0.62, 0.73 and 0.79 V, respectively. The former broad peak corresponds to the delithiation of Li_xSn generated from finer Sn phase, while the latter sharp peaks indicate the two-phase regions of Li_xSn delithiation generated from the coarse Sn particles. However, the intensity of all dQ/dV (V_{Sn}) peaks

diminish dramatically to zero after the 30th cycle in **Fig. 4(a)**, which suggests that almost all Sn lose the lithiation activity in the C-milled Sn-C. On the contrary, as shown in **Fig. 4(b)**, the intensity of dQ/dV (V_{Sn}) peaks decrease but still keep strong after the 30th cycle. This implies that most of Sn in the P-milled Sn-C remains lithiation activity. Nevertheless, the capacity from Sn in P-milled Sn-C reduces largely after 50 cycles. Definitely, as shown in **Fig. 4(c)**, the dQ/dV (V_{Sn}) curve shows only one broad peak among 0.3-0.8 V in the Sn@SnO_x/C, which indicate that no obvious two-phase co-existence region during delithiation in the Sn@SnO_x/C with highly dispersive refined Sn particles. Furthermore, the onset of delithiation voltage of Li_xSn in Sn@SnO_x/C is about 0.3 V, showing a negative shift compared with the C-milled Sn-C and P-milled Sn-C. This shift should be also attributed to the fast Li-ion diffusion in the nanocomposite structure of Sn@SnO_x/C. However, it can be seen that the 0.6-0.7 V peak in the dQ/dV (V_{Sn}) curve of Sn@SnO_x/C becomes a little sharper showing two-phase region formation, which implies that the Sn aggregates lightly after 50 cycles. Nevertheless, the Sn phase still remains high capacity contribution until 100 cycles in Sn@SnO_x/C [20]. This suggests that the Sn@SnO_x/C would perform better capacity retention than the C-milled Sn-C and P-milled Sn-C composite anodes.

Fig.4 Differential capacity vs. voltage (V_{Sn} , delithiation from Li_xSn) curves during charge processing

for (a) C-milled Sn-C, (b) P-milled Sn-C, and (c) O-P-milled Sn@SnO_x/C. (d) The delithiation capacity of Sn versus cycle number from C-milled Sn-C, P-milled Sn-C and O-P-milled Sn@SnO_x/C electrodes.

Fig. 4(d) shows the delithiation capacity of Sn versus cycle number from the C-milled Sn-C, P-milled Sn-C, and O-P-milled Sn@SnO_x/C electrodes. The Sn delithiation capacities are very close in the C-milled Sn-C and P-milled Sn-C electrodes, being 471, and 463 mAh/g, respectively. After 30 cycles, it reduces to 169 mAh/g in the C-milled Sn-C, while it remains 300 mAh/g but decreases to 200 mAh/g after 50 cycles in the P-milled Sn-C. The Sn@SnO_x/C composite shows the best capacity retention with an initial capacity of 661 mAh/g, and retains 461 mAh/g and 391 mAh/g after 30 and 50 cycles, respectively. This result is in good agreement with the above dQ/dV analysis. Obviously, the reversible capacities of the Sn-C composites are dominantly dependent on the amount of active Sn. And thus, the structural stability of Sn phase in the composite is crucial for long-term cycling stability. From the above results, the Sn@SnO_x/C electrode should have the best stability during cycling, following with P-milled Sn-C, while the C-milled Sn-C electrodes already suffer serious structural collapse after 30 cycles.

3.3 Simulation analysis of structural stability of Sn-C composites

The structural stability of the Sn-C electrodes has been analyzed by simulating the designed geometry models. A single-coating model, denoted as Sn-C (21 nm) and having the same spherical Sn particles size of 21 nm (with radius of 10.5 nm) as that in the Sn@SnO_x/C, has been simulated for comparison. Fig. 5(a), (b), (c) and (d) show the total plastic deformation distribution for C-milled Sn-C, P-milled Sn-C, Sn-C (21 nm) and O-P-milled Sn@SnO_x/C after fully lithiating of Sn, respectively. It can be observed that the total deformation of Sn increases, while that of the matrix decreases gradually from the core to the outer edge of the shell. The maximum displacement occurs in the contact interface between Sn and matrix marked in red in Fig. 5. It reveals that the weakest site of these Sn-C electrodes is the contact interface

between Sn and matrix, which coincides with the theoretical damage distribution in Sn/Si-matrix systems reported by Dimitrijevic et al.[28]. The C-milled Sn-C shows the maximum deformation of 12.4 nm, while 7.71 nm in the P-milled Sn-C, and 3.87 nm in the Sn-C (21 nm) model. As for the Sn@SnO_x/C, the maximum total deformation is very small and just 2.17 nm, indicating that the *in-situ* generated stiff Li₂O layer is an ideal matrix to buffer Sn expansion in Sn-C nanocomposites.

Fig.5 Total plastic deformation distribution after fully lithiation in Sn for unit model of (a) C-milled Sn-C, (b) P-milled Sn-C, (c) Sn-C (21 nm), (d) O-P-milled Sn@SnO_x/C composites.

The deformations of the outer edge in carbon matrix in these Sn-C models also show difference, with 8.6 nm in the C-milled Sn-C, 1.8 nm in P-milled Sn-C, and 0.26 nm in Sn-C (21 nm), while the Sn@SnO_x/C has the smallest of 0.22 nm. **Fig. 6(a)** shows the strain distribution in matrix after full lithiation in Sn for the Sn-C unit model, with the zero spot representing the contact interface between Sn and the matrix. Correspondingly, the strain of graphite matrix, 0.25 mm/mm, is the largest in C-milled Sn-C,

and they are 0.21 and 0.18 mm/mm in P-milled Sn-C and Sn-C 21 nm, respectively, while it is only 0.12 mm/mm in the double-coating Sn@SnO_x/C. **Fig. 6(b)** shows the distribution of volume expansion ratio for Sn-C unit calculated from Fig. 6(a). The volume expansion ratio of Sn (zero spot) are 170%, 166% and 156% in C-milled Sn-C, P-milled Sn-C and Sn-C (21 nm), respectively. But it is clear that much smaller volume expansion, being 76% and only half of that in the single-coating Sn-C (21 nm), suffered for the Sn in the double-coating Sn@SnO_x/C. This further consolidates that Li₂O can buffer the Sn expansion efficiently in the Sn-C composites. Therefore, it could be understood that, in the single-coating Sn-C model (Fig.3(c)), the core/shell structure is more stable as with smaller particle size of Sn core, while the double-coating structure with a stiff layer coated the same size Sn is more stable than the single-coating one. Thus, Sn@SnO_x/C has much better ability to maintain its good coating structure and superior capacity retention after long cycling compared with the C-milled Sn-C and P-milled Sn-C anodes.

Fig.6 (a) Strain distribution in matrix after full lithiation in Sn for Sn-C units. (b) Volume expansion ratio distribution after fully lithiated in Sn for Sn-C units.

In order to confirm the structural stability predicted by the simulation analysis, the microstructure of Sn-C electrodes after 50 cycles was characterized by SEM and TEM. **Fig. 7(a), and (b)** show the back-scattered electron SEM images for the C-milled Sn-C, and P-milled Sn-C, respectively. In Fig. 7(a), it is clear that there are many clusters of Sn or Sn-Li whiskers (marked with arrows) in the cycled C-milled Sn-C electrode. In the cycled P-milled Sn-C, as shown in Fig. 7(b), the Sn particles are still very fine and

1 dispersive in the graphite matrix even with partially small aggregations. In contrast, as shown in **Fig.7(c)**
 2 **and (d)**, the Sn particles remain much finer in the cycled $\text{Sn@SnO}_x/\text{C}$, without any obvious aggregation of
 3 Sn on the surface of electrode. TEM images as given in **Fig. 8(a), (b) and (c)**, show more detail
 4 microstructure changes in the C-milled Sn-C, P-milled Sn-C, and $\text{Sn@SnO}_x/\text{C}$ electrodes after cycling.
 5 Completely different from the original structure with Sn dispersing in carbon shown in Fig. 1(a), Sn
 6 whiskers could be detectable and they have fractured the C-milled Sn-C after 50 cycles as shown in
 7 **Fig. 8(a)**. The SAED pattern (inset in Fig.8(a)) reveals that the whisker consists of LiSn compounds.
 8 Compared with those in Fig. 1(b) and (c), it can be found that the typical structures of the cycled P-milled
 9 Sn-C and $\text{Sn@SnO}_x/\text{C}$ maintain their original microstructures with ultrafine Sn particles dispersing in
 10 graphite as shown in **Fig. 8(b) and (c)**. For the P-milled Sn-C, the EDS detected mass ratio of Sn: C is
 11 close to 1:1, meeting well with the original composition. However, some rich-graphite regions can also be
 12 observed in the cycled P-milled Sn-C, as marked by “C” in Fig. 8(b), which should be related to the
 13 coarsening of Sn during cycling. In the cycled $\text{Sn@SnO}_x/\text{C}$, as revealed by dark-field image (inset in Fig.
 14 8(c)) and magnified TEM image in **Fig. 8(d)**, all the nanosized Sn particles are well embedded in the
 15 graphite matrix. These further demonstrate that the C-milled Sn-C shows the most unstable structure while
 16 the $\text{Sn@SnO}_x/\text{C}$ delivers excellent structural stability, which is well consistent with the above deformation
 17 distribution analysis and electrochemical performance evaluations.

Fig.7 Back-scattered SEM images for delithiated electrodes after 50 cycles: (a) C-milled Sn-C, (b) P-milled Sn-C, (c) and (d) O-P-milled Sn@SnO_x/C.

Fig.8 TEM images and SAED pattern (inset) for the electrodes after discharge-charge 50cycles. (a) C-milled Sn-C; (b) P-milled Sn-C; (c) and (d) O-P-milled Sn@SnO_x/C.

3.4 The growth of Sn whiskers in the Sn-C composite and its mechanism

To figure out the Sn/LiSn growth process of the whiskers, the microstructure changes of the cycled C-milled Sn-C electrodes at different lithiation and delithiation states were *ex-situ* characterized by SEM. It is apparent that, as shown in **Fig. 9(a) and (b)**, the Sn particles exist in spherical shape after the first cycle in the C-milled Sn-C. However, the C-milled Sn-C shows distinctly different microstructure after 20 cycles. The number of Sn particles decreases dramatically in the view of SEM observation as shown in **Fig. 9(c)**. This is because that the Sn particles have been peeled off from the carbon matrix, which is resulted by the large deformation in the C-milled Sn-C. Moreover, the Sn spheres turn into clusters, indicating the aggregation of the remaining Sn during cycling. After 30 cycles, as shown in **Fig. 9(d)**, whiskers could be observed on the surface of the cycled C-milled Sn-C electrode.

As reported before, Sn crystal growth was observed in SnO₂ nanowires by *in-situ* TEM[21], and crystalline Sn whiskers could grow on Sn film in Sn-based anodes after cycling [22]. In electrical devices, it is well known that Sn whisker grows spontaneously out from the surface of tin plate coating film, and it is widely accepted that this is in response to a mechanism of stress relief within the tin plating[29, 30]. Accordingly, we speculate that the whisker formation in Sn-C electrode during long-term cycling should be similar to the Sn whisker growth in electronics. The indispensable conditions for tin whisker growth are the free Sn source and the compressive stress as a driving force [31-33]. As illustrated in **Fig. 9(e)**, there are plentiful free Sn in the C-milled Sn-C because the originally fine Sn particles aggregate to form coarse Sn particles. In addition, Sn suffers from compressive stress due to the volume expansion resulting from the reaction of Sn and Li⁺. As revealed by the simulation results, the weakest spot is the interface between Sn and matrix, thus the Sn could break through the restriction of the graphite matrix to aggregate under the stress effect. In this case, Sn clusters extrude out from the weak spots in the surface of the electrode to form whiskers during lithiation/delithiation process [22, 34]. But those aggregated Sn particles or Sn whiskers

still remains electric contact and lithiation activity reacting with Li^+ to form Li_xSn due to the surrounding of carbon. Nevertheless, the brittle Li_xSn cracks easily and falls down on the electrode surface, and then lose electrical contact and delithiation activity as the cycle number increased. In contrast, for the $\text{Sn}@\text{SnO}_x/\text{C}$ composite, the Sn also suffer from compressive stress, but the Sn particles are much finer and restricted by a stiff Li_2O layer which dispersed uniformly in the graphite, thus there is no enough Sn source to form large aggregation. This is the reason why no Sn whiskers grow in the cycled $\text{Sn}@\text{SnO}_x/\text{C}$ electrode even after 50 cycles. Therefore, aggregation of the refined Sn is the most vital factor for Sn whisker formation in Sn-C electrodes during cycling. To enhance the capacity retention of Sn-C composites, it is of great importance to design a suitable Sn-C structure to avoid the long diffusion of Sn and the Sn whisker growth.

Fig.9 SEM images for cycled C-milled Sn-C in different states: (a) lithiation state after the first

discharge, (b) delithiation state after the first charge, (c) delithiation state after 20 cycles, and (d) delithiation state after 30 cycles. (e) Sn whisker growth mechanism in cycled Sn-C electrodes

3.5 The double-coating structural design for Sn-C electrodes

Structural design is conducted with the aim of achieving stable microstructure and capacity for the Sn-C electrodes. As shown in **Fig.10 (a)**, we set the radius of Sn particles and the thickness of matrix as “ R_1 ” and “ R_2 ”, respectively. After full lithiation of Sn, the expansion deformation of Sn edge (zero spot in Fig. 6) is set as ΔR_1 , which is equal to the maximum of compressed deformation of the matrix inner edge; and the expansion deformation of the whole unit is ΔR_2 , which is equal to the deformation of the matrix outer edge. To avoid Sn whisker growth, it needs to meet a basic criterion of $2\Delta R_1 \leq R_2 + \Delta R_2$ so that Sn cannot break through the matrix and aggregate directly.

Fig.10 (a) Schematic of the Sn-C core-shell structure after full lithiation; **(b)** the relationship between ΔR_1 and R_1 ; **(c)** the relationship between ΔR_2 and R_1 when $R_2 = 40$ nm including a 10 nm Li_2O layer for double-coating Sn-C.

Fig.11 (a) The relationship between ΔR_1 and R_2 ; (b) the relationship between ΔR_2 versus R_2 for Sn-C units with a fixed $R_1 = 8, 10.5$ and 25 nm.

Based on the experiment results suggesting that the Sn@SnO_x/C can maintain its coating structure and perform high capacity, the variation of the total deformation versus R_1 in the double-coating Sn-C is investigated by simulation for $R_2 = 40$ including a 10 nm Li₂O layer. **Fig. 10** (b) and (c) show the relationship between ΔR_1 and ΔR_2 versus R_1 , respectively. ΔR_1 linearly increases along with R_1 when R_2 is fixed, and the fitting function is $\Delta R_1 = 0.292 R_1 - 0.93$ (nm). ΔR_2 rises exponentially along with R_1 according to the fitting function of $\ln(\Delta R_2) = 2.438 \ln(R_1) - 7.23$. **Fig. 10(b)** shows the volume expansion ratio of Sn on the right hand side vertical axis for the double-coating Sn-C with different R_1 values and a fixed R_2 . The volume expansion is less than 99% when $R_1 \leq 25$ nm, which is acceptable for alloy electrode design. **Fig. 11(a) and (b)** show the variation of ΔR_1 and ΔR_2 versus R_2 in different Sn-C units with a fixed R_1 ($R_1 = 8, 10.5$ and 25 nm). All the ΔR_2 - R_1 and ΔR_2 - R_2 curves could be fitted by functions as shown in Fig. 11. It can be found that the ΔR_1 extremely slightly decreases, while the ΔR_2 decreases exponentially as R_2 increases. Thus, it is a high priority strategy to obtain Sn-C composites with smaller Sn and thicker matrix in terms of microstructure stability. However, it should be necessary to keep enough Sn mass ratio to ensure high capacity of Sn-C anodes. **Table 2** lists the theoretical capacity and the deformation of matrix

outer edge for a double-coating Sn-C with $R_1 = 10.5$ nm. This would be a brief guidance for designing Sn-C anodes with good combination of high capacity and good cycle ability.

Table 2 The capacity and deformation of matrix outer edge of Sn-C when Sn particle size $R_1 = 10.5$ nm for a double-coating model.

R_2 (nm)	Theoretical capacity (mAh/g)	The deformation of matrix outer edge (nm)
30	739	0.33
35	605	0.26
40	534	0.21
45	492	0.18
50	464	0.15

4. Conclusion

For the Sn-C nanocomposite electrodes, Sn particles tend to aggregate to form Sn clusters or whiskers due to the Sn extruding from the carbon matrix resulted by volume expansion, which leads to the capacity fade during long-term cycling of electrode. It has been demonstrated that the maximum deformation of electrode during lithiation occurs in the contact interface between Sn and carbon matrix. For the double core/shell structured Sn@SnO_x/C composites, which have a structure with Sn nanoparticles coated in a stiff Li₂O layer embedded uniformly in graphite after the first cycle, can maintain the better mechanical stability and capacity retention than the single-coating structural Sn-C composites. With the help of simulation of the internal stress in core/shell structure, as well as controlling the size and distribution of Sn, it could be a possible strategy to obtain double-coating Sn-C composites with smaller Sn particles embedded in matrix with large elastic modulus and proper thickness, as a long-life and high capacity anode for lithium ion battery.

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