Tracking the phase transformation and microstructural evolution of Sn anode using *operando* synchrotron X-ray energy-dispersive diffraction and Xray tomography

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Abstract

Tin (Sn) holds great promise as an anode material for next-generation lithium (Li) ion batteries but suffers from massive volume change and poor cycling performance. To clarify the dynamic chemical and microstructural evolution of Sn anode during lithiation and delithiation, synchrotron X-ray energydispersive diffraction and X-ray tomography are simultaneously employed during Li/Sn cell operation. The intermediate Li-Sn alloy phases during de/lithiation are identified, and their dynamic phase transformation is unraveled which is further correlated with the volume variation of the Sn at particleand electrode-level. Moreover, we find that the Sn particle expansion/shrinkage induced particle displacement is anisotropic: the displacement perpendicular to the electrode surface (z-axis) is more pronounced compared to the directions (x- and y-axis) along the electrode surface. This anisotropic particle displacement leads to an anisotropic volume variation at the electrode level and eventually generates a net electrode expansion towards the separator after cycling, which could be one of the root causes of mechanical detachment and delamination of electrodes during long-term operation. The unraveled chemical evolution of Li-Sn and deep insights into the microstructural evolution of Sn anode provided here could guide future design and engineering of Sn and other alloy anodes for high energy density Li- and Na-ion batteries.

Keywords: Sn anode; Li-Sn phase transformation; X-ray tomography; Operando X-ray diffraction; Anisotropic displacement; Digital volume correlation (DVC)

1. Introduction

With the increasing demands for advanced batteries of higher energy density, lower cost and longer lifetime, battery electrode materials that could offer higher capacities than graphite anode and transition metal oxides (e.g. $\text{LiNi}_{0.33}\text{Mn}_{0.33}\text{Co}_{0.33}\text{O}_2$) hold enormous promise [1,2]. Different from conventional graphite anodes that are based on intercalation mechanism, alloying reaction based on elements in group IVA in periodic table like silicon (Si) and tin (Sn) that form the alloy phase of Li_{4.4}M (M = Si, Ge and Sn) have gained extensive attention for decades due to their relatively high theoretical capacities [3,4]. Amongst them, metallic Sn anode offers a relatively good electronic conductivity ($8.7 \times 10^6 \text{ S m}^{-1}$), a theoretical capacity of 994 mA h g⁻¹ and a low operation voltage, and is thus regarded as a promising anode candidate for next-generation batteries [5].

However, the practical use of Sn anode has been hampered by its massive volume variation (theoretically ~260%) during repetitive Li insertion (*i.e.*, lithiation, $\text{Sn} + x\text{Li}^+ + xe^- \rightarrow \text{Li}_x\text{Sn}$, $0 < x \le 4.4$) into and Li extraction (delithiation) from Sn [6]. This drastic volume change, on one hand, directly leads to severe particle pulverization and the mechanical detachment of the electrode composition from current collectors. On the other hand, it induces an unstable solid electrolyte interface (SEI) layer on the Sn particles and thus results in a low Coulombic efficiency [7,8]. These issues together lead to the low reversible discharge/charge capacities and poor cycling performance during long-term battery operation.

To address these challenges, extensive efforts have been devoted in the last decade and several approaches have been proposed, such as Sn size control [9], optimization of electrolyte composition [10], and rational design of electrode architecture [11,12]. Specifically, compared with micrometer-sized active materials, nano-sized Sn particles have been demonstrated to be able to effectively promote a homogeneous lithiation and delithiation in single particles, mitigate the structural strain/stress change, and improve overall structural stability. Electrolyte additives like fluoroethylene carbonate (FEC) could help remove the highly oxidized carbon compounds and facilitate the formation of a relatively stable SEI layer, thus improving the cycling performance [10]. In addition, various Sn-based composite anodes, e.g., Sn-Si [13,14], and Sn-carbon [9,12,15], have been designed to suppress or tackle the drastic volume change of Sn anode. Although these endeavors have improved the cyclability of Sn-based anode materials, their practical use in achieving long-term stable operation is still challenging, which is fundamentally rooted in the poor reversibility of Sn de/lithiation and the concurrent massive volume change.

To ultimately address these issues, it is critical to fundamentally clarify the dynamic alloying and dealloying mechanisms of Sn anode, i.e., the electrochemical lithiation/delithiation mechanisms. Regarding the Li-Sn alloy phases, relevant binary Li–Sn phase reports [16,17] have identified a series of intermetallic phases at elevated temperatures, including Li₂Sn₅, LiSn, Li₇Sn₃, Li₅Sn₂, Li₁₃Sn₅, Li₇Sn₂ and Li₂₂Sn₅ with increasing Li content. Nevertheless, previous studies using *in-situ* XRD on Sn thin-film electrodes [18] or Sn nanoparticles [19] have only uncovered three intermetallic phases during electrochemical lithiation, i.e., Li₂Sn₅, Li-Sn and Li₂₂Sn₅, while the other Li-Sn phases were regarded energetically unfavorable and thus were not detected during electrochemical reactions. Lopez *et al.* [20] confirmed the three resolved intermetallic phases using *operando* and *ex-situ* ⁷Li NMR, and furthermore, they unraveled the formation of several other phases, i.e., Li₇Sn₃, Li₅Sn₂, Li₁₃Sn₅, and Li₇Sn₂. However, among these newly detected phases, only Li₇Sn₃ was confirmed by a recent report using the same technique [21], making the detailed alloying mechanisms of Sn debatable and inconclusive.

Moreover, it is well known that the volume variation of alloy anodes could lead to interfacial delamination of the active composite layer from the current collector, which could result in a rapid capacity fading [22,23]. For instance, synchrotron X-ray (nano-)tomography [24,25] has been employed, and has successfully enabled the visualization of the gradual delamination of Si composite-based electrodes from the current collector in 3D. However, due to a lack of suitable characterization tools, it is still poorly understood how the volume change of active materials induces the delamination of the electrode. Therefore, it is highly necessary to elucidate the particle and electrode volume evolving behaviors and more importantly, their interplays with the interfacial delamination that deteriorates the long-term cell performance.

Herein, using synchrotron X-ray energy-dispersive diffraction and X-ray tomography (CT) simultaneously under operando conditions, we clarify the dynamic evolution of the phase transformation of intermediate Li–Sn phase during lithiation and delithiation. Compared with lab-based X-ray diffraction, synchrotron X-ray energy-dispersive diffraction in transmission offers a higher temporal resolution and better signal-to-noise ratio due to high X-ray flux. Furthermore, dynamic volume variation of single Sn particles during de/lithiation is tracked and quantified, and is further correlated with the mean particle volume change calculated based on over 2000 particles. Moreover, to the best of our knowledge, we for the first time discovered the anisotropic displacement of Sn particles and anisotropic volume variation of

the Sn electrode. We conclude that this anisotropic volume variation at electrode level results in a higher stress/strain at the interface between the Sn composite electrode and the current collector, leading to the electrode delamination during long-term cycling. The revealed dynamic Li-Sn phase transformation and the anisotropic spatial evolution of individual Sn particles and overall Sn electrode provide new insights for understanding the operation and degradation mechanisms of Sn-based electrodes, and may also shed light on the future development of Sn anodes and other alloying anodes based Li or sodium batteries.

2. Experimental

2.1. Materials

Metallic lithium, Celgard® 2325, polyvinylidene difluoride (PVDF) and carbon black were purchased from MTI Corp., USA. Sn particles and the electrolyte of 1 M LiPF₆ with a mixture of ethylene carbonate (EC) and ethyl methyl carbonate (EMC) (1:1, v/v) were received from Sigma-Aldrich. The housing for the battery made of polyether ether ketone (PEEK) was purchased from Distrelec Schuricht GmbH.

2.2. Cell assembly and electrochemical measurements

The Sn composite electrode was made from slurries that contain Sn particles, carbon black and PVDF binder (45:45:10, wt%) with NMP as dispersion solvent. The slurries were cast on stainless steel before being stored at 65 °C for 20 h to remove NMP solvent. After drying, the free-standing Sn composite electrode was weighted before cell assembly in an Ar-filled Mbraun glovebox. To build the tailor-made cells for X-ray tomography and diffraction measurements, Li disks (2.5 mm diameter, 400 μ m thick), Celgard® 2325 (3.0 mm diameter) and Sn composite electrodes were used as an anode, separator and cathode, respectively. A volume of 30 μ l electrolyte was added before cell sealing. Assembled cells were transferred to the beamline end station and underwent galvanostatic cycling using an Ivium CompactStat station at a current density of 57.2 mA/g for discharge and 28.6 mA/g for charge in the voltage range of 0.01-2.0 V. The current density for cell dis/charge is calculated based on the mass of Sn.

2.3. Synchrotron X-ray tomography and diffraction

Synchrotron X-ray tomography and X-ray diffraction were conducted at the EDDI beamline of BESSY II, Helmholtz-Zentrum Berlin, Germany. This EDDI beamline provides a hard and white X-ray beam generated by 7T multipole wiggler in the X-ray energy range of about 6-120 keV [26]. The detector system is comprised of a 200 µm thick LuAG:Ce scintillator, a Schneider Optics macro lens, and a PCO DIMAX high speed camera with a 2000 × 2000 pixel CMOS chip that locates out of the beam by using a mirror. The optic lens has a magnification of 4.4, generating a pixel size of 2.5 µm. A small exposure time of 0.018 second and a decreased region of interest has been chosen to minimize the beam dose. Synchrotron X-ray tomography and energy-dispersive diffraction were simultaneously conducted every \sim 15 min during the experiments. Each diffraction and tomography scan took \sim 75 s during which the operando cell rotated slightly over 180°. The energy-calibrated diffraction spectra were dead-time corrected to compensate for intensity variations in the incident beam and the channel intensities were grouped in the lattice parameters associated with their energies. After subtracting an interpolated background, a stripe correction, to compensate for the deviating channel widths, and normalization, the intensity plot, arranged consecutively over time, is obtained in logarithmic representation to highlight the lower intensities from the Li-Sn phases accompanied by the strongly scattering Fe and Sn peaks. Therefore, the detailed phase evolution of Sn anode during the first cycle is obtained by operando synchrotron X-ray energy-dispersive diffraction and the detailed Li-Sn phases could be identified. Due to limited beamtime, the structural stability of the generated intermediate Li-Sn phases and their effect on the battery performance could be further studied in the following work.

2.4. Data reconstruction and image analysis

The obtained projections were normalized and reconstructed via filtered back projection using an inhouse reconstruction algorithm written in IDL 8.2. To conduct Sn particle volume analysis, the reconstructed 3D datasets were binarized and segmented followed by particle volume and diameter analysis using software Fiji. The 3D volume rendering of the subvolume was obtained using VGStudio MAX 3.1. The 3D volume displacement was visualized and quantified using XDigitalVolumeCorrelation Extension in Avizo 2020.2. The SEM measurement of Sn particles was performed using Zeiss Merlin, after gold sputtering for 120 s to increase the electronic conductivity.



3. Results and discussion

Fig. 1. The setup for the operando measurement. (a) A schematic of the end station of EDDI beamline at BESSY II. (b) SEM micrography shows the morphology and the size distribution of Sn particles. (c) A radiograph projection displaying the structure of the operando Li/Sn cell from lab micro-CT. (d) 3D rendering of the Li/Sn cell at pristine state obtained at the EDDI beamline; the Sn anode (bottom, colorful Sn particle mixed with carbon/binder matrix (dark grey)), separator (middle, green), and Li electrode (top, light grey).

To reveal and track the compositional and structural evolution of Sn anode during de/lithiation, operando synchrotron X-ray diffraction and tomography of a Li/Sn cell were simultaneously conducted at the Energy-Dispersive DIffraction (EDDI) beamline [26] at BESSY II. As a schematic of the EDDI beamline end station shows in Fig. 1, the incident polychromatic X-ray beam (white beam with a broad X-ray spectrum) is directed on the electrochemically operating Li/Sn cell. The diffracted and transmitted X-rays are collected by the Ge detector and the imaging detector system, enabling the composition resolving and 3D microstructure visualization at the same time under operando conditions [27]. In our experiment, a customized tomography cell (tomo-cell) is designed and employed to meet the characterization guidelines [28,29]. During the assembly of the Li/Sn cell, a composite Sn electrode consisting of spherical Sn particles, carbon black and PVDF binders in a weight ratio of 45:45:10 was used. Fig. 1(b) shows that the Sn particles are sphere-shaped, and the analysis of its size distribution suggests that the Sn particles are generally $\leq 45 \ \mu m$. After cell assembly, laboratory micro-computer tomography (CT) was initially used to scrutinize the cell before operando measurements at EDDI beamline, and a radiography of the Li/Sn cell is shown in Fig. 1(c). Afterward, the cell was mounted on the sample stage at the synchrotron beamline for operando measurements, and Fig. 1(d) shows a 3D rendering of the Li/Sn cell at pristine state. Clearly, a Celgard separator (green) is sandwiched by a Li electrode (grey) and the Sn composite electrode where dark grey denotes carbon/binder matrix and Sn particles are rendered with pseudo colors.



Fig. 2. The dynamic Li-Sn phase transformation during lithiation and delithiation. (a) The voltage profile (blue) during the first cell discharge and charge as well as the mean particle volume variation (red dots) of over 2000 particles. (b) The corresponding diffraction data of the Li/Sn cell during the first cycle, during which in total 100 diffraction scans are implemented. For clarity, two magnified regions showing detailed evolution of the *d* values (c) between 2.26 and 2.44 Å, and (d) between 1.30 and 1.70 Å are provided.

To illustrate the detailed Sn alloying and dealloying process during lithiation and delithiation, the time-dependent contour map of the diffraction data of the Li/Sn cell, which is correlated with the voltage profile during the first discharge and charge of the Li/Sn cell, is analyzed and shown in Fig. 2. Specifically, in Fig. 2(a), the voltage profile (blue curve) depicts the cell's first discharge (blue shadow) and charge (light red shadow), corresponding to diffraction and tomography scan from #4 to #100. Meanwhile, the mean particle volume evolution (detailed calculation in supporting information) of over 2000 particles is plotted with red dots and fitted with a red curve in Fig. 2(a). The spikes on the voltage profile between 1.5 V and 0.5 V are associated with the repetitive exposure of the Li/Sn cell to the X-ray beam with energy roughly from 6 to 120 keV during the measurements. This is supported by the fact that the time interval for adjacent spikes and neighboring X-ray scans are both around 15 min. These voltage spikes during beam exposure commonly exist in operando (synchrotron) X-ray imaging studies [30,31] on battery and fuel cells. In this work, the spikes could be largely attributed to the attenuation of the X-rays by the Sn particles as well the partially exposed stainless steel current collector that may induce transient temperature increase [32]. Correlating the voltage profile with the particle mean volume change, no obvious Sn alloying reactions occur at the beginning of the discharge until scan #30, corresponding to the voltage range between 2.25 and 0.25 V. In this voltage range, decomposition of electrolyte commonly occurs, forming an SEI layer on the particle surface [33]. On this basis, we could conclude that the practical Sn lithiation occurs mostly between scan #30 and scan #71. The corresponding practical lithiation capacity is 567 mA h g⁻¹, accounting for 60 % of the whole discharge capacity (943 mA h g⁻¹). Similarly, based on the voltage profile and the particle mean volume change curve, it can be deduced that the subsequent practical delithiation capacity is around 275 mA h g⁻¹, corresponding to the volume shrink period of Sn particles and making up 67% of the whole charge capacity (412 mA h g⁻¹), as shown in Fig. 2(a). Similar to the discharge process, the remaining 33% of the charge capacity corresponds to a voltage range (between 1.1 and 2.0 V) where side reactions involving electrolyte usually occur, facilitating the formation of a thick and stable SEI layer in the 1st cycle.

Fig. 2(b) gives an overview of the diffraction contour map, while Fig. 2(c) and 2(d) show the zoomed-in evolution of *d* values in two small ranges, i.e., 2.26–2.44 Å and 1.30–1.70 Å, representatively. In addition to the Fe (111), (200) and (220) peaks at *d* values of 2.09, 1.81 and 1.28 Å that are originated from the steel current collectors and are strongest due to their scattering ability, other diffraction signals of the PEEK housing (2.48, 2.18 and 1.68 Å), the LiPF₆ in the electrolyte (2.17 and 1.63 Å) and the Li anode (2.48 Å), which are present over the entire period, can be seen. In Fig. 2(b), the diffraction peaks of Sn (200), (101), (112) and (312) at 2.92, 2.79, 1.48 and 1.20 Å between scan #1 and scan #30, which are stable in position, exemplarily confirm that the lithiation of Sn before scan #30 is negligible. Starting from scan #30, as indicated by *d* values at 2.79 Å (Fig. 2b) and 1.44 Å (Fig. 2d), several diffraction peaks belonging to pure Sn (Sn(101) peak at 2.79 Å in Fig. 2b) gradually narrow, weaken and eventually vanish around scan #50.

With the proceeding of lithiation, diffraction peaks attributed to Li-Sn intermediate phases appear. Several different alloying phases can be identified in the Li-Sn phase evolution map (Fig. 2b-d), such as Li₂Sn₅, LiSn, Li₇Sn₃, Li₅Sn₂, Li₁₃Sn₅, Li₇Sn₂, Li₁₇Sn₄. Specifically, from scan #30 a first peak appears shortly below 2.3 Å in Fig. 2(c), which remains until the end of the cycle with two short interruptions between scan #35 and #40, as well as #75 and #80, which can be assigned to the phase Li₂Sn₅. Also from about scan #30 onwards, two peaks appear at 2.34 and 2.36 Å (Fig. 2c), each caused by two diffraction reflexes of the planes ($\overline{1}04/020$) and ($212/\overline{3}12$) of the phase Li₂Sn₃. In the further course, peaks appear at somewhat higher and lower d values. Here, the (110) and (107) reflexes of Li₅Sn₂ at 2.37 and 2.33 Å in Fig. 2(c), respectively, are worth mentioning, which are among the most intense of this phase. A further broadening up to scan #60 by the appearance of peaks at 2.38, 2.32 and 2.31 Å is caused by the formation of the Li₇Sn₂ phase. From scan #60, the intensity in the upper part of the conglomerate (Fig. 2c) decreases until the end of the cycle, indicating the evolution of Li₇Sn₃, Li₅Sn₂ and Li₇Sn₂ phases before the end of the charge. Between scan #65 and #75, there is an increase in intensity in the range between 2.33 and 2.36 Å, which can be assigned to the phases Li₁₃Sn₅ and Li₇Sn₃. Although two of its most intense peaks of the highly lithiated phase Li₁₇Sn₄ are superimposed by the peaks from the phase Li₇Sn₂, the peaks at 2.41 Å and, in particular at 2.27 Å that appears at almost the end of the lithiation in Fig. 2(c) could confirm the existence of $Li_{17}Sn_4$. Fig. 2(d) shows the appearance of peaks in the range between 1.5 and 1.54 Å from scan #35 onwards, which can be assigned to the LiSn phase. Signals of the Li₇Sn₃ phase also appear in the region around 1.36 Å, as well as a few scans later at 1.47, 1.55, 1.57, 1.65 and 1.67 Å. The reflections measured in the further course above 1.36 Å in Fig. 2(d) are assigned to the phases Li_5Sn_2 and Li_7Sn_2 , those below to the phase $Li_{13}Sn_5$. In the end, from scan #80 onwards, reflections assigned to the Li₂Sn₅ phase also appear here at 1.62, 1.44 and 1.31 Å.

During delithiation, the broad region at around 2.34 Å that is attributed to the different Li-Sn phases gradually narrows with the proceeding of delithiation, as shown in Fig. 2(c), forming a broad peak around 2.34 Å in the end. Meanwhile, *d* values at 2.79 Å (Fig. 2b) and 1.44 Å (Fig. 2d) attributed to Sn reappear in the diffraction map but possess a weaker peak intensity compared to the corresponding peaks at the pristine state. In addition, the LiSn phase also has lattice planes with these spacings. This together with the remaining Li_2Sn_5 signals at the end of the delithiation demonstrates that the particles are not fully delithiated with a portion of Li trapped within the particles. In addition, the diffraction pattern clearly reveals that the dominant compositions that remain at the delithiated state are Li_2Sn_5 and LiSn, as seen from the numerous diffraction peaks over the entire recorded spectrum in Fig. 2(b).



Fig. 3. The volume change and evolution of Sn particles. (a) 3D rendering of five representative particles after lithiation. (b) The volume expansion rate of the 5 particles (P1-P5) after lithiation as well the net expansion after the 1st cycle. (c) For ease of comparison, the volume evolution of three particles (P1, P2, and P5) is present and is compared with the particle mean volume change ratio of over 2000 particles in the Sn electrode of Li/Sn cell. The volume evolution of P3 and P4 is shown in Fig. S3.

Accompanying the Li-Sn chemical evolution of the Sn particles in Fig. 2 is their severe volume variation during de/lithiation. To illustrate this, we randomly chose five representative adjacent Sn particles (particle #1 to #5 denoted thereafter as P1 to P5), and their volume variations analysis results are shown in Fig. 3. Specifically, Fig. 3(a) shows the 3D rendering of these five particles at their pristine state. Fig. 3(b) illustrates the volume expansion ratio of these five particles after the first lithiation (orange bars) and their net volume expansion ratio after the first cycle (green bars). It is clear from Fig. 3(b) that the P2-P5 underwent a volume expansion of respectively 38%, 30%, 22% and 30% after the first lithiation. These 4 particles did not shrink back to the pristine volume after the first cycle with an averaging net volume expansion ratio of around 22% (Fig. 3b). These non-zero net expansion ratios suggest a small volume change during delithiation compared with lithiation, which agrees well with a smaller capacity during delithiation (Fig. 2a). In comparison, P1 has a much smaller volume expansion ratio of only 4.8% after the first lithiation and a negligible volume change thereafter, leaving a net particle expansion of 4.7% at the end of the first cycle. A smaller than average expansion ratio of P1 suggests a lower lithiation extent within the particle compared with P2-P5, implying that the depth of lithiation is particle-dependent (e.g., different particle reactivity, different particle size and morphology, and varying chemical/electronic environment around particles).

Furthermore, the dynamic volume change of five single particles (P1-P5) during the de/lithiation as well as the mean volume change of over 2000 particles are tracked and compared (Fig. 3c and Fig. S3), exhibiting different volume variation behaviors. Specifically, P2 and P5 (Fig. 3c) as well as P3 and P4 (in Fig. S3) exhibit a similar volume change behavior: they retain their particle sizes at the initial stage (from scan #1 to around #40 in Fig. 3c), and then start to expand with a similar slope roughly between scan #41 and scan #58 until reaching the maxima of the volume at around scan #58; unlike the evolution of the mean volume change (red plot in Fig. 3c), for P2 and P5 a period with almost negligible shrinkage (c.a. between scan #71 to #80) can be observed during the initial delithiation before evident volume decrease. In contrast to the volume change dynamics of P2-P5, P1 reaches its maximum particle size earlier at around scan #55 with small volume change both during lithiation and delithiation. Regarding the discrepancies of volume evolution among single particles (P1-P5) and the different volume change behaviors at particle- and electrode-level, we emphasize that the mean particle volume evolution represents the overall volume change of over 2000 Sn particles, while the volume change behaviors of single particles could be largely affected by the locally varying physicochemical environment surrounding them. It has been reported that the locally varying environment of the electronic (carbon matrix) and ionic conductivity (electrolyte distribution) around the electrode particles are essential for the de/alloying reactions [33] as well as the reactivity of the particles (e.g., inert particles [34]).

Apart from single particles, the mean particle volume evolution of over 2000 Sn particles is acquired to represent the overall particle volume dynamics at the electrode level, as shown in Fig. 3(c). The

mean particle volume change starts from scan #30 where the lithiation plateau (0.25 V) appears (Fig. 2a), and reaches its peak at the end of lithiation (scan #71) with an expansion rate of ~37%. During the subsequent delithiation, the mean particle volume decreases immediately without showing a volume stable period, and yields a net volume expansion ratio of around 26%. This irreversible volume change at electrode level directly results from a smaller delithiation capacity of the overall Sn electrode (275 mA h g⁻¹) compared with the lithiation capacity (567 mA h g⁻¹). Although a delithiation current density was set as half of the lithiation current in order to maximize the Li extraction from lithiated Sn particle, around 51.5% of Li were still trapped in the Sn particles at the end of delithiation, calculated based on the practical lithiation (567 mA h g⁻¹) and delithiation capacity (275 mA h g⁻¹). Therefore, strategies that could increase and, more importantly, maintain a high reactivity of the Sn throughout the repetitive de/lithiation are expected to exhibit good reversibility and cycling performance.

It is widely acknowledged that remarkable volume change of alloving type anode materials like Si, Ge, and Sn could induce deformation of the whole electrode [4,35]. However, it is poorly understood how the particle expansion/shrinkage impacts the deformation of the electrode. In Fig. 4, we unravel the particle volume variation induced particle displacement and the anisotropic volume variation behavior at the electrode level. In Fig. 4(a-c), the particle locations after lithiation and delithiation with their pristine positions are compared. In-plane (x-y plane) and cross-sectional (x-z plane) views from these three states are provided, with the Sn particles' initial positions highlighted with blue contours in both in-plane and cross-sectional views for comparison. A careful examination among the in-plane and cross-sectional views reveals a difference regarding the particles' motion during de/lithiation: an evident particle displacement can be found along the zaxis while the particle motion in the x-y plane is relatively small. This indicates that the particles' expansion does not accumulate in the x-y plane and can be well accommodated by their surrounding carbon/binder matrix. In addition, evidenced by the region highlighted by a red dashed square in Fig. 4(b), particles adjacent to the separator tend to have a larger shift along the z-axis compared with particles near the current collector. This could be attributed to the accumulated volume expansion along the z-axis starting from the current collector (steel rods) at the Sn electrode side.

Besides the particle displacement, we further visualize and quantify the volume variation of the Sn electrode. Fig. 4(d-f) shows the separator position in cross-section views at three different states as well as a comparison among them, which can be used to indicate the volume variation of the Sn electrode along the z-axis. Assuming the separator has a stable thickness during the de/lithiation, by comparing Fig. 4(d and e), we found Sn electrode expands for 9.3 pixels (c.a. 23.3 μ m) along the z-axis towards the Li electrode during the lithiation process, while the shrinkage during delithiation (Fig. 4e-f) is around 3.2 pixels (i.e., 8.0 μ m) along the z-axis. The smaller shrinking value in thickness of the Sn electrode during delithiation generates a net expansion of the electrode along the z-axis after the first cycle (indicated by the three dashed lines in Fig. 4f), which agrees well with the electrode expansion at another region shown in Fig. S4.



Fig. 4. The anisotropic displacement of Sn particle and the anisotropic volume variation of the Sn electrode. The virtual in-plane and cross-section view of a sub-volume at (a) pristine state, (b) after lithiation, (c) after delithiation. For position comparison of particles between different states, blue contours showing the pristine positions of particles are superimposed on the images in panels (a-c). Note that the cross-sectional views in panels (a-c) show the same region at different states, and their discrepancy in image height is the result of predominant electrode expansion along the z-axis. (d-f) The separator position at pristine, lithiated and delithiated state is marked with red, green and blue dashes lines. (g) The dashed lines from the three different states are superimposed on the cross-section view of the lithiated state for comparison. 3D visualization and quantification of the spatial volume variation of Sn electrode during (h) lithiation (expansion) and (i) delithiation (shrinkage), using a vector field obtained from digital volume correlation. The vector field is color-coded based on the displacement magnitude of an array of the cuboids that are divided from a sub-volume (250 × 250 × 66 voxels at pristine state) of the Sn electrode during digital volume correlation analysis. Each vector indicates the direction and length of the displacement of a corresponding cuboid. For ease of visibility, all the vectors are rescaled by a factor of 2 during visualization. The overall net volume change of Sn electrode after the first cycle is shown in Fig. S5.

To further unravel the volume variation of the electrode in 3D space, digital volume correlation (DVC), a commonly used method to compute the local geometric change of 3D image datasets, is employed and the results are shown in Fig. 4(h-i) and Fig. S5. A sub-volume of $250 \times 250 \times 66$ voxels at the pristine state from the Sn electrode is used during the DVC analysis, and this sub-volume is further divided into a matrix of cuboids. For each cuboid, a corresponding vector is employed to indicate the motion direction of the cuboid with the length of the vector (rescaled by a factor of 2 during visualization) suggesting the relative motion distance. Note that Fig. 4(h) shows

the displacement results comparing the lithiated state with the pristine state (lithiation process), while Fig. 4(i) represents the displacement comparing the delithiated state with the lithiated state (delithiation process). From Fig. 4(h), it can be found that the whole sub-volume of the Sn electrode has a larger volume expansion along the z-axis during the lithiation process, in line with the particle displacement shown in Fig. 4(a-c). In addition, the displacement extent of the divided cuboids along the z-axis appears to be proportional to the distance to the current collector (z = 0), namely, the further the cuboid from the current collector, the larger the displacement distance (green/blue vectors vs. yellow/orange vectors in Fig. 4h). Fig. 4(i) shows that the displacement of the whole sub-volume during the delithiation is generally smaller than that in the previous lithiation (Fig. 4h). This is also supported by the shift of the separator shown in Fig. 4(d-g) and Fig. S4. The relatively larger extent of volume expansion of the Sn anode after the first lithiation process (Fig. 4h) together with the smaller extent of volume shrinkage of the Sn anode after the first delithiation process (Fig. 4i) collectively results in a net volume expansion of the Sn anode after the first cycle, as shown in Fig. S5. This net irreversible volume expansion originates from a smaller particle shrinkage rate during delithiation that is closely related to the smaller capacity during delithiation (electrochemical curve in Fig. 2a).

The prominent displacement along the z-axis can be rationalized by several aspects. Firstly, the high aspect ratio of the electrode (~2500 μ m in diameter vs. ~200 μ m thick) could lead to a relatively less volume accommodation capability along the z-axis. Assuming that Sn particles expand uniformly in 3D and the carbon/binder matrix can accommodate volume expansion of Sn uniformly in x, y, and z-axis, a high aspect ratio of the electrode (meaning the diameter is much larger than the thickness of the electrode) will lead to a higher volume change accommodation ability across x-y plane, due to more carbon/binder matrix that exists across x-y plane than that along z-axis. Secondly, as the Li/Sn cell is physically confined between two steel rods (Fig. 1c), given its high malleability Li foil is prone to mechanically deform and creep along the x-y plane during the expansion of the Sn electrode, which eventually facilitates the expansion of Sn electrode towards Li along the z-axis [36,37]. Thirdly, the electro-dissolution of Li foil, which will be discussed in the next section, could generate pit-shaped cavities on the Li surface, and these cavities could to some extent, induce a favored local displacement of Sn electrode towards the Li surface along the z-axis.

Based on the aforementioned results, it can be concluded that the volume change induced anisotropic particle displacements during de/lithiation lead to an anisotropic volume change of the Sn/carbon/binder composite electrode (Fig. 4). Finite element modeling revealed that electrode volume expansion exerts greater stress at its contact area with the current collector than that in the bulk electrode [24]. In light of this, we can deduce that this z-direction (perpendicular to current collector) favored volume variation of the Sn/carbon/binder composite imposes a higher mechanical stress/strain at the interface area contacting the current collector compared with the stress/strain in the x-y plane within the Sn composite bulk. Therefore, the adhesive bonding between the Sn electrode and the current collector provided by the binder tends to gradually weaken and deteriorate during repetitive cycling, which eventually leads to the mechanical detachment and delamination of composite electrodes from the current collector during long-term operation.



Fig. 5. The interfacial evolution of Li anode. The virtual in-plane and cross-sectional view of Li surface at pristine (a and b), after first lithiation (c and d), and after first delithiation (e and f), respectively. For better visibility, the cross-sectional views are magnified to present a detailed interfacial structure. The white particles belong to Sn or lithiated Sn particles. Note that panel (b, d, and f) shows the same region at different states and their discrepancy in image height is due to predominant electrode expansion along the z-axis.

Apart from the chemical, volume and structure evolution of Sn electrode, Li anode also plays an important role in the irreversibility of the Li/Sn cell. The root cause for the poor electrochemical performance of metallic Li-based batteries is closely associated with the uneven and unstable Li plating and stripping during electrochemical cycling [38,39]. This uneven Li plating and stripping could not only lead to continuous electrolyte consumption due to notorious parasitic side reactions between electrolyte and fresh Li electrodeposits [40], but also dendritic structures [41,42] that could bring about cell short-circuit. In light of this, we further investigated the morphological evolution of Li anode and the results are shown in Fig. 5. At pristine state (Fig. 5a and b), one can note that the Li anode exhibits a smooth surface at micrometer level (Fig. 5a) and intimate contact between Li and separator can be observed from the cross-sectional view (Fig. 5b). After the first discharge process, pit-shape structures are formed at the Li anode side, as shown in Fig. 5(c and d). The inhomogeneous distribution of the pit-shape structures indicates an uneven electrochemical dissolution of Li [28,40,43]. These inhomogeneously distributed pit-shape structures on the Li surface could provide accommodation space for the volume-expanded Sn composite electrode and thus, to some extent, induce a favorable local expansion of the Sn electrode along the z-direction towards the pit regions. During the charging process of the Li-Sn cell, Li ions were extracted from Sn particles at Sn electrode while at the Li electrode Li ions electrochemically deposited on Li surface (Fig. 5e and f). As a thinner SEI layer is expected on the surface of the newly-exposed pits during electrochemical dissolution, these pits tend to be the preferential deposition sites, forming light grey deposits as indicated in Fig. 5(e and f). Instead of fully refilling, partial µm-sized pits are covered or filled with new Li deposition. This can be rationalized by a lower amount of Li deposition as a result of the decreased charge capacity.

We highlight that several Li-Sn intermetallic phases (e.g., Li₇Sn₃, Li₅Sn₂, Li₁₃Sn₅) are identified during the de/lithiation of Sn by *operando* synchrotron X-ray energy-dispersive diffraction in transmission mode in this work, but were not observed in previous *in-situ* XRD studies. This could be attributed to a better signal-to-noise ratio at the synchrotron X-ray beamline originated from a much higher X-ray flux, and a stronger X-ray penetration ability with a white beam (6-120 keV) at the synchrotron beamline compared to a laboratory-based XRD facility with a typical X-ray generator voltage of 40 kV. Nevertheless, there are also uncertainties in this measurement. One problem is that the main peaks of most Li-Sn phases occur at ~4 Å, i.e. in the low energy range, which leads to strong attenuation due to absorption in transmission geometry and thus poor comparability of intensities, making the quantitative estimation of the phase fractions very difficult. However, the occurrence of peaks gives a good indication of the formation of the associated phases. Another problem is the volume fraction of the Sn particles in combination with the small scattering volume, which on the one hand produces less diffraction signal and on the other hand less statistics from the measurement. Also, the superposition of closely neighbouring signals often makes it difficult to clearly separate individual phases, but this can usually be checked by the presence of reflections elsewhere in the spectrum.

Although the alloy-type anode materials (Si, Ge, and Sn) all undergo characteristic volume change during de/lithiation, discrepancies regarding their expansion behavior still exist. It has been previously reported that Si anodes could continue to expand during the initial stage of delithiation, and this expansion prolongation after the reverse of polarization has been explained by the different expansion mechanisms of the cores and outer regions of the cracked Si particles [33,44]. In contrast, the extent of the expansion of Sn anode peaks at the end of the lithiation process and no expansion prolongation is observed in this work. This discrepancy could be attributed to the enhanced structural integrity [45] of the Sn particles during the de/lithiation process, compared with Si particles that crack and pulverize repetitively. Without notable cracks, assuming a good electric conductivity around the Sn or Si particles and a low lithiation rate, the de/lithiation of intact Sn particles is likely to be kinetic-control, which is different from the cracked Si particles' scenario where the electrolyte diffusion within the particle cracks are non-negligible and the de/lithiation of cracked Si particles tend to be mixed kinetic-diffusion control even at a low current.

From the aforementioned results, it can be anticipated that a higher amount of Sn loading (45 wt% in this work) in the Sn anode could also lead to an anisotropic volume variation of the Sn electrode, as well as a more pronounced shift along the z-direction perpendicular to the current collector. Therefore, the unraveled anisotropic behaviors imply that when alloy-type material is mixed with graphite forming a composite anode to increase its practical capacity, a rational mass loading of the alloy-type materials is crucial rather than negligible, and should be optimized to avoid a sacrifice of the long-term cell performance.

Meanwhile, the current findings corroborate that strategies such as building a robust and elastic carbon/binder matrix [46,47] or 3D current collector [48] as well as designing hollow or core-shell structures that are able to accommodate the large volume variation of the alloy-type materials are expected to effectively mitigate or even suppress the irreversible volume expansion of alloy-type anodes.

Furthermore, it can be deduced that other alloy-type anode materials that suffer from massive volume change, e.g., Si and Ge anodes as well as their derived oxide and sulfide materials, could also exhibit such an anisotropic behavior at particle and electrode levels. In the last, we emphasize that the anisotropic particle displacement and volume variation may also be found during the alloying reactions with Na ions when the alloy-type anodes are used in Na-ion batteries. Therefore, the currently presented experimental findings and the accompanying informative implications are also applicable to the alloy-type anodes in Na-ion batteries.

4. Conclusions

Operando synchrotron X-ray energy-dispersive diffraction and X-ray tomography were simultaneously employed to clarify the chemical evolution of Sn and illustrate the microstructural evolution of Sn anode during lithiation and delithiation. Several intermediate alloying phases have been identified in the Li-Sn phase evolution map, including Li₂Sn₅, LiSn, Li₇Sn₃, Li₅Sn₂, Li₁₃Sn₅, Li₇Sn₂, Li₁₇Sn₄. Furthermore, we for the first time discovered the anisotropic displacement phenomenon of Sn particles and the concurrent anisotropic volume variation of the Sn composite electrode during lithiation and delithiation, showing a more pronounced motion or expansion along the direction perpendicular to the current collector (z-axis) compared to that laterally in the x-y plane within the electrode bulk. The z-axis (perpendicular to the current collector) favored volume variation of the Sn composite electrode could be one of the root causes that leads to the delamination of electrodes. Also, the expansion is found irreversible, generating a net expansion after the first cycle. Additionally, inhomogeneous Li stripping and plating at the Li electrode surface was

visualized, forming pit-like structure on the Li surface during Li stripping but was not fully re-filled by Li deposition. These results provide new understanding towards the phase, microstructural and mechanical evolution of alloy-type electrodes, and could guide future design and engineering of Sn anode and other alloy reaction based electrodes.

Author Contributions

K.D.: Conceptualization, Investigation, Data analysis and interpretation, Writing-Original draft preparation and Editing; F.S.: Conceptualization, Investigation, Data analysis and interpretation, Writing-Review and Editing; A.H.: 3D reconstruction, Image analysis; P.H.K.: Experiment assistance at beamline, Diffraction data analysis; M.O.: Image analysis and visualization, SEM measurement and analysis; F.G.M: Experiment assistance at beamline, Diffraction data analysis; I.M.: Conceptualization, Data analysis and interpretation, Supervision, Project administration, Funding acquisition.

Notes

The authors declare no competing financial interest.

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Graphic Abstract

Using synchrotron X-ray energy-dispersive diffraction and X-ray tomography, Li-Sn phase evolution during de/lithiation is identified, and the Sn expansion-induced particle and electrode displacement is found preferentially along z-axis.

