Highlighting a study on in situ TEM investigation of large crystals formation in lithiated SnO₂ anode assisted by electron beam irradiation by a group of researchers led by Prof. Kuibo Yin and Prof. Litao Sun from Southeast University.

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The formation mechanism of large Li₄.₄Sn crystals formed in lithiated SnO₂ particles and their suppressing methods are represented. The high Li⁺ concentration within the lithiated SnO₂ can promote the large Li₄.₄Sn’s formation. Theoretical calculation results revealed that the Li₄.₄Sn/Li₂O interface is unstable, which drives the aggregation of Li₄.₄Sn nanocrystals. Moreover, by reducing the Li⁺ concentration as well as by reducing the size of SnO₂ below 15 nm the formation of large Li₄.₄Sn crystals can be effectively suppressed.

In situ TEM investigation of large crystal formation in lithiated SnO$_2$ anode assisted by electron beam irradiation

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The formation of large crystals in an anode during the working cycle is harmful to the lithium-ion battery’s capacity and cycling performance. However, the underlying mechanism is not clearly revealed, which significantly hinders the development of strategies to suppress the formation of large particles. Here, we studied the formation mechanism of large crystals with the assistance of electron beam irradiation. The large crystal formed after the lithiation of SnO$_2$ was identified as Li$_{4.4}$Sn. The formation of such large Li$_{4.4}$Sn is significantly promoted by the high Li$^+$ concentration in the sample, which contributes to the formation of more Li$_{4.4}$Sn/Li$_2$O interfaces. Within the Li$^+$ supersaturation environment, a considerable number of Li$_{4.4}$Sn nanocrystals with larger size are formed. Theoretical calculation results revealed that the Li$_{4.4}$Sn/Li$_2$O interface is unstable, which thus drives the aggregation of Li$_{4.4}$Sn nanocrystals. Moreover, by reducing the Li$^+$ concentration and the size of SnO$_2$ below 15 nm, the formation of large Li$_{4.4}$Sn crystals can be effectively suppressed. This work reveals the formation mechanism of large crystals in lithiated SnO$_2$, which may supply enlightening insights into the structural engineering of tin-based anode materials.

1. Introduction

Lithium-ion batteries (LIBs) have been widely recognized as one of the most promising energy storage systems due to their high energy capacity and conversion efficiency. The past few decades have seen the soaring demands to develop high-performance anode materials for LIBs to replace the conventional graphite anode.\(^1\)–\(^5\) SnO$_2$ has attracted considerable attention as an ideal anode material for the next generation LIBs due to its easy feasibility, natural abundance, and high theoretical capacity (1494 mA h g\(^{-1}\)).\(^6\)–\(^8\) The superior electrochemical performance of the SnO$_2$ anode is attributed to its two-step reaction kinetics. First, the insertion of Li$^+$ drives the breakdown of the Sn–O bond to form reduced nano-sized Sn and amorphous Li$_2$O (SnO$_2$ + 4Li$^+$ + 4e$^-$ → Sn + 2Li$_2$O). After that, Li$^+$ further alloys with Sn to form the Li$_x$Sn nanocrystal (Sn + xLi$^+$ + xe$^-$ ↔ Li$_x$Sn).\(^9\)–\(^12\) However, the SnO$_2$ anode suffers from the aggregation of tiny Sn/Li$_x$Sn nanocrystals as the discharge/charge cycle progresses,\(^13\)–\(^15\) giving birth to the formation of large particles. These large crystals account for the crucial factor of the impairment of anode integrity,\(^16\)–\(^18\) and are the important contributor to the low coulombic efficiency (CE) of batteries,\(^19\)–\(^21\) resulting in the continuous decay in reversible capacity as the charge/discharge cycle progresses.

Numerous efforts have focused on alleviating the formation of large crystals in the SnO$_2$ anode, mainly by inhibiting the contact among the anode materials. By introducing a secondary transition metal or metal oxide phase in the form of composites,\(^22\)–\(^24\) as well as optimizing the working surface in the form of coating,\(^9\),\(^13\),\(^17\) multiple state-of-the-art nanoengineering techniques demonstrate their exceptional capability in suppressing the formation of large particles in the first few working cycles. However, the inhibition on the contact among anode materials could not sustain long-term working cycles, and the large crystals are likely to reappear.\(^9\),\(^20\),\(^21\) Consequently, it is important to develop a fundamental method to suppress the formation of large crystals. In terms of this goal, a deep understanding of the formation mechanism of the large crystals in the SnO$_2$ anode is of significant importance to guide the further design and preparation of tin-based LIBs. The in situ technique is indispensable in understanding the nanoscale mechanism due to its incomparable ability to capture the materials’ dynamic behaviors under mimicked conditions. Among various in situ characterization techniques, in situ transmission electron microscopy (TEM) has a powerful capability to disclose the
structural and compositional evolutions, which can be applied in analyzing the working mechanism of the electrochemical nanomaterials.26–28 Zhang and Liu et al. studied the growing mechanism of Sn particles during the electrochemical process in the SnO2 nanowire.29 During lithiation, the Joule heat resulted from a large current and the chemical bond breaking contributed to the aggregation of Sn nanoparticles. During delithiation, the high surface stress triggered the coarsening process. However, it is hard to adjust the discharge current and the surface stress distribution in the SnO2 nanowires in situ, which is of vital importance to derive a quantitative result. Moreover, only a narrow time window for investigating the intermediate state is reserved due to the fast and violent lithiation/delithiation process, which may hinder the observation and analysis of the tiny phenomenon. Electron beam irradiation, as one of the important energy sources in TEM, is extensively exploited to drive the in situ processes. For example, Cheong et al. used electron beam irradiation to directly drive the Sn particles’ coarsening in the SnO2 anode.28 Chang et al. investigated the kinetics of conversion and agglomeration of SnO2 nanoparticles under electron beam irradiation.31 The flexibility and controllability of electron beam irradiation is extremely beneficial for studying the mechanism of the nanocrystal aggregation in SnO2 and developing the corresponding solutions.

In this work, we identified the formed large crystals as Li4.4Sn, and further investigated the formation mechanism. Electron beam irradiation was exploited as the energy source to trigger the formation process. The formation of large Li4.4Sn crystals is closely related to the Li+ concentration in the sample. The high Li+ concentration drives the nanocrystals’ aggregation by creating an unstable Li4.4Sn/Li2O interface. The formation of large Li4.4Sn crystals can be effectively suppressed by reducing the Li+ concentration or by using smaller SnO2 particles as the anode. This work is expected to provide valuable insights into understanding the particle aggregation mechanism of tin-based LIBs during the working cycle, which might be helpful for guiding the design of a more robust and competitive energy storage system.

2. Experiment section

Materials synthesis

The small-sized 5 nm SnO2 nanoparticles were prepared via an one-pot hydrothermal method. In particular, 15 mmol SnCl2 was first added to 50 mL deionized water (DI water), followed by ultrasonication for 10 min. Subsequently, 4.5 mL KOH solution (1 M) was added dropwise into the as-prepared solution to obtain a white suspension. After being stirred for 12 h, the resulting suspension was transformed into a 100 mL autoclave, followed by a reaction at 150 °C for 48 h. Finally, the resultants were collected and washed by water and ethanol for several times.

The 30 nm and 50 nm SnO2 nanoparticles were prepared through the calcination of the 5 nm SnO2. To obtain 30 nm SnO2 particles, 0.15 g 5 nm SnO2 was dispersed into 30 mL DI water, followed by ultrasonication for 10 min. Graphene oxide solution (GO, 1.65 wt%, 0.61 g) was added into the suspension, and stirred for 12 h to ensure the efficient SnO2 adsorption onto the GO flake. The SnO2@GO composites were collected by centrifugation with water, and then calcined at 800 °C for 12 h. The 50 nm SnO2 particles were facely prepared by the calcination of 5 nm SnO2 at 800 °C for 12 h without the addition of GO.

Sample preparation and experimental setup

The in situ experiments were performed on a PicoFemto® Zues in situ biasing holder. The holder enables the investigation of the phase transition of the nanoscale battery in the TEM environment. The schematic diagram of the in situ electrochemical device is shown in Fig. S1. A half lacy carbon TEM grid was directly loaded on the holder. SnO2 particles with different sizes were dispersed onto the carbon grid via various methods. Particles larger than 50 nm were directly used as the sample of the in situ experiments. In comparison, smaller SnO2 particles and graphene were first dispersed into DI water with the weight ratio of 10 : 1. The suspension was then magnetically stirred for 12 h so that SnO2 particles can be uniformly loaded onto the graphene sheets. The SnO2@graphene composites were then collected via centrifugation, and used as the sample of the in situ experiments. The employed sample was dispersed in ethanol at a concentration of 1–2 mg mL⁻¹, followed by intensive ultrasonication for 10 min. Finally, the 50 μL suspension was dropped onto the clean half carbon grid. Both carbon grid and graphene can serve as the charge transporter, allowing for the conduction of ions and electrons between the anode and cathode, and the charge buffer, providing an extended time window for in situ observation. On the other side of the holder, a shaped tungsten tip was placed, by which the lithium metal cathode was scratched. The lithium metal was intentionally exposed to air (~2 s) to coat a thin film of Li2O that allows for transportation of the Li+ ion, serving as the solid electrolyte. In working conditions, the lithium source can contact the carbon grid or graphene by manipulating the piezo-driven stage through an external computer. As soon as the contact was made, a potential of −3 V was applied to the SnO2 electrode concerning the lithium electrode in the lithiation process. In comparison, a potential of +5 V was involved in the delithiation process.

TEM characterization

TEM characterizations were performed on an aberration-corrected FEI Titan 80/300 microscope equipped with a Gatan Quantum ER electron energy loss spectrometer. The investigation and identification of the phase of materials during in situ observations were assisted by selected area electron diffraction (SAED) and fast Fourier transformation (FFT). All the observations were performed at the accelerating voltage of 300 kV.

Theoretical calculation

The interface energy was calculated by using the Forcite package in BIOVIA® Materials Studio at the level of the molecular mechanics. The employed {700} facets of Li4.4Sn were
measured at 14.03 Å × 14.03 Å along the a- and b-directions, respectively. The amorphous models of Li2O and LixSnOy (x = 1, 2, 3, 4, 5, 6 and y = 1, 2) were built using the Anneal task in the Ewald electrostatic interaction. Calculations were performed until each self-consistency cycle was converged in energy to within 4.2 × 10^-6 eV. The interface energy between crystalline Li4.4Sn and amorphous was calculated by using the following equation:

$$E_{\text{interface}} = E_{\text{total}} - E_{\text{crystal}} - E_{\text{amorphous}}$$

The $E_{\text{interface}}$ is the resulting interface energy, $E_{\text{total}}$ is the total energy of the entire system, and $E_{\text{crystal}}$ and $E_{\text{amorphous}}$ stand for the energy of crystalline Li4.4Sn and amorphous Li2O and Li,SnOy (x = 1, 2, 3, 4, 5 for y = 1 and x = 1, 2, 3, 4, 5 for y = 2), respectively.

### Electrochemical measurement

The electrochemical measurement was conducted by assembly of CR2025-type coin cells. Pure lithium fill was used as the counter electrode. The electrolyte consisted of 1 M LiPF6 in a mixture of ethylene carbonate (EC)/diethyl carbonate (DEC)/dimethyl carbonate (DMC) (1 : 1 : 1 vol%). 1 vol% vinylene carbonate (VC) and 10 vol% fluoroethylene carbonate (FEC) were added to the electrolyte. The anodes were prepared via a slurry casting method. The active material, carbon black, and polyacrylic acid (PAA) were mixed at the weight ratio of 8 : 1 : 1 to form a homogenous slurry with N-methyl-2-pyrrolidone (NMP). The slurry was casted onto a copper foil at the mass loading rate of ~1 mg cm^-2 and being dried at 120 °C in a vacuum oven for 8 h. The cells were assembled in a nitrogen-filled glovebox and aged for 12 h to ensure full electrolyte interface (SEI) can be found on the particle surface (Fig. S3†). The lithiated sample was immediately irradiated by electron beam (dose rate: 2.0 × 10^2 Â m^-2 s^-1, duration: 7 min) with the lithium source removed, ensuring no lithium insertion during the irradiation. Under continuous electron beam irradiation, the lithiated sample gradually shrank, accompanied by SEI thinning. Finally, large crystals could be found in the sample. The Li-K EELS spectra (Fig. S4†) were collected to study the effect of lithium on carbon support on the lithiated SnO2 during irradiation. The Li^+ concentration was significantly reduced on the irradiated sample or the placed carbon support. In consideration that the volume of the lithiated SnO2 sample continuously decreased during irradiation and placement, the decrease in Li^+ concentration might result from the Li^+ diffusion out of the carbon area rather than the Li^+ insertion into the sample. Consequently, the impact of secondary Li^+ insertion into lithiated SnO2 from the carbon support can be safely ignored. Fig. 1d shows the TEM image of the lithiated SnO2 sample after irradiation. Three large crystals were observed. To identify the phase of the large crystals, a HRTEM image of one representative crystal was acquired and analyzed. This large crystal (Fig. 1e) exhibited an elliptical-like shape with the major axes of about 31 nm and minor axes of about 23 nm. The atomic resolution image (Fig. 1f) shows two mutually perpendicular lattices with interplanar spacings of 0.29 nm and 0.28 nm, respectively. This 2-dimensional (2D) lattice was previously reported and considered as the (200) and (020) facets of tetragonal metallic tin (JCPDS No. 65-2631).46 However, it is noteworthy that the facets of the lithium tin alloy Li4.4Sn, e.g., the Li4.4Sn (700) and (063) planes, can also exhibit similar lattice spacings and interplanar angle. Thus, it is unconvincing to assert that the large crystal formed after lithiation is composed of metallic tin. Further analysis is required to identify the solid phase.

After delithiation, as shown in Fig. 1g, three previously observed large crystals were still embedded in the amorphous matrix. Fig. 1h shows the elliptical delithiated large crystal more clearly. Compared to that before delithiation, the ellipse’s major axe was reduced to about 27 nm and minor axe reduced to about 21 nm, accompanied by the smooth edge. More importantly, the corresponding HRTEM image (Fig. 1i) indicated the lattice transformation from the previous cubic lattice to the hexagonal lattice, which can be exclusively identified as the (200) and (101) planes of tetragonal tin. These results indicate the large crystal formed after lithiation might consist of Li4.4Sn rather than metallic Sn.

To convincingly evidence the formation of Li4.4Sn after lithiation, three sets of 2D lattices were extracted and analyzed from a rotating nanocrystal (Fig. 2 and ESI Movie S1†). These 2D lattices were carefully compared with each possible candidate of cubic Sn, tetragonal Sn, or Li4.4Sn (see details in the ESI†). Table S1† shows that the only possible phase that satisfies the three sets of 2D lattices is cubic Li4.4Sn, which is reported as the theoretically final lithiation products of SnO2.74 Consequently, we identify the large crystal formed via electron beam irradiation as Li4.4Sn.
Effect of different irradiation parameters on the formation process
The effect of the electron beam irradiation intensity on the formation process is first discussed. The instantaneous dose rate of the electron beam (A m⁻²) passing through the sample is used to characterize the irradiation intensity. The dose rate is measured by a sensitive ammeter placed at the fluorescent screen, collecting the electrons passing through the sample. In our experiments, the dose rate was adjusted by manipulating the TEM magnification. As shown in Fig. S5, the dose rate increases quadratically with increasing magnification. Fig. S6 shows the lithiated SnO₂ particle after irradiating by various electron beam dose rates. The dose rate was raised from $1.19 \times 10^3$ A m⁻² to $2.19 \times 10^4$ A m⁻², and each session endured 180 s.

The freshly lithiated SnO₂ sample shown in Fig. S6a was completely converted into an amorphous phase due to ESA, accompanied by the formation of a thin SEI layer on the surface. During the initial three irradiation sessions, the sample remained amorphous, and no apparent changes were observed except the gradual decomposition of the SEI layer (Fig. S6a–c). However, as the beam dose rate was increased to $2.19 \times 10^4$ A m⁻², lateral structures with light contrast (marked in yellow areas) gradually grew upon the previously smooth surface. Such lateral structures might be Li metal, which is reduced from the Li₂O in the amorphous sample under electron beam irradiation with a high dose rate. As the irradiation time was extended (Fig. S6d), large spherical nanocrystals (marked in orange areas) gradually formed on the sample surface. The HRTEM image of the irradiated sample (Fig. S7b) shows that the
A nanocrystal exhibited a 2D lattice with the interplanar spacings of 0.38 nm and 0.20 nm at a lattice angle of 72°, exclusively corresponding to the {511} and {362} facets of Li₄.₄Sn. Moreover, the SAED image (Fig. S7c†) demonstrates a pair of diffraction spots with a lattice spacing of 0.28 nm, validating the presence of Li₄.₄Sn's {362} facet. Both results suggest the observed large crystals after irradiation as Li₄.₄Sn.

The effect of the cumulative amount of electron beam irradiation on the formation of large crystals was also investigated via a controlled experiment. The cumulative irradiation is characterized by the electron dose (C m⁻²). Fig. S8† shows a lithiated SnO₂ particle irradiated by an electron beam with an extended time under a moderate beam dose rate. Similar to the samples in Fig. 1 and S3,† the freshly lithiated SnO₂ sample in Fig. S8† was immediately irradiated by electron beam with the lithium source and bias removed. The irradiation dose rate was 6.13 × 10⁴ A m⁻² and the irradiation time was 30 min. As mentioned before (Fig. S4†), the lithium on the carbon grid in such situation cannot cause a significant effect on the lithiated sample. It can be seen in Fig. S8† that although the electron beam irradiation results in volume reduction, surface destruction, and inhomogeneous contrast in the sample, no large crystal formation was observed. The sample's low crystallinity was further confirmed by the SAED image, in which only weak diffraction rings could be observed. The controlled experiment has demonstrated that the effect of a higher cumulative irradiation dose on the lithiated SnO₂ sample is far less significant than that of an intense electron beam dose rate, suggesting the dose rate threshold in the formation process.

The electron dose rate on the nucleation and growth kinetics was extensively researched in the era of the in situ graphene liquid cell TEM (GLC-TEM) system.⁴⁰–⁴² The high dose rate in the GLC-TEM environment can decompose the liquid solution and generate a supersaturated ionic species, which are favorable for crystal nucleation and growth. In addition, the nucleation process cannot be initiated under the low generation rate of the ionic species, even if a high cumulative dose is applied. Here, we assume a similar crystallization mechanism in our experiments as that in GLC-TEM, where the amorphous matrix after lithiation serves as the liquid solution in GLC-TEM. A high-energy electron can break the chemical bonds in the amorphous matrix to generate free atoms for crystal nucleation and growth. However, these free atoms may be consumed by re-bonding to the amorphous matrix. By increasing the electron dose rate, the possibility of chemical bond breakage is increased, which further results in a higher generation rate of free atoms. As the generation rate exceeds a certain threshold (the intrinsic consumption rate of the system), the nucleation and growth of crystals are triggered.

It should be noted that the method of exploiting electron beam irradiation to study the formation process can mimic the real formation mechanism of Li₄.₄Sn in working condition. Electron beam irradiation can supply the energy for the formation of large Li₄.₄Sn crystals. The irradiation dose rate threshold (2.19 × 10⁴ A m⁻²) found in this article is not far away from the current density reported to drive large Sn formation in SnO₂ nanowires during lithiation (20 A cm⁻²).²⁹ Such divergence might arise from the difference in the sample's...
dimension. The reported SnO2 nanowires were hundreds of nanometers in width and tens of micrometers in length, while the SnO2 nanoparticles in this article were only tens of nanometers in size. Meanwhile, electron beam irradiation is now widely applied as the trigger of nanoscale reaction in various in situ experiments. Park et al.48 and Huang et al.49 used electron beam irradiation to induce the electrochemical reaction between Na/Li and the anode materials in the in situ open cell battery. Seo et al.48 and Chang et al.50 exploited electron beam irradiation to drive the lithiation of SnO2 in the in situ G/LC-TEM system. All these reports have proven the good consistency between the in situ and ex situ results. Thus, the formation mechanism of large Li4.4Sn crystals investigated with the assistance of electron beam irradiation can provide a reliable reference for an actual working SnO2 anode.

Effect of placement on the formation mechanism of large Li4.4Sn crystals

Of the many controlled experiments, it is interesting to note that no large crystals were formed during the subsequent irradiation session if we removed the electron beam source and deliberately placed the lithiated amorphous SnO2 sample for enough time. This phenomenon is further described in Fig. S9.† The freshly lithiated sample was totally converted to the amorphous phase due to the ESA (Fig. S9af). The sample was deliberately placed in a TEM column for 30 minutes with the lithium source removed and the electron beam turned off. As Fig. S9bf demonstrates, the sample remained amorphous after the placement. The placed sample was later irradiated by an electron beam with a dose rate of 1.19 × 10⁵ A m⁻² for 15 minutes. Nevertheless, after the irradiation, no large crystals were found, and only the formation of nanocrystalline Li4.4Sn was confirmed by the SAED (Fig. S7cf). This finding demonstrates that placing the sample without electron beam irradiation cannot significantly affect the amorphous structure. Moreover, the standing sample demonstrated more robust tolerance to the electron beam irradiation.

To probe the structure and phase transformation of the deliberately placed SnO2 sample, a set of controlled experiments were carefully designated, as schematized in Fig. 3m. The pristine SnO2 particle was first lithiated to the amorphous phase and labeled as the 1st sample. The freshly lithiated 1st sample was deliberately placed in a TEM column for 60 minutes with the lithium source removed, and the electron beam was turned off. Afterward, the 1st sample underwent 25 minutes irradiation (EELS characterization, dose rate: 2.0 × 10⁵ A m⁻², 15 min, intensive irradiation, dose rate: 1.32 × 10⁵ A m⁻², 10 min). After irradiation, the 1st sample was re-lithiated and labeled as the 2nd sample. The 2nd sample underwent the same experimental procedure as the 1st sample, except that placement was shortened to 30 minutes. After the irradiation, the 2nd sample was further irradiated for the third time and labeled as the 3rd sample. Unlike the previous step, the freshly lithiated 3rd sample was immediately irradiated by an electron beam with the same irradiation condition as the former two samples.

The structure and phase evolution in the 1st, 2nd, and 3rd samples were studied via TEM and SAED analyses. Diffraction rings of the sample are highlighted by the colorful dash-line circles in Fig. 3d, h, and i. After carefully analyzing these three SAED patterns, it was found that all diffraction rings could be assigned to a corresponding facet of Li4.4Sn. Moreover, the diffraction rings with a lattice spacing of 0.280 nm (red dash-line circle in Fig. 3h, orange dash-line circle in Fig. 3i) and 0.294 nm (red dash-line circle in Fig. 3i) match well with the Li4.4Sn’s {630} and {700} facets, which are two representative facets of Li4.4Sn, as analyzed above (Fig. 1f, 2b and c). All these findings confirm the formation of crystalline Li4.4Sn in the 1st, 2nd, and 3rd lithiated samples. The 1st sample was initially amorphous phase (Fig. 3a and b). After the placement and irradiation (Fig. 3c), the sample underwent volume shrinkage, which might be caused by the irradiation-induced lithium diffusion out of the sample.46 The SAED image in Fig. 3d suggests that only a small number of Li4.4Sn crystallites with extremely tiny size were embedded in the amorphous matrix. The volume of the amorphous 2nd sample expanded violently due to the re-injection of Li⁺. After irradiation, numerous nanocrystalline Li4.4Sn were found, disclosed by the {842} ring of Li4.4Sn in the SAED. However, despite the crystal nucleation, these nanocrystals’ ensuing coarsening was not triggered, as reflected from the absence of a large visible crystal. The nanocrystalline 2nd sample returned to be mainly amorphous after the 3rd lithiation with only a small amount of diffraction spots, which can be recognized in the SAED. These diffraction spots are possibly ascribed to the remaining nanocrystals in the 2nd lithiated particle, which is not re-converted to an amorphous form during the ESA. After the immediate irradiation, the apparent formation of large crystals was confirmed by the TEM and SAED images. It is suggested that the observed nanocrystals of the 2nd sample act as the intermediate phase in the formation of large crystals of the 3rd sample.

EELS analyses were introduced to investigate the variance in the chemical status of the samples. The EELS spectra were sequentially collected under the same experimental conditions on the same sample after the 1st, 2nd, and 3rd lithiation, where the same thickness of the analyzed region can be assumed. Consequently, the concentration of Li⁺ ions can therefore be directly compared by using the raw intensity data.47 The EELS spectra of the sample with different placement times are illustrated in Fig. 3n with different colors. It can be clearly observed that the Li⁺ concentration decreases with the increase of standing time, proving our previous assumption that the lithium ions can diffuse out during placing. Meanwhile, the fine structure shows a clear difference in the spectra of freshly lithiated samples to standing samples. In both 1st and 2nd samples, the Li–K edge spectra showed a major peak at 65 eV, indicating a similar phase of the amorphous matrix in the deliberately placed samples. However, the Li–K edge spectrum of the 3rd lithiated sample demonstrated two peaks at 59 eV and 65 eV, respectively, and a broad shoulder from 68 eV to 80 eV, well-matched with the previously reported EELS spectrum of Li2O.47,48 The intense Li2O peak in the 3rd sample demonstrates that the amorphous form in fresh lithiated SnO2 was partly
composed of Li₂O, in accordance with previous reports. However, after being left for standing for a certain period, Li₂O almost disappeared. Other amorphous unknown Li-containing materials then formed the amorphous lithiated SnO₂. Such change in material phase might be caused by the continuous diffusion of Li⁺ or the spontaneous phase transition in a low-energy environment without electron beam irradiation, which is left for further study. Lee et al. also observed a similar transformation in the chemical status.

They further proved that the new Li-containing phase is different from LiH, LiOH, and Li₂CO₃. Considering the incomplete participation of LiSn crystals in the 1st and 2nd samples, it is assumed that the Sn element is present in an amorphous form in the standing sample. As a result, the molecular formula of the new amorphous phase is inferred as LiₓSnO₉.

The high concentration of Li⁺ ions is assumed to be a key reason for forming large Li₄.4Sn crystals in the lithiated SnO₂. As reflected from the SAED patterns in Fig. 3d and h, Li₄.4Sn nanocrystals with increased dimension and number were formed in the 2nd sample compared to that in the 1st sample. This finding demonstrates that the Li₄.4Sn’s formation is significantly facilitated by the high Li⁺ concentrations. Such preference in formation is understood based on the classic nucleation theory, in which the supersaturation dramatically

Fig. 3 Formation process of Li₄.4Sn large crystals in the lithiated SnO₂ particle. The TEM and SAED images of the 1st (a and b) and 2nd (e and f) lithiated sample before irradiation show the amorphous phase of both samples. The TEM image (i) also confirms the 3rd sample before irradiation to be mainly amorphous with only a small number of nanocrystals, as suggested by the SAED pattern (j). However, different structures and phase evolutions are observed in the 1st (c and d), 2nd (g and h), and 3rd (k and l) samples after the irradiation. The schematic experiment setup is illustrated by (m). (n) Li–K edge EELS obtained in the lithiated sample after 60 min’s placement (black line), 30 min’s placement (red line), and 0 min’s placement (blue line).
contributes to the nucleation of crystals. Meanwhile, the amorphous Li$_2$O (a-Li$_2$O) only exists in the sample with higher Li$^+$ concentration. To explore the role of a-Li$_2$O in the formation progress of large Li$_{4.4}$Sn, the interface model between the (700) plane of crystalline Li$_{4.4}$Sn (c-Li$_{4.4}$Sn) and different amorphous (a-Li$_2$O and a-Li$_x$SnO$_y$) was built, as shown in Fig. 4a. In consideration of the continuous loss of Li and O in the TEM environment, the ratio of Li and O in a-Li$_x$SnO$_y$ were set to be within a certain range, rather than fixed values. The simulated interface energy of Li$_{4.4}$Sn towards a different amorphous form is shown in Fig. 4b. The interface energy between {700} of c-Li$_{4.4}$Sn’s and a-Li$_x$SnO$_y$ fluctuated with Li content. On the other hand, as O increases, the interface becomes more unstable. However, the interface energy towards a-Li$_x$SnO$_y$ was always significantly lower than that towards a-Li$_2$O, regardless of the Li and O atomic ratio changes. This finding demonstrates that with the same interface area, the net energy of c-Li$_{4.4}$Sn/a-Li$_x$SnO$_y$ is always lower than that of c-Li$_{4.4}$Sn/a-Li$_2$O. The unstable c-Li$_{4.4}$Sn/a-Li$_2$O interfaces are more prone to coarsen in order to reduce the total interface area. Consequently, the formation of coarse particles becomes favorable in the freshly lithiated sample since more c-Li$_{4.4}$Sn/a-Li$_2$O interfaces exist in the fresh sample.

Size effect of SnO$_2$ on the formation mechanism of large Li$_{4.4}$Sn crystals

It should be noted that the size of the SnO$_2$ particles might have significant effects on the formation kinetics. Three sets of controlled experiments were performed on SnO$_2$ particles with different sizes (15 nm, 30 nm, and 50 nm), as illustrated in Fig. 5. The freshly lithiated samples were immediately irradiated by electron beam with a dose rate of 1.32 × 10$^7$ A m$^{-2}$ for 700 s. Time-resolved TEM images were acquired to probe the structure evolution during irradiation. The 15 nm and 30 nm SnO$_2$ particles were assembled by nanocrystals. After lithiation, the nanocrystalline assembly was transformed into the

![Fig. 4](image-url) Molecular dynamic simulation of the interface between the crystalline Li$_{4.4}$Sn (700) plane and various amorphous structures. (a) Optimized atomic structures for the interface of c-Li$_{4.4}$Sn/a-Li$_x$SnO$_y$ ($x = 1, 2, 3, 4, 5, 6$ for $y = 1$ and $x = 1, 2, 3, 4, 5$ for $y = 2$) and c-Li$_{4.4}$Sn/a-Li$_2$O. (b) The simulated interface energy. The results reveal that a-Li$_x$SnO$_y$, compared with a-Li$_2$O, can significantly stabilize the crystal/amorphous interface.
amorphous phase and merged as a whole. Fig. 5a–d shows the structure evolution of the small 15 nm lithiated SnO₂. During the irradiation, the sample underwent a volume decrease and shape reconstruction. Nevertheless, no crystal structure was observed, proved by both HRTEM and FFT images. The small lithiated sample remained amorphous even after irradiation for 700 s. As for the medium 30 nm SnO₂ particle (Fig. 5e–h), many tiny crystalline seeds were immediately formed after being irradiated. With the extension of the irradiation time, the formation of one 8 nm nanocrystal was confirmed by HRTEM, accompanied by the disappearance of other crystal seeds. Finally, after irradiation for 700 s, only two nanocrystals were left, as indicated by the deficiency of diffraction spots in the FFT (inset in Fig. 5h). Fig. 5i–l demonstrates the structural evolution of the 50 nm lithiated SnO₂ particle under irradiation. After irradiation for 260 s, a large crystal was observed in the amorphous matrix. The diffraction rings in SAED confirm the formation of many small nanocrystals besides the large visible crystal. With increasing irradiation time, the diffraction rings were gradually reduced to discrete spots, suggesting the small nanocrystals’ coarsening.

The formation process of large crystals in 50 nm SnO₂ is similar to the previously discussed one. Li₄.₄Sn nanocrystals were first formed under the electron beam irradiation. These nanocrystals further aggregated to large particles. As the size of SnO₂ reduced to 30 nm, the formation of numerous Li₄.₄Sn nanocrystals could be directly viewed (Fig. 5f). The size of these nanocrystals was around 5 nm, and they were relatively uniformly dispersed in the amorphous matrix. As the irradiation extended, these nanocrystals gradually aggregated into 8 nm crystals. However, after irradiation for 700 s, tiny Li₄.₄Sn nanocrystals were almost consumed, as reflected from the disappearance of diffraction spots in the FFT images. The aggregation process thus stopped naturally. Furthermore, the time-resolved distribution of nanocrystals in the 30 nm sample was analyzed. It was found that nanocrystals located near the surface were easily dissolved. Lifshitz et al. concluded this mechanism as the enhanced diffusion at the surface to dominate the competing dissolving/growing process. This kinetics becomes more significant in small-sized materials as the surface/volume ratio rises sharply. Therefore, with the dimension decreasing below 15 nm, Li₄.₄Sn nanocrystals become even more unstable, suppressing the formation of large crystals.

The electrochemical performance of SnO₂ with different sizes was evaluated. Fig. S10† shows the cycling performance of 5 nm SnO₂ and 50 nm SnO₂ anode between the voltage range of...
0.01 V and 3 V vs. Li⁺/Li. The cell was first discharged/charged under the current density of 50 mA g⁻¹ in the initial 5 cycles to activate the electrode material, and discharged/charged at 1000 mA g⁻¹ for the remaining 95 cycles. The 5 nm SnO₂ anode shows a stable cycling performance with the 20th capacity of 543 mA h g⁻¹ and the 100th capacity of 554 mA h g⁻¹. The CE of the anode is maintained above 99% during the 7th to 100th cycles. In contrast, the capacity of the 50 nm SnO₂ anode decreased continuously from 626 mA h g⁻¹ in the 20th cycle to 169 mA h g⁻¹ after the 100th cycle. During the 7th to 100th cycles, the lowest CE of this anode is as low as 95% and the highest CE is no more than 99%. These results demonstrate the improvement of the cycling stability and reversibility of the SnO₂ anode by reducing the particle size below 15 nm, in accordance with the superior electrochemical performance of the small-sized electrode materials reported in other literature studies.⁵,¹⁸

The batteries were dissembled in a nitrogen-filled glovebox after cycling under a charged state and characterized by ex situ TEM (Fig. S11†). The cycled 5 nm SnO₂ preserved its structure without any formation of large particles inside. The corresponding HRTEM (Fig. S11b†) discloses that nanocrystalline SnO₂ were embedded in the electrode, demonstrating the good reversibility of the 5 nm SnO₂ anode. In sharp contrast, numerous spherical particles were found in the cycled 50 nm SnO₂. Fig. S11d† shows two sets of lattice spacings of 0.29 and 0.21 nm, corresponding to the {200} and {220} facets of Sn. The formation of SnO on the 50 nm SnO₂ anode is consistent with the in situ observation (Fig. 1i). This comparison validates the higher structural stability and better reversibility of the small-sized SnO₂ anode, leading to its superior electrochemical performance. The X-ray photoelectron spectroscopy (XPS) data of 5 nm and 50 nm SnO₂ anodes after 100 cycles were also collected to investigate the chemical state of Sn in the employed samples (Fig. S12†). Both sets of spectra of the charged 5 nm and 50 nm SnO₂ anodes exhibit two intensive peaks around 495.2 and 486.7 eV, which can be assigned to the Sn 3d₅/₂ and Sn 3d₇/₂ of the pristine SnO₂,⁵³ respectively, demonstrating the presence of Sn⁴⁺ in both the electrode and indicating the reversibility of Sn to SnO₂. However, an obvious difference can be observed in the Sn 3d₅/₂ spectra of the discharged 5 nm and 50 nm SnO₂ anodes. The Sn 3d₅/₂ peaks of the discharged 5 nm SnO₂ shift to higher binding energy, while the peaks of discharged 50 nm SnO₂ shift to lower energy. Such difference may result from the formation of Li₂SnO₃ (peak centered at 487.0 eV) in the 5 nm SnO₂ anode, and the formation of Sn and LiₓSn (peak centered at 485.3 eV and ~484.5 eV, respectively) in the 50 nm SnO₂ anode.⁵⁴ These results agree well with the in situ results, demonstrating the outstanding ability of the 5 nm SnO₂ anode to suppress the formation of Li₄.₄Sn crystals.

Fig. 6 summarizes the formation mechanisms of the large Li₄.₄Sn crystal in lithiated SnO₂ particles with different placement times and different sizes. Electron beam irradiation with a considerable dose rate is used to drive the formation process. For large SnO₂ particles with the size surpassing 50 nm, the formation mechanism is closely related to the Li⁺ concentration in the sample. Not only does the Li⁺ supersaturation lead to the formation of numerous Li₄.₄Sn nanocrystals, but the a-Li₂O...
present in the high Li\(^+\) concentration environment can also destabilize the nanocrystals’ interface and induce particle aggregation. The Li\(^+\) concentration can be modulated by placing the fresh lithiated SnO\(_2\) for a certain time. As the placing time was extended, the Li\(^+\) concentration in the sample decreased, resulting in the reduced number and dimension of the Li\(_{4.4}\)Sn nanocrystals. More importantly, the c-Li\(_{4.4}\)Sn/a-Li\(_2\)O interface present in the low Li\(^+\) concentration environment stabilizes the Li\(_{4.4}\)Sn nanocrystal and effectively blocks the aggregation. It was also found that reducing the size of SnO\(_2\) below 15 nm can suppress the formation of large crystals. Li\(_{4.4}\)Sn nanocrystals in small SnO\(_2\) become exceptionally unstable due to the increased surface/volume ratio, and tend to dissolve in the amorphous matrix. Consequently, small lithiated SnO\(_2\) can show robust tolerance to any formation of crystalline structures, even under intense electron beam irradiation.

4. Conclusion

In summary, we have elucidated the formation mechanism of large crystals in the lithiated SnO\(_2\) particles with the assistance of electron beam irradiation with a considerable irradiation dose rate (2.19 \times 10^4 \text{ A m}^{-2}). The large crystals were identified as Li\(_{4.4}\)Sn. The high Li\(^+\) concentration in lithiated SnO\(_2\) was revealed as one of the key contributors to the formation via in situ TEM and EELS analyses. The supersaturation created in the high Li\(^+\) concentration environment promotes the Li\(_{4.4}\)Sn nanocrystals’ formation. Meanwhile, the unstable c-Li\(_{4.4}\)Sn/a-Li\(_2\)O interfaces enhanced the aggregation of the nanocrystals. By placing the lithiated sample in the TEM column for a certain time or by reducing the size of the pristine SnO\(_2\) below 15 nm, the formation of large Li\(_{4.4}\)Sn can be suppressed and the structural stability of the lithiated SnO\(_2\) anode can be boosted. Our results can provide valuable insights into the kinetics of the large crystal coarsening in the tin-based anode, which is of great significance for the rational design of next-generation LIBs.

Conflicts of interest

There are no conflicts to declare.

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References

18 B. B. Jiang, C. P. Han, B. Li, Y. J. He and Z. Q. Lin, ACS Nano, 2016, 10, 2728–2735.