Pulverization is a major cause of the capacity fade and poor cyclability of Sn-based anodes in lithium-ion batteries. We study the structural evolution of Sn nanoparticles during electrochemical lithiation-delithiation cycling by in situ transmission electron microscopy (TEM). The β-Sn nanoparticles in the size range of 79–526 nm are lithiated to the crystal Li$_2$Sn phase via a two-step mechanism, and no cracking or fracture is observed, distinct from the lithiation-induced fracture in micron-sized Sn particles. Lithiation can induce the aggregation of small Sn nanoparticles with diameter in tens of nanometers, while delithiation can lead to the pulverization of large Sn nanoparticles. Similarly, the aggregation and pulverization of Sn nanoparticles are also observed during sodiation and desodiation, respectively. The delithiation/desodiation induced pulverization of Sn nanoparticles is attributed to the high deallloying rate that results in cracks and voids in deallloyed Sn anodes. Based on our in situ TEM results, a size-dependent pulverization mechanism of Sn particles is proposed. Our work advances the mechanistic understanding of the pulverization and degradation mechanisms of Sn particle-based electrodes in Li-ion batteries.

We observe a two-step lithiation mechanism without cracking or fracture in Sn NPs with a wide size range of 79–526 nm. In addition, we find that small Sn NPs can fuse together during lithiation. Also, small NPs are frequently generated from the mather NPs during delithiation, leading to pulverization. Similar pulverization processes are also observed during sodiation-desodiation cycling. Based on in situ observations, a size-dependent pulverization mechanism of Sn particles is proposed, shedding light onto how the Sn particle-based electrodes degrade in Li-ion and Na-ion batteries.

**Experiments and Results**

Figure 1a shows a schematic of the nanoscale battery setup in TEM. The Sn NPs with different diameters (purchased from Skyspring Nanomaterials Inc.) are single crystals with a tetragonal lattice structure (β-Sn), as shown in our recent work.26 They are dispersed on a platinum (Pt) rod to serve as the working electrode. The bulk Li metal on a tungsten (W) rod is used as the counter electrode, and the native Li$_2$O on the Li surface acts as the solid electrolyte. This all-solid setup enables a real-time observation of the structural evolution in individual NP electrodes during electrochemical cycling.26–30 The experiments are conducted under either the electron beam-on condition with a low current density or the beam-blank condition, so as to reduce the beam effect on the lithiation-delithiation processes. A negative potential of −1 V is applied against the Li electrode to initiate the lithiation. Figure 1b–1h shows the typical structural changes of Sn NPs during the first lithiation. The lithiation of Sn NPs is dominated by a two-step mechanism, similar to the sodiation of Sn NPs.26 That is, Sn NPs are initially lithiated with a limited volume expansion, yielding a Li-poor amorphous Li$_x$Sn (α-Li$_x$Sn) phase (Figure 1b–1e); then they are further lithiated with a much larger volume expansion, resulting in the final product of a Li-rich crystalline Li$_2$Sn$_3$ (c-Li$_2$Sn$_3$) phase (Figure 1e–1h). More specifically, in the first step of lithiation, a phase boundary migrates (indicated by the yellow arrows in Figure 1e–1d), pristine Sn is consumed, forming a new α-Li$_x$Sn phase. After the phase boundary sweeps through the entire Sn NP, the volume expansion only...
reaches ∼55%, indicating a relatively low Li content in the resultant α-Li,Sn phase. In the second step of lithiation, the α-Li,Sn phase is further lithiated without an observable phase boundary. The final product after full lithiation is c-Li22Sn5, giving a total volume expansion of ∼239% relative to pristine Sn. Figure 1i shows the electron diffraction pattern (EDP) after full lithiation, which is identified as the c-Li22Sn5 phase with a cubic structure. The inserted curve in Figure 1i is the simulated powder diffraction of the c-Li22Sn5 phase, which agrees well with the measured EDP. (j) High resolution TEM (HRTEM) image, fast Fourier transform (FFT) pattern and inverse FFT (IFFT) image of the product c-Li22Sn5 phase. The HRTEM image is taken from another sample.

Table I. Measured volume expansions after the first step of lithiation and the full lithiation.

<table>
<thead>
<tr>
<th>Pristine NP sizes (nm)</th>
<th>1st-step lithiation</th>
<th>Full lithiation</th>
</tr>
</thead>
<tbody>
<tr>
<td></td>
<td>86</td>
<td>63%</td>
</tr>
<tr>
<td></td>
<td>156</td>
<td>50%</td>
</tr>
<tr>
<td></td>
<td>292</td>
<td>55%</td>
</tr>
<tr>
<td></td>
<td>423</td>
<td>255%</td>
</tr>
<tr>
<td>Volume expansion</td>
<td>132</td>
<td>267%</td>
</tr>
<tr>
<td></td>
<td>291</td>
<td>242%</td>
</tr>
<tr>
<td></td>
<td>350</td>
<td>271%</td>
</tr>
<tr>
<td></td>
<td>423</td>
<td>255%</td>
</tr>
</tbody>
</table>

between 50–63%, close to the theoretical value of the LiSn phase (52%). Previous studies showed that the Li2Sn5 phase formed after the initial lithiation.23-24 The discrepancy between the present study and the earlier tests23,24 might be caused by different experimental setups, sample conditions and lithiation rates, which could affect the reaction kinetics and accordingly product phase.25 After full lithiation to the c-Li22Sn5 phase, the measured volume expansions in our experiments are in the range of 239–271%, close to the theoretical value of 258% for c-Li22Sn5.

Figure 3 and Figure 4 present additional in situ TEM results on lithiation of Sn NPs with different sizes. Figure 4a–4c shows a typical core-shell structure observed during the first step of lithiation, which
The linear relationship between the theoretical volume expansion and the Li content for different Li₅Sn alloy phases. The blue line connects the calculation data points (squares), and the red line represents the linear fitting result.

Figure 2. The linear relationship between the theoretical volume expansion and the Li content for different Li₅Sn alloy phases. The blue line connects the calculation data points (squares), and the red line represents the linear fitting result.

Table II. Theoretical values of volume expansion for different Li₅Sn phases.

<table>
<thead>
<tr>
<th>Phase</th>
<th>Li₂Sn₅</th>
<th>Li₅Sn</th>
<th>Li₇Sn₃</th>
<th>Li₇Sn₂</th>
<th>Li₉Sn₅</th>
<th>Li₁₃Sn₅</th>
<th>Li₁₇Sn₂</th>
<th>Li₂₂Sn₅</th>
</tr>
</thead>
<tbody>
<tr>
<td>Volume expansionb</td>
<td>22%</td>
<td>52%</td>
<td>126%</td>
<td>138%</td>
<td>142%</td>
<td>197%</td>
<td>258%</td>
<td></td>
</tr>
</tbody>
</table>

a The different Li-Sn crystal phases are based on the ICSD. 31
b The theoretical volume expansions of different Li₅Sn phases are calculated based on the following methods. The unit cell of β-Sn contains four Sn atoms, while the unit cell of Li₅Sn phases contains n Sn atoms. The theoretical volume expansions are estimated according to:

\[ \text{Volume expansion} = \left( \frac{V_{\text{Li₅Sn}}}{V_{\text{Sn}}} - 1 \right) \times 100\% \]

where, \( V_{\text{Li₅Sn}} \) and \( V_{\text{Sn}} \) are the volume of the unit cell of Li₅Sn and β-Sn, respectively.

Figure 4. Lithiation of large Sn NPs without cracking. (a-c) Lithiation of a Sn NP with the initial diameter of 350 nm. A core-shell structure forms during lithiation. (d-e) Lithiation of a Sn NP with the initial diameter of 526 nm. No cracking or fracture is observed in both cases after full lithiation.

Table II. Theoretical values of volume expansion for different Li₅Sn phases.

<table>
<thead>
<tr>
<th>Phase</th>
<th>Li₂Sn₅</th>
<th>Li₅Sn</th>
<th>Li₇Sn₃</th>
<th>Li₇Sn₂</th>
<th>Li₉Sn₅</th>
<th>Li₁₃Sn₅</th>
<th>Li₁₇Sn₂</th>
<th>Li₂₂Sn₅</th>
</tr>
</thead>
<tbody>
<tr>
<td>Volume expansionb</td>
<td>22%</td>
<td>52%</td>
<td>126%</td>
<td>138%</td>
<td>142%</td>
<td>197%</td>
<td>258%</td>
<td></td>
</tr>
</tbody>
</table>

a The different Li-Sn crystal phases are based on the ICSD. 31
b The theoretical volume expansions of different Li₅Sn phases are calculated based on the following methods. The unit cell of β-Sn contains four Sn atoms, while the unit cell of Li₅Sn phases contains n Sn atoms. The theoretical volume expansions are estimated according to:

\[ \text{Volume expansion} = \left( \frac{V_{\text{Li₅Sn}}}{V_{\text{Sn}}} - 1 \right) \times 100\% \]

where, \( V_{\text{Li₅Sn}} \) and \( V_{\text{Sn}} \) are the volume of the unit cell of Li₅Sn and β-Sn, respectively.

Figure 2. The linear relationship between the theoretical volume expansion and the Li content for different Li₅Sn alloy phases. The blue line connects the calculation data points (squares), and the red line represents the linear fitting result.

Figure 3. Lithiation of a large Sn NP without fracture and aggregation of smaller Sn NPs during lithiation. (a) A large Sn NP with the initial diameter of 440 nm and adjacent small NPs before lithiation. (b) After full lithiation under the beam-blank condition, no cracking or fracture is observed in all NPs. (c) A zoom-in image before lithiation, showing a cluster of three separated small pristine Sn NPs with the diameter of 105 nm, 79 nm and 68 nm, respectively. (d) A zoom-in image after lithiation, showing that the three small NPs are fused together to form a large c-Li₂Sn₅ NP.
Figure 5. Structural evolution of Sn NPs during sodiation-desodiation cycling. (a-c) Sodiation causes aggregation of smaller Sn NPs, which yields a single Sn NP larger than its parent NPs during the subsequent desodiation. (e, g) Desodiation could induce pulverization of large Sn NPs. That is, the new small Sn NPs are generated after several sodiation-desodiation cycles. The blue arrows indicate several individual Sn NPs before sodiation-desodiation cycles, while the red arrows indicate the new small Sn NPs formed during desodiation.

several micrometers, the lithiation-induced hoop stress and accordingly the driving force of crack extension could become sufficiently large to fracture the micron-sized particles from the lithiated surface layer.

Interestingly, the fusions of small Sn NPs are often observed during in situ TEM experiments of lithiation. Figure 3c shows three neighboring Sn NPs with the diameter of 105 nm, 79 nm and 68 nm, respectively. After lithiation, they are fused to form a single large NP of c-Li22Sn5. Such kind of fusion has been previously observed during the lithiation of Sn nanowires and NPs,36–38 which were attributed to the lithiation-induced material flow and surface welding.40 Subsequent dealloying (e.g., desodiation) yields a single Sn NP larger than its parent NPs (Figure 5). While previous ex situ observations have showed aggregation of Sn-based NPs after charge-discharge cycles,15–17 the mechanism of aggregation remains unclear. Our in situ TEM directly reveals that the fusion of Sn NPs can occur during the initial lithiation/sodiation. The resultant large alloy particles can undergo further morphological changes and even pulverize during subsequent cycling (Figure 5).

Figure 6a–6c presents the TEM images of a pair of Sn NPs in the first lithiation-delithiation cycle. The experiment is conducted under the beam-blank condition. Of particular note are the morphological changes occurring during the delithiation. The spherical Sn NPs are transformed into irregular shapes after one cycle, and smaller Sn NPs (∼20 nm in diameter) appear near the mother NPs after full delithiation, as indicated by red arrows in Figure 6c. Similar morphological changes are also observed in Sn NPs after sodiation-desodiation cycles (Figure 5). This provides a direct evidence of pulverization occurring during the dealloying process. Such delithiation/desodiation-induced morphological changes are possibly owing to the high dealloying rate associated with the applied large voltage load in Sn, Li-Sn, and Na-Sn alloys. This could induce a large concentration gradient and thus a high stress/strain in the dealloyed Sn region. The high stress/strain can lead to cracking and facilitate void formation in dealloyed Sn anodes,41 resulting in the production of smaller daughter NPs. Figure 6d–6g shows another in situ TEM result of the delithiation process. In this case, the lithiation-induced surface oxide layer forms a stable shell (Figure 6d), which effectively serves as the SEI layer. After delithiation, the surface SEI shell exhibits negligible shrinkage, and a large void forms inside the shell (Figure 6f–6g). This void accommodates the volume loss (i.e., the production of free volumes) associated with the extraction of Li ions, thereby reducing the overall volume change of the Sn NP after delithiation. The dealloying-induced voids have also been observed in the delithiation/desodiation of Sn particles with different sizes (from several micrometers to hundreds of nanometers).25,26 Such dealloying-induced voids are presumably caused by the vacancy-mediated diffusion, while the specific dealloying morphologies are controlled by the particle size, Li content and dealloying rate, etc.42 In addition, some small individual Sn NPs can be generated on the SEI shell after full delithiation (indicated by the red arrows and inset in Figure 6g). However, those NPs can be further lithiated due to their connections with the surface Li source. As a result, the capacity fade could be effectively reduced. Similar behaviors are also observed during the sodiation-desodiation cycling (Figure 5).

Figure 6a–6c presents the TEM images of a pair of Sn NPs in the first lithiation-delithiation cycle. The experiment is conducted under the beam-blank condition. Of particular note are the morphological changes occurring during the delithiation. The spherical Sn NPs are transformed into irregular shapes after one cycle, and smaller Sn NPs (∼20 nm in diameter) appear near the mother NPs after full delithiation, as indicated by red arrows in Figure 6c. Similar morphological changes are also observed in Sn NPs after sodiation-desodiation cycles (Figure 5). This provides a direct evidence of pulverization occurring during the dealloying process. Such delithiation/desodiation-induced morphological changes are possibly owing to the high dealloying rate associated with the applied large voltage load in Sn, Li-Sn, and Na-Sn alloys. This could induce a large concentration gradient and thus a high stress/strain in the dealloyed Sn region. The high stress/strain can lead to cracking and facilitate void formation in dealloyed Sn anodes,41 resulting in the production of smaller daughter NPs. Figure 6d–6g shows another in situ TEM result of the delithiation process. In this case, the lithiation-induced surface oxide layer forms a stable shell (Figure 6d), which effectively serves as the SEI layer. After delithiation, the surface SEI shell exhibits negligible shrinkage, and a large void forms inside the shell (Figure 6f–6g). This void accommodates the volume loss (i.e., the production of free volumes) associated with the extraction of Li ions, thereby reducing the overall volume change of the Sn NP after delithiation. The dealloying-induced voids have also been observed in the delithiation/desodiation of Sn particles with different sizes (from several micrometers to hundreds of nanometers).25,26 Such dealloying-induced voids are presumably caused by the vacancy-mediated diffusion, while the specific dealloying morphologies are controlled by the particle size, Li content and dealloying rate, etc.42 In addition, some small individual Sn NPs can be generated on the SEI shell after full delithiation (indicated by the red arrows and inset in Figure 6g). However, those NPs can be further lithiated due to their connections with the surface Li source. As a result, the capacity fade could be effectively reduced. Similar behaviors are also observed during the sodiation-desodiation cycling (Figure 5).

After full delithiation, NPs are transformed back to the crystalline Sn with a tetragonal structure (β-Sn), as shown by both the EDP and HRTEM image (Figure 6h–6i). This is consistent with the phase transformation of cycled Sn anodes reported in the literature.13,18,20,24 However, in a recent study of Sn NPs (∼10 nm in diameter) by Xu et al.,33 α-Sn with a cubic structure was obtained after delithiation, in contrast to β-Sn in the present and previous studies.13,15–18,20,24,26 It is well known that α-Sn is a semiconductor with low conductivity; it is brittle, powdery, and only stable under low temperature (<13.2°C).43 Moreover, the phase transformation from β-Sn to α-Sn can result in Sn and Sn-based alloys crumbled into powders (referred to as the so-called tin pest or tin disease, i.e., pulverization),41,44 leading to the well-known failure of “Napoleon’s buttons”.44 Therefore, the drastic mechanical damage and pulverization of Sn NPs observed by Xu et al.33 could probably be related to the formation of brittle α-Sn. However, it remains unclear regarding the key factors governing the formation of α-Sn, such as electrochemical load, temperature and particle size.

Discussion

Based on the above in situ studies of Sn NPs and in conjunction with the earlier results of Sn microparticles,20,22,26 we summarize, in Figure 7, a size-dependent pulverization mechanism of Sn particles upon electrochemical cycling. In Sn microparticles, cracking and fracture occur during lithiation due to the high stress generated by the large, non-uniform volume expansion.20,27,29 Repeated fractures subdivide the particles, causing the pulverization of electrodes during cycling (Figure 7a). In contrast, in Sn NPs, the volume expansion occurring during lithiation can be effectively accommodated without fracture (Figure 7b). This can be attributed to the small particle size and the unique two-step lithiation mechanism, which reduce the driving force of cracking. However, due to the low melting point of Sn and Li-Sn alloys, in conjunction with the small particle size promoting fast Li transport, drastic morphological changes occur during delithiation, leading to the generation of smaller NPs, i.e., pulverization (Figure 7b). For the smaller pristine or pulverization-generated NPs with sizes about tens of nanometers (Figure 7c), they can aggregate together during delithiation, forming larger NPs that pulverize upon subsequent cycling. This corresponds to a dynamic process of damaging and/or self-healing. During such process, some small-sized Sn NPs can be isolated from others by the SEI, causing a difficulty in
Figure 6. Structural changes of Sn NPs during lithiation-delithiation cycling. (a-c) Morphological evolution of Sn NPs during the first lithiation-delithiation cycle under the beam-blank condition. The spherical pristine NPs become irregular shapes with some smaller NPs generated after delithiation. The blue arrow indicates a pre-existing small Sn NP, while the red arrows point to the newly formed Sn NPs with diameters of ~20 nm. (d-g) Delithiation of a NP with a stable surface shell. A surface shell is formed from the lithiated surface oxide layer, serving as the SEI. Upon delithiation, a void forms inside the surface shell. After full delithiation, some small Sn NPs are generated on the surface SEI shell, as indicated by the red arrow and inset in (g). The blue arrow in (f) indicates the void. (h-i) EDP and HRTEM images showing that the NPs are transformed back to β-Sn after full delithiation.

Figure 7. A summary of the size-dependent pulverization mechanisms in Sn particles. (a) In micron-sized Sn particles, the lithiation induces cracking. The SEI grows on fresh new surfaces, so as to prevent the small Sn pieces to be fused together. Pores form after delithiation due to the high rate of Li diffusion. Electrochemical cycling causes the pulverization of Sn particles. (b) In Sn nanoparticles with sizes in hundreds of nanometers, no cracking or fracture occurs after full lithiation, and pulverization is dominated by structural reconstruction during delithiation. (c) In Sn nanoparticles with sizes in tens of nanometers, the lithiation induces aggregation, resulting in larger nanoparticles, which further pulverizes upon cycling. (d) For Sn-C nanocomposites, although the pulverization may generate some small nanoparticles, the electrical contacts are retained in the confined volume of the carbon shell and the nanoparticles can be fused together during cycling, thereby slowing down the capacity fade.
aggregation (Figure 7a-7c). Thus the self-healing capability and the electrode capacity will decay gradually as the cycle number increases. Recently, uniform Sn-C nanocomposites are reported to exhibit excellent electrochemical performance.7–11,19 In these nanocomposites, Sn NPs are enclosed by the carbon shell that can serve as a barrier to the aggregation of Sn NPs as well as the SEI formation on the surface of Sn NPs.7,11,19 Even if pulverization yields smaller NPs inside the carbon shell, direct contacts between those Sn NPs and Sn/carbon shell could be retained due to the confined volume, such that the pulverized NPs could be effectively fused together in subsequent cycles due to the presence of fresh surface (no SEI formation on the surface of NPs) (Figure 7d). As a result, the pulverization-induced capacity loss can be reduced, thereby enhancing the cyclability.7–9,11,12

In this regard, our in situ TEM observation provides a direct evidence that the architecture of Sn NPs embedded in a closed shell would be a favorable design for the Sn-based nanocomposite anode, which could facilitate the retention of a high energy density by mitigating the pulverization during electrochemical cycling. Finally, we note that since Sn particles exhibit similar behaviors during lithiation-delithiation and sodiation-desodiation cycling, the size-dependent pulverization mechanism revealed in this work could hold true in the application of Sn particle anodes in Na-ion batteries.

Conclusions

In conclusion, the structural evolutions of Sn NPs during lithiation-delithiation cycling are studied with in situ TEM. The β-Sn NPs in the size range of 79–526 nm undergo a two-step lithiation, resulting in c-Li22Sn5 with a total volume expansion of about 258%. No cracking or fracture occurs after full lithiation of Sn NPs, in contrast with the lithiation-induced cracking in micron-sized Sn particles. In addition, lithiation/sodiation can lead to the fusion of small Sn NPs. Delithiation/sodiation desodiation causes the pulverization of the relatively large Sn NPs, which can be attributed to the high dealloying rate that induces a large concentration gradient of lithium/sodium and thus a high stress/strain in the dealloyed Sn region. The high stress/strain can induce cracking and facilitate void formation in dealloyed Sn anodes, resulting in smaller Sn particles. Based on the different lithiation-delithiation behaviors of Sn particles, a size-dependent pulverization mechanism is identified. Our results advance the fundamental understanding of the pulverization and degradation mechanisms in Sn-based anodes, which is critical to the design of the mechanically robust Sn-based anodes for high-performance Li-ion batteries. This work also provides a valuable basis for the systematic study of structural evolution and pulverization in Sn-based anodes for Na-ion batteries.

Acknowledgments


Acknowledgments

T.Z. acknowledges the support by the NSF grants CMMI 1100205 and DMR 1410936. S.X.M. acknowledges the NSF grant CMMI 08010934 through University of Pittsburgh and Sandia National Lab support. This work was performed, in part, at the Center for Integrated Nanotechnologies, a US Department of Energy, Office of Basic Energy Sciences user facility. Sandia National Laboratories is a multiprogram laboratory managed and operated by Sandia Corporation, a wholly owned subsidiary of Lockheed Martin Corporation, for the US Department of Energy’s National Nuclear Security Administration under Contract DE-AC04-94AL85000.