Supplementary Materials for

Visualization and Quantification of Electrochemical and Mechanical Degradation in Li Ion Batteries

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Materials and Methods

Material Synthesis

The synthesis of SnO particles closely followed the report of Wang et al. (33): 18 mmol tin chloride dihydrate (SnCl₂·2H₂O) and 24 mmol tri-sodium citrate dihydrate (Na₃C₆H₅O₇·2H₂O) were dissolved in 25 ml DI water, and, after complete dissolution, 10 ml of potassium hydroxide solution (64.3 mmol KOH) was added drop wise during 150 s under continuous ultrasonic agitation in an ultrasonic bath with a power of 25 W. The resulting milky white suspension was then rested for about 2 h until a black precipitate formed and the supernatant turned clear. The reaction product was then centrifuged and washed with DI water and ethanol several times before it was dried in a vacuum oven at 60 °C overnight. A scanning electron micrograph (Fig. S1A) of the SnO particles shows tetragonal particles with good uniformity in shape and size (~30 µm). As indicated by the red arrows, multiple defects in the (001) plane are observed in the synthesized material. Particle cross-sections (Fig. S1B and C), prepared by focused-ion-beam milling, reveal the existence of grain boundaries in the (001) planes as well as singular voids and cracks. An X-ray diffractogram, shown in Fig. S1D, was recorded with a Brucker D8 diffractometer using Cu Kα radiation at 40 kV and 40 mA, and indicates the purity of tetragonal SnO.

Cell preparation & electrochemical test procedure

An electrochemical cell (Fig 1. B) was fabricated as described below. Electrode slurries with 25 wt.% solid content were prepared by dispersing 80 wt.% SnO, 10 wt.% carbon black (TIMCAL) and 10 wt.% PVDF (Arkema) in N-methyl-pyrrolidone (NMP, Sigma Aldrich) using a ULTRA-TURRAX high shear mixer for 10 min, followed by ultra-sonication for 10 min. Electrodes were prepared by coating the tip of one current collector pin with the slurry, followed by drying at 80 °C under vacuum over night. Active mass was estimated by weighing the current collector before and after electrode deposition. Current collectors were then transferred into an argon-filled glovebox (O₂ and H₂O <1 ppm). Finally, half-cells with metallic lithium as a combined counter and reference electrode, a glass fiber separator, and electrolyte (1 M LiPF₆ in 1:1 ethylene carbonate:dimethyl carbonate, LP30 from Merck) were assembled. Galvanostatic reduction and oxidation was performed at 110 mAg⁻¹ to 10 mV vs. Li/Li⁺ and 167 mAg⁻¹ rate to 2.5 V vs Li/Li⁺, respectively, using a Bio-logic SP-150 potentiostat with low current module. The electrochemically active mass was determined from the measured lithiation capacity and a theoretical capacity of 1273 mAhg⁻¹, and is in good agreement with the mass estimation determined by weighing. The potential during galvanostatic reduction and oxidation at 127.3 mAhg⁻¹ in a 1.3 cm² coin-type half-cell with ~20 mg active material is shown in Fig. S1C. We note that this electrochemistry recorded without radiation exposure is comparable to the electrochemistry recorded during the SRXTM experiment as the sample undergoes radiation exposure. This indicates that no beam-induced degradation of the sample relevant to electrochemistry occurs during the SRXTM experiment. Furthermore, we can estimate the absorbed x-ray dosage and determine that it should induce at most in what is classified as “some damage” (37). In particular, for a 28 keV beam energy, 1 mm of PVDF (density 1.78 g cm⁻³) absorbs 3.4 % of the incident photon flux of 10¹¹ mm⁻² s⁻¹, resulting in an absorbed does of about 5*10⁵ J kg⁻¹ over 15 h of permanent radiation exposure.
The design of a stable electrochemical cell is critical to the success of the experiment. As the technical drawing of our cell shows (Fig. S1D), we customize a polymeric tube fitting (Swagelock PFA-220-6). The electrochemical cell remains functional for weeks, due to the excellent seal provided by the commercial fitting and the custom machined stainless steel current collectors. The gap between the two current collectors after cell assembly is precisely controlled by the stable positioning and accurate machining of the stainless steel pins. To improve x-ray transmission through the cell, we machine a groove around the entire circumference of the tube fitting, leaving a 2 mm PFA sidewall thickness.

**Supplementary Text**

**Tomography settings & reconstruction**

SRXTM radiographs were recorded at the TOMCAT beamline of the Swiss Light Source (25) at Paul Scherrer Institut in Villigen, Switzerland, using parallel, monochromatic synchrotron radiation at 28 keV (selected using a [W/Si]100 multi-layer monochromator), a 20 µm LAG:Ce scintillator, and an optical 10 x objective in conjunction with a PCO.edge sCMOS camera with a chip size of 2560(h) x 2160(v) pixel. 700 radiographs during 180° sample rotation with 700 ms exposure time were recorded. The radiographs were flat- and darkfield-corrected and rearranged into sinograms. A highly optimized routine based on the Fourier transform method and a gridding procedure was employed to reconstruct the full tomographic dataset (26). A Hamming window in conjunction with the standard ramp filter was used in the reconstruction process to minimize noise contamination. The resulting voxel size of the dataset was 0.65x0.65x0.65 µm³.

**Histogram calculation and normalization of attenuation coefficients**

Histograms were calculated by selecting 10⁶ voxels from a central region of the reconstructed tomograms that contains only electrochemically active particles and the electrolyte, carbon black, and binder mixture. The numerical gray-scale value of each voxel in a tomogram is linearly related to the attenuation coefficient of the sample at the position of the voxel. In order to yield absolute values, the numbers have to be normalized. Here, the SnO and the background peaks were utilized as internal standards for this normalization. Based on known elemental mass attenuation coefficients (38), densities, and molar masses, the theoretical attenuation coefficients of SnO and the background can be calculated (Tbl. S1). The background results from low absorbing, carbon-containing materials. For normalization, the attenuation of elemental carbon is chosen, which is an acceptable approximation since, at two orders of magnitude smaller than the attenuation coefficient for SnO, the exact value used is not significant. A sum of two normal distributions is fitted to the histogram calculated from the tomogram acquired before electrochemical reduction to determine the gray-scale values (w) of the pure SnO and the background. Associating the theoretical attenuation coefficients with the gray-scale values determined for the SnO and the background phase, determines the normalization function **Equ. S1** with a = 149.4 cm⁻¹ and b = -46.2 cm⁻¹.

\[ \mu(w) = a \cdot w + b \]  

**Equ. S1**
Microstructure preprocessing

The 74 reconstructed tomograms (2650x2650x250 voxel) were partitioned into regions of 512x512x250 voxels to enable numerical processing of the $>10^{11}$ 16-bit values on a 600 core linux cluster. Each region was subjected to 3D median filtering with a 5 voxel cubic kernel. Subsequently, the regions were binarized with a variable threshold. The threshold value for each tomogram was calculated as the arithmetic mean of the attenuation coefficient of the carbon black, electrolyte, and binder background and the Li$_x$Sn + Li$_2$O mixed phase. For the first 13 tomograms, a constant attenuation coefficient equal to the attenuation coefficient of the mixed phase in the 14th tomogram was taken. The mixed phase peak does not shift in value as it emerges from the noise, but fitting the broad peak near the noise floor is fault-prone. The evolution of the attenuation coefficients of the identified phases, determined by fitting the peak in the histogram, as well as the calculated threshold values are depicted in Fig. S2A. In Fig. S2B, close-ups of the histograms of the Li$_x$Sn + Li$_2$O and SnO peaks are shown.

The resulting datasets after binarization represent the microstructure of the sample constituents with absorption coefficients higher than the electrolyte, carbon black, and binder background: the SnO particles, the current collector, and the glass fiber separator. To facilitate quantification of the volume-change of the SnO particles alone, the current-collector and the glass fiber separator have to be removed from the datasets. This was achieved in two steps: First, region masks that exclude the separator were calculated based on the separators fiber shape by applying the morphological hole-filling operator imfill() in Matlab, followed by the morphological opening operator imopen() with spherical structure element of radius 5 voxel to copies of the thresholded datasets. Applying voxel-by-voxel Boolean AND operations between the original thresholded datasets and these region masks retained the shape of the SnO particles while efficiently removing the glass fiber separator. In a second step, the planar current-collector, which was slightly tilted with respect to the coordinate system of the tomograms, was removed by determining the offset and inclination of the current collector-electrode interface plane and removing all voxels on the current-collector side of this plane.

Calculation of volume expansion

To calculate the volume expansion of the active material, the entire dataset, including all particles in the cell, was considered. The considered volume was selected such that no particle leaves or enters the volume; otherwise the calculated volume change would be incorrect. To compute the volume change, the volume of particles in the electrode $V_i$ was calculated for every tomogram by counting the number of voxels associated with particles. The volume expansion was then calculated with Equ. S2.

$$E_i = \left(\frac{V_i}{V_0} - 1\right) \cdot 100\%$$

Equ. S2

The theoretical volume expansions can be calculated with Equ. S3 from the molar volumes of the phases in relation to SnO.

$$\varepsilon_i = \left(\frac{M_i}{\rho_l} / \frac{M_{SnO}}{\rho_{SnO}} - 1\right) \cdot 100\%$$

Equ. S3

They are 252 % for Li$_x$Sn + Li$_2$O and 49 % for Sn + Li$_2$O. From the molar volumes of the Li$_x$Sn and Li$_2$O + Li$_x$Sn phases reported in Tbl. S1, the change in molar volume with lithium content (x) can be estimated with Equ. S4 (6).
\[ v(x) = v_0 + kx \] \hspace{1cm} \textbf{Equ. S4}

In agreement with Ref. 6, we find \( k = 9.73 \text{ cm}^3\text{ mol}^{-1} \) and \( k = 9.74 \text{ cm}^3\text{ mol}^{-1} \) for the Li\(_3\)Sn and Li\(_2\)O + Li\(_3\)Sn phases, respectively.

\textbf{Estimation of lost capacity}

We estimated the state of charge, parameterized by the mean lithium content, \( \bar{x} \), from the attenuation coefficient histograms, \( f(\mu) \). We estimated the relation between lithium content for each attenuation coefficient, \( x(\mu) \), by linear interpolation between the values of equilibrium phases reported in Tbl. S1.

\[ \bar{x} = \frac{\int_{\mu=13 \text{ cm}^{-1}}^{30 \text{ cm}^{-1}} x(\mu)f(\mu)\,d\mu}{\int_{\mu=13 \text{ cm}^{-1}}^{30 \text{ cm}^{-1}} f(\mu)\,d\mu} \] \hspace{1cm} \textbf{Equ. S5}

\textbf{Equ. S5} calculates the state of charge, which is plotted as a function of oxidation capacity in Fig. S3. The mean lithium content at 550mAh\(_g\)^{-1} is found to be \( \bar{x} = 1.9 \), resulting in a lost capacity of \( 1.9/4.4 = 43\% \).
Fig. S1.

(A) Close-up scanning electron micrograph of active particles highlighting the tetragonal particle shape and grain boundaries in the (001) plane. (B) Particle cross-section prepared by focused-ion-beam milling with grain boundaries indicated by dotted line and (C) close up of grain boundaries. (D) X-ray diffractogram showing the purity of the SnO. Reference diffractogram for the tetragonal phase is indicated in red. (E) Potential during galvanostatic reduction and oxidation of SnO in coin-type half-cell recorded at 127 mAg⁻¹. (F) Technical drawing of the electrochemical cell.
(A) Evolution of the attenuation coefficients of materials determined by fitting normal distributions to the attenuation coefficient distributions shown in close up in (B).
Fig. S3.

(A) Evolution of attenuation coefficient distribution and (B) quantification of peak broadening during oxidation. (C) Average lithium content, $\hat{\chi}$, estimated from integrating the attenuation coefficient distribution as a function of oxidation capacity.
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<th>Symbol</th>
<th>Unit</th>
<th>Mass density $\frac{\mu}{\rho}$</th>
<th>Molar mass $\rho$</th>
<th>Molar volume $M$</th>
<th>Molar mass density $\frac{\mu}{\rho}M$</th>
<th>Attenuation coefficient $\mu$</th>
<th>Gray-scale value $w$</th>
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<td>150.97</td>
<td>34.72</td>
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<td>174.73</td>
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<td>934.54</td>
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</table>

Attenuation coefficients of all constituents of the electrode can be calculated (shaded cells) from literature values (unshaded cells). The values for SnO and the electrolyte, carbon black, and binder matrix are used to calculate the linear scaling transformation **Equ. S1** between the attenuation coefficients and the recorded grey-scale values (bold).
Movie S1.
**Electrode cross-section parallel to current collector.** Sequence of 74 unprocessed tomograms show individual SnO particles in the electrode against low attenuating carbon black, binder, and electrolyte phase as they undergo core-shell lithiation, volume expansion and fracture during reduction followed by volume contraction during oxidation.

Movie S2.
**Evolution of particle fracture: cross-sections.** Coronal (left) and transverse (right) cross-sections through a particle during electrochemical reduction and oxidation showing the growth of multiple cracks in parallel (001) planes leading to zig-zag particle morphology.

Movie S3.
**Evolution of particle fracture: 3D rendering.** Preferential crack initiation and growth in the (001) planes leading to zig-zag morphology is shown for multiple particles.

Movie S4.
**Evolution of an electrode subvolume: 3D rendering.** During reduction, particle volume expansion leads to expansion of the entire electrode and particle fracture. During oxidation, the particles contract, but the electrode is permanently distorted.
References and Notes


29. Materials and methods are available as supplementary materials on Science Online.


