Tracking sodium-antimonide phase transformations in sodium-ion anodes; insights from operando pair distribution function analysis and solid-state NMR spectroscopy

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SI.1: Calculations of level of sodiation for amorphous phases

S1-a: a-Na$_{3.3}$Sb

The amorphous a-Na$_{3.3}$Sb is the dominant phase at a sodiation level of Na$_{2.7}$Sb. From high-$r$ (20 – 50 Å) PDF refinements the scale factor for c-Sb phase is 0.1504. In the pristine electrode the refined scale factor is 0.988. A ratio of the scale factors calculates the amount of c-Sb there still is in the electrode:

c-Sb = 0.1504/0.988 = 0.1522, so approximately 15% of the antimony still exists as c-Sb

This means that 85% of the antimony is present as sodiated phases: either Na$_{3}$Sb or a-Na$_{3.3}$Sb. It is assumed that 0.375 Na per Sb is contained as the SEI (as 3.375 Na per Sb are inserted during the first sodiation, forming Na$_{3}$Sb). Therefore, there are 2.325 Na per Sb contained within 85% of the Sb present in the electrode. Therefore, per Sb in the sodiated phases there are 2.325/0.85 = 2.73 Na per Sb: average stoichiometry of the two sodiated phases is Na$_{2.7}$Sb

From high-$r$ PDF refinements, the scale factor for c-Na$_{3}$Sb is 0.2181 compared to 0.9682 at the end of sodiation (end of S1-b) where 100% of the Sb is present as c-Na$_{3}$Sb.

c-Na$_{3}$Sb = 0.2181/0.9682 = 0.2252 therefore 22.5% of the total c-Na$_{3}$Sb has been formed (NB: this accounts for approx. 0.68 Na per Sb). This represents 0.2181/0.85 = 0.26 = 26% of the sodiated phase (accounting for the fact that only 85% of the Sb is in sodiated phases).

2.73 Na per Sb = 0.26(#Na per Sb in c-Na$_{3}$Sb) + 0.74(#Na per Sb in a-Na$_{3.3}$Sb)

Therefore: 2.73 = 0.26*3 + 0.74(3-x) => 2.73 = 0.78 + 2.22 – 0.74x => x = 0.36

To one significant figure (accounting for possible errors in the calculations, this gives x = 0.4).

If we don’t account for any sodium being present in the SEI, the calculation gives x = -0.17 (this would imply that it is over-sodiated). This is unlikely to be the case, given that a surplus of 0.375 Na per Sb are added throughout the sodiation, and the $^{23}$Na NMR indicate that these are formed as surface species. The least-squares refinement of the Na$_{3}$Sb structure against PDF data for this structure implies a contracted c-parameter, suggesting that there are vacancies in the structure which cause the layers to sit closer together, consistent with a undersodiated version.

At the end of D-1a

At the end of sodiation, Na$_{3}$Sb is formed, but 3.375 Na per Sb have been inserted. We assume that the 0.375 Na per Sb used in side reactions and are no longer active in the electrode. Therefore, the starting electrode stoichiometry is 3 Na per Sb. During D1-a, 1.125 Na per Sb are removed from the electrode, resulting in a whole electrode stoichiometry Na$_{1.875}$Sb. The electrode is a mixture of c-Na$_{3}$Sb and the new amorphous phase, a-Na$_{3}$Sb.

From high-$r$ (20 – 50 Å) PDF refinements, the scale factor of the c-Na$_{3}$Sb phase is 0.140, compared to 0.9682 at the end of sodiation. Therefore, 0.140/0.9682 = 0.144 (14%) of the Sb is still present as c-Na$_{3}$Sb, 0.8556 as the a-Na$_{3.3}$Sb phase.

Therefore, 1.875 = 0.1444(#Na per Sb in Na$_{3}$Sb) + 0.8556(x in a-Na$_{3.3}$Sb phase)

x = (1.875 - 0.144(3)) / 0.8556, x = 1.68

Therefore, the stoichiometry of the a-Na$_{3}$Sb phase is approximately Na$_{1.7}$Sb

At the end of D1-b

We use the same assumption about SEI as above. During D1-b, 0.9 Na per Sb are removed, making the overall stoichiometry Na$_{0.975}$Sb. No c-Na$_{3}$Sb remains, but a very small amount of c-Sb appears (Scale factor = 0.036 => 0.036/0.988 = 0.037 is present as c-Sb. 0.963 is present as the amorphous
antimony network. Therefore, the stoichiometry of the amorphous Sb network: $0.975 = 0.963(x)$, $x = 1.01$.

**At the end of D1-c**

0.3375 Na per Sb are removed during D1-c, making the overall electrode stoichiometry Na$_{0.6375}$Sb. The electrode is a mixture of c-Sb and an amorphous Sb phase. From high-r (20 – 50 Å) PDF refinements, the scale factor for the c-Sb is 0.404 (compared to 0.988 for the pristine electrode). Therefore, $0.395/0.988 = 0.3998$ (40%) of Sb present as c-Sb, 0.6002, as amorphous phase, Na$_x$Sb. $x = 0.6375/0.6002$, $x = 1.0425$, so the amorphous phase stoichiometry is approximately Na$_{1.0}$Sb.

Note, that comparing the area of the amorphous-component PDF extracted from the residual from high-r refinements against c-Sb, and the crystalline component PDF first peaks (assuming that both represent 3 x Sb-Sb bonds – no significant defects in the a-Sb) gives 33% c-Sb, 67% amorphous a-Na$_{1.0}$Sb phase: a similar result to the previous calculation.

**Figure S1:** Comparison of the first peaks of the amorphous (left) and crystalline (right) PDF components at the top of charge. Open circles show experimental data, red line is the fit to experimental data. Grey lines give Gaussian peaks fitted for first (solid line) and second (dashed line) peaks in the experimental PDF. Relative areas of the first peaks to each other labelled.

**At the end of S2-a**

During S1-a, 0.5625 Na per Sb are added to the electrode. Total electrode stoichiometry is Na$_{1.2}$Sb. The electrode is a mixture of c-Sb and an amorphous Sb phase. From high-r (20 – 50 Å) PDF refinements, the scale factor for the c-Sb is 0.357 meaning $0.375/0.988 = 0.3613$: 36% is as c-Sb, 63% as a-Na$_x$Sb. The stoichiometry of the amorphous phase is: $1.2 = 0.63(x) = 1.90$, the amorphous phase is Na$_{2.0}$Sb.

**At the end of S2-b**

During S2-b, 0.675 are added into the electrode, making the total electrode stoichiometry Na$_{1.875}$Sb. Scale factor for Sb is 0.0501, meaning $0.0501/0.988 = 5.1\%$ of the c-Sb remains. Therefore, total stoichiometry of the amorphous phase(s) is Na$_{2.0}$Sb.

**At this point it is a mixture of the Na$_{1.7}$Sb and the Na$_{3.5}$Sb.** The amount of each amorphous phase can be estimated by using a linear combination of Na$_{1.7}$Sb (amorphous PDF from end of D1-a - this was scaled by 0.821818 to account for the fact only 86% of the Sb was in this phase at the end of D1-a) and Na$_{3.5}$Sb (from end of S2-c). Linear combination = $x$(PDF for a-Na$_{1.7}$Sb) + $(1-x)$(PDF for Na$_{3.5}$Sb). The sum of squared differences between the linear combination of these phases and the
experimental data is minimised by varying the relative amounts of each phase and an overall scale factor:

\[ \text{Sum of differences} = \sum_r (G(r)_{\text{expt}} - G(r)_{\text{linear combination}})^2 \]

This gives a reasonable match to the experimental PDF (below) using a phase distribution of **53% as Na}_{1.7}Sb, 47% as a-Na}_{3.4}Sb**. If this is the case, then the total electrode stoichiometry should be:

\[ y = 0.53(1.7) + 0.47 (2.43) = 2.04 \Rightarrow \text{Na}_{2}Sb \text{ (compared to Na}_{1.90} \text{ from electrochemical measurements)} \]

**Figure S 2:** Linear combination fit to PDF at the end of S2-b using the PDFs for Na}_{1.7}Sb (from the end of D-1a) and the Na}_{3.4}Sb (from the end of S2-c). The difference between the linear combination and the experimental data is shown offset for clarity.

**The end of S2-c:**
During D1-c 0.5625 per Sb are added to electrode, making stoichiometry Na}_{2.4625}Sb. At this stage, there is no c-Na or c-Na}_{3}Sb in the electrode, so all sodiation is present in an amorphous phase. There is no peak left at 2.85 Å, indicating that all the Na}_{1.7}Sb has been sodiated further. Therefore, all sodium is present as a-Na}_{3.4}Sb. **In this case, x is estimated to be 0.54 (compared to 0.4 from 1st sodiation).**

The total charge capacity of the electrode is 79% of the theoretical value. In the above calculations, we assume that this is due to sodium being trapped within Na}_{x}Sb phases in the electrode, and that the whole electrode remains in electrical contact during the desodiation and 2nd sodiation processes, for the reasons discussed in the text. However, for completeness we also consider the sodiation level of the amorphous phases, were loss of electrical contact responsible for the lower desodiation capacity, below:

D1-a: 1.125 Na per Sb removed.
If only 79% of electrode “active”, then this is equivalent to 1.42 being removed from this.
0.144 % of the **whole electrode** (including inactive/dead component) is still present as c-Na}_{0}Sb. This is 0.144/0.79 = 18.2% of the 79% active material. 85.6 % is as a-Na}_{x}Sb phase
This would make the calculation for x: \[ x = (1.576 - 0.182(3)) /0.856, x = 1.2 \]
**a-Na_{1.2}Sb**

D1-b: 0.9 Na per Sb
if only 79% active, then this is equivalent to 1.13 Na per Sb removed
0.037 of *whole electrode* is c-Sb, equal to 0.037/0.79 = 4.7% of active Sb
0.45 = 0.953(x), x = 0.47

**a-Na_{0.8}Sb**

D1c: No sodium left in the electrode (except for 0.375 within the SEI) => Na_6Sb

S2-a: 0.5625 Na per Sb added, equivalent to 0.63 Na per Sb in the 79% active electrode
Total electrode stoichiometry is Na_{0.63}Sb
0.3613 of whole electrode is c-Sb, equivalent to 46% of the active electrode, 54% as a-Na_0Sb
0.63 = 0.54(x), x = 1.17: **a-Na_{1.2}Sb**

S2-b: 0.675 Na per Sb added, equivalent to 0.85 Na per Sb in the 79% active electrode
Total stoichiometry is Na_{1.48}Sb
From linear combinations, around 53% as the amorphous component from S2-a/D1-a, 47% as the amorphous component from S2-c

S2-c: 0.5625 Na per Sb added, equivalent to 0.63 Na per Sb in the 79% active electrode
Total electrode stoichiometry is Na_{2.11}Sb
All present as a-Na_{3.8}Sb
x = 0.89 (compared to x = 0.35 – 0.41 from S1-a)

S2-d: 0.7875, equivalent to 1.0 Na per Sb in the 79% active electrode
Total electrode stoichiometry is 3.10

Comparison of stoichiometries calculated using 100% “active” electrode and 79% “active” electrode:
**a-Na_{3.8}Sb**: S1-a and S2-c (after 450 mV process):
if we consider 100% of the electrode to be “active”: S1-a: x = 0.31-0.36, S2-c: x = 0.53
if we consider 79% of the electrode to be “active”: S1-a x = 0.31-0.36, S2-c: x = 0.89

**Dumbbell phase**: 100% active electrode D1-a = Na_{1.7}Sb; S2-a = Na_{1.9}Sb
79% active electrode: D1-a = a-Na_{1.2}Sb; S2-a = Na_{1.2}Sb
Table S 1: Previous reports of capacities of Sb anodes

| Report       | Formulation                              | Rate | 1st sodiation capacity /mAhg\(^1\) (Numbers in brackets show in terms of #Na per Sb) | 1st Desodiation capacity /mAhg\(^1\) (Numbers in brackets show in terms of #Na per Sb) | Irreversible capacity /mAhg\(^1\) (Numbers in brackets show in terms of #Na per Sb) | Irreversible capacity excluding SEI /mAhg\(^1\) (Numbers in brackets show in terms of #Na per Sb) |
|--------------|-------------------------------------------|------|--------------------------------------------------------------------------------------|--------------------------------------------------------------------------------------|------------------------------------------------------------------------------------|------------------------------------------------------------------------------------------------|
| Darwiche et al.\(^1\) | Sb: -300 mesh, carbon, CMC                | C/6  | 726 (3.3)                                                                            | 572 (2.6)                                                                            | 154 (0.7)                                                                          | 88 (0.4)                                                                                     |
| Baggetto et al.\(^2\) | Thin film                               | C/10 | 750 (3.41)                                                                           | 542 (2.46)                                                                           | 208 (0.95)                                                                         | 118 (0.54)                                                                                   |
| He et al.\(^3\) | Nanoparticles (20 nm)                     | 1C   | 1100 (5.00)                                                                          | 520 (2.36)                                                                           | 580 (2.64)                                                                         | 140 (0.64)                                                                                   |
| This study   | Sb: -300 mesh, carbon, CMC                | C/20 | 743 (3.375)                                                                          | 520 (2.36)                                                                           | 223 (1.01)                                                                         | 80 (0.36)                                                                                   |
SI.2 PDF data for first sodiation, first desodiation and second sodiation.

Data are offset for clarity. The colour of the curve corresponds to colours of the points on the electrochemical curve.

Figure S3: PDFs for the first sodiation
Figure S4: PDFs for the first desodiation
Figure S5: PDFs for the second sodiation
SI.3 PDFs for amorphous and crystalline components of electrode

PDFs for the amorphous (left) and crystalline phases (right) as a function of sodiation. Amorphous phases are extracted from the residual of a two-phase (c-Sb and c-Na₃Sb) refinement over the full r-range (2 – 50 Å) with structural parameters fixed to those values determined from refinements at high-r (20 – 50 Å). These have been r-averaged over the period of the termination ripples. The PDFs for the crystalline phases were calculated from structural parameters in the same two-phase refinements using PDFGui. Where the crystalline and amorphous component data are shown on different scales, this is indicated on the y-axis.

Figure S6: Amorphous (left) and crystalline (right) components of the electrode for the first sodiation
Figure S7: Amorphous (left) and crystalline (right) components of the electrode for the first desodiation
Figure S8: Amorphous (left) and crystalline (right) components of the electrode for the second sodiation
SI.4 Density-functional theory calculations

A simple species-swapping procedure was used to generate likely candidate structures of Na$_x$Sb, this method has been used to successfully generate low-energy structures in the Li-Si, Li-Ge$^4$ and Li-S$^5$ systems. All of the known stoichiometric crystal structures of Li-P, Li-As, Li-Sb, Na-P, Na-As, Na-Sb, K-P, K-As and K-Sb were obtained from the International Crystallographic Structure Database (ICSD). For each structure the anions were replaced by Na and the cations by Sb. All of the structures were then relaxed using forces calculated using the CASTEP$^6$ density-functional theory (DFT) code. The Perdew-Burke-Ernzeof (PBE) exchange-correlation functional was used with CASTEP on-the-fly Vanderbilt ultrasoft pseudopotentials, (Na 2[1.3]1.3[1.0|16|19|21|20U:30U:21(qc=8) and Sb 2[2.0|2.0|1.6|4|7|8|50:51). The Kohn-Sham eigenvalues were represented by a basis set containing plane waves with energies of up to 700 eV and Fourier Transform grids were set to represent without aliasing frequencies up twice the size of the basis set. A Monkhorst−Pack grid corresponding to a Brillouin zone sampling grid finer than $2\pi \times 0.03$ Å$^{-1}$ was used.

A convex hull was generated between Na (Im-3m) and Sb (R-3m) see Figure S9. Average voltages were calculated from ground state energies$^7$.

![Figure S9](image-url)

**Figure S9:** Convex hull between Na (Im-3m) and Sb (R-3m). The purple line is the tie-line indicating the stable phases at 0 K predicted by DFT. The dots indicate the formation enthalpy of a structure.
SI.5 Model compounds Sb, NaSb and Na$_3$Sb

**Figure S 10:** XRD (Cu K$_\alpha$, $\lambda = 1.54$ Å) patterns of NaSb (top) and Na$_3$Sb (bottom) powders obtained by ball milling.

The red circles show the experimental data and the black line is the calculated pattern. The residual from the refinement (blue line) is shown offset.
**Figure S 11:** Refinement of crystalline Sb\(^8\) against ex situ PDF data.

For these, and all subsequent refinements shown, black circles show experimental data, green lines shows the calculated PDF. The difference between the experimental and model PDFs (defined as \( G(r)_{\text{experiment}} - G(r)_{\text{calculated}} \)) is shown by the black line, offset for clarity.

**Table S 2:** Structural parameters for NaSb determined from Rietveld refinement and least-squares refinement against PDF data. * = parameter not refined

| Parameter | Literature structure\(^9\) | Le Bail refinement of XRD data | Ex situ PDF |
|-----------|-----------------------------|-------------------------------|-------------|
| a /Å      | 6.8000                      | 6.7765(7)                     | 6.797       |
| b /Å      | 6.3400                      | 6.3295(7)                     | 6.330       |
| c/ Å      | 12.4800                     | 12.468(2)                     | 12.45       |
| β /Å      | 117.6000                    | 117.512(4)                    | 117.6*      |
| U\(_{(Sb)}\) | 0.030                       |                               | 0.030       |
| U\(_{(Na)}\) | 0.10                        |                               | 0.10        |

**Table S 3:** Comparison of structural parameters obtained from structural refinements for antimony from model compound and from pristine electrode from in situ PDF experiment, and the structure obtained at the end of desodiation.

| Parameter | Literature structure\(^8\) | Le Bail refinement of XRD data | Ex situ PDF | End of desodiation |
|-----------|-----------------------------|-------------------------------|-------------|--------------------|
| a /Å      | 4.3072                      | 4.307                         | 4.315       | 4.308              |
| c/ Å      | 11.2754(6)                  | 11.28                         | 11.29       | 11.38              |
| U\(_{11}/U_{22}\) | 0.01                       | 0.011                         | 0.017       | 0.0203             |
| U\(_{33}\) | 0.01                        | 0.016                         | 0.023       | 0.0389             |
| sp diameter / Å | -                          | -                             | -           | 197                |
| Sb z-coordinate | 0.2664(1)                  | 0.266                         | 0.267       | 0.267              |
Table S 4: Comparison of structural parameters for Na₃Sb obtained from structural refinements of data for model compound, at the end of the first sodiation and at the end of the second sodiation during in situ PDF experiments.

Na₁ sits within the hexagonal layers of Sb/Na, Na₂ sits between the layers

|                  | Literature structure¹⁰ | Le Bail refinement of XRD data | Ex situ PDF | End of first sodiation | End of second sodiation |
|------------------|-------------------------|--------------------------------|-------------|------------------------|------------------------|
| a /Å              | 5.3550                  | 5.3500(6)                      | 5.346       | 5.364                  | 5.368                  |
| c / Å             | 9.4960                  | 9.493(2)                       | 9.489       | 9.520                  | 9.519                  |
| U₁₁/U₂₂(Sb)      | 0.018                   | 0.014                          | 0.018       | 0.014                  | 0.016                  |
| U₃₃(Sb)          | 0.024                   | 0.023                          | 0.024       |                        |                        |
| U₁₁/U₂₂(Na₁)     | 0.076                   | 0.064                          | 0.076       | 0.064                  | 0.069                  |
| U₃₃(Na₁)         | 0.050                   | 0.060                          | 0.050       | 0.060                  | 0.069                  |
| U₁₁/U₂₂(Na₂)     | 0.042                   | 0.039                          | 0.042       | 0.039                  | 0.048                  |
| U₃₃(Na₂)         | 0.147                   | 0.142                          | 0.147       | 0.142                  | 0.116                  |

Figure S 12: Deconvolution of peaks in spectrum for model compound Na₃Sb collected at 268 K. Spectra were recorded at MAS rate of 10 kHz in an external field of 16.4 T.
Table S 5: Parameters for isotropic chemical shifts, $\delta_{\text{iso}}$, quadrupolar coupling constants, $C_Q$, asymmetry parameters, $\eta_Q$, and broadening parameters for the two sites in Na$_3$Sb when fitted to the experimental NMR data collected at 268 K.

Fits were performed using the SOLA function in Topspin. All parameters were refined during the fit. The expected ratio of the two peaks is 2:1. Due to the larger $C_Q$ of site 2, some intensity is lost to spinning sidebands, resulting in a slightly larger ratio of integrals.

|                      | Na1  | Na2  |
|----------------------|------|------|
| $\delta_{\text{iso}}$/ppm | 83   | 52   |
| $C_Q$/MHz            | 4.61 | 0    |
| $\eta_Q$             | 0.06 | 0.15 |
| Gaussian line broadening/Hz | 239  | 283  |
| Lorenzian line broadening/Hz | 199  | 4354 |
| Integral (normalised by site 1) | 1    | 2.25 |
Figure S 13: Comparison of experimental variable temperature data with simulated spectra with varying hopping rates between sodium sites.

Variable-temperature $^{23}$Na NMR spectra were recorded at MAS rate of 10 kHz in an external field of 16.4 T. The temperature was determined using a previous calibration of gas-flow rates performed using Pb(NO$_3$)$_2$. Simulations were carried out using the EXPRESS simulation package within Matlab. For the simulations, the $^{23}$Na quadrupolar and chemical shift parameters extracted from the experimental spectrum for Na$_3$Sb at 268 K were used. Powder averaging was performed using a ZCW1597 tiling scheme and 500 Hz Gaussian line broadening was applied prior to Fourier transformation of the simulated free induction decays.
**Figure S14:** $^{23}$Na Multiple Quantum MAS (MQMAS) spectrum for the NaSb model compound.

Two sites are observed at 22 ppm and 17 ppm which integrate to approx. 1:1 intensity, with very small quadrupoles, corresponding to the two Na-sites in the structure. The MQMAS spectrum was recorded using a z-filtered pulse. Asterisks denote spinning sidebands.
SI.6 Operando PDF measurements – additional information and figures

**Figure S 15:** Contribution to the PDF of sodium metal as a function of sodiation level calculated from PDFGui.

The amount of sodium residual in the electrode grows during the desodiation process due to plating of the removed sodium onto the counter electrode resulting in texture which could not be removed from the PDF. The amount of sodium shows little change during the second sodiation. At all times, the contribution to the PDF of the sodium is very small compared to the peaks from the Na,Sb phases at low-r.

**Figure S 16:** $^{23}$Na NMR spectra for the pristine electrode (top) and a 3:2 ratio Super P:CMC electrode discharged to 0 V. Spectra were recorded at 10 kHz MAS with an external field of 16.4 T.
Table S6: Residual values for different refinement strategies. For three-phase refinements, where the addition of a-Na$_3$Sb improved the value of $R_w$ by $< 0.01$ compared to the two-phase refinement with fixed parameters, cells are highlighted in green; where the difference was between 0.01 and 0.1, cell are highlighted in yellow; where the difference is $> 0.1$, cells are highlighted in orange.

| Sodiation level calculated from electrochemical measurements (Number of Na per Sb) | $R_w$: 2 phase, 20 - 50 Å | $R_w$: 2 phase, 2 - 50 Å (fixed parameters from 20 - 50 Å refinement) | $R_w$: 2 phase, 2 - 50 Å, free parameters | $R_w$: 3 phase, 2 - 50 Å |
|---|---|---|---|---|
| 0 | 0.0854281 | 0.122403 | 0.13581821 | 0.13646 |
| 0.1125 | 0.100226 | 0.1315 | 0.1456721 | 0.1546207 |
| 0.225 | 0.0892131 | 0.131641 | 0.1463736 | 0.138377 |
| 0.3375 | 0.0887858 | 0.131008 | 0.1463537 | 0.141418 |
| 0.45 | 0.0912381 | 0.134853 | 0.15200942 | 0.148833 |
| 0.5625 | 0.0912381 | 0.137028 | 0.1546207 | 0.152509 |
| 0.675 | 0.0959591 | 0.139879 | 0.15868978 | 0.158836 |
| 0.7875 | 0.103441 | 0.150948 | 0.16577395 | 0.182607 |
| 0.9 | 0.0971645 | 0.1555 | 0.17305851 | 0.202095 |
| 1.0125 | 0.100585 | 0.163855 | 0.17989056 | 0.218383 |
| 1.125 | 0.100632 | 0.174443 | 0.1888977 | 0.23611 |
| 1.2375 | 0.10255 | 0.226309 | 0.19856172 | 0.220325 |
| 1.35 | 0.101682 | 0.200506 | 0.21338084 | 0.21436 |
| 1.4625 | 0.107517 | 0.217925 | 0.22889006 | 0.222674 |
| 1.575 | 0.113417 | 0.24861 | 0.25580464 | 0.219914 |
| 1.6875 | 0.115238 | 0.24861 | 0.28325656 | 0.236446 |
| 1.8 | 0.144409 | 0.285008 | 0.33954649 | 0.257094 |
| 1.9125 | 0.14474 | 0.338433 | 0.340794 | 0.257094 |
| 2.025 | 0.17321 | 0.340289 | 0.40480997 | 0.21436 |
| 2.1375 | 0.144143 | 0.435421 | 0.44509466 | 0.222674 |
| 2.25 | 0.158662 | 0.562885 | 0.51117389 | 0.219914 |
| 2.3625 | 0.1643 | 0.639437 | 0.54648632 | 0.236446 |
| 2.475 | 0.203411 | 0.68673 | 0.52346962 | 0.209339 |
| 2.5875 | 0.246382 | 0.703827 | 0.46101268 | 0.221444 |
| 2.7 | 0.22535 | 0.633175 | 0.41383742 | 0.244187 |
| 2.8125 | 0.217813 | 0.544762 | 0.34979319 | 0.242341 |
| 2.925 | 0.20341 | 0.407297 | 0.2468847 | 0.267849 |
| 3.0375 | 0.182821 | 0.318102 | 0.18442733 | 0.267849 |
| 3.15 | 0.153045 | 0.273135 | 0.19469936 | 0.267849 |
| 3.2625 | 0.106217 | 0.156309 | 0.11356645 | 0.267849 |
| 3.375 | 0.0937 | 0.132332 | 0.10074404 | 0.267849 |
Table S7: Sodiation level calculated from the distribution of unit cells calculated from refinements in PDFGui. * indicates that a one-phase refinement was done for this data set, because additional phases were not stable in the refinement.

| Sodiation level from electrochemical measurements | Proportion of unit cells | Sodiation calculations | Proportion of unit cells | Sodiation calculations | Proportion of unit cells | Sodiation calculations |
|--------------------------------------------------|--------------------------|------------------------|--------------------------|------------------------|--------------------------|------------------------|
| Sb                                              | Na3Sb                    | a-Na3Sb                | #Na                      | #Sb                    | #Na per Sb                | Unit cells Sb          | Unit cells Na3Sb       | #Na                      | #Sb                      | #Na per Sb                |
| 0.000*                                           | 0.000                    | 0.000                  | 0.000                    | 0.000                  | 0.000                    | 1.000*                 | 0.000                    | 0.000                    | 0.000                    | 0.000                    |
| 0.1125                                           | 1.000*                   | 0.000                  | 0.000                    | 0.000                  | 0.000                    | 1.000*                 | 0.000                    | 0.000                    | 0.000                    | 0.000                    |
| 0.225                                            | 1.000*                   | 0.000                  | 0.000                    | 0.000                  | 0.000                    | 1.000*                 | 0.000                    | 0.000                    | 0.000                    | 0.000                    |
| 0.3375                                           | 1.000*                   | 0.000                  | 0.000                    | 0.000                  | 0.000                    | 1.000*                 | 0.000                    | 0.000                    | 0.000                    | 0.000                    |
| 0.45                                             | 1.000*                   | 0.000                  | 0.000                    | 0.000                  | 0.000                    | 1.000*                 | 0.000                    | 0.000                    | 0.000                    | 0.000                    |
| 0.5625                                           | 0.859                    | 0.000                  | 0.141                    | 0.702                  | 0.000                    | 6.000                   | 0.000                    | 6.000                   | 0.000                    | 6.000                    |
| 0.675                                            | 0.749                    | 0.000                  | 0.251                    | 1.251                  | 0.000                    | 4.995                   | 0.000                    | 4.995                   | 0.000                    | 4.995                    |
| 0.7875                                           | 0.629                    | 0.000                  | 0.371                    | 1.847                  | 0.000                    | 4.517                   | 0.000                    | 4.517                   | 0.000                    | 4.517                    |
| 0.9                                              | 0.532                    | 0.000                  | 0.468                    | 2.330                  | 0.000                    | 4.128                   | 0.000                    | 4.128                   | 0.000                    | 4.128                    |
| 1.0125                                           | 0.453                    | 0.000                  | 0.547                    | 2.723                  | 0.000                    | 3.813                   | 0.000                    | 3.813                   | 0.000                    | 3.813                    |
| 1.125                                            | 0.407                    | 0.000                  | 0.593                    | 2.955                  | 0.000                    | 3.627                   | 0.000                    | 3.627                   | 0.000                    | 3.627                    |
| 1.2375                                           | 0.358                    | 0.000                  | 0.642                    | 3.195                  | 0.000                    | 3.433                   | 0.000                    | 3.433                   | 0.000                    | 3.433                    |
| 1.35                                             | 0.309                    | 0.002                  | 0.689                    | 3.443                  | 0.000                    | 3.236                   | 0.000                    | 3.236                   | 0.000                    | 3.236                    |
| 1.4625                                           | 0.271                    | 0.006                  | 0.723                    | 3.637                  | 0.000                    | 3.083                   | 0.000                    | 3.083                   | 0.000                    | 3.083                    |
| 1.575                                            | 0.231                    | 0.008                  | 0.760                    | 3.837                  | 0.000                    | 2.925                   | 0.000                    | 2.925                   | 0.000                    | 2.925                    |
| 1.6875                                           | 0.191                    | 0.013                  | 0.796                    | 4.044                  | 0.000                    | 2.762                   | 0.000                    | 2.762                   | 0.000                    | 2.762                    |
| 1.8                                              | 0.135                    | 0.042                  | 0.823                    | 4.348                  | 0.000                    | 2.542                   | 0.000                    | 2.542                   | 0.000                    | 2.542                    |
| 1.9125                                           | 0.142                    | 0.013                  | 0.846                    | 4.287                  | 0.000                    | 2.567                   | 0.000                    | 2.567                   | 0.000                    | 2.567                    |
| 2.025                                            | 0.093                    | 0.015                  | 0.891                    | 4.530                  | 0.000                    | 2.374                   | 0.000                    | 2.374                   | 0.000                    | 2.374                    |
| 2.1375                                           | 0.078                    | 0.021                  | 0.901                    | 4.613                  | 0.000                    | 2.312                   | 0.000                    | 2.312                   | 0.000                    | 2.312                    |
| 2.25                                             | 0.065                    | 0.027                  | 0.908                    | 4.685                  | 0.000                    | 2.260                   | 0.000                    | 2.260                   | 0.000                    | 2.260                    |
| 2.3625                                           | 0.050                    | 0.040                  | 0.910                    | 4.771                  | 0.000                    | 2.200                   | 0.000                    | 2.200                   | 0.000                    | 2.200                    |
| 2.475                                            | 0.039                    | 0.056                  | 0.905                    | 4.842                  | 0.000                    | 2.157                   | 0.000                    | 2.157                   | 0.000                    | 2.157                    |
| 2.5875                                           | 0.031                    | 0.077                  | 0.892                    | 4.905                  | 0.000                    | 2.123                   | 0.000                    | 2.123                   | 0.000                    | 2.123                    |
| 2.7                                              | 0.025                    | 0.164                  | 0.811                    | 5.023                  | 0.000                    | 2.099                   | 0.000                    | 2.099                   | 0.000                    | 2.099                    |
| 2.8125                                           | 0.018                    | 0.249                  | 0.733                    | 5.143                  | 0.000                    | 2.073                   | 0.000                    | 2.073                   | 0.000                    | 2.073                    |
| 2.925                                            | 0.013                    | 0.432                  | 0.555                    | 5.353                  | 0.000                    | 2.054                   | 0.000                    | 2.054                   | 0.000                    | 2.054                    |
| 3.0375                                           | 0.009                    | 0.828                  | 0.163                    | 5.778                  | 0.000                    | 2.038                   | 0.000                    | 2.038                   | 0.000                    | 2.038                    |
| 3.15                                             | 1.000*                   |                     |                       |                       |                         |                       |                         |                       |                       |                         |
| 3.2625                                           | 1.000*                   |                     |                       |                       |                         |                       |                         |                       |                       |                         |
| 3.375                                            | 1.000*                   |                     |                       |                       |                         |                       |                         |                       |                       |                         |
Figure S17: Refinement of the Sb structure against PDF data for the pristine electrode extracted from the in situ electrochemical cell. $R_w = 11.2\%$

Figure S18: Left axis (red crosses): change to the antimony phase scale factor during the first sodiation in one-phase refinements (normalised with respect to the scale factor for the pristine electrode). Right axis (green circles): change to $R_w$ for one-phase least-squared refinement of Sb versus PDF data in the distance range 20 – 50 Å. Very little change to the scale factor is observed until approximately 0.8 Na per Sb has been added to the electrode.
**Figure S 19:** Contributions of c-Sb, c-Na$_3$Sb and a-Na$_{2.7}$Sb to the PDF obtained at a total electrode stoichiometry of Na$_{2.7}$Sb on the first sodiation. Contribution of phases is calculated using the parameters obtained during a three-phase least-squares refinement against PDF data.

**Figure S 20:** Comparison of the PDF a-Na$_{2.7}$Sb obtained at the end of S2-c with that obtained during the S1-a.
Figure S 21: Refinement of the Na₃Sb structure against PDF data for the electrode at the end of sodiation extracted from the in situ electrochemical cell. $R_w = 10.1\%$

Figure S 22: Comparison of different Sb-connectivities with the experimental PDF.

Calculated PDFs for NaSb, NaSb-helix and parallel dumbbell connectivities were calculated using PDFGui. For NaSb, the PDF was calculated from the structure of Cromer et al. For the NaSb helix, a supercell containing only a single helix with no additional correlations in the $a$ and $c$ directions within 10 Å. For the PDF of dumbbells, a subset of the NaSb structure containing pairs of dumbbells with the correct orientation was chosen and all other atoms removed.
**Figure S 23:** Peak fitting of the PDF extracted at the end of D2-b. Open circles show experimental data, red line shows fit to the experimental data. Centres of the fitted peaks are labelled.
Linear combinations of the PDFs for \( c-Na_3Sb \), \( a-Na_{1.0}Sb \) and \( a-Na_{1.7}Sb \) were used to model the intermediate datasets during D1-a and D1-b using both two and three phase models. The PDF for \( c-Na_3Sb \) was taken from the end of S1-b, the PDF for \( a-Na_{1.0}Sb \) from the end of D1-b and the PDF for \( a-Na_{1.7}Sb \) was taken from the amorphous component of the PDF obtained at the end of D1-a.

The sum of the squared differences between the data and the linear combination \( (G(r)_{\text{experiment}} - [xG(r)_a + yG(r)_b])^2 \) (where \( a \) and \( b \) are the PDFs for the two phases) over the whole \( r \)-range, was minimised by varying the phase fraction of the two phases. A three phase fit was achieved by using three phase scale factors and a global scale factor.

When only \( c-Na_3Sb \) and \( a-Na_{1.0}Sb \) were used, the fit to the data at the end of D1-a was very poor, as shown in the figures below and is reflected in the large value for the sum of least-squares. The fit after incorporation of the additional \( a-Na_{1.7}Sb \) phase was at least as good as the two phase fit in all regions, with a significant improvement shown in the intermediate region.

It is on the basis of these results and from the visual change in amorphous component of the electrode during desodiation (Figure S8b), as well as the \(^{23}\text{Na} \) NMR results presented in the text, that we propose the formation of the additional phase, \( a-Na_{1.7}Sb \), during D1-a.

**Figure S 24:** Linear combination of \( c-Na_3Sb \) and \( a-Na_{1.0}Sb \) at a sodiation of \( Na_{1.7}Sb \) after minimisation of the squared difference between the function over the whole \( r \)-range. A very poor fit is achieved, indicating that an additional intermediate structure exists during desodiation.
Figure S 25: Results of linear combinations of PDFs to fit the intermediate PDFs during D1-a and D1-b.

Top: Linear combination at a total electrode sodiation level of Na$_{2.1}$Sb using the PDFs obtained at the start of D1-a (c-Na$_3$Sb) and at the end of D1-a (top left) and combination of c-Na$_3$Sb and a-Na$_{1.0}$Sb (top right). The linear combination using only c-Na$_3$Sb and a-Na$_{1.0}$Sb shows a considerably worse fit to the data in the intermediate region, confirming the presence of a separate intermediate phase: a-Na$_{1.7}$Sb. Bottom left: phase fractions determined by minimisation of squared differences by varying phase fraction using two phase (c-Na$_3$Sb, a-Na$_{1.7}$Sb crosses, c-Na$_3$Sb, a-Na$_{1.0}$Sb open circles) and three phase (triangles) fits. Red = c-Na$_3$Sb, blue = a-Na$_{1.7}$Sb, green = a-Na$_{1.0}$Sb. Bottom right: sum of the squared difference for two-phase c-Na$_3$Sb and a-Na$_{1.0}$Sb (orange circles) and three-phase (blue squares) combinations. The data indicate a two-phase region between c-Na$_3$Sb and a-Na$_{1.7}$Sb during D1-a, and conversion of a-Na$_{1.7}$Sb to a-Na$_{1.0}$Sb and the breakdown of remaining c-Na$_3$Sb during D1-b. c-Na$_3$Sb is still present at the end of D1-a, and is broken down further during D1-b.
Figure S 26: Refinement of c-Sb against PDF data obtained at the end of desodiation

Top: Refinement in high-r region (20 – 50 Å, $R_w = 14.1\%$); bottom: parameters fixed to values obtained at high-r and refinement extended to the full r-range. The residual of the refinement shows the amorphous Na$_{1.0}$Sb which remains in the electrode. The residual has been r-averaged over termination ripples.
Table S8: Structural parameters of c-Sb during D1-c, S1-a and S1-b from refinements against PDF data in the distance range 20 – 50 Å

| Sodiation level (Number of Na per Sb) | a /Å | c /Å | Scale | U11/U22 /Å$^2$ | U33 /Å$^3$ | Fraction atomic coordinate | R_w |
|--------------------------------------|------|------|-------|-----------------|-------------|---------------------------|-----|
| 0.975 D1-c                           | 4.307| 11.367| 0.036 | 0.013           | 0.053       | 0.271                     | 0.34|
| 0.8625                               | 4.305| 11.402| 0.166 | 0.021           | 0.049       | 0.267                     | 0.22|
| 0.75                                 | 4.303| 11.400| 0.369 | 0.022           | 0.048       | 0.267                     | 0.15|
| 0.6375 S2-a                          | 4.308| 11.380| 0.404 | 0.020           | 0.040       | 0.267                     | 0.14|
| 0.75                                 | 4.310| 11.373| 0.420 | 0.019           | 0.037       | 0.267                     | 0.14|
| 0.8625                               | 4.311| 11.365| 0.396 | 0.018           | 0.034       | 0.267                     | 0.14|
| 0.75                                 | 4.312| 11.354| 0.389 | 0.016           | 0.030       | 0.267                     | 0.13|
| 0.975 S2-b                           | 4.312| 11.345| 0.357 | 0.015           | 0.028       | 0.267                     | 0.13|
| 1.0875                               | 4.312| 11.341| 0.320 | 0.014           | 0.027       | 0.267                     | 0.12|
| 1.2                                  | 4.311| 11.333| 0.262 | 0.014           | 0.028       | 0.268                     | 0.17|
| 1.3125                               | 4.311| 11.321| 0.176 | 0.013           | 0.024       | 0.268                     | 0.20|
| 1.425                                | 4.311| 11.308| 0.110 | 0.011           | 0.024       | 0.267                     | 0.24|
| 1.5375                               | 4.310| 11.306| 0.069 | 0.011           | 0.023       | 0.268                     | 0.29|
| 1.65                                 | 4.307| 11.305| 0.050 | 0.009           | 0.015       | 0.271                     | 0.32|

Figure S 27: Comparison of the dumbbell Na$_{1.7}$Sb phase at the end of D1-a and end of S2-a.
Figure S 28: Refinement of Na$_3$Sb structure against PDF data obtained at the end of S2-c.

The difference curve is shown offset in grey for clarity. Below the structure refinement data are the calculated contributions to the PDF of sodium-metal (which is modelled as an additional phase as discussed in the Experimental Methods section) and the a-Na$_3$Sb calculated from the refined structures in PDFGui.

Table S9: Structural parameters for a-Na$_3$xSb determined from the refinement of Na$_3$Sb structure against PDF data determined at the end of S2-c. * indicates parameters fixed in the refinement.

|                  | c-Na$_3$Sb (ex situ PDF) | a-Na$_3$Sb at the end of S2-c |
|------------------|--------------------------|-------------------------------|
| $a$ /Å           | 5.346                    | 5.398                         |
| $c$ /Å           | 9.489                    | 9.197                         |
| Na occupancy     | 1                        | 0.830*                        |
| $U_{11}/U_{22}$(Sb) | 0.018                    | 0.180                         |
| $U_{33}$(Sb)     | 0.024                    | 0.839                         |
| $U_{11}/U_{22}$(Na1) | 0.076                    | 0.180                         |
| $U_{33}$(Na1)    | 0.050                    | 8.302                         |
| $U_{11}/U_{22}$(Na2) | 0.042                    | 0.170                         |
| $U_{33}$(Na2)    | 0.147                    | 0.231                         |
| Sp-diameter /Å   | -                        | 21.7                          |
SI.7 Calculation of error bars for sodiation level

Errors on the sodiation level were considered by considering the highest and lowest sodiation which could be achieved within the errors for phase fraction obtained from PDFGui refinements.

The least Na per Sb would be achieved when the maximum amount of Sb was present as c-Sb:

- The amount of c-Sb = F_1 + Δ
- The amount of a-Na_{3,δ}Sb = F_2 + Δ, or in the case that 1 − (F_1 + Δ) > F_2 + Δ, the amount of a- Na_{3,δ}Sb was set to 1 − (F_1 + Δ).
- The amount of c-Na_{3,δ}Sb = 1 − (F_1 + Δ) − (F_2 + Δ), or in the case that 1 − (F_1 + Δ) − (F_2 + Δ) = 0, the amount of c-Na_{3}Sb was set to 0.

where F_1, F_2 and F_3 are the phase fractions for c-Sb, a-Na_{3,δ}Sb and c-Na_{3,δ}Sb, and Δ the error given by PDFGui.

- The most amount of Na per Sb would be achieved when:
  - The amount of c- Na_{3,δ}Sb = F_3 + Δ
  - The amount of a- Na_{3,δ}Sb = F_2 + Δ, or when 1 − (F_3 + Δ) < F_2 + Δ, the amount of a- Na_{3,δ}Sb was set to 1 − (F_3 + Δ)
  - The amount of c-Sb = 1 − (F_3 + Δ) − (F_2 + Δ), or in the case that 1 − (F_3 + Δ) − (F_2 + Δ) = 0, the amount of c- Na_{3}Sb was set to 0.

The amount of Na per Sb was calculated in the same manner as outlined in section 2 of the main text. The difference between the these values and the values calculated for the phase fractions were used as error bars in Figure 4. A similar procedure was used for the two-phase refinement.
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