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Supporting Information

Characterizing multiple continuous phase transitions at an alloying anode with

voltammetric measurement and density functional theory

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1. Atomic configurations of structural motifs



Figure S1. Supercell structures of the stable (a) β -Sb, (b) α -Sb, (c) NaSb, and (d) Na₃Sb phases reported in previous works ^{S1, 2} and their fundamental structural motifs (see the insets) composed of Sb atoms. (e) Example metastable structure of the NaSb phase predicted in this study and its structural motif (see the inset) composed of Sb atoms.

In order to predict the plausible intermediate Na_xSb phases formed during battery cycles, we first obtained the fundamental frameworks of Sb atoms constructing the intermediate Na_xSb phases. This was done by extracting the frameworks of Sb atoms of the stable Na_xSb phases (i.e., β -Sb, α -Sb, NaSb, and Na₃Sb) reported elsewhere ^{S1, 2}. The Sb frameworks were classified according to their atomic configurations, where chemical bonds within the cut-off length of 3.2 Å are indicated for better visibility (Figs. S1a-d). When examining the stable Na_xSb phases, they are composed of four differing types of Sb frameworks, i.e., layered-zigzag, layered-armchair, 1D-armchair, and independent atom structures. However, in addition to these fundamental structural motifs, inflowing Na ions into the

stable phases can distort/transform these fundamental structures, which can promote the formation of additional Sb frameworks. To confirm this concept, we assessed whether the changes in Na contents of stable phases promote the formation of additional Sb frameworks (for the detailed procedures for constructing metastable phases, see Section 4.2. in Supporting Information). Calculations show that, when *x* of Na_{*x*}Sb becomes greater than 1.0, Na ions flowing into the layered-armchair structure break Sb-Sb bonds, which transform the layered-armchair structure to the 1D-zigzag structure (Fig. S1e). The above analyses on the fundamental structural motifs indicate that the intermediate Na_{*x*}Sb phases formed during battery cycles are composed of five different structural motifs of zigzag-armchair, layered-armchair, 1D-zigzag, 1D-armchair, and independent atom structures.



2. Prediction of the intermediate phases formed during sodiation of Sb anode

Figure S2. Formation energies per atom of various intermediate Na_xSb phases plotted as a function of (a) *x* of Na_xSb and (b) atomic percent of Na. Note that, of all 19 intermediate Na_xSb phases, nine phases (denoted by the red symbols) are likely to form during battery cycles.

Table S1. Results of phase selection performed on 19 different Na_xSb structures predicted in this study. Among these phases, unlikely phases are denoted by \times , whereas metastable and stable phases are indicated by Δ and \bigcirc , respectively.

Transition stage		$Stage I (Sb \leftrightarrow NaSb) \qquad Stage II (NaSb \leftrightarrow$				Na ₃ Sb)									
Na contents	x of Na_xSb	0	0.11	0.25	0.5	0.75	1.0	1.0	1.25	1.5	1.75	2	2.5	2.75	3
	Atomic percent of Na	0	10	20	33	43	50	50	56	60	64	67	71	73	75
Fundamental structural motifs	Layered-zigzag	0	×		×		×	×							
	Layered-armchair			\bigtriangleup	\bigtriangleup	×									
	1D-zigzag						\bigtriangleup	\bigtriangleup	\bigtriangleup	\bigtriangleup	\bigtriangleup				
	1D-armchair						0	0	×	×					
	Independent atoms										×	\bigtriangleup	×	×	0

3. Determination of charge and discharge voltages for the Stage II transition of the Na-Sb battery



Figure S3. Changes in the Gibbs free energy (G_i^{II} and $G_{i,U}^{II}$) calculated for the intermediate reaction states occurring during the Stage II transition (NaSb \leftrightarrow Na₃Sb) of the Na–Sb system imposed on various external voltages. 1, 2, 3, 4, 5 and 6 indicated on the *x*-axis denote the intermediate reaction states corresponding to 2Na + NaSb, 1.75Na + Na_{1.25}Sb, 1.5Na + Na_{1.5}Sb, 1.25Na + Na_{1.75}Sb, Na + Na₂Sb, and Na₃Sb, respectively. The insets are the intermediate Na_xSb phases formed in each reaction state.

In this section, by applying a thermodynamic model similar to that explained in Fig. 5 in the manuscript, we calculated the theoretical charge and discharge voltages for the Stage II transition. As shown in Figure S2 and Table S1 in Supporting Information, during the Stage II transition, the continuous/reversible phase transition between the two stable phases of NaSb and Na₃Sb proceeds with the formation of five different intermediate metastable phases, i.e., Na_{1.25}Sb (1D-zigzag), Na_{1.75}Sb (1D-zigzag), Na₂Sb (independent atom structures) according to:

Stage II transition: $2Na + NaSb \leftrightarrow 1.75Na + Na_{1.25}Sb \leftrightarrow 1.5Na + Na_{1.5}Sb \leftrightarrow 1.25Na$ + $Na_{1.75}Sb \leftrightarrow Na + Na_2Sb \leftrightarrow Na_3Sb.$ (S1) Therefore, under the absence of applied potential, the Gibbs free energy at i^{th} intermediate state in the Stage II transition, i.e., G_{i}^{II} , can be calculated by:

$$G_i^{II} = (1 - x)G_{Na} + G_{Na_xSb}, \quad i = 1, 2, 3, 4, 5 \text{ and } 6,$$
(S2)

where G_{Na} and G_{Na_xSb} are the Gibbs free energies of Na and the intermediate stable/metastable Na_xSb phases, respectively, and *x* is the number of Na ions (Na⁺) reacted with pristine Sb. When the external potential (*U*) is imposed on the Na-Sb system, the Gibbs free energy of each intermediate state decreases in proportion to the numbers of Na⁺, i.e., (1 - *x*) in Eq. (S2) that do not participate in the reaction responsible for the formation of Na_xSb phases. Therefore, under the external potential *U* imposed on the battery system, the Gibbs free energy of each intermediate state in the Stage II transition can be evaluated as:

$$G_{i,U}^{II} = G_i^{II} - (1 - x)U, \quad i = 1, 2, 3, 4, 5 \text{ and } 6.$$
(S3)

Using Eq. (S3), the $G_{l,U}^{II}$ values for various external potentials *U* are calculated and shown in Figure S3. When examining the $G_{l,U}^{II}$ values calculated under the absence of external potentials (see the black line in Fig. S3), all intermediate reaction states are in the decreasing trend of free energy, indicating that the spontaneous phase transition occurs along the direction of sodiation. When an external potential is imposed on the system, the $G_{l,U}^{II}$ value of each intermediate state begins to decrease but is reduced at different rates by the amount of (1 - x)U, rendering the overall shape of the Gibbs free energy curves to change. The decreasing tendency in $G_{l,U}^{II}$ values continues along the direction of sodiation until U <0.28 V (denoted by the red line in Figure S3). When U = 0.28 V, some $G_{l,U}^{II}$ values are no longer in the decreasing trend along sodiation. This suggests that the discharging process is no more spontaneous beyond U = 0.28 V (see the purple line U = 0.28 V in Figure S3). As the *U* value increases beyond 0.78 V, the $G_{l,U}^{II}$ values exhibit the increasing trend, indicating that the desodiation process becomes spontaneous (see the blue and orange lines in Figure S3). The above calculation results indicate that 0.28 and 0.78 V are the threshold/minimal potential for sodiation and desodiation, respectively, and thus, are the theoretical discharge ($U_{th,dis}$) and charge ($U_{th,chg}$) voltages of the Stage II transition.

4. METHODS

4.1. Calculation of theoretical voltages using stable intermediate phases: previous method

In order to reproduce the theoretical polarization curves of batteries, previous studies have considered only the stable phases, which correspond to both edges of the voltage plateaus in the experimental polarization curve $^{S3-5}$. In case of the Na-Sb battery, the polarization curve exhibits two distinct voltage plateaus enclosed by *x* of Na_{*x*}Sb in the ranges of $0 \le x \le 1.0$ and $1.0 \le x \le 3.0$, indicating that the charge and discharge processes of this battery are accompanied by the formation of three different stable phases of Sb, NaSb, and Na₃Sb. The phase transition that occurs during discharging (charging) between these three stable phases releases (absorbs) a transition energy (transition enthalpy), the degree of which is revealed as voltage values of the plateaus observed from polarization curves. Therefore, the theoretical voltage values (U_{th}) of the plateaus can be expressed in terms of transition enthalpy ($^{\Delta H_t}$);

$$U_{th} = \Delta H_t / \Delta e = \frac{\Delta H_{Na_{x_1}Sb} - \Delta H_{Na_{x_2}Sb}}{(x_2 - x_1)e}, \qquad (S4)$$

where ${}^{\Delta H_{Na_{x1}Sb}}$ and ${}^{\Delta H_{Na_{x2}Sb}}$ are the enthalpy of formation of the Na_{x1}Sb and Na_{x2}Sb phase, respectively, x_i the amount of Na reacted with the pristine Sb, and e the charge of an electron (for the calculation methods of enthalpy of formation of phases, see Section 4.4. below). Therefore, the U_{th} values of two different voltage plateaus observed from the Na-Sb battery are given by;

$$U_{th,Sb\to NaSb} = \frac{\Delta H_{Sb} - \Delta H_{NaSb}}{e},$$
(S5.1)

$$U_{th,NaSb\to Na_3Sb} = \frac{\Delta H_{NaSb} - \Delta H_{Na_3Sb}}{2e}.$$
(S5.2)

4.2. Identification of metastable phases

To identify the plausible metastable phases formed during battery cycles, we constructed the representative metastable Na_xSb structures; we first constructed three fundamental structural motifs of Sb atoms (i.e., layered-zigzag, layered-armchair, and 1D-armchair structures). The Sb frameworks with layered-zigzag and layered-armchair structures were obtained by generating the supercell structures of $(3 \times 3 \times 1)$ β -Sb and $(2 \times 2 \times 1) \alpha$ -Sb, whereas the Sb framework with 1D-armchair structure was obtained by removing constituent Na atoms from the $(2 \times 2 \times 1)$ NaSb supercell structure. We next added differing numbers of Na atoms to the Sb frameworks such that they distribute uniformly in the free spaces of the Sb frameworks, to produce 28 different initial Na_xSb model structures (see Table S2). Subsequently, these initial Na_rSb model structures were relaxed under isothermal-isobaric ensemble to obtain the metastable Na_xSb structures with differing Na contents. During relaxation, the electronic wave functions were expanded in plane waves with an energy cutoff of 30 Ry, and $(4 \times 4 \times 4)$ 4) k-point mesh was sampled with Monkhorst and Pack scheme. During this process, some Sb frameworks undergo spontaneous transformation into more stable structures, such as layered-zigzag, layered-armchair, 1D-zigzag, 1D-armchair, independent-atom structures, and amorphous structures (see Table S3). Lastly, we discarded phases with amorphous Sb structures (because these phases are less likely to retain their structures during battery cycles) and selected 19 different candidate metastable phases. The energy convergence was achieved using a conjugate gradient method ^{S6} until the residual forces were below 10⁻³ eV/Å. Three-dimensional periodic boundary conditions were applied to all model structures. All calculations were performed based on the Perdew-Burke-Ernzerhof S7 exchangecorrelation functional, as implemented in the Quantum Espresso package ^{S8}.

Table S2. List of initial Na_x Sb model structures with differing structural motifs and Na compositions.All structures were constructed by adding Na atoms in free spaces of Sb structural motifs.

Initial structural motifs	Initial model structures of Na_xSb before relaxation	Total number of phases
β-Sb (Layered-zigzag)	Sb, Na _{0.11} Sb, Na _{0.17} Sb, Na _{0.33} Sb, Na _{0.5} Sb, Na _{0.67} Sb, NaSb, Na _{1.5} Sb	8
α-Sb (Layered-armchair)	$Na_{0.13}Sb, Na_{0.25}Sb, Na_{0.5}Sb, Na_{0.75}Sb, NaSb, Na_{1.25}Sb, Na_{1.5}Sb, Na_{1.75}Sb$	8
NaSb (1D-armchair)	Na _{0.5} Sb, Na _{0.75} Sb, NaSb, Na _{1.25} Sb, Na _{1.5} Sb, Na _{1.75} Sb, Na ₂ Sb, Na _{2.25} Sb, Na _{2.25} Sb, Na _{2.75} Sb, Na ₃ Sb	11
Na ₃ Sb (Independent atoms)	Na ₃ Sb	1

Table S3. Results of structural relaxation performed on 28 different initial Na_xSb model structures.

Among these phases, total of 19 structures remain their crystallinity during relaxation and can be

regarded as metastable Na_xSb phases.

Initial structural motifs	Model structures of Na_xSb structures after relaxation									
	Layered-zigzag	Layered-armchair	1D-zigzag	1D-armchair	Independent atoms	Amorphous				
β-Sb (Layered-zigzag)	Sb, Na _{0.11} Sb, Na _{0.5} Sb, NaSb					Na _{0.17} Sb, Na _{0.33} Sb, Na _{0.67} Sb, Na _{1.5} Sb				
α-Sb (Layered-armchair)		Na _{0.25} Sb, Na _{0.5} Sb, Na _{0.75} Sb	NaSb, Na _{1.25} Sb, Na _{1.5} Sb. Na _{1.75} Sb			Na _{0.13} Sb				
NaSb (1D-armchair)				NaSb, Na _{1.25} Sb, Na _{1.5} Sb	Na _{1.75} Sb, Na ₂ Sb, Na _{2.5} Sb, Na _{2.75} Sb	Na _{0.5} Sb, Na _{0.75} Sb, Na _{2.25} Sb, Na ₃ Sb				
Na ₃ Sb (Independent atoms)					Na ₃ Sb					

4.3. Calculation of the free space of intermediate Na_xSb phases

Voronoi analyses were performed to estimate the volume fraction of the free space of the intermediate Na_xSb phases. For this purpose, we first moved the spherical probes through the free space of the intermediate Na_xSb phases using the tunnel detection algorithms implemented in CAVER[®] software ^{S9}. We then visualized the distribution of the free space by tracking the traces of the spherical probes that migrate through the free space (for the distribution of the free space of phases, see Figure 3 in the manuscript). The volumes of the free space were calculated for various intermediate Na_xSb phases to compare the relative magnitude of spaces to which Na ions can be stored. In this calculation, Sb atoms constituting the Na_xSb phases were assumed to be hard spheres with radius of 2.06 Å.

4.4. Computation of the enthalpy of formation of phases

The plausible phases that can develop during charge-discharge cycles were then filtered out by evaluating the formation energies of 19 different Na_xSb structures/phases listed in Figure S2 and Table S1. For this purpose, the total energies were calculated for (2 2 2) supercell structures of the intermediate phases using the isothermal-isobaric ensemble at 0 K. Since the influence of pressure on the condensed phases was ignored and the energy evaluated at 0 K does not contain any entropic (*TS*) contributions, the calculated total energies of phases can be regarded as the enthalpy (*H*) of phases ^{S10}. ¹¹. Accordingly, the enthalpy of phases were calculated for (2 2 2) supercell structures of the intermediate Na_xSb ^{(H_{Na_xSb})</sup>, Sb (^{H_{Sb}}), and Na ^(H_{Na}) phases using first-principles calculations with the Norm-conserving pseudopotentials ^{S12, 13} and plane-wave basis set as shown in Quantum Espresso ^{S8}. The sampling of the Brillouin zone was conducted utilizing the theory proposed by Monkhorst and Pack by setting the k-point mesh to $4 \times 4 \times 4$. The cutoff energy for plane wave was fixed at 30 Ry, while the convergence in the total energy was obtained until the residual forces were below 10^{-3} eV/Å. Utilizing the calculated enthalpy of the Sb and Na solid phases, the enthalpy of formation (Δ H) of stable intermediate phases of NaSb and Na₃Sb were calculated using Eq. (S6);</sup>}

$$\Delta H_{Na_xSb} = (1+x)H_{Na_xSb}/n_{Na_xSb} - xH_{Na}/n_{Na} - H_{Sb}/n_{Sb},$$
(S6)

where ${}^{n_{Na_{x}Sb}}$, n_{Na} , and n_{Sb} correspond to the atom numbers in the supercell structures of the phases of Na_xSb, Na, and Sb, respectively. The enthalpies of formation calculated for the stable NaSb and Na₃Sb phases are consistent with previous calculation results ^{S14} (Table S4). After confirming the reliability of calculation methods employed in this study, we evaluated the enthalpy of formation of the other metastable phases using procedures similar to those employed for the stable NaSb and Na₃Sb phases.

Table S4. Calculated enthalpy of formation $({}^{\Delta H_{Na_x}Sb})$ of the stable NaSb and Na₃Sb phases. For comparison, the ${}^{\Delta H_{Na_x}Sb}$ values calculated from previous studies are also shown.

Internet liste March allocation	Formation energies ($\Delta H_{Na_{\chi}Sb}$, eV/atom)						
Intermediate Na_xSb phases	Present study	Previous studies ^{S14}					
NaSb (1D-armchair)	-0.34	-0.33					
Na ₃ Sb (Independent atoms)	-0.46	-0.44					

4.5. Calculation of the Gibbs free energies of the model systems

Using the enthalpy of phases calculated based on Eq. (S6), the theoretical charge and discharge voltages of the Na-Sb battery were evaluated by analyzing the changes in the Gibbs free energy for phase transformation in charge-discharge cycles. We obtained this by computing the Gibbs free energy changes related to the *i*th intermediate reaction in each transition stage of I and II (referred to as G_i^I , and G_i^{II} ; see Table 1 for the detailed equations). The Gibbs free energies of pure Na, pure Sb, and intermediate metastable Na_xSb phases (namely, G_{Na} , G_{Sb} , and $G_{Na_xSb}^{II}$) in these computations are given by Eqs. (S7-9),

$$G_{Na_{\chi}Sb} = \frac{(1+x)(H_{Na_{\chi}Sb} - TS_{Na_{\chi}Sb})}{n_{Na_{\chi}Sb}},$$
(S7)

$$G_{Na} = \frac{H_{Na} - TS_{Na}}{n_{Na}},\tag{S8}$$

$$G_{Sb} = \frac{H_{Sb} - TS_{Sb}}{n_{Sb}}.$$
(S9)

Here, ${}^{S_{UC,Na_x}Sb}$, ${}^{S_{UC,Na}}$, and ${}^{S_{UC,Sb}}$ correspond to the entropy of each unit cell of the intermediate Na_xSb, Na, and Sb phases. Since the entropic (*TS*) contribution for a two-phase reaction in alloying anodes is

usually very small (an order of ~10 meV) at ambient temperatures ^{S15, 16}, it is assumed that the Gibbs free energies in Eqs. (S7-9) is roughly the same as the enthalpic contribution (i.e., H_{Sb}/n_{Sb}).

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