Supplementary Information

Evaluation of energy loss at Sn anodes based on phase transition behaviors and formation of electrically resistive phases of the Na-Sn battery

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Calculation of the voltage values via Gibbs free energy curves for Stage I − IV transitions.

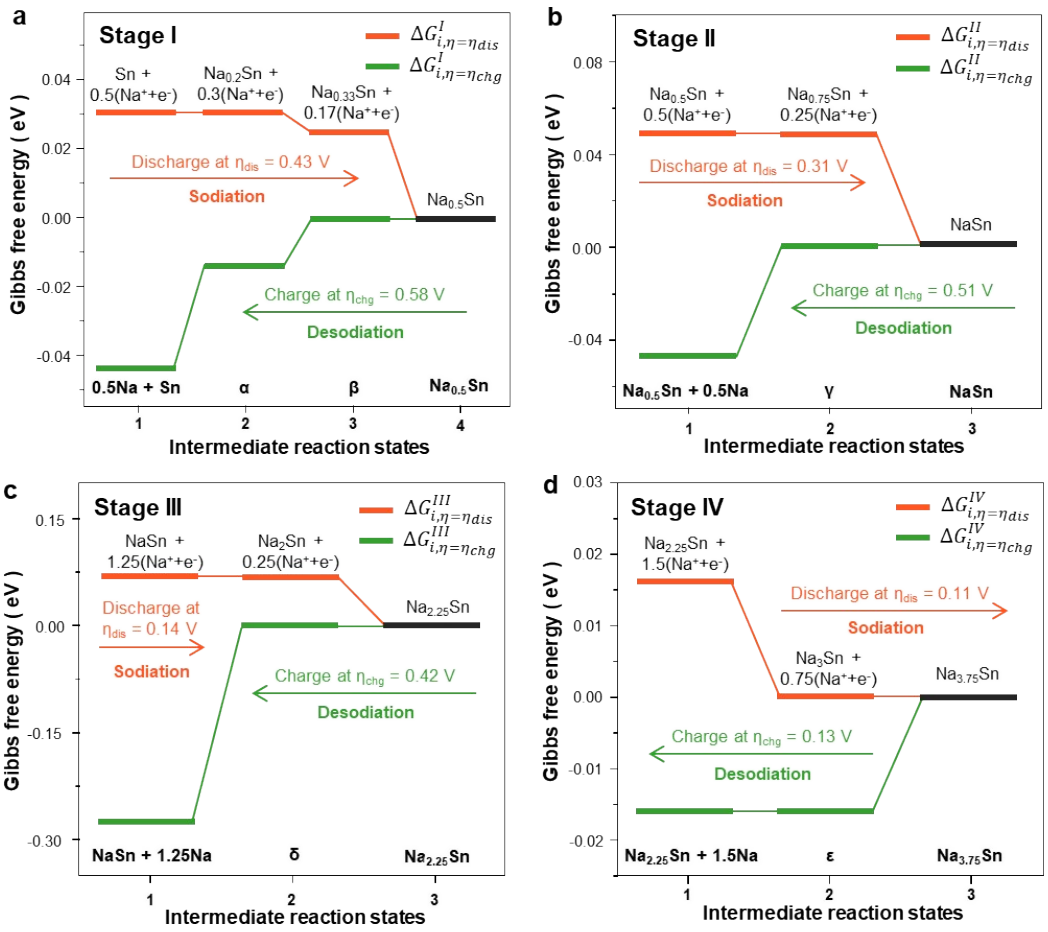

Figure S1. Changes in the Gibbs free energy calculated for the intermediate reaction states occurring during (a) Stage I ($\Delta G^{I}_{i,\eta}$), (b) Stage II ($\Delta G^{II}_{i,\eta}$), (c) Stage III ($\Delta G^{III}_{i,\eta}$), and (d) Stage IV ($\Delta G^{IV}_{i,\eta}$) transitions under the external voltage η. In these graphs, two representative voltage value corresponding to discharge (η_{dis}) and charge (η_{chg}) are chosen. The greek alphabets indicated in the *x*-axis denote the intermediate states comprising metastable phases; α = 0.3Na + $Na_{0.2}Sn$, β = 0.17Na + $Na_{0.33}Sn$, γ = $Na_{0.75}Sn$ + 0.25Na, δ = Na_2Sn + 0.25Na, ε = Na_3Sn + 0.75Na.

By applying the same thermodynamic model as explained in Fig. 2 in the manuscript, the discharge (η_{dis}) and charge voltages (η_{chg}) corresponding to Stage I − IV can be determined. In this section, we evaluate the η_{dis} and η_{chg} values by calculating the changes in the Gibbs free energy in Stage I − IV during charging and discharging. For this purpose, we first evaluated the Gibbs free energy change (ΔG_i^I) associated with the i^{th} intermediate reaction in Stage I− IV. This was achieved by add up the Gibbs free energies of all phases (Na, Sn, and Na_xSn phases) comprising the i^{th} intermediate reaction state according to;

(Stage I transition) $$\Delta G_{i,\eta}^{I} = 0.5G_{Na} + G_{Sn}, \; i = 1. \qquad \text{(S1.1)}$$

$$\Delta G_i^I = (0.5 - x)G_{Na} + xG_{Na_xSn}, \; i = 2, 3, 4. \qquad \text{(S1.2)}$$

(Stage II transition) $$\Delta G_i^{II} = (1.0 - x)G_{Na} + G_{Na_xSn}, \; i = 1, 2, 3. \qquad \text{(S2)}$$

(Stage III transition) $$\Delta G_i^{III} = (2.25 - x)G_{Na} + G_{Na_xSn}, \; i = 1, 2, 3. \qquad \text{(S3)}$$

(Stage IV transition) $$\Delta G_i^{IV} = (3.75 - x)G_{Na} + G_{Na_xSn}, \; i = 1, 2, 3. \qquad \text{(S4)}$$

When an external voltage/potential (η) is applied to the Na-Sn system, the Gibbs free energy of each intermediate reaction in Eqs. (S1−4) decreases linearly in proportion to the x value of Na in Na_xSn. Therefore, under the application of the external voltage η, the Gibbs free energy of each intermediate state in Stage I − IV transitions can be evaluated from

(Stage I transition) $$\Delta G_{i,\eta}^{I} = 0.5G_{Na} + G_{Sn} - (0.5 - x)\eta, \; i = 1. \qquad \text{(S5.1)}$$

$$\Delta G_{i,\eta}^{I} = (0.5 - x)G_{Na} + xG_{Na_xSn} - (0.5 - x)\eta, \; i = 2, 3, 4. \qquad \text{(S5.2)}$$

(Stage II transition) $\Delta G_i^{II} = (1.0 - x)G_{Na} + G_{Na_xSn} - (1.0 - x)\eta$, i = 1, 2, 3. (S6)

(Stage III transition) $\Delta G_i^{III} = (2.25 - x)G_{Na} + G_{Na_xSn} - (2.25 - x)\eta$, i = 1, 2, 3. (S7)

(Stage IV transition) $\Delta G_i^{IV} = (3.75 - x)G_{Na} + G_{Na_xSn} - (3.75 - x)\eta$, i = 1, 2, 3. (S8)

As shown in Eqs (S5−8), the external voltage (η) changes the Gibbs free energies of the i^{th} intermediate reaction states and thus, alters to overall shape of the Gibbs free energy curve during charging and discharging. According to the definitions made in the manuscript, the η_{dis} value can be determined as the highest voltage that makes the all intermediate states for discharge process to be the free-energy downhill, while the η_{chg} value as the lowest voltage that causes the all intermediate states for charge process to be the free-energy downhill. By substituting the various η values, we obtained the η_{dis} and η_{chg} values for Stage I − IV transitions that satisfied the above-mentioned criteria (Fig. S1). Therefore, the η_{dis} and η_{chg} corresponding to Stage I – IV transitions are determined to be η_{dis} = 0.43 (Stage I), 0.31 (Stage II), 0.14 (Stage III), 0.11 V (Stage IV) and η_{chg} = 0.58 (Stage I), 0.51 (Stage II), 0.42 (Stage III), 0.13 V (Stage IV), which is also summarized in Table 2 in the manuscript.