Electronic Supplementary Material (ESI) for Journal of Materials Chemistry A.

Supplementary Information

Phase transition behaviors and formation of electrically resistive phases at the anodes: Major factors determining the energy efficiency of Li-ion batteries

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1. Calculation of the voltage values via Gibbs free energy curves for the Li−Sb battery.

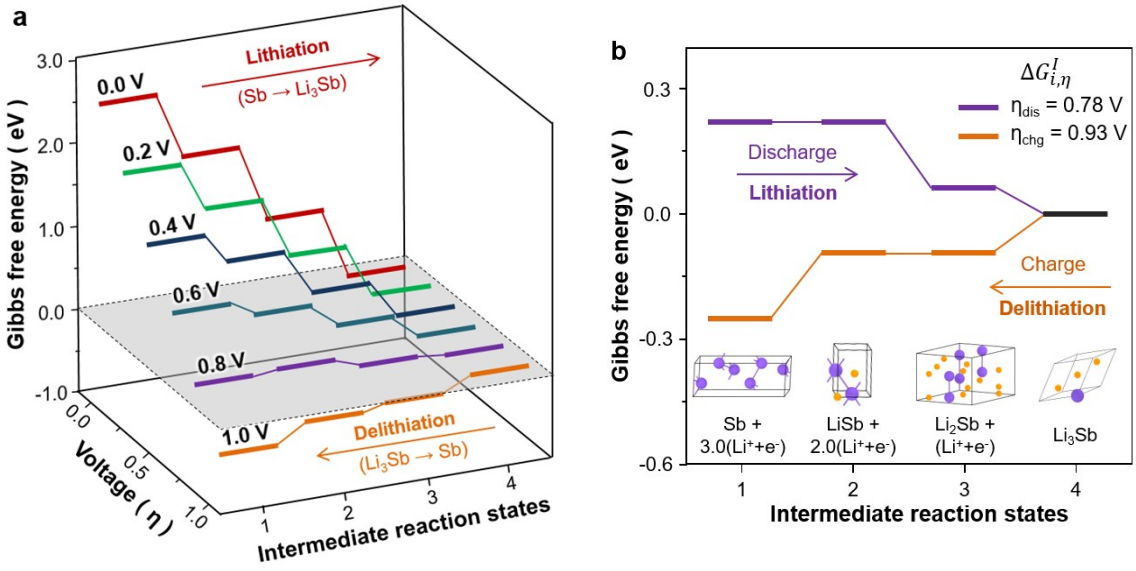

Figure S1. (a) Changes in the Gibbs free energy ($^{\Delta G^{I}_{i,\eta}}$) calculated for the intermediate reactions occurring during Stage I transition (Sb ↔ Li_3Sb) of the Li−Sb battery under various external voltages. 1, 2, 3 and 4 indicated on the *x*-axis denote the intermediate states corresponding to 3.0Li + Sb, 2.0Li + LiSb, Li + Li_2Sb and Li_3Sb, respectively. (b) Representative graphs selected from (a), showing the changes in the Gibbs free energy of the intermediate reactions at the critical voltages corresponding to the discharge (η_{dis}) and charge (η_{chg}) in Stage I transition. The structures in the inset of (b) are four Li_xSb phases formed by the intermediate reactions in the Li−Sb battery. In these structures, Li and Sb atoms are distinguished by yellow and purple shperes, respectively.

During the charge and discharge processes, the Li−Sb system undergoes a single phase transition corresponding to Sb ↔ Li_3Sb, which is referred to as the Stage I transition. In order to replicate the voltage curves associated with the battery cycles at the Sb anode of the Li−Sb system, it is therefore

necessary to evaluate the discharge (η_{dis}) and charge voltages (η_{chg}) corresponding to the Stage I transition. In this section, using procedures similar to those discussed in Fig. 5 of the manuscript, we evaluated the η_{dis} and η_{chg} values by calculating the changes in the Gibbs free energy of the intermediate reactions in the Stage I transition of the Li−Sb battery. For this purpose, we first evaluated the Gibbs free energy change ($^{\Delta G_i^I}$) associated with the i^{th} intermediate reaction in Stage I transition. This was achieved by using the Gibbs free energies of all phases (Li, Sb, and Li_xSb phases) comprising the i^{th} intermediate reaction state according to:

(Stage I transition) $$\Delta G_{i,\eta}^{\ I} = 3G_{Li} + G_{Sb},\ i = 1. \quad \text{(S1.1)}$$

$$\Delta G_i^I = (3 - x)G_{Li} + xG_{Li_xSb},\ i = 2, 3, 4. \quad \text{(S1.2)}$$

When the external voltage/potential η is imposed on the Li−Sb system, the Gibbs free energy of each intermediate reaction in Eq. (S1) decreases further in proportion to the number of Li atoms that do not participate in the reaction forming the lithiated compound of Li_xSb, i.e., (3 - x). Therefore, under external voltages imposed to the system, the Gibbs free energy of each intermediate state in Stage I transition can be evaluated as:

(Stage I transition) $$\Delta G_{i,\eta}^{\ I} = 0.5G_{Li} + G_{Sb} - (3.0 - x)\eta,\ i = 1. \quad \text{(S2.1)}$$

$$\Delta G_{i,\eta}^{\ I} = (3.0 - x)G_{Li} + xG_{Li_xSb} - (3.0 - x)\eta,\ i = 2, 3, 4. \quad \text{(S2.2)}$$

As shown in Eq. (S2), the external voltage (η) changes the Gibbs free energies ($^{\Delta G_{i,\eta}^{\ I}}$) of each i^{th} intermediate reaction state in Stage I and thus, alters the overall shape of the Gibbs free energy curve during charging and discharging. According to the definitions in the manuscript, the η_{dis} value is the

highest voltage at which all intermediate reactions are in the free-energy downhill in the direction of the discharge process (i.e., 3.0Li + Sb → Li_3Sb), whereas the η_{chg} value is the lowest voltage at which all intermediate reactions are in the free-energy downhill in the direction of the charge process (i.e., Li_3Sb → 3.0Li + Sb). By substituting the various η values, we obtained the η_{dis} and η_{chg} values satisfying the above-mentioned criteria (Fig. S1). The calculated values of the η_{dis} and η_{chg} corresponding to the Stage I transition are 0.78 and 0.93 V, respectively, and are summarized in Table 3 in the manuscript.

2. Predicted intermediate phases of Li−Sb and Li−Si battery.

Table S1. Predicted Li_xSb phases formed during the battery cycle predicted by the current and previous works [S1]. The phases predicted by atomic simulations (○) and those identified by both theory and experiments (●) are distinguished by different symbols.

Space group of predicted structures	x of Li_xSb								
	Stage I (Sb ↔ Li_3Sb)								
	0	0.33	0.43	0.5	0.6	1	2	2.7	3
$Fm\bar{3}m$							○		○
$P6_3/mmc$									○
$R\bar{3}m$	●								
C2/m								○	
$Im\bar{3}m$		○	○	○	○	○	○		●

Table S2. Predicted Li_xSi phases formed during the battery cycle predicted by present and previous works [S1, 2]. Among these phases, the phases predicted by atomic simulations (○) and those identified by both theory and experiments (●) are distinguished by different symbols.

Space group of predicted structures	x of Li_xSi								
	Stage I ($Si \leftrightarrow Li_{3.75}Si$)								
							Stage II ($Li_{2.33}Si \leftrightarrow Li_{3.75}Si$)		
	0	0.33	1	1.71	2	2.33	3.25	3.5	3.75
$Fd\bar{3}m$	●								
$P6_3/mmc$		○					○		
$R\bar{3}m$					○				
$I\bar{4}3d$									●
$I4_1/a$			○○						
Pnma				○					
Pbam							○	○	
$P3_212$						○			
$P\bar{3}m1$						○			

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(S2) Braga, M. H.; Dębski, A.; Gąsior, W., Li–Si Phase Diagram: Enthalpy of Mixing, Thermodynamic Stability, and Coherent Assessment. *J. Alloys Compd.* **2014,** *616*, 581-593.