Experimental investigation and thermodynamic assessment of the Li-Sb system

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Abstract: Sb and Sb-containing compounds have been attracting a great interest as promising alternative materials for commercial anodes and liquid batteries. The Li-Sb system was studied experimentally by investigating 6 alloys with X-ray diffraction measurement, scanning electron microscopy and electron probe microanalyses. Two binary phases Li_2Sb and Li_3Sb were confirmed to be stable in this system. Two invariant reactions $\text{L} \rightarrow (\text{Sb}) + \text{Li}_2\text{Sb}$ and $\text{L} + \text{Li}_3\text{Sb} \rightarrow \text{Li}_2\text{Sb}$ were identified experimentally based on the microstructures of the as-cast alloys. The eutectic point was determined to be about 40 at.% Li. The enthalpies of formation for Li_2Sb , $\alpha\text{Li}_3\text{Sb}$ and $\beta\text{Li}_3\text{Sb}$ at 0 K were calculated by means of density functional theory and the transition enthalpy between $\alpha\text{Li}_3\text{Sb}$ and $\beta\text{Li}_3\text{Sb}$ was obtained. Then, the presently obtained results, combined with a critical review of literature data, were used to develop the thermodynamic description of the Li-Sb system by means of CALPHAD method. The liquid phase was treated as (Li, Li_3Sb , Sb) using an associate model. The calculated phase diagram and thermodynamic properties can reproduce the available experimental data reasonably.

Keywords: Li-Sb system, Calphad, Phase diagram, thermodynamic description, Sb anode

1. Introduction and literature review

Development of the new materials for energy storage and conversion is a challenging task. Sb and its compounds have been attracting a great interest as energy storage materials due to their relative abundance in the earth's crust, their

comparatively low cost and the relative capacities [1]. In addition, Sb is one important additive to the liquid Li batteries and Sn anode [2-5]. Therefore, knowledge of phase equilibria in the Li-Sb system is very important and critical to design one applicable Li-Sb-containing material. However, the phase diagrams of the Li-Sb system reported by previous studies [6-8] are contradictory and the phase relationship is not totally explicit. The main objective of this work is to clarify the phase relationship of the Li-Sb system via the binary alloys combining the techniques of scanning electron microscopy (SEM), electron probe microanalyses (EPMA) and X-ray diffraction measurement (XRD). Thermodynamic parameters of this system were then obtained by CALPHAD (CALculation PHase Diagram) method based on the reliable data in available.

The Li-Sb system was critically evaluated by Sangster and Pelton [6]. They firstly calculated the phase diagram based on the experimental work from Braue and Zintl [9] and Weppner and Hugins [10] by assuming that the thermodynamic properties of the liquid Li-Sb alloys are the same as those of the liquid Li-Bi alloys. The main experimental data of the phase equilibria in the assessed work were the melting temperature of $\beta\text{Li}_3\text{Sb}$ and transition temperature between $\alpha\text{Li}_3\text{Sb}$ and $\beta\text{Li}_3\text{Sb}$. The melting temperature was considered to be in the range of 1150 to 1300 °C measured by Brauer and Zintl [9] and higher than 950 °C reported by Lebeau [11]. The $\alpha\text{Li}_3\text{Sb}$ phase transforms to $\beta\text{Li}_3\text{Sb}$ at a temperature above 650 °C measured by Braue and Zintl [9]. Apparently, the phase diagram drawn by Sangster and Pelton [6] was not accurate due to many hypotheses. Three binary compounds were presented in the assessed phase diagram, viz. Li_2Sb , $\alpha\text{Li}_3\text{Sb}$ and $\beta\text{Li}_3\text{Sb}$ (high temperature phase). Then Fedorov [7] proposed a different phase diagram based on thermal analysis with the unannealed alloys. As presented in Fig. 1a, two additional compounds Li_3Sb_2 and LiSb_2 were included. It is questionable whether these two phases are stable since no XRD patterns were presented in his work. Besides, the melting point of $\beta\text{Li}_3\text{Sb}$ was determined to be higher than 1000 °C, which is consistent with the work of Braue and Zintl [9]. The transition temperature between the $\alpha\text{Li}_3\text{Sb}$ and $\beta\text{Li}_3\text{Sb}$ seems to be 456 °C, which is lower than the work of Braue and Zintl [9]. Recently, Kane et al. [8]

determined the Li-Sb system using the electromotive force (EMF) measurement, but neither Li_3Sb_2 nor LiSb_2 was confirmed to be stable. As shown in Fig. 1b, the eutectic temperature of $\text{L} \rightarrow (\text{Sb}) + \text{Li}_2\text{Sb}$ was measured to be 460 °C and Li_2Sb was reported to be formed by the peritectic reaction at a temperature of 584 °C in the work of Kane et al. [8]. In addition, the eutectic point was considered to be about 40 at.% Li.

Enthalpies of formation of the Li_3Sb and Li_2Sb phases have been investigated by many authors [10, 12-15]. Shchukarev et al. [12] and Kubaschewski and Catterall [13] determined the enthalpies of formation of Li_3Sb using solution calorimetry (SC) and direct reaction calorimetry (DRC), respectively. Their results are quite different. In addition, Nikitin et al. [14] and Weppner and Huggins [10] measured the enthalpies of formation of the Li_3Sb and Li_2Sb phases by the cathodic polarization technique (CP) and EMF, respectively. Their experimental data are close to each other and inconsistent with the work of Shchukarev et al. [12] and Kubaschewski and Catterall [13]. Recently, Terlicka et al. [15] have determined the enthalpies of formation of Li_3Sb and Li_2Sb using the DRC technique, which are similar with the data reported by Nikitin et al. [14] and Weppner and Huggins [10]. Besides, enthalpies of formation of the Li_3Sb and Li_2Sb phases were calculated by Chang et al. [16] using First-principles calculations. Their calculated results [16] were a little larger than the experimental data [10, 14-15]. Thermodynamic properties of the liquid Li-Sb alloys were investigated by two groups [8, 15]. Kane et al. [8] measured the thermodynamic properties of the Li-Sb alloys by EMF technique with the temperature ranges of 425–775 °C and composition ranges of 1–75 at.% Li. Terlicka et al. [15] determined partial and integral mixing enthalpy of the liquid Li-Sb alloys at 547 °C, 669 °C, 649 °C and 751 °C by drop calorimetry. The thermodynamic data reported by Kane et al. [8], Weppner and Huggins [10], Nikitin et al. [14] and Terlicka et al. [15] are agreement with each other and accepted in this work.

2. Experimental procedures

In order to clarify the phase relationship and the stability of the binary compounds in the Li-Sb system, 6 Li-Sb binary alloys as shown in Table 1 were selected based on the literature review and prepared as described below. Sb (99.99 wt.%) and Li (99.9

wt.%) were used as starting materials. Before weighting, the oxide layers on the surfaces of the lithium and antimony pieces were mechanically removed and accurately weighed in the glove box, which are filled with the high-purity argon. Then the Li and Sb blocks were melted in an induction furnace under high-purity argon atmosphere. In order to improve the homogeneity, the melt was stirred and then was poured before it started to volatilize. Finally, the as-cast samples were obtained. The slices of the as-cast alloys were sealed in the quartz tubes and were annealed in an L4514-type diffusion furnace (Qingdao Instrument & Equipment Co. Ltd., China) at 300 °C for 30 days. Subsequently, the samples were quenched into water without breaking the quartz tubes and the equilibrated Li-Sb alloys were prepared.

The metallographic samples of the alloys in the as-cast and equilibrated states were firstly examined using optical microscopy and then analyzed with the scanning electron microscopy (SEM)/back-scattered electron image (BSE) and EPMA (JXA-8530, JEOL, Japan) employing pure Sb (99.99 wt.%) as the standard materials. XRD was performed using a Cu-K α radiation on a X-ray diffractometer (D8-advance, Bruker, Germany) at 40 kV and 40 mA. EPMA were analyzed at 15 kV and 2×10^{-8} A. It is worth noting that the element Li cannot be determined using EPMA. Therefore, only the composition of Sb was obtained in this work and the phases were identified based on the degree of weight loss in the total mass fraction.

3. Experimental results and discussion

The as-cast samples were prepared in order to clarify and confirm the phase equilibria of the Li-Sb system. Table 1 listed the alloy compositions, the primary phases of the as-cast alloys and phase identification by XRD, SEM and EPMA.

Fig. 2 presents the micrographs of the as-cast alloys # 1-6 and the XRD patterns are shown in Fig. 3. From the XRD patterns, only (Sb), Li₂Sb and α -Li₃Sb could be identified, which confirm that no other binary compounds exist when the composition of Sb exceeds 33.33 at.%. It is worth mentioning that the reason that no characteristic peaks of Li₂Sb could be observed in the as-cast alloy #1 is that the peak intensities of Li₂Sb is too weak and could not be exhibited. Figs. 2a and 2b present the microstructures of alloys # 1 and # 2 with the similar results. Two parts (primary (Sb)

and eutectic structure (Sb)+Li₂Sb) could be easily seen in the pictures, which means that the liquid melt firstly forms the primary (Sb) and then forms (Sb)+Li₂Sb with the eutectic reaction. Fig. 2c shows the micrograph of the as-cast alloy # 3 and only eutectic structures (Sb)+Li₂Sb can be observed. The composition of this alloy is 40 at.% Li and therefore we can consider this composition as the eutectic point. The primary phase changes to be Li₂Sb along with the increase of the concentration of Li, as shown in Figs. 2d and 2e (the as-cast alloys # 4 and # 5). In these two pictures, the primary phases are Li₂Sb and then eutectic structure (Sb)+Li₂Sb forms. The micrograph of as-cast alloy # 6 is presented in Fig. 2f. From this image, it is easy to be identified that the primary phase is the chapped α Li₃Sb phases and it is surrounded by the Li₂Sb phase, which means that the peritectic reaction $L+\alpha\text{Li}_3\text{Sb}\rightarrow\text{Li}_2\text{Sb}$ happened. In the amplification image as shown in the upper left, the eutectic structures (Sb)+Li₂Sb could be observed, which implied that the solidification process ended in the eutectic reaction.

Table 1 Nominal compositions and phase analysis results by SEM/EPMA/XRD on the as-cast Li-Sb alloys.

Alloy No.	Composition (at. %)	Primary phase	Phase identification	
			XRD	SEM/EPMA
1	Li ₁₅ Sb ₈₅	(Sb)	(Sb)	(Sb) Eutectic (Sb)+ Li ₂ Sb
2	Li ₂₅ Sb ₇₅	(Sb)	(Sb) Li ₂ Sb	(Sb) Eutectic (Sb)+ Li ₂ Sb
3	Li ₄₀ Sb ₆₀	—	(Sb) Li ₂ Sb	Eutectic (Sb)+ Li ₂ Sb
4	Li ₄₅ Sb ₅₅	Li ₂ Sb	(Sb) Li ₂ Sb	Li ₂ Sb Eutectic (Sb)+ Li ₂ Sb
5	Li ₅₀ Sb ₅₀	Li ₂ Sb	(Sb) Li ₂ Sb	Li ₂ Sb Eutectic (Sb)+ Li ₂ Sb
6	Li ₆₀ Sb ₄₀	α Li ₃ Sb	(Sb) Li ₂ Sb α Li ₃ Sb	Li ₃ Sb Li ₂ Sb Eutectic (Sb)+ Li ₂ Sb

Table 2 Summary of the experimental phase diagram and thermodynamic data in the Li-Sb system.

Type of experimental data	Experimental technique	Quoted mode ^a	Reference
Melting temperature of Li ₃ Sb	XRD	□	[9]
Transformation temperature of αLi ₃ Sb and βLi ₃ Sb	XRD	□	[9]
Melting temperature of Li ₃ Sb	XRD	□	[11]
Phase diagram from 0 to 20 at. % Sb and 90 to 100 at. % Sb	TA	□	[7]
Phase diagram from 20 to 90 at. % Sb	TA	+	[7]
Phase diagram from 30 to 100 at. % Sb	EMF	■	[8]
Enthalpy of formation for Li ₃ Sb	SC	+	[12]
Enthalpy of formation for Li ₃ Sb	DRC	+	[13]
Enthalpies and entropies of formation for Li ₃ Sb and Li ₂ Sb	CP	■	[14]
Enthalpies and entropies of formation for Li ₃ Sb and Li ₂ Sb	EMF	■	[10]
Enthalpies of formation for Li ₃ Sb and Li ₂ Sb	DRC	■	[15]
Variation of electromotive force with temperature of the Li-Sb alloys	EMF	■	[8]
Partial mixing enthalpy of Li in liquid Li-Sb alloys	EMF	■	[8]
Enthalpy of mixing of liquid	DC	■	[15]
Partial mixing enthalpy of Li and Sb in liquid Li-Sb alloys	DC	■	[15]
Phase diagram and solidification information from 40 to 85 at. % Sb	XRD EPMA SEM	■	This work

XRD, X-ray diffraction; TA, thermal analysis; EMF, electromotive force; SC, solution calorimetry; DRC, direct reaction calorimetry; CP, cathodic polarization; DC, drop calorimetry.

^a Indicates whether the data are used or not used in the parameter optimization: ■ used; □ used but only treat as a reference data; + not used.

Table 3 Summary of the thermodynamic parameters in the Li-Sb system.^a

Liquid: (Li, Li₃Sb, Sb)

$${}^0G_{Li_3Sb}^{liq} = 3 {}^0G_{Li}^{Liq} + {}^0G_{Sb}^{Liq} - 294669.26 + 68.57T$$

$${}^0L_{Li,Sb}^{liq} = -128946.98 + 1.68T \quad {}^1L_{Li,Sb}^{liq} = -46409.75 + 0.46T$$

$${}^0L_{Li,Li_3Sb}^{liq} = -13210.72 - 6.61T \quad {}^1L_{Li,Li_3Sb}^{liq} = 6156.66$$

$${}^0L_{Li_3Sb,Sb}^{liq} = 12645.50 - 47.62T$$

Li₂Sb: (Li)₂(Sb)₁

$${}^0G_{Li_2Sb}^{Li_2Sb} - 2 {}^0G_{Li}^{SER} - {}^0G_{Sb}^{SER} = -197620.01 + 25.93T$$

αLi₃Sb: (Li)₃(Sb)₁

$${}^0G_{Li_3Sb}^{\alpha Li_3Sb} - 3 {}^0G_{Li}^{SER} - {}^0G_{Sb}^{SER} = -298322.23 + 45.88T$$

βLi₃Sb: (Li)₃(Sb)₁

$${}^0G_{Li_3Sb}^{\beta Li_3Sb} - 3 {}^0G_{Li}^{SER} - {}^0G_{Sb}^{SER} = -295511.06 + 43.45T$$

^a Temperature (T) in Kelvin and Gibbs energy in J/mol.

Table 4 Summary of the invariant equilibria in the Li-Sb system.

Reaction	Type	T(°C)	at.% Li in Liq	Remark
Liquid→(Sb)+Li ₂ Sb	Eutectic	460	40	[8]
	Eutectic	466	15	[7]
	Eutectic	—	40	This work, exp
	Eutectic	466	40.5	This work, cal
Liquid+αLi ₃ Sb→Li ₂ Sb	Peritectic	584	—	[8]
	Peritectic	583	54.5	This work, cal
βLi ₃ Sb→αLi ₃ Sb	Allotropic	>650	—	[9]
	Allotropic	887	—	This work, cal
Liquid→βLi ₃ Sb	Melting	1150-1300	—	[9]
	Melting	>950	—	[11]
	Melting	1184	75	This work, cal
Liquid→(Li)+ αLi ₃ Sb	Eutectic	176	—	[7]
	Eutectic	168	97.9	This work, cal

Table 5 Calculated enthalpies and entropies of formation of Li_2Sb and Li_3Sb with the experimental data.

Reaction	ΔH_f , kJ/mol	ΔS_f , J/mol	Temperature	Remark
$2\text{Li(L)}+\text{Sb(S)}=\text{Li}_2\text{Sb(S)}$	-197.3	-31.9	355-500 °C	[10]
	-195	-27	377-450 °C	[14]
	-203.6	-39.2	355-500 °C	This work, cal
$3\text{Li(L)}+\text{Sb(S)}=\text{Li}_3\text{Sb(S)}$	-293.3	-49.2	355-500 °C	[10]
	-301	-60	377-450 °C	[14]
	-307.3	-65.75	355-500 °C	This work, cal

In order to determine the stabilities of the binary compounds at the equilibrated state, alloys # 2-3 were selected as a representative and annealed at 300 °C for 30 days. As presented in Fig. 4a, the XRD patterns of these two annealed alloys show that only (Sb) and Li_2Sb can be identified. BSE image of the annealed alloy # 2 confirm the results from XRD, as shown in Fig. 4b.

Based on our experimental investigation, we can get the following characteristics about the Li-Sb system: (1) no other binary compounds (such as Li_3Sb_2 and LiSb_2 reported by Fedorov [7]) exist when the concentration of Sb is above 33.3 at.% except Li_2Sb and $\alpha\text{Li}_3\text{Sb}$; (2) eutectic reaction $\text{L} \rightarrow (\text{Sb}) + \text{Li}_2\text{Sb}$ was confirmed and the eutectic point was considered to be at about 40 at.% Li; (3) the peritectic reaction $\text{L} + \alpha\text{Li}_3\text{Sb} \rightarrow \text{Li}_2\text{Sb}$ happened. Compared with our experiment, it is distinct that the phase diagram reported by Kane et al. [11] in Fig.1b is more accurate and could totally express our experimental results and their experimental data are accepted as the optimized input data in this work. However, it is surprised that the experimental data reported by Fedorov [7] are quite consistent with those reported by Kane et al. [11] when the concentration of Sb is more than 80 at.% as shown in Fig. 5. It seems that the nonequilibrium diagram reported by Fedorov [7] would not dramatically deviate from the equilibrium phase diagram when the compositions of the alloys are close to the end member. Therefore, in this work the phase equilibria at the Li-rich corner reported by Fedorov [7] are also considered to be the input data for the optimization with a low weight due to no other available experimental data at the Li-rich region.

4. Thermodynamic modeling

4.1 Unary phase

The Gibbs energy functions of pure elements Li, Sb are taken from the SGTE compilation by Dinsdale [17] and described by:

$$G_i(T) - H_i^{SER} = A + BT + CT \ln T + DT^2 + ET^{-1} + FT^3 + IT^7 + JT^{-9} \quad (1)$$

where H_i^{SER} is the molar enthalpy of the element i at 1 bar and 298.15 K in its standard element reference (SER) state, and T is the absolute temperature. The last two terms in Eq. (1) are used only outside the ranges of stability, the term IT^7 for a liquid below the melting point and JT^{-9} for solid phases above the melting point.

4.2 Liquid phase

The liquid phase of the Li-Sb system exhibits a sharp minimum versus composition in its enthalpy of mixing near the Li_3Sb stoichiometry [15], which indicates strong short-range order interactions. Therefore, the associate model is used to describe the liquid phase in this work. In CALPHAD terminology, the term “associate” is used to denote an association between unlike atoms when the attractive forces between the atoms are not strong enough to form a stable chemical molecule. In this work the liquid phase is assumed to contain three species (Li, Li_3Sb , Sb). The molar Gibbs energy is expressed by the following Redlich–Kister equation [18]:

$$G_m^{Liq} - H^{SER} = \sum y_i {}^0G_i^{Liq} + RT \sum y_i \ln y_i + \sum_i \sum_{j \neq i} y_i y_j \sum_k {}^kL_{i,j}^{Liq} (y_i - y_j)^k \quad (2)$$

where $i, j = \text{Li}, \text{Li}_3\text{Sb}, \text{Sb}$, R is the gas constant and T is the temperature. y_i and y_j are the mole fractions of each species in the liquid. ${}^0G_{\text{Li}_3\text{Sb}}^{Liq}$ is the Gibbs energy of formation of the specie Li_3Sb in the liquid phase, which is described as $3{}^0G_{\text{Li}}^{Liq} + {}^0G_{\text{Sb}}^{Liq} + a + bT$ (a and b are the assessed parameters). In addition, ${}^kL_{i,j}^{Liq}$ are the k th order of the interaction parameters and considered to be linearly temperature dependent, which evaluated based on the experimental data.

4.3 Intermetallic phases

The Li_2Sb , $\alpha\text{Li}_3\text{Sb}$ and $\beta\text{Li}_3\text{Sb}$ phases were modeled as stoichiometric phases in view of the negligible homogeneities. The Gibbs energy of Li_2Sb is presented in Eq.

(3) as a representative.

$${}^0G_{Li:Sb}^{Li_2Sb} = 2 {}^0G_{Li}^{SER} + {}^0G_{Sb}^{SER} + A + BT \quad (3)$$

where A and B are corresponding to the enthalpy and entropy of formation of the compound, respectively.

4.4 BCC_A2 and RHO_A7

The standard reference phases of Li (bcc) and Sb (rhombus) were modeled with no solubilities as previous experimental results indicate.

5. Energetics of intermetallic phases by first-principles calculations

In the present work, first-principles calculations were employed to obtain ΔH_f for the compounds Li_2Sb (space group P-62c), αLi_3Sb (space group Fm-3m) and βLi_3Sb (space group P6₃/mmc). The total energies of the Li_2Sb , αLi_3Sb , βLi_3Sb , Li and Sb were calculated by using density functional theory (DFT) as implemented in the Vienna ab initio simulation package [19-20]. The electron-ion interactions were described through projector augmented wave (PAW) [21] and the exchange correlation functional was constructed by the generalized gradient approximation (GGA) proposed by Perdew-Burke-Ernzerhof (PBE) [22]. Brillouin zone integrations were performed by using a Monkhorst–Pack mesh [23]. The energy cut-off of 400 eV was used to converge total energy to be less than 1.0 meV/atom. Structural relaxations of atomic positions, cell shapes and cell volumes were carried out using the conjugate gradient method until the residual forces were less than 0.02 eV Å⁻¹. A final self-consistent static calculation via the tetrahedron smearing method with Blochl corrections [24] was performed.

To obtain the formation energies of Li-Sb compounds, we take the energies of a Li atom (E_{Li}) and a Sb atom (E_{Sb}) in bulk Bcc-Li and Rho-Sb as reference energies. The formation energy of a compound can be defined as the difference between the total energy of the compound and the energies of its constituent elements and shown below:

$$\Delta_f H_{Li_aSb_b} = \Delta E_{Li_aSb_b} = E_{Li_aSb_b} - aE_{Li} - bE_{Sb} \quad (4)$$

where $E_{Li_aSb_b}$ is the total energy of the compound Li_aSb_b , meanwhile E_{Li} and E_{Sb} are the energies of Li and Sb in their bcc and rho states, respectively. The calculated enthalpies of formation at 0 K for Li_2Sb , αLi_3Sb and βLi_3Sb were -167499.6, -246587.1, and -245372.7 J/mol (per formula unit), respectively. Our present calculated results are consistent with the results of Li_2Sb and Li_3Sb by Chang et al. [16] using First-principles calculations. Based on our first-principles calculations, the transition enthalpy of $\beta Li_3Sb \rightarrow \alpha Li_3Sb$ is considered to be -1214.4 J/mol. This value is an important input data for the thermodynamic optimizations.

6. Thermodynamic results and discussion

The assessment was carried out by using the PARRAOT module of Thermo-Calc [25], which works by minimizing the square sum of the errors between calculation and experiment. The step-by-step optimization procedure was utilized in the present assessment. During the optimization, each piece of experimental information was given a certain weight based on the uncertainties of the data. The available experimental data of the Li-Sb system were summary in Table 2. The optimization started with the thermodynamic properties of the liquid phase, including the electromotive force [8], mixing enthalpies of liquid [15] and partial mixing enthalpies of liquid [8, 15]. Then, the optimization was carried out from the Sb-rich side to the Li-rich side and the intermetallic phases were introduced in the modeling one by one. Finally, all the parameters were optimized simultaneously based on the experimental data to obtain the self-consistent thermodynamic parameters. The finally obtained thermodynamic parameters for the Li-Sb binary system are listed in Table 3.

Fig. 5 shows the presently calculated Li-Sb phase diagram along with the experimental data from literature [7-9]. The experimental data at the Li or Sb rich sides reported by Fedorov [7] and all the experimental data reported by Kane et al. [8] are exhibited in the figure for comparison. It can be seen that the present modeling could reproduce the available experimental data reasonably. The calculated eutectic and peritectic reaction temperatures of $L \rightarrow (Sb) + Li_2Sb$ and $L + \alpha Li_3Sb \rightarrow Li_2Sb$ are 466 and 583 °C, which are consistent with those reported by Kane et al. [8]. The

calculated eutectic point is 40 at.% Li, which is agreement with the results of our experiment and Kane et al. [8]. In this optimization, the melting temperature of $\beta\text{Li}_3\text{Sb}$, transition temperature between $\alpha\text{Li}_3\text{Sb}$ and $\beta\text{Li}_3\text{Sb}$ measured by Braue and Zintl [9] and the transition enthalpy of $\alpha\text{Li}_3\text{Sb}$ and $\beta\text{Li}_3\text{Sb}$ calculated by first-principles calculations in this work were used to obtain the parameters of the $\beta\text{Li}_3\text{Sb}$ phases. The eutectic temperature of reaction $\text{L} \rightarrow (\text{Li}) + \alpha\text{Li}_3\text{Sb}$ determined by Fedorov [7] is also included in our optimization with a low weight due to their unannealed alloys. The calculated melting temperature of $\beta\text{Li}_3\text{Sb}$, transition temperature of $\alpha\text{Li}_3\text{Sb} \rightarrow \beta\text{Li}_3\text{Sb}$ and eutectic temperature of $\text{L} \rightarrow (\text{Li}) + \alpha\text{Li}_3\text{Sb}$ are 1184 °C, 887 °C and 168 °C, which are consistent with the reported data [7-9, 11]. The calculated transition enthalpy of $\beta\text{Li}_3\text{Sb} \rightarrow \alpha\text{Li}_3\text{Sb}$ is -2811.16 J/mol, which is close to the data obtained by DFT (-1214.4 J/mol). The compositions of the as-cast alloys in the present work were also presented in the figure, which indicate that our calculated phase diagram can reproduce our experimental observed microstructures reasonably. The whole calculated invariant temperatures and compositions with the experimental data are listed in Table 4. In comparison with the experimental data from literature and present work, the present calculations are considered to be reasonable.

The calculated enthalpies of mixing for liquid at 649 °C along with the experimental data [15] were presented in Fig. 6. It is obvious that the enthalpies of mixing exhibit a sharp minimum versus composition, which shows the necessity to use the associate model to describe the liquid phase. Fig. 7 shows the calculated partial mixing enthalpy of Li in liquid Li-Sb alloys at 649 °C and partial mixing enthalpy of Sb at 669 °C, which could reasonably reproduce the experimental data [8, 15]. The calculated variation of electromotive force with temperature at various compositions along with the experimental data [8] was exhibited in Fig. 8, which shows that the calculated results exhibit a good agreement with the experimental data.

Fig. 9 shows the calculated enthalpies of formation at 25 °C and compared with the available experimental data [10, 12-15] and first-principles calculations from the literature [24]. In addition, the calculated enthalpies of formation for Li_2Sb and Li_3Sb by first-principles calculations in this work were also listed in this picture.

Furthermore, the calculated and measured enthalpies and entropies of formation of Li_2Sb and Li_3Sb at the temperature range between 300 °C and 600 °C with the reference states of liquid Li and solid Sb are listed in Table 5. This shows that our calculation could well reproduce the work of [10, 14]. The calculated coulometric titration curves of the Li–Sb system at 633 K along with the experimental data [10] were presented in Fig. 10, which exhibit a good agreement with each other. In comparison with the experimental data from literature and present work, the thermodynamic description of the Li-Sb system is reasonable and the thermodynamic parameters can be used for the establishment of the thermodynamic database for Li-Sb-based system.

5. Conclusion

The Li-Sb system was investigated with 6 alloys by means of XRD, SEM and EPMA. Two invariant reactions were confirmed based on the microstructures of the as-cast alloys and only two binary compounds were determined to be stable. The enthalpies of formation of Li_2Sb , $\alpha\text{Li}_3\text{Sb}$ and $\beta\text{Li}_3\text{Sb}$ at 0 K were calculated from first-principles calculations and the transition enthalpy between $\alpha\text{Li}_3\text{Sb}$ and $\beta\text{Li}_3\text{Sb}$ was obtained. Then a set of self-consistent thermodynamic parameters was obtained based on the available experimental data of this work and literature, which can be used to serve as a part of the thermodynamic database for Li-Sb-based system.

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Tables and Figures captions

Table 1 Nominal compositions and phase analysis results by SEM/EPMA/XRD on

the as-cast Li-Sb alloys.

Table 2 Summary of the experimental phase diagram and thermodynamic data in the Li-Sb system.

Table 3 Summary of the thermodynamic parameters in the Li-Sb system.^a

Table 4 Summary of the invariant equilibria in the Li-Sb system.

Table 5 Calculated enthalpies and entropies of formation of Li_2Sb and Li_3Sb with the experimental data.

Fig. 1 Experimental phase diagrams of Li-Sb system: (a) reported by Fedorov [7], (b) reported by Kane et al. [8]

Fig. 2 SEM/BSE images of the Li-Sb alloys at the as-cast state: (a) alloy # 1 ($\text{Li}_{15}\text{Sb}_{85}$), (b) alloy # 2 ($\text{Li}_{25}\text{Sb}_{75}$), (c) alloy # 3 ($\text{Li}_{40}\text{Sb}_{60}$), (d) alloy # 4 ($\text{Li}_{45}\text{Sb}_{55}$), (e) alloy # 5 ($\text{Li}_{50}\text{Sb}_{50}$), (f) alloy # 6 ($\text{Li}_{60}\text{Sb}_{40}$).

Fig. 3 XRD patterns of the Li-Sb alloys at the as-cast state.

Fig. 4 XRD patterns and SEM/BSE images of the Li-Sb alloys at the equilibrated state: (a) XRD patterns of alloys # 2-3, (b) SEM/BSE images of alloy # 2.

Fig. 5 Calculated Li-Sb phase diagram with the experimental data in literature [7-9]. The blue arrows indicate the compositions of alloys in this work.

Fig. 6 Calculated enthalpies of mixing for liquid at 649 °C along with the experimental data [15]

Fig. 7 Calculated partial mixing enthalpies of Li and Sb at 649 °C and 669 °C along with the experimental data [8, 15]

Fig. 8 Calculated temperature variation of EMF at various compositions in comparison with experimental data [8].

Fig. 9 Calculated enthalpies of formation at 25 °C along with the available experimental data in literature [10, 12-15] and first-principles calculations [16]. FP=First-principles.

Fig. 10 Calculated open circle voltage of Li–Sb alloy against pure Li at 360 °C in comparison of the experimental data [10].