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THERMODYNAMIC MODELING OF THE BINARY INDIUM-LITHIUM SYSTEM, A PROMISING Li-ION BATTERY MATERIAL

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Abstract

The binary In – Li system is a promising Li-ion battery anode material as well as a part of the important ternary Ge – In – Li system. The thermodynamic descriptions of metallic systems are widely used to retrieve information necessary for alloy applications. In this work, a thermodynamic model of a binary indium – lithium system prepared by the Calphad approach is proposed. The liquid phase was described by an associate model, and the solid phases determined by the ab-initio calculation were included in the thermodynamic modeling. The obtained set of self-consistent thermodynamic parameters well reproduces the available experimental data and enables further calculations of multi-component systems. A good agreement between the calculations and the available experimental data was found. The proposed model can be used for further descriptions of ternary systems.

Keywords: *Li-ion batteries; Calphad; Thermodynamics; Indium; Lithium*

1. Introduction

The binary indium – lithium system is one of the constituent binaries of Ge – In – Li. These ternary alloys have found various fields of applications: germanium – indium alloys are used in the electronic industry [1], [2] whereas In – Li compounds are promising materials of electrodes in Li-ion batteries [3], [4]. The knowledge of phase stability, equilibrium and transformations is the basic information needed by materials scientists and engineers. All the information can be retrieved from thermodynamic databases; therefore, it seems reasonable to have one that describes the ternary Ge – In – Li system. It is obvious that a description of a ternary system needs descriptions of all the constituent binary systems. In this work, a thermodynamic model of the binary In – Li system is proposed. The proposed model can be used in the future modeling of a ternary Ge – In – Li system.

2. Literature review

The phase equilibria investigations in the binary In – Li system were started by Zintl and Brauer [5], who determined the crystal structure of the InLi intermetallic compound (IMC) as isostructural with NaTl (B_{32}). Grube and Wolf [6] measured the congruent melting temperature of the InLi phase at 898 K and determined the liquidus line as well. Lamprecht and Crowther [7] examined the system by thermal analysis and solubility studies. Based on the experimental results, they concluded that, in the binary In – Li system, InLi and $InLi_4$ phases exist, and also that the melting temperature of the InLi phase equals 902 K. Later, the investigations conducted by Schneider and Hilmer [8] and by Thummel and Klemm [9] showed that the congruent melting of InLi IMC is at 903±5 K and 908 K, respectively. Thummel and Klemm [9] also proposed a phase diagram of the In – Li system based on thermal analysis. They proposed that there are ten solid phases, six of them stable at room temperature, and that InLi and In_4Li_9 decompose by congruent transformation. The other phases decompose through a peritectic or peritectoid reaction. According to Thummel and Klemm [9], who determined the solidus line, the homogeneity range of the InLi phase is quite wide at temperature c.a. 700 K and stretches from about 0.45 to roughly 0.75 mole fraction of Li.

An extensive study of solid phase equilibria was conducted by Alexander et al. [10], who used the X-ray diffraction method (XRD) and thermal analysis. The In – Li phase diagram proposed by Alexander et

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al. [10] includes 10 different solid phases. Six of them are stable at room temperature, while others are formed by eutectoid reactions. Among the phases proposed by [10], only InLi decomposes by a congruent transformation, whereas the other phases disintegrate through a peritectic or peritectoid transformation. The results of a study of the liquidus line, for the concentration of Li smaller than 0.5 mole fraction, by way of thermal analysis, obtained by Alexander et al. [6] were a bit higher than those by Grube and Wolf [6] and lower than those by Thummel and Klemm [9]. For alloys of higher concentrations of Li (X_{LI}>0.5), the thermal analysis data of [2], [5], and [6] show similar characteristics.

The homogeneity range of the InLi phase reported by Alexander et al. [6] is much smaller in comparison to that suggested by Thummel and Klemm [9], and it extends between 0.45 and roughly 0.62 mole fraction of Li at c.a. 743 K.

The enthalpy of fusion of InLi IMC was investigated at 688 K by Schneider and Hilmer [8] with the use of the drop calorimetry method and by Bushmanov and Yatsenko [11] by a direct calorimetry measurement, who obtained 12.8 kJ/ mol atom and 13.5 kJ/mol, respectively, while the formation enthalpy change of the InLi phase at 800 K was measured by Sommer et al. [12], who obtained the value of -24.5 kJ/mol atom.

The ab initio energies of formation of the IMCs in the In – Li system reported in the Materials Project [13] database revealed that only five intermediate phases: In_3Li, InLi, In_2Li_3, $InLi_2$, and In_3Li_{13} are stable at 0 K.

The electromotive force measurement (EMF) method and the coulometric titration technique were used by Wen and Huggins [14] to investigate the activity of Li in solid and liquid phases of the In – Li system at 688 K. The experiments were carried out in the area of the InLi phase and for dilute liquid solutions. They also calculated the formation Gibbs energy of InLi and $InLi_2$, which are: -24 kJ/ mol atom and -34.1 kJ/mol atom, respectively. Gąsior and Schwitzgebel [15] applied the same EMF method to investigate solid and liquid In – Li alloys at the temperature range of 733 K – 923 K. The activity of the elements in liquid alloys was determined at the temperature range of 120 – 150 deg above liquidus by Yatsenko and Saltykova [16], who also utilized the EMF method, similarly to Morachevski et al. [17], who measured the activities in a dilute solution of Li in In and in the temperature range between 783 K – 823 K. Recently, Gąsior [18] measured the Li activity in liquid alloys in the temperature range of 673 K – 772 K using the EMF technique.

The mixing enthalpy of liquid In-Li was investigated with the application of calorimetry by Predel and Oehme [19] at 985 K, Bushmanov and Yatsenko [11] at 923 K, and Dębski et al. [20] at 653 K, 940 K, 994 K, and 1076 K. All the data are in good agreement, showing the minimum value around 0.6 mole fraction of Li, which suggests short-range ordering.

The binary In – Li system was assessed in 1991 by Sangster and Pelton [21], who proposed a phase diagram based on the available literature information. In his work, the phase equilibria followed the results given by Thummel and Klemm [9] and they showed congruent decomposition of the $InLi_2$ phase found by Alexander et al. [6]. However, most of the IMCs are drawn by dashed lines, indicating uncertainty. Because, to the best of the authors' knowledge, there is no thermodynamic optimization of the In – Li system reported in the literature, the main aim of this work is to optimize the thermodynamic properties of the phases and to calculate the In-Li phase equilibria with the Thermo-Calc software [22].

3. Thermodynamic models

Due to different intermediate phases reported by Thummel and Klemm [9] and by Alexander et al. [10], it was decided to include in the optimization only those phases which are stable from the ab initio calculation [13], plus the $InLi_6$ phase, which is indicated by the liquidus slope [10], [9], [21]. The phase In_3Li was excluded from this work due to a lack of report in the works of Thummel and Klemm [9] or Alexander et al. [10].

Detailed information about the crystal structures of the phases involved in this work is given in Table 1.

The Gibbs free energies of pure elements with respect to temperature $^0G_i(T) = G_i(T) - H_i^{SER}$ are represented by Equation 1:

$$^0G_i(T) = a + bT + cTln(T) + dT^2 + eT^{-1} + fT^3 + iT^4 + jT^7 + kT^{-9} \tag{1}$$

The $^0G_i(T)$ data are referred to the constant enthalpy value of the standard element reference H_i^{SER} at 298.15

Table 1. *Crystal structures of In-Li phases involved in this work*

Phase	Pearson symbol	Space group	Strukturbericht designation	Reference
(In)	*tI*2	$I4/mmm$	A6	[21]
InLi	*cF*16	$Fd\bar{3}m$	B32	[21]
In_2Li_3	*hR*5	$R\bar{3}m$	C33	[21]
$InLi_2$	*oC*12	$Cmcm$	…	[21]
In_3Li_{13}	*cF*128	$Fd\bar{3}m$	…	[21]
$InLi_6$	…	…	…	[10]
(Li)	*cI*2	$Im\bar{3}m$	A2	[21]

K and 1 bar, as recommended by Scientific Group Thermodata Europe (SGTE) [23]. The reference states are: Tetragonal_A6 (In), and BCC_A2 (Li). The expression may be given for several temperature ranges, where the coefficients *a, b, c, d, e, f, i, j, k* have different values. The functions are taken from SGTE Unary (Pure elements) TDB v.5 [23].

The BCC_A2 (Li) terminal phase was treated as a pure element due to the negligible solubility of In in Li. Its Gibbs energy was taken directly from the SGTE Unary database [23].

The tetragonal_A6 phase was described by the substitutional solution model and its Gibbs energy is given as follows:

$$\begin{aligned} {}^{m}G_{In,Li}^{Tetragonal\_A6} &= x_{In}\,{}^{0}G_{In}^{Tetragonal\_A6} + x_{Li}\,{}^{0}G_{Li}^{Tetragonal\_A6} + \\ RT\left(x_{In}lnx_{In} + x_{Li}lnx_{Li}\right) &+ x_{In}x_{Li}\sum {}^{i}L_{In,Li}^{Tetragonal\_A6} \end{aligned} \tag{2}$$

where R is the gas constant, T is the absolute temperature, ${}^{i}L_{In,Li}^{Tetragonal\_A6}$ are adjustable parameters, and *i* is an integer (i = 0, 1, 2…).

The liquid phase was described by the associated solution model proposed by Sommer [24]. The model has been previously used for Me-Li systems. In the case of the In – Li system, the model includes the InLi species.

The Gibbs energy for one mole of atoms is given by the following formula:

$${}^{0}G_{m}^{Liquid} = \begin{bmatrix} y_{In}\,{}^{0}G_{In}^{Liquid} + y_{Li}\,{}^{0}G_{Li}^{Liquid} + \\ y_{InLi}G_{InLi}^{Liquid} + RT\begin{pmatrix} y_{In}lny_{In} + \\ y_{In}lny_{In} + \\ y_{InLi}lny_{InLi} \end{pmatrix} + \\ {}^{xs}G_{m}^{Liquid} \end{bmatrix} / \left(1 + 2y_{InLi}\right) \tag{3}$$

where y_i is the site fraction of specie *i* (*i* = In, Li, InLi) in the liquid phase, ${}^{0}G_{i}^{Liquid}$ is the Gibbs energy of pure specie *i* in the liquid state, ${}^{xs}G_{m}^{Liquid}$ is the excess Gibbs energy of the liquid, *R* is the molar gas constant, and *T* is the absolute temperature.

The liquid phase contains three species: In, Li, and InLi, which are at internal equilibrium:

$$In + Li = InLi \tag{4}$$

The mass balance of the species gives the following constraints:

$$n_{In} = n_{In}^{'} + n_{InLi}^{'} \tag{5a}$$

$$n_{Li} = n_{Li}^{'} + n_{InLi}^{'} \tag{5b}$$

where n_{In} and n_{Li} are the numbers of end-members, n_{In}*'*, n_{Li}*'*, n_{InLi}*'* are the numbers of moles of the InLi associate and of the unassociated In and Li atoms.

Therefore, the fraction y_i (*i = In, Li, InLi*) is defined as:

$$y_i = \frac{n_i^{'}}{\sum_j n_j^{'}} \tag{6}$$

where the summation is done over all the species (*j = In, Li, InLi*).

The excess Gibbs energy of the liquid is described by the expression:

$$\begin{aligned} {}^{xs}G_{m}^{Liquid} &= y_{In}y_{InLi}\sum_{k} {}^{k}L_{In,InLi}^{Liquid}\left(y_{In} - y_{InLi}\right)^{k} + \\ &y_{InLi}y_{Li}\sum_{k} {}^{k}L_{InLi,Li}^{Liquid}\left(y_{InLi} - y_{Li}\right)^{k} \end{aligned} \tag{7}$$

where y_i is the site fraction of specie *i* (*i*=In, Li, InLi) in liquid, *k* is an integer number (*k* = 0, 1, 2,…), and $m \cdot GH$is an adjustable parameter. This adjustable parameter has a form of ${}^{0}G_{m}^{InLi} = y$, where A and B denote the adjustable coefficients and *T* is the absolute temperature.

The In_2Li_3, $InLi_2$ In_3Li_{13}, and $InLi_6$ phases.

All those phases were treated as line compounds, and their Gibbs energies were modeled as follows:

$$\begin{aligned} {}^{0}G_{In:Li}^{In_mLi_n} &= a + bT + cTlnT + \\ &m \cdot GHSERIN + n \cdot GHSERLI \end{aligned} \tag{8}$$

where *a*,*b* and *c* are adjustable parameters, *T* is the absolute temperature, *m, n* are the stoichiometric coefficients, and *GHSERIN* and *GHSERLI* are the Gibbs energies of In and Li in their SER reference state, respectively.

The InLi phase.

The InLi phase has a crystal structure B32, which is isostructural to AlLi [25] and GaLi [26]. These kinds of phases show non-stoichiometry due to a double effect [26]: on the one hand anti-structural defects, and on the other hand vacancies of the nominal stoichiometric composition. Therefore, the InLi phase can be modeled as (In,Li)0.5:(Li,Va)0.5. The Gibbs energy of the InLi phase is given by Equation 6:

$$\begin{aligned} {}^{0}G_{m}^{InLi} &= y_{In}^{I}y_{Li}^{II}\,{}^{0}G_{In:Li}^{InLi} + y_{In}^{I}y_{Va}^{II}\,{}^{0}G_{In:Va}^{InLi} + y_{Li}^{I}y_{Li}^{II}\,{}^{0}G_{Li:Li}^{InLi} \\ &+y_{Li}^{I}y_{Va}^{II}\,{}^{0}G_{Li:Va}^{InLi} + RT\begin{bmatrix} 0.5\left(y_{In}^{I}lny_{In}^{I} + y_{Li}^{I}lny_{Li}^{I}\right) + \\ 0.5\left(y_{Li}^{II}lny_{Li}^{II} + y_{Va}^{II}lny_{Va}^{II}\right) \end{bmatrix} + \\ &+y_{In}^{I}y_{Li}^{I}y_{Li}^{II}L_{In,Li:Li}^{InLi} + y_{In}^{I}y_{Li}^{I}y_{Va}^{II}L_{In,Li:Va}^{InLi} + \\ &y_{In}^{I}y_{Li}^{II}y_{Va}^{II}L_{In:Li,Va}^{InLi} + y_{Li}^{I}y_{Li}^{II}y_{Va}^{II}L_{Li,Li:Va}^{InLi} \end{aligned} \tag{9}$$

where is the site fraction *m* (*m* = *I* or *II*) occupied by element *i* (*i* = In, Li, Va),${}^{0}G_{i,j}^{InLi}$ is the Gibbs energy of the end-member when sublattice *I* is occupied by element *i* and sublattice *II* is occupied by element *j, R* is the molar gas constant, and T is the absolute temperature. The $L_{i,j:k}^{InLi}$ is an adjustable parameter in the form ${}^{k}A + {}^{k}BT$, *k* is an integer number (*k* = 0, 1, 2,…), *i, j, k* represent the elements (i,j, k = In, Li, Va), and colon ":" indicates different sublattices.

4. Ab-initio calculations

The stabilities of In_2Li_3, $InLi_2$, InLi, In_3Li_{13}, and $InLi_6$ were calculated with the aid of the ab-initio method within the Density Functional Theory (DFT), which was implemented in the Quantum Espresso package [27], [28]. The calculation used the General Gradient Approximation (GGA) pseudopotential functional parametrized by Padrew, Burke, and Emzerhof revised for the solids (PBEsol) approach [29]. For all the calculations, the cut-off energy and the k-point distance were set to 300 eV and 0.15 1/Å, respectively. Before the final calculation, a convergence test with respect to the cut-off energy and the k-point density was carried out. The input file for the ab-initio calculation was prepared with the aid of the cif files downloaded from the Crystallography Open Database [30] and Materials Project [13]. During the calculation, the crystal structures were fully relaxed and the self-consistent field (scf) calculation was completed. Next, the obtained energies were used for the calculation of the formation energy of the IMCs, following Equation 10:

$$\Delta E^0 = \left(E^0_{In_mLi_n} - mE^0_{In} - nE^0_{Li} \right) / \left(m + n \right) \qquad (10)$$

Where ΔE^0 is the formation energy per atom, $E^0_{In_nLi_m}$ is the energy of phase, E^0_{In} is the energy of In, E^0_{Li} is the energy of Li, *m* and *n* are the numbers of atoms In and Li, respectively.

The formation energies obtained in this step were used as the input values for the Calphad-type optimization.

5. Results and discussion

The optimization was carried out with the use of the following steps. First, the liquid phase was optimized, and after that, the InLi phase was assessed. Next, both phases were adjusted to obtain the best fitting of the experimental data. After that, the line compounds were added to the optimization. The last step was to optimize all the parameters together to find the best set of thermodynamic parameters describing the binary In – Li system. For this optimization, the available information on the thermodynamic properties of liquid and solid phases as well as phase equilibria was used. Each piece of the selected information was given a certain weight based on personal judgment and experimental uncertainty. For example, it can be observed that mixing enthalpy is a function independent of temperature; therefore, all the experimental data showing a small discrepancy from each other got the same weight. On the other hand, the dataset, which represents more negative heat of mixing, got a smaller weight because it was assumed that this particular dataset was burdened with error.

Since the Gibbs energy of lithium in the Tetragonal_A6 structure is not presented in the SGTE Unary [23] database, the ab-initio [13] calculation

Table 2. *Thermodynamic parameters obtained in this work [J/mol]*

Phase	Function
Liquid	$^0G^{Liquid}_{InLi} = -41511.85 + 3.7319 \cdot T + GLIQIN + GLIQLI$
	$^0L^{Liquid}_{In,InLi} = -9400.39 - 15.3466 \cdot T$
	$^0L^{Liquid}_{InLi,Li} = -50379.64 + 20.5279 \cdot T$
	$^1L^{Liquid}_{InLi,Li} = 3820.32 - 1.1837 \cdot T$
Tetragonal_A6	$^0G^{Tetragonal\_A6}_{Li} = 96.4 + GHSERLI$
	$^0L^{Tetragonal\_A6}_{In,Li} = -58600.23$
InLi	$^0G^{InLi}_{In:Li} = -98434.41 + 55.3295 \cdot T + GHSERIN + GHSERLI$
	$^0G^{InLi}_{Li:Li} = 20000 + 2 \cdot GHSERLI$
	$^0G^{InLi}_{In:Va} = 10000 + GHSERIN$
	$^0G^{InLi}_{Li:Va} = -18914.52 + 100 \cdot T$
	$^0L^{InLi}_{In,Li:*} = -18464.71 - 70.5668 \cdot T$
	$^1L^{InLi}_{In,Li:*} = 47382.29 - 37.3892 \cdot T$
	$^0L^{InLi}_{*:Li,Va} = 61209.82 - 95.9394 \cdot T$
In_2Li_3	$^0G^{In2Li3}_{In:Li} = -254024.89 + 792.4355 \cdot T + 95.5259 \cdot T \cdot LN\left(T\right) + 2GHSERIN + 3GHSERLI$
$InLi_2$	$^0G^{InLi2}_{In:Li} = -134998.27 + 437.0727 \cdot T - 53.8317 \cdot T \cdot LN\left(T\right) + GHSERIN + 2GHSERLI$
In_3Li_{13}	$^0G^{In3Li13}_{In:Li} = -402819.03 + 134.8964 \cdot T + 10.4201 \cdot T \cdot LN\left(T\right) + 3GHSERIN + 13GHSERLI$
$InLi_6$	$^0G^{InLi6}_{In:Li} = -134228.95 + 20.6122 \cdot T + 6.6984 \cdot T \cdot LN\left(T\right) + GHSERIN + 6GHSERLI$

was applied in this work. A very similar approach was successfully applied in calculation of Ir – Mo and Ir-W done by Huang et al. [31].

Figure 1 shows the calculated phase diagram superimposed with the experimental data given by Lamprecht and Crowther [7], Alexander et al. [10], Thummel and Klemm [9], Wen and Huggins [14], Grube and Wolf [6], and Gąsior and Schwitzgebel [15]. It can be seen that the literature data shows some discrepancies, especially for low and high concentrations of lithium. For example, the liquidus line determined for the concentration x_{Li} equal to 0.2 mole fraction varies from 680 K to 730 K, according to Lamprecht and Crowther [7] and Thummel and Klemm [9], respectively. Similarly, the liquidus determination for the concentration of Li bigger than 0.9 mole fraction lies in a range of temperatures with a difference of up to 100 degrees. A much smaller discrepancy can be observed around the equimolar concentration, where all the literature data are in agreement.

It can be seen that the calculated liquidus line for the concentration of lithium smaller than 0.5 is well reproduced in the calculation and the liquidus line covers most of the experimental data. For a higher concentration of Li, one can see a bit bigger discrepancy between the calculation and the experiments. The biggest difference can be found for the liquidus line of the In_3Li_{13} and In_6Li primary solidification phases. The experimental determination shows an almost straight line from a peritectic reaction In_3Li_{13}+Liquid ⇄ $InLi_6$ to a eutectic reaction Liquid ⇄ $InLi_6$+(Li). This kind of line was impossible to reproduce due to the shape of the Gibbs energies functions used for the description of these phases. Although it was achievable to obtain a less concave shape of the liquidus in that area, it cost a much higher number of interaction parameters in the liquid phase. Taking into account the basic rule of thermodynamic optimization, which says the model should be as simple as possible, it was decided to allow for a small inconsistency between the calculations and the experiments in this area. The solidus line is reproduced well for a whole range of concentrations. It was decided to follow the Thummel and Klemm [9] and Gąsior and Schwitzgebel [15] determination of the InLi homogeneity range. The consequence of this decision is a congruent decomposition of the $InLi_2$ phase. Moreover, one can notice that the phase boundary of the calculated InLi agrees well with the

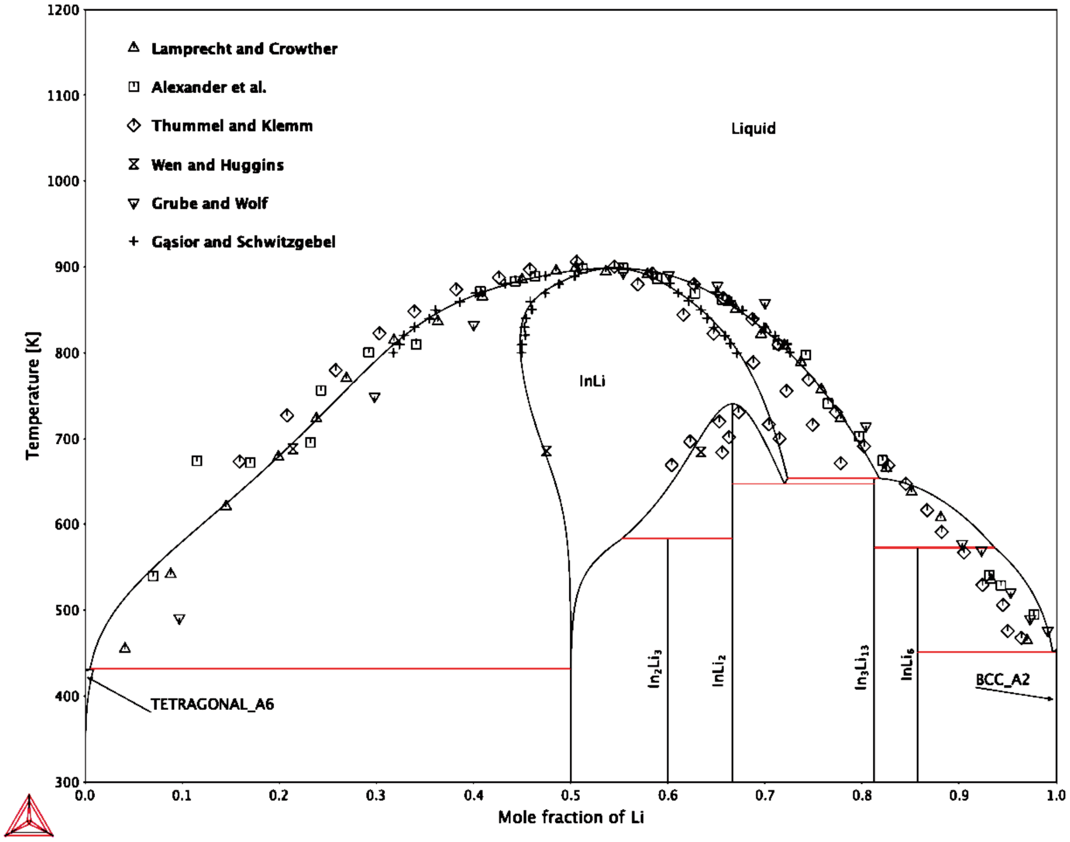

Figure 1. *Calculated phase diagram of In – Li system superimposed with experimental data given by Lamprecht and Crowther [7], Alexander et al. [10], Thummel and Klemm [9], Wen and Huggins [14], Grube and Wolf [6], and Gąsior and Schwitzgebel [15]*

data reported by Gąsior and Schwitzgebel [15] and Thummel and Klemm [9]. A small difference between the calculations and the Thummel and Klemm [9] data can be found around the eutectoid reaction InLi⇄$InLi_2$+In_3Li_{13}, where the experimental data reports the composition of InLi poorer in Li. A detailed comparison of the calculated reaction temperatures with the experimental determinations is given in Table 3.

Figure 2 displays the calculated liquidus and solidus lines of the InLi intermetallic phase superimposed with the data given by Gąsior and Schwitzgebel [15].

The depiction shows that the calculation agrees well with the experimental determination given for this particular area of the In-Li phase diagram. The picture also reveals that the congruent melting composition of InLi is shifted towards the lithium side. The calculated congruent melting occurs at the temperature 898 K and the composition equals 0.544 mole fraction of Li.

The calculated enthalpy of mixing of the liquid In-Li alloys is displayed in Figure 3. The same figure shows the experimental data given by Dębski et al. [20], Predel and Ohme [19], and Bushmanov and Yatsenko [11].

It can be seen that the measurements reported by Dębski et al. [20] are independent of temperature. The data given by Predel and Ohme [19] agree well with those given by Dębski et al. [20]. The data by Bushmanov and Yatsenko [11] show a slightly more

Table 3. *Calculated temperatures of reactions compared with literature data*

Reaction	Temperature [K]	Reference
Liquid ⇄ (In)+InLi	432±10	[21]
	431	[10]
	432	This work
Liquid ⇄ InLi	907±5	[21]
	898	[6]
	902	[7]
	903±5	[8]
	903±5	[9]
	898	This work
InLi+$InLi_2$ ⇄ In_2Li_3	568±20	[21]
	573	This work
InLi ⇄ $InLi_2$	733	[21]
	732	This work
InLi ⇄ $InLi_2$+In_3Li_{13}	647	This work
InLi+Liquid ⇄ In_3Li_{13}	673±10	[21]
	668	This work
In_3Li_{13}+Liquid ⇄ $InLi_6$	580	This work
Liquid ⇄ $InLi_6$+(Li)	452	[21]
	453.5	[10]
	453	This work

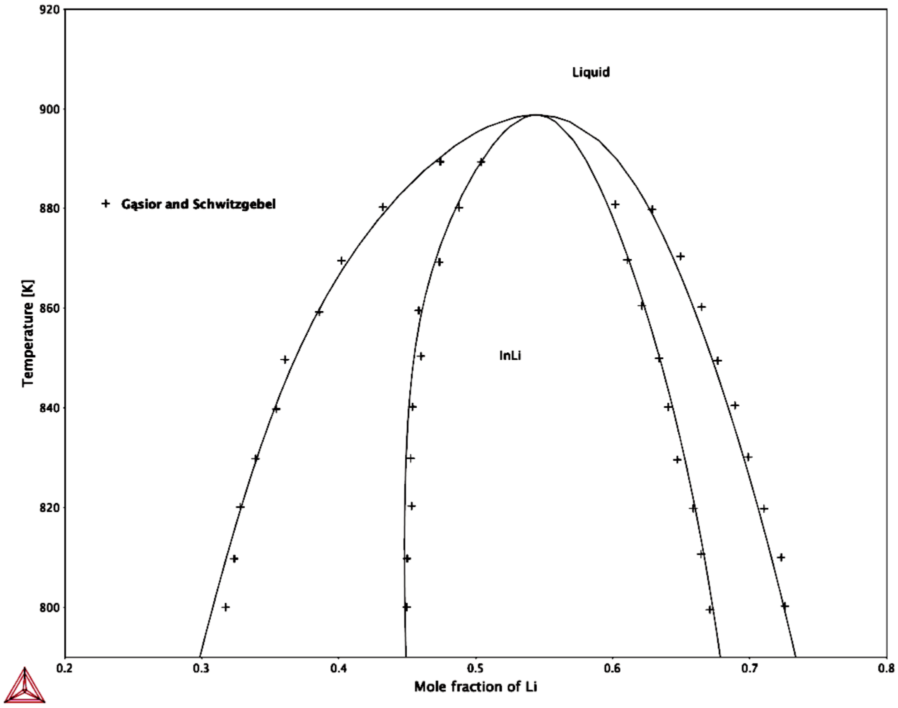

Figure 2. *Equilibrium between InLi and liquid phases compared to experimental determination given by Gąsior and Schwitzgebel [15]*

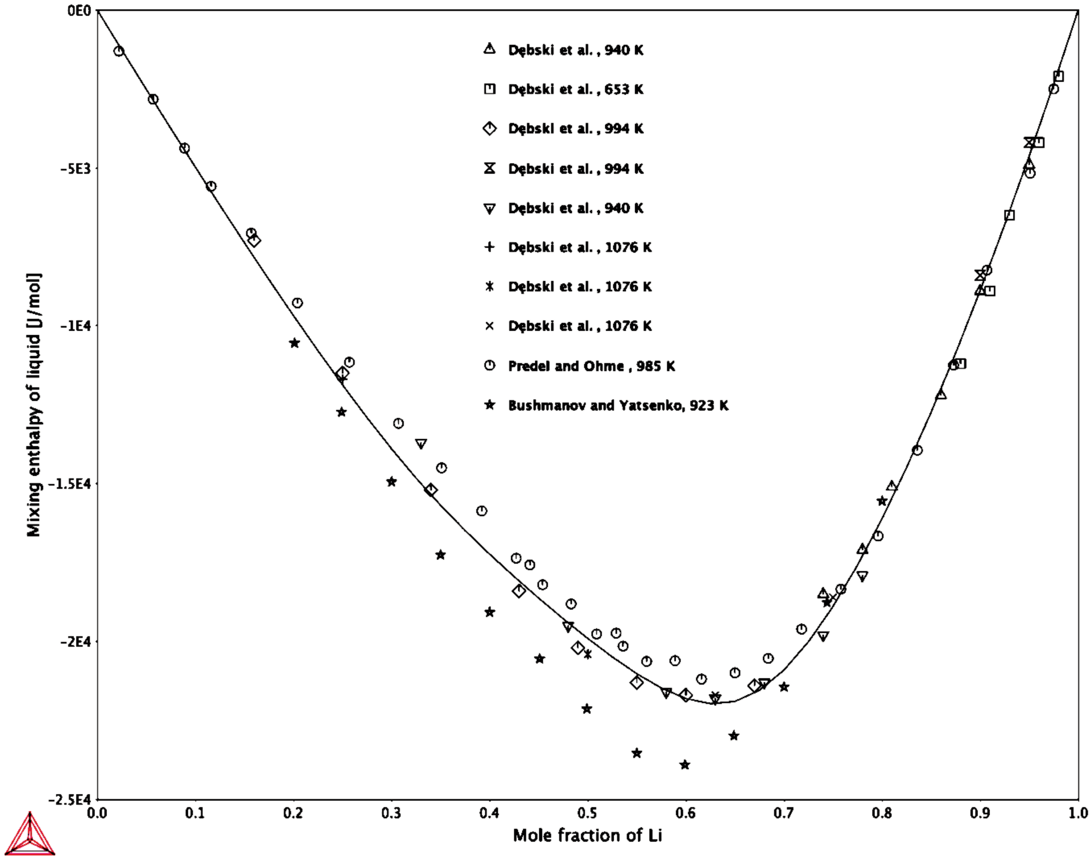

Figure 3. *Calculated enthalpy of mixing of liquid In-Li alloys together with data given by Dębski et al. [20], Predel and Ohme [19], and Bushmanov and Yatsenko [11]*

exothermic effect of mixing. The marginal discrepancy between the datasets obtained at different temperatures can be explained by experimental errors, which, in the case of calorimetric measurements, can be assumed to be 250 J. Since the calculation follows the majority of the experimental data, the points reported by Bushmanov and Yatsenko [11] show a small disagreement with the modeling.

Figure 4 shows the calculated activity of lithium in liquid In-Li at 900 K superimposed with the experimental determinations given by Morachevsky et al. [17] at 800 K, Gąsior and Schwizgebel [15] at 900 K, and Gąsior [18] at 772 K.

The calculation well reproduces the experiment and shows near zero activity of Li for its concentration smaller than 0.4 mole fraction. For the equimolar concentration of Li and In, the activity of lithium grows to circa 0.02, according to Gąsior and Schweitzgebel [15] and Gąsior [18]. The calculated activity at 900 K agrees well with the experiment. It can be noticed that the two sets of lithium activity determinations given at 772 K and 800 K are located above and below the Li activity at 900 K, which is in contradiction to the literature information. To avoid this problem, it was decided not to use the data given by Morachevsky [17].

Figure 5 displays the calculated activity of lithium in the solid phase at 850 K together with the experimental data obtained by Gąsior and Schwitzgebel [15].

As it can be found in the phase diagram (Fig. 1), at the temperature of 850 K, two phases exist: Liquid and InLi. The experimental data shown in Figure 4 exhibit the activity of Li in the solid InLi phase. One can see that the calculation fairly reproduces the experiment. A disagreement can be found between the experimental determination for the composition equalling 0.65 mole fraction of Li and the calculation. The experimental point indicates a single-phase region, whereas the calculation shows a binary (InLI + Liquid) region. The explanation of this inconsistency lies in Figure 1, where the data given by Thummel and Klemm and Gąsor and Schwitzgebel [15] are entered. The second dataset shows a bigger homogeneity range of the InLi phase than that reported by Thummel and Klemm [9]. Since the calculation is located in-between both datasets, it is obvious that the binary region will be covered by the area determined by Gąsior and Schwitzgebel [15] as a single region.

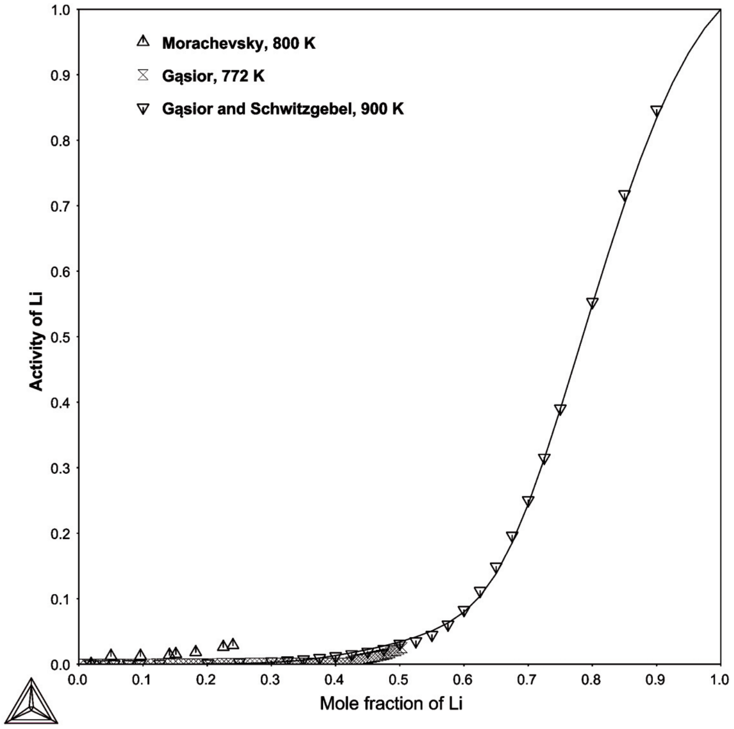

Figure 4. *The calculated activity of lithium in liquid In-Li at 900 K compared with experimental determinations given by Morachevsky et al. [17] at 800 K, Gąsior and Schwizgebel [15] at 900 K, and Gąsior at 772 K [18] (in liquid and Liquid +InLi region)*

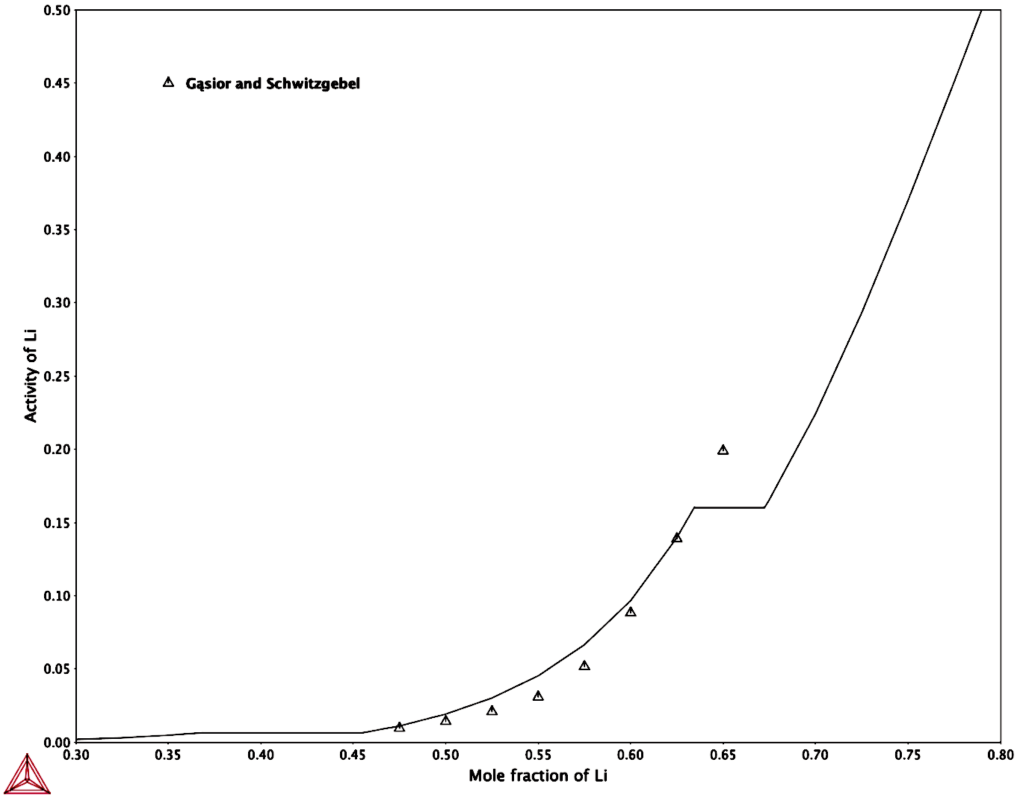

Figure 5. *Calculated activity of lithium in solid phase at 850 K together with experimental data obtained by Gąsior and Schwitzgebel [15]*

6. Conclusions

Applying the available literature data on the thermodynamics and phase equilibria in the In-Li system, a thermodynamic description of a binary In-Li system is proposed in this work.

The liquid phase was described by an associate model and the solid phases determined by the ab-initio calculation were included in the thermodynamic modeling. This approach seems to be correct in reference to the available thermodynamic data of the liquid, which strongly suggests the existence of a liquid associate, as well as to the unambiguous information on the In – Li phase diagram topology. The obtained set of self-consistent thermodynamic parameters well reproduces the available experimental data and allows for further calculations of multi-components systems.

Additional investigations of solid In-Li solutions with the Li concentration higher than 0.5 mole fraction are necessary in the future for a more precise determination of the number of intermetallic phases, their transition temperatures and the regions of homogeneity.

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Author's contributions

W. Gierlotka – calculations, writing manuscript; W. Gąsior – correcting manuscript, supervising; A. Dębski – correcting manuscript, literature research; M. Zabrocki – correcting manuscript, iterature research.

Data availability

The database is available upon request.

Conflicts of interest

Authors claim no conflict of interest.

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TERMODINAMIČKO MODELOVANJE BINARNOG INDIJUM - LITIJUM SISTEMA, MATERIJALA KOJI JE PERSPEKTIVAN ZA LITIJUM - JONSKE BATERIJE

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Apstrakt

Binarni In – Li sistem je perspektivni materijal za anode litijum-jonskih baterija, kao što je i deo važnog trojnog Ge – In – Li sistema. Termodinamički opisi metalnih sistema se često koriste da bi se prenele informacije neophodne za primenu legura. U ovom radu predložen je termodinamički model binarnog indijum-litijum sistema pripremljen Calphad pristupom. U termodinamičko modelovanje bile su uključene tečna faza opisana pridruženim modelom, i čvrste faze određene ab-initio proračunima. Dobijeni set samo-konzistentnih termodinamičkih parametara dobro reprodukuje dostupne eksperimentalne podatke i omogućava dalje proračune višekomponentnih sistema. Proračuni su bili u skladu sa dostupnim eksperimentalnim podacima. Predloženi model se može koristiti za dodatno opisivanje trojnih sistema.

Ključne reči: *Litijum-jonske baterije; Calphad; Termodinamika; Indijum; Litijum*