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Li–Si phase diagram: Enthalpy of mixing, thermodynamic stability, and coherent assessment

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ABSTRACT

Silicon has been recently used as negative electrode in Li-ion batteries which makes the Li–Si system the focus of numerous studies. In this work, the Li–Si system was studied by means of drop calorimetry, differential scanning calorimetry, first principles calculations and the CALPHAD method. The enthalpies of mixing of the liquid phase were determined for the first time. The optimization started by the liquid phase and was performed using the experimental data. The following steps of the optimization of the thermodynamic properties and assessment of the phase diagram were conducted using the CALPHAD method. According to very recent studies in the literature and with our calculations, $Li_{17}Si_4$, $Li_{21}Si_5$ and $Li_{4.13}Si$ phases were considered as the Li-rich phases instead of $Li_{22}Si_5$. The LiSi phase was also considered for the first time in the assessment. The $Li_{13}Si_4$, Li_7Si_3 and $Li_{12}Si_7$ phases were also taken into account. Additionally, the crystal structure of the Li–Si phases was established by optimization of the electronic structure of each phase and phonon calculations were performed to attain the thermodynamic data at $T > 0$ K. The first principles thermodynamic data was compared with experimental and CALPHAD results.

1. Introduction

Most of the thermochemical data for the Li–Si system was obtained by means of electrochemical measurements in the late seventies or eighties of the 20th century [1–4].

Binary lithium alloys have been considered to be possible negative electrode materials because they exhibit much higher specific capacities than graphite used in Li-ion batteries. For comparison, the Li–Si electrodes are characterized by the highest theoretical capacity which for the $Li_{22}Si_5$ compound equals ~4200 mA h g^{-1}, while for graphite it reaches only 372 mA h g^{-1}[5].

However, the lifecycle of these binary alloys negative electrodes is poor, as large volume variations associated to repeatedly charge/discharge cycles lead to the pulverization of the electrode [5]. Large improvements have been achieved in these areas, essentially due to nanostructuration [6–8].

Other alternative is adding another element to silicon, for example Mg [9]. Such alloys show high capacity at low potential which makes them attractive as negative electrodes, however their cycle life is still small. Subsequently, good knowledge of the binary phase diagrams is likewise essential to avoid dissemination of errors to higher order phase diagrams.

Thought the Li–Si system has been investigated for years there are still data inconsistencies for the liquidus temperature for the Si-rich alloys and discrepancies concerning the composition of the Li–Si intermetallic phases of high Li-concentration ($x_{Li} > 0.75$).

Generally, there is an agreement regarding the existence of three Li–Si phases: $Li_{12}Si_7$, Li_7Si_3, and $Li_{13}Si_4$. The LiSi phase was identified for first time in 1997 by Evers et al. [10] and then in 2003 by Stearns et al. [11]. It was prepared under very high pressure (1–2.5 GPa) and at temperatures between 773 and 973 K and also by mechanical alloying [12]. Finally, the LiSi phase was accepted by Okamoto [13] in the critical evaluation of Li–Si system that had been previously assessed by Braga et al. [14]. Additionally, Chevrier et al. [15] using lattice dynamics simulations, found that LiSi is stable at room temperature up to $T < 600$ K and Mihalkovic, Widom and coworkers [16] and Kim et al. [17] confirmed LiSi electronic structure to be stable.

Different data concerning the intermetallic phase(s) of highest concentration of Li can be found in literature. Based on the electrochemical investigations of Li–Si solid alloys, Wen and Huggins [4] suggested the $Li_{22}Si_5$ phase. However based on experimental or theoretical studies, some authors [15,18,19] were in agreement that $Li_{15}Si_4$ and $Li_{21}Si_5$ phases were the Li's richest phases. Very recently, Zeilinger and co-workers published their work focusing on the phases: $Li_{17}Si_4$ [20], $Li_{15}Si_4$ [21], $Li_{4.11}Si$ [22] and $Li_{13}Si_4$ [23]. They found $Li_{17}Si_4$ to be stable at room temperature up to

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~761 K, and $Li_{4.11}Si$ stable between ~754 K and ~892 K. The phase $Li_{15}Si_4$ was found to be metastable. Moreover, the cited authors refined the crystal structure of $Li_{13}Si_4$.

Very recently Fima et al. [24] measured the electromotive forces for some liquid alloys by EMF method. The measurements were carried out in the temperature range between 880 and 1020 K for liquid alloys containing 0.570, 0.610, 0.815, and 0.850 mole fractions of Li.

In Table 1S – Supplement some of the phases that were considered by various authors since the Li–Si system was firstly studied, up to very recently, and whose consideration followed experimental efforts [1–4,8,10–12,18,20,22,23,25–47]. In Table 2S – Supplement it is shown a similar content to Table 1S, but for studies that proceeded from data optimization [13], CALPHAD assessments [14,48,49] or first principles calculations [15–17].

The most recent CALPHAD assessment was performed by Wang et al. [49]. Their assessment takes into account $Li_{22}Si_5$ as the Li-rich phase instead of $Li_{17}Si_4$, $Li_{21}Si_5$ and $Li_{4.13}Si$ and LiSi was not considered. Furthermore, their liquidus assessed line is not in agreement with the experimental data, especially on the Li-rich side. Their liquid phase enthalpies of mixing are also deviated from the experimental data presented in this work.

The aim of the present work is to critically assess all the experimental data, especially that related with the crystal structure of the Li–Si system's phases and phase diagram [1–3,8,10,11,18,20–23,25–47].

Furthermore, it is our goal to present the enthalpies of mixing of the liquid phase measured by means of drop calorimetry, which were never investigated for this system before. Moreover, first principles data and phonon calculations (lattice vibrations) are compared with experimental results and CALPHAD assessment, which from the best of our knowledge, is an additional novelty for this system. The optimization of the Li–Si thermodynamic data and phase diagram calculations were our goals as well. The $Li_{17}Si_4$, $Li_{21}Si_5$, and $Li_{4.13}Si$ Li-rich phases, $Li_{13}Si_4$, Li_7Si_3, $Li_{12}Si_7$ and the LiSi (for the first time assumed in calculations) were taken into consideration as well as all the available thermodynamic experimental data.

2. Experimental and calculations

2.1. Calorimetric measurements

To determine the integral enthalpy of mixing of liquid Li–Si alloys, lithium (99.9 wt% Li) and silicon (99.9999 wt.% Si) Alfa Aesar were used. All calorimetric measurements were carried out within a protective atmosphere of high purity argon (Air Products 99.9999 wt%) using a Setaram MHTC 96 Line evo calorimeter at 1081, 1089 and 1093 K. The impurities of nitrogen, oxygen and water in the course of preparation of samples and experiments were much lower that 1 ppm. To the calorimetric study, tantalum crucibles with protective alumina tube were used. At the beginning of series 1, the calorimeter was calibrated using lithium pieces. The prepared lithium pieces were closed inside the glovebox with high purity argon in a calorimetric antechamber. Subsequently, the calorimetric antechamber was removed from the glove box and connected to the calorimeter. For the series 2–5, the calorimeter was calibrated at the end of the series using pieces of tantalum. Before each experimental run and before dropping the pieces of Li or Si into the calorimeter the apparatus was evacuated several times with a turbomolecular pump and then flushed with high purity argon of the same quality as that inside the glovebox.

The measured enthalpy of mixing of liquid Li–Si alloys (integrated heat flux at constant pressure) is defined by the relationship:

$$H_{DISS-X} = (\Delta H_{signal} \cdot K) - (H_X^{T_D \to T_M} \cdot n_X) \quad (1)$$

$$\Delta H_{mix} = \frac{\sum H_{DISS\text{-}X}}{n_{Li} + n_{Si}} \quad (2)$$

where ΔH_{signal} is the heat effect of each drop of metal (Li or Si) which equalled the added drop enthalpy, K is calorimeter constant, T_D and T_M are the drop and calorimeter absolute temperatures, respectively. The $H_X^{T_D \to T_M}$ is the enthalpy of the pure metals (Li or Si) which was obtained from Thermo-Calc database [50], n_{Li} and n_{Si} are the number of moles of lithium and silicon, respectively. The $H_{DISS\text{-}X}$ is the enthalpy of dissolution of pure lithium or silicon.

2.2. Differential Thermal Analysis (DTA)

Phase transformations and liquidus temperature measurements of Li–Si alloys were conducted by means of the DTA technique using Q-1500 (Paulik–Paulik–Erdey) derivatograph. The samples were prepared in the glovebox filled with the high purity argon similarly as used in the calorimetric measurements. The alloys were prepared by melting metals in Ta crucibles which were sealed in the Ti crucibles using a hydraulic press. Ti crucibles were preliminary heated in air up to 1073 K to avoid subsequent effects of the reactions of Ti with N_2 and/or O_2 in the course of DTA measurements. Weights of test samples were ~0.2 g. Afterwards the DTA measurements were performed in air with a temperature rate of 5 K per minute. Empty crucibles of Ta inside Ti were used as the reference state.

The intermetallic Li–Si phases were produced from Li and Si by melting the stoichiometric amounts in a Mo crucible protected from the inside by a Ta foil. Melting took place in the glovebox with high purity Ar. Subsequently, the liquid alloy was cooled together in the furnace and after solidification it was studied by X-ray diffraction. It was found that generally in such prepared samples only the assumed Li–Si phases were present; therefore the samples could be used for DTA measurements. Other Li–Si alloys were prepared directly during the DTA studies as follows. In the glovebox the suitable amounts of Li and Si were weighed and put into the inner Ta crucible which was placed in the outer Ti crucible. Afterwards the Ti crucible was closed by the cover pressed inside crucible. Such prepared sample was drown out from the glove box, set into the DTA apparatus and slowly heated to the temperature above the liquidus. After about 5 min equilibration the cooling was started with the rate of 5 °C/min. After reaching the room temperature, the heating run started and was performed up to above the liquidus temperature.

2.3. First principles calculations

One of the most important methods of quantum mechanical modeling of solids is the framework of Density Functional Theory (DFT) [51] using the Generalized Gradient Approximation (GGA) [52]. The basic notion of this method is to replace the true interacting many-electron-system with a system of one electron in an effective potential due to all of the other electrons and nuclei. From a fundamental point of view, the one-electron functions are a unique tool for calculating the total energy and the electronic density of states; these functions have no particular physical meaning but this simplification of the problem needs a self-consistent calculation and it is one of the major technical issues in the *ab initio* approach [53]. DFT calculations with Projector Augmented Wave (PAW) pseudopotentials [54], and the Perdew–Burke–Ernzerhof (PBE) functional [55] were used as implemented in the Vienna *Ab Initio* Simulation Package (VASP) code [56]. A plane wave cutoff of at least 400.00 eV and k-spacings of 0.230 × 0.230 × 0.230 $Å^{-1}$ were used. Calculations were performed in the real space and performed for: Li-bcc A2, $Li_{22}Si_5$, $Li_{17}Si_4$, $Li_{21}Si_5$, $Li_{4.19}Si$–Li_4Si (five different structures), $Li_{15}Si_4$ (two different structures), $Li_{13}Si_4$ (two different structures), Li_7Si_3 (two different structures), $Li_{12}Si_7$, LiSi and Si-diamond A4. Additionally, the anti-phases of Li and Si, Li as diamond-A4 and Si as bcc-A2 were calculated, since this data is also required in the CALPHAD assessment. The total energy was minimized with respect to the volume (volume relaxation), the shape of the unit cell (external relaxation), and the position of the atoms within the cell (internal relaxation). More details on the crystal structures will be given later.

The Phonon direct method [57] was engaged to predict the lattice dynamics using the harmonic approximation on VASP's minimized structures that had the lowest ground state energy. Therefore, the electronic structure at ground state was calculated using VASP and the zero point energy, the phonons' energy and the entropy was calculated using Phonon direct method. In fact, we have calculated the Helmholtz free energy, which can be approximated to the Gibbs free energy at zero stress.

The Helmholtz free energy, the internal energy – that can be approximated to the enthalpy – and the entropy were calculated after the vibration frequencies, ω, as follows:

$$F_{phonon} = 3Nk_BT\int_0^{\omega_L} ln\left(2sinh\frac{\hbar\omega}{2k_BT}\right)g(\omega)d\omega \quad (3)$$

$$E_{phonon} = 3N\frac{\hbar}{2}\int_0^{\omega_L} \omega coth\left(\frac{\hbar\omega}{2k_BT}\right)g(\omega)d\omega \quad (4)$$

$$S_{phonon} = 3Nk_B\int_0^{\omega_L}\left[\frac{\hbar\omega}{2k_BT}coth\left(\frac{\hbar\omega}{2k_BT}\right) - ln\left(2sinh\frac{\hbar\omega}{2k_BT}\right)\right]g(\omega)d\omega \quad (5)$$

where N is the number of atoms in the cell, k_B is Boltzmann's constant, T the absolute temperature, ω_L the maximal frequency and $g(\omega)$ the frequency distribution function. The electronic contribution (calculated using DFT as implemented in VASP), the *ZPE* zero-point energy of the quantum harmonic oscillator, $E(0\ K) = \frac{1}{2}\hbar\omega$, plus the phonon contribution (calculated using phonon) define $E(T) = E_{elec} + ZPE + E_{phonon}(T)$. The