Electromotive Force Measurements in Liquid Li-Si Alloys

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Abstract

Electromotive force measurements on the Li-Si system were initiated by the concentration cell method with an $(\text{LiCl-LiF})_{\text{eut}}$ electrolyte and the $(\text{Bi, Li}_3\text{Bi}_{(l)} + \text{Li}_3\text{Bi}_{(s)})$ two phase alloy as a reference electrode. The measurements are carried out in the temperature range between 880 and 1020 K for liquid alloys containing 0.57, 0.61, 0.815, and 0.85 mole fractions of Li. The activities of Li in liquid Li-Si alloys determined in this work are compared with the activities calculated from the set of thermodynamic parameters optimized by Braga et al. Present results are in reasonable agreement with calculated data.

Keywords activity, electromotive force (emf), liquid, Li-Si system

1. Introduction

The Li-Si system is interesting because of its potential application as an anode material in thermally activated batteries^[1] and for hydrogen storage. In the Li-Si system, according to assessments of Braga et al.^[2] and Okamoto,^[3] four intermetallic compounds (IMC) are present ($\text{Li}_{22}\text{Si}_5$, $\text{Li}_{13}\text{Si}_4$, Li_7Si_3 , $\text{Li}_{12}\text{Si}_7$), as reported by Wen and Huggins^[4] they were assumed to be thermodynamically most stable. Recently, based on work of Stearns et al.,^[5] Okamoto^[6] suggested a new version of the phase diagram that includes an LiSi compound decomposing on heating at 743 K. Stearns et al.^[5] found that the LiSi compound is formed at pressures higher than 1 GPa and at temperatures between 773 and 973 K. At normal pressures it is a stable compound, but its formation cannot be observed due to slow kinetics.

Regardless, the relatively new controversy concerning the LiSi IMC, Braga's and Okamoto's phase diagrams^[2,3] are different from an earlier assessment,^[7] moreover some of preceding experimental data do not support it. Thermodynamic studies of Li-Si system in the solid state were performed by means of the electromotive force (emf) method by a few groups, and these reported data of Gibbs free energy of formation of IMC^[4,8-10] in good mutual agreement. The literature survey indicates, however, that there is no experimental data regarding thermodynamics of the liquid phase of the Li-Si system. Because of the lack of experimental data for liquid phase the recommended thermodynamic parameters^[2] should be verified experimentally. Reversing the problem, experimental thermodynamic data for liquid Li-Si alloys will be used in future reassessment of the Li-Si system. Therefore the aim of this work is to perform emf measurements of the liquid Li-Si alloys over a concentration range from 0.57 to 0.85 mole fractions of Li.

2. Experimental

The electrochemical concentration cell method was used for the investigation of the thermodynamic properties of Li-Si alloys. Such a galvanic cell can be schematically represented by the formula below, and the cell's construction details are shown in Fig. 1.

The cell consisted of two molybdenum crucibles (1 and 2). The $(\text{Bi, Li}_3\text{Bi}_{(l)} + \text{Li}_3\text{Bi}_{(s)})$ reference electrode was placed at the bottom of the outer

crucible (1) filled with LiCl-LiF electrolyte. The inner crucible (2) with the studied Li-Si alloy was fixed on Mo wire (1.5 mm in diameter) support. In the bottom of the inner crucible there were three holes, each of 0.5 mm in diameter. The electrode connections (3) and (4) were prepared from Mo wire (0.5 mm in diameter). The temperature was measured by a Ni-Mo thermocouple (5), calibrated with Pt-PtRh10 one, screwed onto the outer crucible (1) (Fig. 1). The liquid eutectic salt mixture LiCl-LiF was prepared by bubbling a gaseous HCl through the melted salt solutions. In the next step, the absorbed residual HCl was removed by Ar flux (of 99.999% purity) in the same bubbler. Each cell was assembled under high purity argon (99.9999%) in the glove-box provided with the purification system. The protective gas circulated continuously between the purification system and the glove-box at the rate 35 m³/h removing oxygen, water and nitrogen. The amounts of O₂ and H₂O in Ar were continuously monitored and kept at the level lower than 1 ppm. N₂ was removed in the Ti-reactor at 1273 K and its concentration was not monitored. The cell was introduced into the gas tight vertical quartz vessel with the tapered glass joint and valves for argon inlet and outlet. After assembling, the cell was placed in the resistance furnace equipped with a programmable temperature control unit.

The Li-Si alloys were prepared directly in the cell crucible from the pure Si (99.9999%, Alfa-Aesar) and Li (99.9%, Alfa-Aesar). First, the samples were heated to the temperatures about 100 K above the liquidus. The alloys were prepared by relatively fast dissolution of solid Si in liquid Li. The preparation process was monitored by continuous emf measurements. After stabilization of the emf the activity measurements were

Fig. 1 The scheme of the concentration cell used for the emf measurements

Fig. 2 Electromotive force (emf) vs. $\text{Bi, Li}_3\text{Bi}_{(l)} + \text{Li}_3\text{Bi}_{(s)}$ reference electrode dependence on temperature

carried out at alternating temperatures. Before the measurements for Li-Si alloys, the emf of $\text{Bi, Li}_3\text{Bi}_{(l)} + \text{Li}_3\text{Bi}_{(s)}$ versus Li was measured and it was found in very good agreement with the data reported in Gasior et al.,^[11] therefore the formula describing temperature dependence of the data reported in that investigation was used in present calculations.

3. Results and Discussion

The results of the emf measurements by the concentration cell (1) are presented in Fig. 2 and the regression

equations describing their temperature dependences are listed in Table 1. The emf of the studied alloys versus reference $\text{Bi, Li}_3\text{Bi}_{(l)} + \text{Li}_3\text{Bi}_{(s)}$ electrode decreases linearly with increasing temperature. The partial excess Gibbs free energy $G_{\text{Li}}^{\text{ex}}$ and the activity a_{Li} of Li in the liquid phase were calculated applying the following relations:

$$G_{\text{Li}}^{\text{ex}} = -nF(E_{\text{Bi, Li}_3\text{Bi}_{(l)} + \text{Li}_3\text{Bi}_{(s)}} + E) - RT \ln x_{\text{Li}} \quad (\text{Eq 2})$$

$$a_{\text{Li}} = \exp\left(\frac{-nF(E_{\text{Bi, Li}_3\text{Bi}_{(l)} + \text{Li}_3\text{Bi}_{(s)}} + E)}{RT}\right) \quad (\text{Eq 3})$$

$$E_{\text{Bi, Li}_3\text{Bi}_{(l)} + \text{Li}_3\text{Bi}_{(s)}} = 547.1 + 3.695 \times T - 0.5229 \times T \times \ln(T) \quad (\text{Eq 4})$$

where E is the emf of cell (1), $E_{\text{Bi, Li}_3\text{Bi}_{(l)} + \text{Li}_3\text{Bi}_{(s)}}$ is the emf of $\text{Bi, Li}_3\text{Bi}_{(l)} + \text{Li}_3\text{Bi}_{(s)}$ electrode versus liquid Li^[11] according to Eq 4, x_{Li} denotes the mole fraction of Li, n is the valence of Li ions (i.e. $n = 1$), R is the gas constant, T and F are the temperature and Faraday constant, respectively.

For the interpretation of thermodynamic properties of liquid solutions, the polynomial proposed by Redlich and Kister^[12] is commonly used (Eq 5). The resulting expression for the partial excess Gibbs energy of Li is expressed by Eq 6.

$$G_{\text{Li, Si}}^{\text{ex}} = x_{\text{Li}} x_{\text{Si}} \sum_{i=0}^n L_{\text{Li, Si}}^i (x_{\text{Li}} - x_{\text{Si}})^i \quad (\text{Eq 5})$$

$$G_{\text{Li}}^{\text{ex}} = x_{\text{Si}}^2 \left(L_{\text{Li, Si}}^0 + \sum_{i=1}^n L_{\text{Li, Si}}^i (x_{\text{Li}} - x_{\text{Si}})^{i-1} \times ((2n+1)x_{\text{Li}} - x_{\text{Si}}) \right) \quad (\text{Eq 6})$$

$$L_{\text{Li, Si}}^0 = -87689.8 + 2.667T \quad (\text{Eq 7})$$

$$L_{\text{Li, Si}}^1 = -130002.8 + 88.84T \quad (\text{Eq 8})$$

$$L_{\text{Li, Si}}^2 = 33387.9 - 57.13T \quad (\text{Eq 9})$$

The partial Gibbs free energy of Li $G_{\text{Li}}^{\text{ex}}$ (Eq 6) calculated at 973 K from optimized parameters recommended by Braga et al.^[2] (Eq 7-9) varies with composition as shown in Fig. 3, with weak inflection points around $x_{\text{Li}} = 0.3$, 0.71. The experimental $G_{\text{Li}}^{\text{ex}}$ (calculated from the emf measurements in this work) deviate from the calculated line as much as 5 kJ/mol for $x_{\text{Li}} = 0.815$ composition. The relatively large difference between the $G_{\text{Li}}^{\text{ex}}$ for $x_{\text{Li}} = 0.815$ (Fig. 3) calculated from the Redlich-Kister equation and

Table 1 Results of emf measurements vs. $\text{Bi}, \text{Li}_3\text{Bi}_{(l)} + \text{Li}_3\text{Bi}_{(s)}$ reference electrode, partial Gibbs free energy of Li ($G_{\text{Li}}^{\text{ex}}$) and activity of Li (a_{Li}) at 973 K, respectively

x_{Li}	emf = $a + b T$, mV	$G_{\text{Li}}^{\text{ex}}$ (973 K), J mol^{-1}	a_{Li} (973 K)
0.57	$-868.6 + 0.5888 T$	-28949	0.016
0.61	$-647.5 + 0.2987 T$	-23559	0.033
0.815	$-746.9 + 0.3373 T$	-19950	0.069
0.85	$-927.5 + 0.3400 T$	-3164	0.575

Fig. 3 $G_{\text{Li}}^{\text{ex}}$ vs. Li concentration at 973 K; present data (points) compared with values calculated from optimized thermodynamic parameters^[2] (dotted line)

Fig. 4 Activity of Li vs. Li concentration at 973 K; present data (points) compared with activity calculated from optimized thermodynamic parameters^[2] (dotted line)

thermodynamic parameters (Eq 7-9)^[2] and $G_{\text{Li}}^{\text{ex}}$ determined from emf measurements in this work is the result of two factors. The first is the model used by Braga et al.^[2] to describe the excess Gibbs free energy of liquid alloys with strong deviations from ideal behavior, and a number of intermetallics in the solid state, while the second is a large decline in the value of $G_{\text{Li}}^{\text{ex}}$ of liquid

alloys in the vicinity of concentration matching one of the intermetallics occurring in the solid state.

Such rapid changes of $G_{\text{Li}}^{\text{ex}}$ have been observed also in emf studies of liquid Li-Pb,^[13-15] Li-Sn^[14,16-18] and Li-Bi^[11,14] alloys. Most likely, the situation is analogous in the case of liquid Li-Si alloys as in the binary systems of Li and elements of 4-th

group of periodic system (Si, Ge, Sn, and Pb), in which a number of intermetallics are present with the same or similar concentrations of the components, similar deviations from ideal solutions of thermodynamic functions for liquid alloys are observed. It should therefore be inferred that in the Li-Si system in the vicinity of the concentration corresponding to the Li-richest phase ($\text{Li}_{22}\text{Si}_5$) a sharp decline of $G_{\text{Li}}^{\text{ex}}$ should also be observed. We observed it in our results but it is in disagreement with the values calculated from the Redlich-Kister equation and optimized thermodynamic parameters (Eq 7-9). According to Saboungi et al.,^[13] Gasior^[14] and Gasior et al.^[15] for Li-Pb system it is impossible to describe excess Gibbs free energy of Pb using a polynomial with such a low degree, precisely because of the very large decrease of the excess Gibbs free energy values in the vicinity of $\text{Li}_{22}\text{Pb}_5$ phase with relatively low variation of Li concentration. Using a different model such as Sommer's associates model^[19] to interpret the thermodynamic properties of liquid phase in Li-Si system would give better agreement of the calculated and measured values.

The second factor that increases the analyzed divergence of the $G_{\text{Li}}^{\text{ex}}$ is the change of concentration of alloy electrode due to the transport of Li through the electrolyte from the electrode with higher potential to the electrode with lower potential of Li. This process is well known to experimenters engaged in the studies of activity of Li in alloys by measuring the emf, and is characterized by a change of the emf during measurement. For large values of the emf of the concentration cell and long (1-3 h) time required by the cell to reach thermodynamic equilibrium or thermal (temperature) stabilization there is always certain change in the composition of the alloy electrode and the reference electrode (change in concentration of the reference electrode has no influence on its potential relative to Li), as the system seeks to reduce the emf of the concentration cell (alignment of concentrations in both electrodes). Thus, if in the Li-Si solution of composition matching the

Li-richest phase ($\text{Li}_{22}\text{Si}_5$) a change of concentration occurs (in the Li-Si alloy, concentration of Li in alloy electrode is reduced as the potential of Li in the reference electrode is much lower) then the measured emf relative to Li is higher (but relative to the reference electrode is lower) than it should be for nominal concentration, and as a result the calculated value of $G_{\text{Li}}^{\text{ex}}$ is lower. Of course, both of the analyzed factors contributed to the relatively large difference between the calculated and measured $G_{\text{Li}}^{\text{ex}}$ for $x_{\text{Li}} = 0.815$. Future re-optimization of the thermodynamic properties of liquid phase of Li-Si, taking into account the results of present work and describing the thermodynamics of liquid alloys with the use of, for example, the associates model^[19] should greatly reduce the discussed discrepancy of $G_{\text{Li}}^{\text{ex}}$ for the concentrations close to the phase $\text{Li}_{22}\text{Si}_5$.

The activity of Li calculated at 973 K from recommended optimized parameters shows strongly negative deviation from additivity (Fig. 4). In particular at $x_{\text{Li}} = 0.7$ the activity value equals 0.08, and it rapidly increases for higher Li concentrations. Present results are in good agreement with calculated activity for $x_{\text{Li}} = 0.57$ and 0.61 alloys, whereas the agreement is worse for alloys containing $x_{\text{Li}} = 0.815$ and 0.85. For $x_{\text{Li}} = 0.815$ present result 0.069 is much lower than the calculated 0.298, while for $x_{\text{Li}} = 0.85$ the present 0.575 is higher than the 0.420 calculated from recommended optimized parameters. The fact that activity of Li in liquid alloys shows strongly negative deviation from additive behavior can be explained by local arrangement in the liquid resulting from intermetallics that are present below the liquidus. For Li concentrations higher than $x_{\text{Li}} = 0.815$, which corresponds to $\text{Li}_{22}\text{Si}_5$ IMC, activity of Li in the liquid rapidly increases as the activity of pure liquid Li is equal to 1. For alloys containing $x_{\text{Li}} = 0.815$ and 0.85, the disagreement between experimental activity and the one calculated from recommended thermodynamic parameters,^[2] can be to some extent explained by experimental

errors such as change of the alloy composition during the experiment that were discussed above. In such case even a very small change of alloy composition in Li-rich concentration range results in significant change of activity. For this reason it is necessary to continue investigations of the thermodynamics of liquid phase of Li-Si alloys.

4. Conclusions

Electromotive force (emf) versus a $\text{Bi}_3\text{Li}_3\text{Bi}_{(l)} + \text{Li}_3\text{Bi}_{(s)}$ reference electrode determined for four compositions of liquid Li-Si alloys decreases with increasing temperature. Using well known relations, excess Gibbs free energy and activity of Li were derived from measurements results. Present results were compared with activity and excess Gibbs free energy of Li calculated from optimized thermodynamic parameters. Generally, good agreement is observed between the two sets of data, however, in order to clarify activity dependence on composition further research is necessary in the concentration range $0.6 < x_{\text{Li}} < 1$.

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