Journal of Molecular Liquids 269 (2018) 501–510

Contents lists available at ScienceDirect

Journal of Molecular Liquids

journal homepage: www.elsevier.com/locate/molliq

Enthalpy of mixing of liquid Ag-Li-Sb alloys

Monika Bugajska [a], Siegfried Fürtauer [b], Hans Flandorfer [b], Przemyslaw Fima [a],*

[a] Institute of Metallurgy and Materials Science, Polish Academy of Sciences, 25 Reymonta St., 30-059 Krakow, Poland
[b] Department of Inorganic Chemistry - Functional Materials, University of Vienna, Althanstraße 14, 1090 Wien, Austria

ARTICLE INFO

Article history:
Received 8 February 2018
Received in revised form 11 July 2018
Accepted 11 August 2018
Available online 11 August 2018

Keywords:
Ag-Li-Sb
Drop solution calorimetry
Enthalpy of mixing
Liquid alloys

ABSTRACT

Ag-Li-Sb is a ternary system that has not yet been studied in terms of thermodynamic investigations. The partial and integral enthalpies of mixing of liquid Ag-Li-Sb alloys at 980 K were determined applying drop calorimetry. The investigations were performed along five sections by the addition of lithium to alloys with fixed Ag to Sb molar ratio of 1:1 and 1:4, by the addition of silver to alloys with fixed Li to Sb molar ratio equal to 1:9, 3:7 and 1:1. Experimental data were compared and discussed with Muggianu and Toop extrapolation models. From experimental ternary data the range of liquid at 980 K was deduced.

1. Introduction

Currently, lithium-ion batteries are the main source of power used in portable electronics and their specific energy hardly exceeds 250 Wh/kg. Alternative power supply with renewable energy sources like wind and solar energy as well as full-electric vehicles require energy storage systems with high specific energy, energy and power densities. The low weight and high voltage of Li-ion batteries make them promising candidates for such applications [1,2]. However, they have to be improved mandatory in respect to their specific energy, energy and power density as well as lifetime and costs [3]. In the most common Li-ion batteries, cathodes are built of layered lithiated metal oxides while anodes are built of layered graphite, which upon lithiation forms LiC_6 [4]. These lithium-ion batteries are characterized by high voltage, high cyclability and reliability, no memory effect and low costs. Their capacity is sufficient for low power applications.

To make Li-ion batteries suitable for high power applications as mentioned above all parts of the battery have to be fundamentally improved, especially the electrodes charge capacities and kinetic performance. This is, however, not possible based on same materials which have been hitherto used. Concerning the anodes, among the most promising new materials are intermetallic compounds. The Li_3Sb intermetallic compound has a relatively high theoretical capacity (660 mAh/g) [5], but due to drastic volume change upon lithiation and delithiation of Sb such electrodes degrade after a few charge/discharge cycles. It has been found that alloying of Sb with other elements (either less active or inactive towards Li) limits volume expansion effects on the electrode material by the precipitation of an inactive matrix which buffers the mechanical stress [4]. Vaughey et al. [6] electrochemically studied lithiation of Ag_3Sb at room temperature, but for a systematic investigation of such processes the knowledge of phase diagrams and thermodynamics is indispensable. Little is known regarding thermodynamics and phase relations in the ternary Ag-Li-Sb system. Batteries operate at −20 to 50 °C, however, experimental thermodynamic investigations are hardly practicable in this temperature regime. Nevertheless, high temperature investigations of Ag-Li-Sb system can shed some light on this matter and provide the essential data for future thermodynamic assessment of Ag-Li-Sb system with CALPHAD method and calculation of its phase diagram. Such a thermodynamic assessment allows the extrapolation of data down to lower temperatures. Therefore, our aim is to study mixing enthalpies of liquid Ag-Li-Sb alloys.

2. Literature survey

According to a literature survey there are no thermodynamic data available for liquid ternary Ag-Li-Sb alloys. Thermodynamic properties of constituent binary alloys were reported earlier, on the other hand.

2.1. Ag-Li system

There are only a few sets of thermodynamic data for liquid Ag-Li alloys. Mixing enthalpy of liquid Ag-Li alloys was obtained calorimetrically by Predel et al. [7] at 1250 K, while Becker et al. [8] studied the activity of Li at 830 K with an electromotive force method (EMF) in the concentration range of 0.435–0.95 mol fraction Li. Debski et al. [9] published a study of the mixing enthalpy of the Ag-Li liquid-alloy based on drop calorimetry at two temperatures, 1253 K and 873 K. Their studies were conducted over the entire range of lithium concentrations, and do not show any dependence on temperature. The integral enthalpy values from [9] are more negative in the concentration range $x(\mathrm{Li}) = 0.2$–0.8, as

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* Corresponding author.
E-mail address: p.fima@imim.pl (P. Fima).

https://doi.org/10.1016/j.molliq.2018.08.067
0167-7322/

compared to [7]. In particular, in [9] the minimum of mixing enthalpy (-11.7 kJ·mol^{-1}, at $x(\mathrm{Li}) = 0.55$) is about 3 kJ·mol^{-1} more negative than the minimum of -9 kJ·mol^{-1} given in [7]. Gąsior et al. [10] have developed a thermodynamic description of liquid phase based on literature data and their own EMF measurements of liquid alloys. According to [10] the mixing enthalpy is negative and does not depend on temperature. The maximum difference between calculated enthalpy [10] and experimental data is 1 kJ·mol^{-1} in the case of [7] and 2 kJ·mol^{-1} in the case of [9].

2.2. Ag-Sb system

The molar mixing enthalpy of liquid Ag-Sb alloys was investigated by Castanet et al. at 950, 1000 and 1300 K [11]. Their results show a temperature dependence of the integral mixing enthalpy. Predel and Emam [12] measured the integral mixing enthalpy at 1250 K, and their results coincided with Castanet's results at 1300 K [11]. The antimony activity in liquid Ag-Sb alloys was determined by Hino et al. [13], measuring the vapor pressure of antimony in a temperature range of 1273 K - 1473 K. Nozaki et al. [14], and Vacher and Gerasimov [15] used a galvanic cell with liquid salts electrolyte and solid silver as the reference electrode, to determine the activity of silver with EMF method in the range of $0.157 \leq x(\mathrm{Sb}) \leq 0.829$ at 1300 K. The results of these independent investigations have both shown large deviations of silver activity from Raoult's law.

First Oh et al. [16], published a thermodynamic assessment of the Ag-Sb system based on the available data from the literature. Later Krzyżak and Fitzner [17] used their own results of antimony activity, measured with EMF method in the 950–1100 K temperature range, and earlier calorimetric data to develop a thermodynamic description of the liquid phase of Ag-Sb. The mixing enthalpy calculated from their description well reproduces most values known from the literature. Only the values obtained by Castanet differ slightly. Castanet and co-authors [11] received a lower minimum enthalpy of mixing in the liquid Ag-Sb system. According to [17], on the silver side enthalpy is negative and its minimum is ~ -2.5 kJ·mol^{-1}, while on the antimony side enthalpy values are positive and its maximum is equal to ~ 1.2 kJ·mol^{-1}. A further thermodynamic description was developed by Zoro et al. [18] in 2006. All three descriptions show similar enthalpy of mixing dependence on concentration.

2.3. Li-Sb system

Until recently little was known regarding thermodynamic properties of liquid Li-Sb alloys. Kubaschewski and Seith measured the enthalpy of mixing of the Li-Sb alloys at 1223 K in the lithium molar fractions range of 0.0–0.6 [19]. Kane et al. [20] performed EMF measurements at a temperature range of 698 K to 998 K for Li-Sb alloys containing up to 0.6 mol fraction of lithium. From EMF data they determined activity of Li, which shows strong negative deviation from Raoult's law. Terlicka et al. measured the enthalpy of mixing of liquid Li-Sb in the range of 820 to 1024 K, using drop calorimetry [21]. Their results were confirmed with latest work on the thermodynamic assessment of the Li-Sb system published by D. Li et al. [22]. Their results of calorimetric enthalpy studies are consistent with earlier data, and confirm that integral mixing enthalpy does not depend on temperature. D. Li et al. [22] assessed the phase diagram of Li-Sb also based on experimental phase diagram data published earlier by Beutl et al. [23]. Their experimental enthalpy of mixing is strongly negative with an estimated minimum close to the lithium molar fraction of 0.75. Such a shape of mixing enthalpy suggests the existence of an associate "$\mathrm{Li_3Sb}$" in the liquid [22] which was implemented into the thermodynamic assessment. The calculated minimum of the enthalpy of mixing of metastable liquid is ~ -55 kJ·mol^{-1}.

3. Experimental procedure

Measurements were performed at 980 K along five cross-sections of constant ratios: $x(\mathrm{Ag}){:}x(\mathrm{Sb}) = 1{:}1$; $x(\mathrm{Ag}){:}x(\mathrm{Sb}) = 1{:}4$; $x(\mathrm{Li}){:}x(\mathrm{Sb}) = 1{:}9$; $x(\mathrm{Li}){:}x(\mathrm{Sb}) = 3{:}7$; $x(\mathrm{Li}){:}x(\mathrm{Sb}) = 1{:}1$, as illustrated in Fig. 1. The starting binary alloys were synthesized by melting in a resistance furnace in a glovebox with Ar atmosphere, which was purified from oxygen, nitrogen and water vapor traces by passing through Ti-shavings heated to 1073 K. Stoichiometric amounts of the pure components of silver and antimony were weighed and placed into graphite crucible, as well as pure lithium and antimony were placed into tungsten crucible. For the homogenization, the contents of the crucible were stirred with graphite or tungsten rods, respectively, during melting.

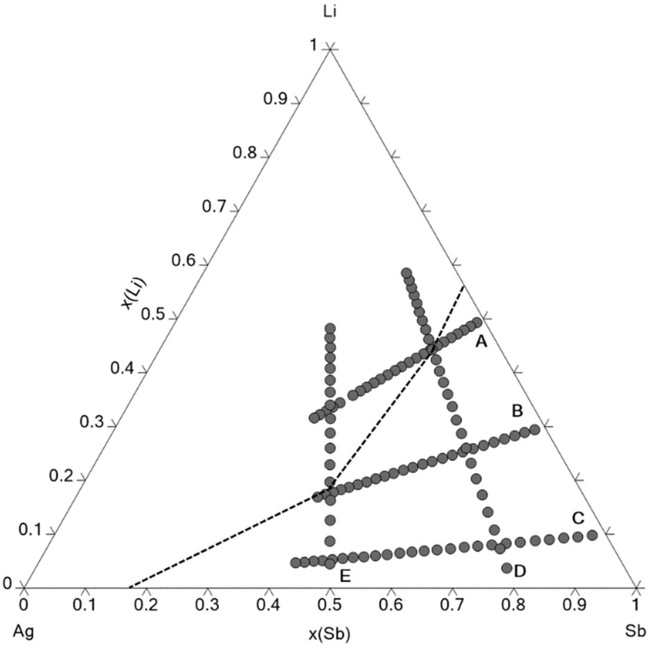

Fig. 1. Measured sections in the ternary Ag-Li-Sb system (points) at 980 K, dashed line indicates approximate position of liquidus, deduced from changes in partial and integral enthalpies.

For all measurements, a pure Li wire (Alfa Aesar, 3.2 mm, 99.8%, with oil coating) which was stored in a glovebox under Ar atmosphere (Ar 5.0; $O_2 < 1$ ppm; $H_2O < 1$ ppm), was used. All the substances used and their purity are included in Table 1. The calorimetric measurements were conducted in a Calvet-type twin calorimeter with two thermopiles containing >200 thermocouples each. A self-constructed auto-sampler was used to perform drops without any interruption of the measurement or contamination of the atmosphere. In particular, pieces of Li were weighed, loaded into the auto-sampler in the glovebox and sealed shortly before the auto-sampler was attached to the calorimeter. The calorimeter and the mechanical sampler were controlled by a self-written software based on LabView. For detailed information see Flandorfer et al. [24]. Measurements of all alloys were performed in BN crucibles. To prevent oxidation, the measurement chamber was evacuated and flushed with Ar (99.999 further purified with Gas Clean Oxygen Filter) three times. Pieces of Ti-foil were placed into the measurement chamber as an oxygen getter and subsequently heated up to 980 K. The temperature was stabilized for approximately 12 h. After this, up to 25 pieces of silver (the masses of pieces ranged from 80 mg to 200 mg) or lithium (the masses of pieces ranged from 10 to

Table 1
Substances used in this study, purity as certified by suppliers.

Substance	Purity [wt%]	Supplier
Ag granules	99.99	Innovator
Li wire	99.8	Alfa Aesar
Sb pieces	99.99	Alfa Aesar
Sapphire rods	99.95	NIST
Ar gas	99.999	Messer