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Short communication

Phase formation in the ternary systems Li-Sn-C and Li-Sn-Si

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ABSTRACT

First results on the constitution of the ternary systems Li-Sn-C and Li-Sn-Si are presented. Extrapolation calculations from the binary boundary systems allow identifying three alloys with key compositions that yield substantial information about the ternary phase diagrams. These alloys were characterized after long-term annealing using X-ray diffraction (XRD) and differential scanning calorimetry (DSC). The XRD and DSC measurements suggest the formation of a solid solution of the isostructural phases Li_5Sn_2 and Li_7Si_3 instead of predicted three phase equilibrium in the Li-Sn-Si system. Ternary phases are not observed.

1. Introduction

The performance of rechargeable Li-ion batteries is a direct function of their electrode materials. For extending the applicability of Li-ion batteries, further requirements need to be fulfilled, e.g. higher energy density and improved cycling behavior, while cost and safety of the battery should be maintained. Graphite is still the most common anode material considering its low volume expansion during Li uptake and its high cycling stability. However, the limited uptake capacity leads to relatively low energy density (372 mAh/g) [1,2]. Si and Sn offer a significantly higher specific Li storage capacity (Si: 3600 mAh/g, Sn:990 mAh/g) [3,4]. These materials form intermetallic compounds during lithium uptake, resulting in a pronounced volume expansion of up to 400% and, as a consequence, a fast degradation of the electrode. An anode material combing Si, Sn, and C and taking advantage of the favorable properties of each constituent appears to be a promising alternative to pure graphite anodes. For the systematic establishment of composition-property relationships of C, Si, and Sn in combination with Li, the corresponding phase diagrams are indispensable. In contrast to the well documented binary phase diagrams Li-Si [5,6], Li-C [7,8] and Li-Sn [9], there is no information reported about phase stability in the corresponding ternary systems. Recently, the phase stabilities in the ternary Li-Si-C system have been investigated [8,10]. In Fig. 1 the most recently reported phase diagrams of the relevant binary subsystems are displayed. References [8,9] provide a comprehensive and critical literature review of constitutional and thermodynamic data.

In the present work, the first study on the ternary phase diagrams Li-Sn-C and Li-Sn-Si is presented. Based on preliminary calculations of the ternary systems extrapolating from the binary systems key compositions are identified that allow distinguishing between different possible variants of equilibria. After long-term annealing of alloys with key compositions, XRD and DSC characterization was carried out to determine phase stabilities in the ternary systems.

2. Experimental

2.1. Identification of key compositions

Preliminary ternary phase diagrams Li-Sn-C and Li-Sn-Si were calculated by extrapolation from the well-assessed binary systems using the commercial software package Pandat® (Fig. 2). The black triangles in Fig. 2 represent calculated three-phase equilibria. Each black line thus represents a two-phase equilibrium (tie-line). Ternary phases are not considered at this stage.

In the Li-Sn-C system, two key compositions were selected according to the extrapolation calculation (see Table 1, compositions marked by red crosses in Fig. 2a). The first key alloy composition (marked ‘1’ in Fig. 2a) is chosen with the aim to verify whether a two phase region $Li_7Sn_2 + Li_2C_2$ or a three-phase region $Li_{17}Sn_4 + Li_2C_2 + C$ (Graphite) exists in the Li-rich corner. According to the preliminary calculation, a two-phase equilibrium of the Li_7Sn_2 and Li_2C_2 phases is to be expected at this composition. The second key alloy composition (marked ‘2’ in Fig. 2a) is chosen to verify which option of a three-phase equilibrium exists: $Li_{13}Sn_5 + Li_2C_2 + C$(Graphite) or $Li_{17}Sn_4 + Li_2C_2 + C$(Graphite) or

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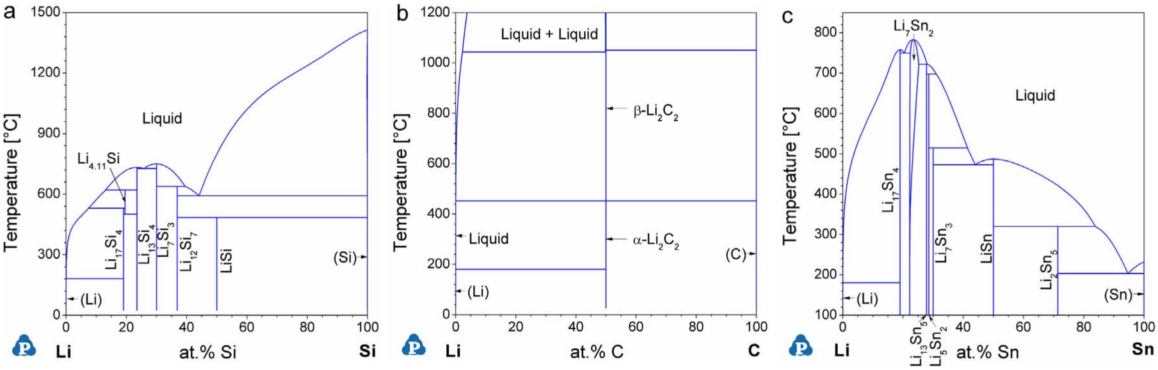

Fig. 1. phase diagrams of the Li containing binary sub-systems a) Li-Si [6], b) Li-C [8], c) Li-Sn [9].

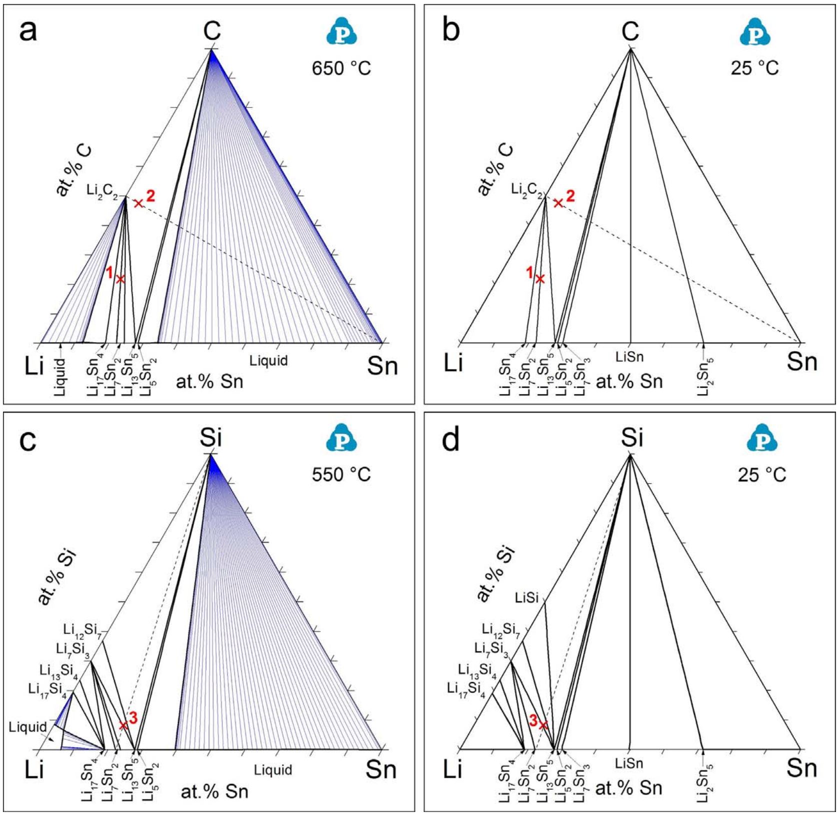

Fig. 2. Preliminary calculation of the ternary phase diagrams at annealing and room temperature, the dashed line connects initial phases competing with the predicted tie lines a) Li-Sn-C at 650 °C; b) Li-Sn-C at 25 °C; c) Li-Sn-Si at 550 °C; d) Li-Sn-Si at 25 °C.

Table 1
Composition, expected phases, initial phase assembly, and annealing conditions of key alloys.

System	Alloy No.	Li (at%)	Sn (at%)	C (at%)	Si (at%)	Expected phases	Initial phase assembly	Annealing
Li-Sn-C	1	65.7	12.5	21.8	–	Li_2C_2 + Li_7Sn_2	Li_2C_2 + Li_7Sn_2	650 °C for 96 h
	2	47.5	5	47.5	–	$Li_{13}Sn_5$ + Li_2C_2 + C(Graphite)	Li_2C_2 + Sn	
Li-Sn-Si	3	71.3	20.4	–	8.3	Li_7Si_3 + $Li_{12}Si_7$ + $Li_{13}Sn_5$	Li_7Sn_2 + Si	550 °C for 168 h

Li_7Sn_2 + Li_2C_2 + C(Graphite). At this composition, the first of these options (three-phase equilibrium $Li_{13}Sn_5$ + Li_2C_2 + C(Graphite)) is predicted by the preliminary calculation.

In the Li-Sn-Si system, one key alloy composition was identified (Table 1, marked ‘3’ in Fig. 2c). This key composition is chosen to confirm the three-phase equilibrium Li_7Si_3 + $Li_{12}Si_7$ + $Li_{13}Sn_5$ as predicted from the preliminary calculation (Fig. 2c). However, the possible equilibrium $Li_{12}Si_7$ + Li_7Sn_2 + $Li_{13}Sn_5$ needs also to be considered at this composition.

All alloy compositions were selected from preliminary isothermal sections calculated for annealing temperature (Fig. 2a and c) and room temperature (Fig. 2b and d). The composition was set such that each alloy consists of the same constituting phases at both temperatures to avoid phase transitions during cooling.

2.2. Synthesis of ternary alloys and adjustment of key compositions

Due to the fact that Li is volatile and evaporates during heat treatment and considering that metallic elements generally feature poor wetting on graphite, the formation of phases containing Li and/or C may be delayed and strongly impeded [10]. Thus, the targeted overall compositions cannot be obtained by synthesis from the pure elements