Electrochemical Investigation of the Ternary Phase Diagram Lithium-Indium-Antimony at 400 °C

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The phase diagram of the ternary system Li – In – Sb is determined at 400 °C by electrochemical techniques. The lithium content of samples with different In : Sb ratios is varied by coulometric titration. The equilibrium lithium activities are obtained from emf measurements. Two new ternary compounds, Li_3InSb_2 and Li_6InSb_3 with a wide range of stoichiometry, exist along the quasibinary cut InSb – Li_3Sb. Both compounds are in equilibrium with In and Sb. Li_3Sb co-exists with all Li – In phases. Semiconducting phases of narrow ranges of stoichiometry show generally fast chemical diffusion rates. The In rich phases have large stoichiometric widths and equilibrate much more slowly.

1. Introduction

Semiconducting lithium compounds are interesting materials for fast solid electrodes in high power density batteries [1]. Several binary phases in systems such as Li – Sb, Li – Bi, Li – Al, Li – Sn or Li – In have shown fast effective ionic diffusion coefficients which are of the same order of magnitude as in liquids [2 – 5]. In the present work we extended our interest to ternary systems which combine two of the previously mentioned binary systems. Among those we have chosen the system Li – In – Sb because of the presence of the semiconductor InSb in which the electronic species are very mobile as required for enhanced diffusion [1]. Multinary systems have in general the advantage to provide additional degrees of freedom compared to binary systems in order to select the kinetically and thermodynamically most favorable path of local composition during equilibration processes of homogeneous phases or chemical reactions.

No previous information is available from the literature on the ternary system Li – In – Sb. Previous knowledge is restricted to the three binary systems. The binary system Li – Sb shows two phases, Li_2Sb and Li_3Sb, with narrow widths of stoichiometry [2, 3, 6 – 9]. The formation of Li_2Sb is kinetically impeded [2, 3]. The lithium and antimony activities vary only slightly within the Li_2Sb phase [7]. The well known compound semiconductor InSb has also a small range of stoichiometry [7] and is the only compound which exists in the binary system In – Sb [10]. A large solubility of antimony in liquid indium (about 17 atom-% at 400 °C) is reported [10]. In contrast, a large number of compounds with wide ranges of stoichiometry was observed for the binary system Li – In [11 – 21]. More than 25% Li may be dissolved in In at 400 °C. The Zintl phase "LiIn" shows a variation in composition of more than 15%. Several other compounds exist with higher lithium content such as "Li_2In" and "$Li_{13}In_3$". Further work is necessary to resolve the stoichiometric ranges of all lithium rich phases.

The electrochemical method employed in the present study was recently developed [22, 23] and previously applied to the predominantly electronically conducting systems Cu – Ge – O [24], Y – Fe – O [25] and Li – Fe – S [26] and in principle in one case also to study the phase equilibria of the ionic conductor $LiAlCl_4$ [27]. The lithium content of several samples with different In : Sb ratios is varied with the help of an auxiliary lithium electrolyte. The cell potential for the equilibrated samples is measured as a function of composition. This electrochemical technique has several important advantages compared to conventional methods: Only a comparatively small number of samples needs to be prepared; electrical quantities are readily measured with high precision; even the width of extremely narrow phases may be resolved; equilibria are

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studied in a non-destructive way and in-situ at the temperature of interest; no quenching is required; and the equilibration of the sample may be readily detected from recording the time dependence of the cell voltage.

2. Theoretical Aspects

The variation of the overall composition of the sample which is employed as an electrode in a galvanic cell occurs along straight lines connecting the starting composition and the lithium corner of the Gibbs triangle Li−In−Sb. Local deviations from this path may occur during the transient process of charge transport across the galvanic cell and reequilibration of the sample, but only the equilibrium values of the cell potential are important for the present phase diagram studies. The integral of the current I as a function of time t is proportional to the variation of the lithium content of the sample according to Faraday's law. The stoichiometry of Li of the sample with the nominal overall composition "$\mathrm{Li}_x\mathrm{InSb}_y$" is varied by

$$\Delta x = \frac{M_{\mathrm{In}} + y\,M_{\mathrm{Sb}}}{F\,m_{\text{“}\mathrm{InSb}_y\text{”}}} \int_t^{t+\Delta t} I\,\mathrm{d}t \tag{1}$$

if m, M_{In}, M_{Sb} and F are the mass of the indium plus antimony content of the sample, the atomic weight of In and Sb, and Faraday's constant, respectively. The percentage of lithium [Li] is given by integration over the total charge flux:

$$[\mathrm{Li}] = \frac{100}{1 + \dfrac{m_{\text{“}\mathrm{InSb}_y\text{”}}\,F}{(M_{\mathrm{In}} + y\,M_{\mathrm{Sb}}) \int_0^t I\,\mathrm{d}t}}\,. \tag{2}$$

The equilibrium cell voltage is independent of the composition as long as the same three phases co-exist within three-phase regions. The cell voltage E is related to the standard Gibbs energies of formation $\Delta G_{\mathrm{f}}^{0}$ of the three phases according to

$$E = \frac{1}{q\,d} \sum_{i=1}^{3} (-1)^i\, d_{i1}\, \Delta G_{\mathrm{f}}^{0}(\mathrm{Li}_{x_i}\mathrm{InSb}_{y_i}) \tag{3}$$

if elemental lithium is used as reference electrode material at the left hand side of the galvanic cell. d is the determinant formed by the stoichiometric numbers of the three phases. d_{i1} is the minor derived from d by eliminating the first column and i-th line. q is the elementary charge. The voltages of those three-phase regions which have one side in common with parts of the binary Li−In and Li−Sb legs are identical with the voltages observed for the same region of the binary systems. The third phase is not involved in the cell reaction during titration in these three-phase regions.

The voltage drops with increasing lithium content as long as the composition passes through two-phase or single-phase regimes. The stoichiometries of the existing phases change during titration and the cell potential is a function of the corresponding change of the chemical potential of lithium. In contrast, the chemical potentials and cell voltage remain unchanged in three-phase regions according to Gibbs phase rule. The limits of three-phase regions may be readily recognized in this way from the limits of the voltage plateaus. Identical voltages for different In : Sb ratios indicate the same three-phase regime.

3. Experimental

The starting materials of all samples were In powder (− 325 mesh, metallic purity 99.999%) and Sb powder (− 100 mesh, metallic purity 99.9999%), both from Alfa Ventron. The powders were carefully mixed and pressed to pellets of 5 mm in diameter. The samples were then heated in evacuated quartz tubes (10^{-3} Torr) to 750 °C for 5 min until the material became molten. No reaction of the In−Sb mixtures with the quartz tube was observed. The samples were quenched to room temperature and subsequently annealed for 4 days at the experimental temperature of the phase diagram analysis at 400 °C. The pellets were ground in an agate mortar and again pressed to pellets of 10 mm in diameter and about or less than 0.5 mm in thickness under loads of 2−4 to, depending on the In:Sb ratio. The higher pressure was required for the antimony rich specimen. The final composition was checked by atomic emission spectroscopy with inductively coupled plasma (Applied Research Laboratories, Zürich, model 35000C ICP). The following In−Sb mixtures were prepared: 6, 12, 18, 25, 31, 37, 44, 48, 50, 56, 62, 69, 75 and 88 atom-% In.

The samples were placed into a pocket made of thin molybdenum sheet (thickness 0.025 mm; metallic purity 99.97%, Alfa Ventron) which was open at the top and large enough to allow expansion of the pellet by the following electrochemical reaction with lithium. Molybdenum wires were used as electronic leads.

Eutectic mixtures of LiCl and KCl (58 mole-% LiCl) were employed as molten salt lithium electrolytes at 400 °C. Both salts (p.a.) were purchased from Fluka, Buchs, Liechtenstein. Alumina crucibles (Haldenwanger, Berlin) of 4 cm in diameter and 6 cm in height were used and did not show any attack at lithium activities lower than the corresponding value of the equilibrium between "LiAl" and Al. The salt mixtures were slowly heated to 300 °C for 4 hrs and then held at 400 °C overnight inside an argon filled dry box.

Two-phase mixtures of "LiAl" and Al were used as reference and counter electrodes. This type of electrodes has the advantage to be solid at the experimental temperature in contrast to elemental lithium and also provides a lower electronic leakage current of the molten salt electrolyte due to the lower lithium activity. The voltage of a "LiAl", Al electrode against elemental lithium is about 300 mV at 400 °C [7].

The two-phase mixtures of "LiAl" and Al were prepared by coulometric titration of lithium into aluminum using LiCl–KCl eutectic molten salt electrolytes and molten lithium counter electrodes. The total concentration of lithium was eventually approximately 30 atom-%. Aluminum wire (1 mm diameter, 99.999% metallic purity) was wound to a spiral which is very suitable to accomodate for the large expansion which occurs by alloying the metal with lithium. A small piece of about 3 windings was used as reference electrode. The lithium capacity of the "LiAl", Al counter electrode was at least three times as large as necessary for the coulometric titration of lithium into the In–Sb samples.

The experimental arrangement of the galvanic cell for our phase equilibrium studies of the system Li–In–Sb is schematically shown in Figure 1. All experiments were run inside an argon dry box with a water vapor pressure lower than 0.1 ppm. Figure 2 illustrates the paths of all coulometric titrations of lithium into In–Sb mixtures followed in the present investigation. All previous knowledge of the ternary system Li–In–Sb is also included in this Figure. Constant current sources (Keithley, 227, Knick J400 and Knick J40) provided currents between the counter electrode and the sample which were in most cases in the range between 1 and 10 mA/cm^2, depending on the kinetics of incorporation of lithium into the sample. One complete titration run between 0 and about 75 atom-% lithium required a total of 4–6 days in each direction. All titrations were reversed for at least one complete run in order to detect possible deviations of the cell potential readings from equilibrium values. The voltages were measured between the reference electrode and the sample by electrometers (Keithley 616) with high input impedance (> 2 × 10^{14} Ω). The charge transport was determined by a coulometer (Jaissle CM50T). The temperature of the melts was automatically controlled (Eurotherm, model 021) and kept constant at 400 ± 2 °C.

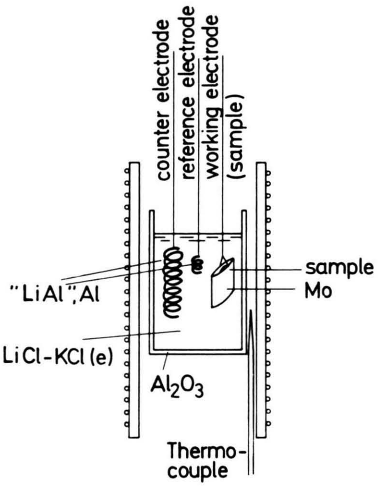

Fig. 1. Experimental arrangement of the galvanic cell employed for phase equilibrium studies of the ternary system Li–In–Sb. The sample is wrapped in molybdenum sheet and in contact with the molten LiCl–KCl (eutectic composition) electrolyte. Two-phase mixtures of "LiAl" and Al are used as reference and counter electrodes.

4. Results and Discussion

Typical coulometric titration curves are presented in Figs. 3–6 for several samples with increasing In:Sb ratios of 12:88, 44:56, 56:44 and 75:25, respectively. The data obtained for forward and backward titration are indicated as crosses and circles, respectively. The small hysteresis in some fields is attributed to slow kinetics of equilibration of the samples. Higher lithium contents than those

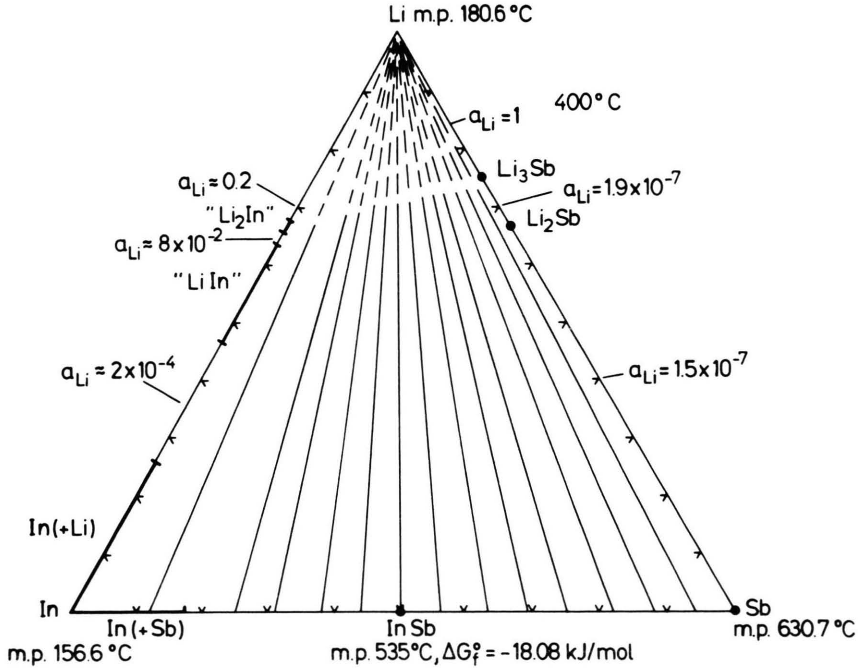

Fig. 2. Paths of compositions of all samples followed by coulometric titration in the present investigation. Previous knowledge of the system Li−In−Sb is also included.

shown in the figures (see also broken lines in Fig. 2) result in small irreversible shifts of the cell voltages in the course of several days. This behavior seems to be caused by a slow reaction of indium containing phases of high lithium activities with the melt.

It is apparent from the figures that the system Li−In−Sb has a large number of different three-phase regions (or plateaus of cell potentials). Many two- and single-phase regions are very wide, often comparable in width to three-phase regions, especially in the indium rich regime of the phase diagram.

The results of the coulometric titrations are analysed in view of the ternary Gibbs' phase digram of Li−In−Sb at 400 °C as shown in Figure 7. The widths of the two- and single-phase regions are indicated by shaded and dotted areas. The high resolution of the employed electrochemical technique for the determination of phase equilibria is clearly visible from the figure.

The binary Li−In compounds have a lower energy of formation compared to the Li−Sb compounds. This results in the experimentally observed thermodynamic equilibrium between Li_3Sb and elemental In.

Two new phases exist along the tie line Li_3Sb−InSb. Both compounds have wide ranges of stoichiometry. The Sb:In ratios vary from 1.94 to 2.06 and from 2.84 to 9.88, respectively. The ideal stoichiometric compositions are assumed to be Li_3InSb_2 and for simplicity "Li_6InSb_3". The last compound may show a large excess of Li_3Sb. The existence of such ternary phases was also confirmed by powder X-ray diffraction using the Guinier-Simon technique. Both ternary phases are in thermodynamic equilibrium with elemental indium and antimony but may not co-exist with elemental lithium. The lithium activities range from 6.6×10^{-8} to 3.6×10^{-7} and 9.3×10^{-8} to 1.1×10^{-5} for Li_3InSb_2 and "Li_6InSb_3", respectively. The energy density of Li−In−Sb as cathode material increases with increasing antimony content.

The equilibration rates for the various regimes of the Gibbs triangle vary essentially. Equilibria are reached rapidly (liquid like) after the variation of overall composition during coulometric titration processes for the three-phase regions Li_3InSb_2−Sb−InSb and Li_3InSb_2−Li_6InSb_3−In, at an intermediate rate for the regimes Li_3InSb_2−InSb−In and Li_3Sb−LiIn−In and slowly (within about 10 hrs) for the

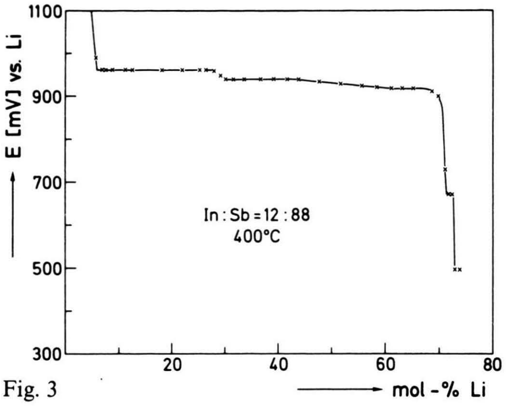

Fig. 3

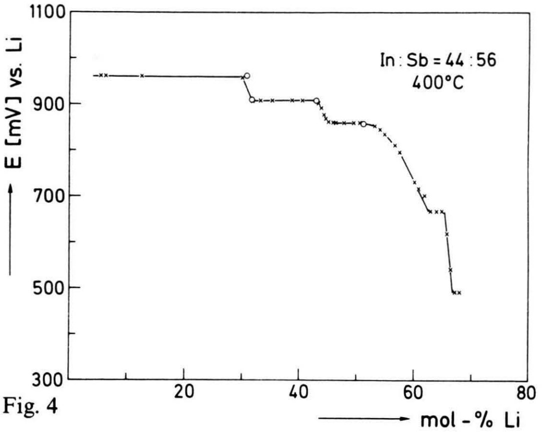

Fig. 4

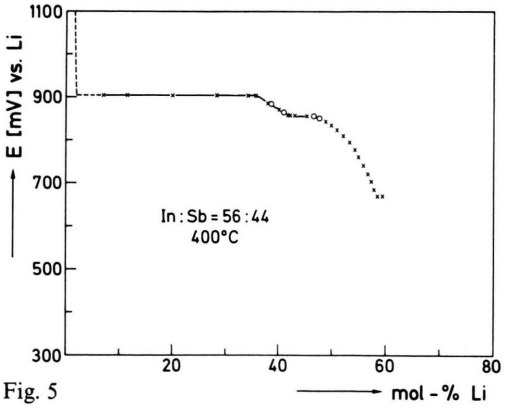

Fig. 5

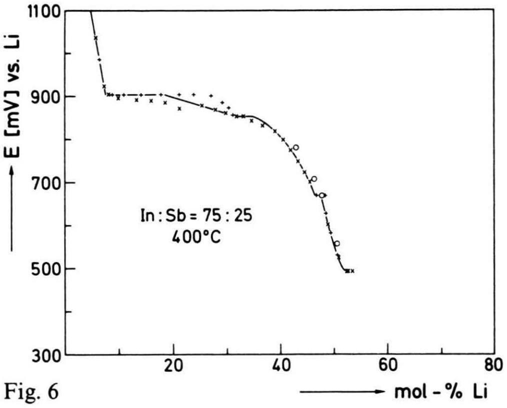

Fig. 6

Figs. 3–6. Experimental coulometric titration curves for representative samples with In:Sb ratios of 12:88, 44:56, 56:44 and 75:25. Data observed for forward and backward titration of Li are indicated by crosses and circles, respectively. Small hysteresis in a few cases is related to slow kinetics.

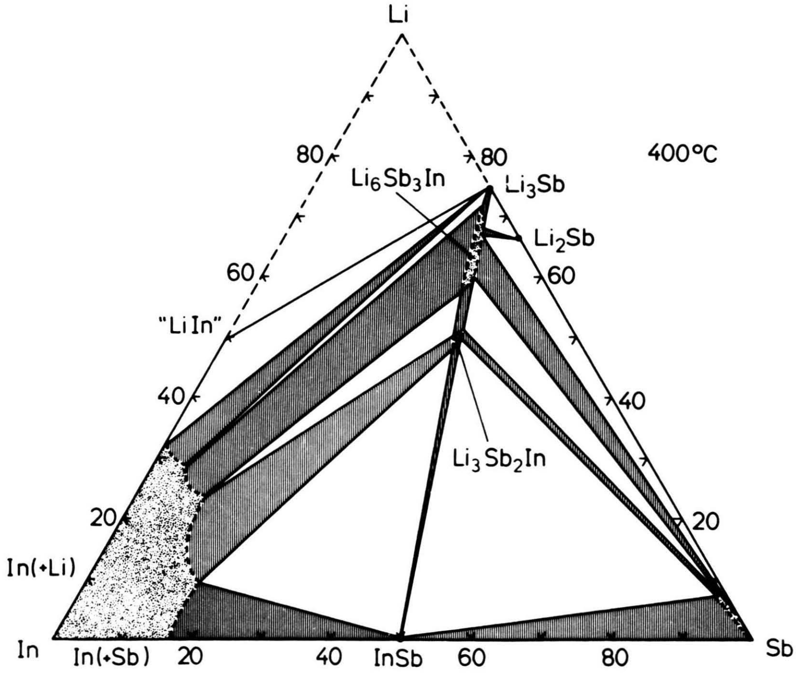

Fig. 7. Ternary phase diagram (Gibbs triangle) of the system Li–In–Sb at 400 °C as derived from the present electrochemical investigation. Two new ternary phases, Li_3InSb_2 and "Li_6InSb_3" (with wide range of stoichiometry) exist along the quasi-binary cut InSb–Li_3Sb.

regions $Li_6InSb_3-Li_3Sb-In$ and $Li_6InSb_3-Li_3InSb_3-Sb$.

These findings are in agreement with the general rule of fast chemical diffusion for phases with narrow ranges of stoichiometry and electronic semiconducting properties while phases with wide ranges of stoichiometry have commonly much lower chemical diffusion rates and higher electronic conductivities [1]. A large number of electronic charge carriers will shield any potentially formed electrical field which acts as an effective driving force for the motion of ions in excess of Fick's diffusion in concentration gradients.

Regions of slow kinetics required long equilibration times. The agreement of both forward and backward titration data and thermodynamic consistency did not indicate any irreversible drift. This will become a problem, however, in the region of higher lithium activities than studied in the present investigation because of the electronic leakage of the $LiCl-KCl(e)$ electrolyte. Studies in this field will require a different solid or molten salt electrolyte.

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