

Kinetics of Li insertion into polycrystalline and nanocrystalline ‘SnSb’ alloys investigated by transient and steady state techniques

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Abstract

Two different methods for studying the kinetics of electrochemical insertion of lithium into thick-film polycrystalline SnSb and thin-film nanocrystalline ‘SnSb’ alloys (nanocrystalline SnSb alloys with an excess of Sn as second phase) are presented. In each case, the composition dependence of the chemical diffusion coefficient has been obtained from galvanostatic polarization experiments on the asymmetric cell, Li|1 M LiClO₄ in PC|SnSb, with Li as additional reference electrode. Coulometric titrations were employed for composition variation with high stoichiometric resolution. Polycrystalline SnSb alloys have been prepared from the elements and incorporated as cathode into the cell. The chemical diffusion coefficient \tilde{D} as function of lithium content has been obtained from a combination of short-time transient and steady state measurements. Values of \tilde{D} for polycrystalline Li_δSnSb-alloys are in the range of 10⁻¹⁰ cm² s⁻¹ at 25°C. Alternatively, for the thin-film nanocrystalline ‘SnSb’ alloy, the short- and long-time approximation of the polarization voltage is used to obtain the chemical diffusion coefficients without taking into account the slope of the coulometric titration curve. The low \tilde{D} -value resulting for the nanocrystalline ‘SnSb’ alloy ($\tilde{D} < 4 \times 10^{-12}$ cm² s⁻¹) may be attributed to its complex morphology as well as to the existence of additional Sn domains acting as diffusion barriers. © 1999 Elsevier Science S.A. All rights reserved.

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1. Introduction

Metals, which can form Li alloys reversibly, are attractive anode materials for rechargeable Li-ion batteries, as they show much higher Li storage capacities than the presently used carbonaceous anodes [1–3]. However, the formation of Li alloys is accompanied by large volume changes, which result in a rapid disintegration of coarse-grained host metals and consequently, in failure of the electrode. One strategy to overcome this problem is to use precursor materials such as Sn oxides or Sn-containing glasses (e.g., Refs. [4–7]), where during the first reduction, nanosized or even amorphous Sn domains are irreversibly formed, which can then reversibly react with Li. In these systems, the excellent cycling stability is achieved at the expense of a large irreversible capacity in the first cycle, which is due to oxide reduction and Li₂O formation. A different approach is to start directly with nanocrystalline metals (e.g., Sn) or nanocrystalline intermetallics (such as

SnSb or SnAg_{3–4}) [3,8,9]. Here, the absolute volume changes are smaller than for the polycrystalline alloys, and, moreover, are limited to the first few cycles. For the application of these alloys as anodes in ambient temperature Li-ion batteries, as well as for a further optimization, their thermodynamic and kinetic properties are of great interest.

Though a number of works have been published on the diffusion of Li in intermetallics such as various Li_xSn_y phases at 415°C [10] and room temperature [11], Li₃Sb at 360°C [12], or other intermetallics at high temperatures [2] and room temperature [13], to the best knowledge of the authors, no data exist for Li diffusion in SnSb alloys.

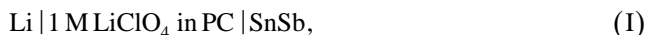
It is the aim of this paper to contribute to the knowledge of the kinetic properties of the Li_δSnSb alloys by applying two different kinds of diffusion experiments. On the one hand, lithium will be inserted into a polycrystalline SnSb-alloy to obtain the coulometric titration curve with high stoichiometric precision and to measure the chemical diffusion coefficient as a function of lithium content by combining transient and steady state measurements. On the other hand, a thin film of nanocrystalline ‘SnSb’-alloy

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(with excess of Sn as second phase) will be investigated by applying DC-polarization measurements on the asymmetric cell and using the short- and long-time approximation of the polarization voltage.

2. Theory

The chemical diffusion coefficient as a function of lithium activity can be obtained with high stoichiometric resolution by performing galvanostatic polarization experiments on the cell:



with lithium as additional reference electrode using the technique introduced by Weppner and Huggins [12]. In this case, the chemical diffusion coefficient as a function of lithium content is available from galvanostatic polarization experiments on cell (I), taking into account both transient and steady state measurements. Coulometric titrations allow the in situ variation of the lithium content in binary and ternary alloys with high stoichiometric resolution [14,15]. Once the slope $dE/d\delta$ of the coulometric titration curve (Fig. 1) and the time dependence of the (short-time) polarization voltage are known (Fig. 2), the chemical diffusion coefficient \tilde{D} can be calculated from:

$$\tilde{D} = \frac{4}{\pi} \left(I \frac{V_m}{zFS} \right)^2 \left(\frac{dE}{d\delta} / \frac{dE}{d\sqrt{t}} \right)^2, \quad (1)$$

with I , V_m , S , z , and F denoting the polarization current, the molar volume, the surface area of the sample, the charge number and the Faraday constant, respectively. The short-time approximation $dE/dt^{0.5}$ is valid for times $t \ll L^2/\tilde{D}$ [where L is the length (thickness) of the sample]. This method was applied for the determination of chemical diffusion coefficients from galvanostatic experiments on polycrystalline $\text{Li}_\delta\text{SnSb}$ alloys.

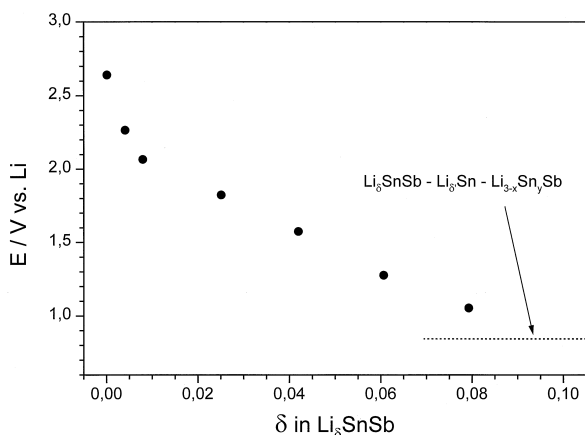


Fig. 1. Coulometric titration curve E vs. δ in polycrystalline $\text{Li}_\delta\text{SnSb}$ at 25°C .

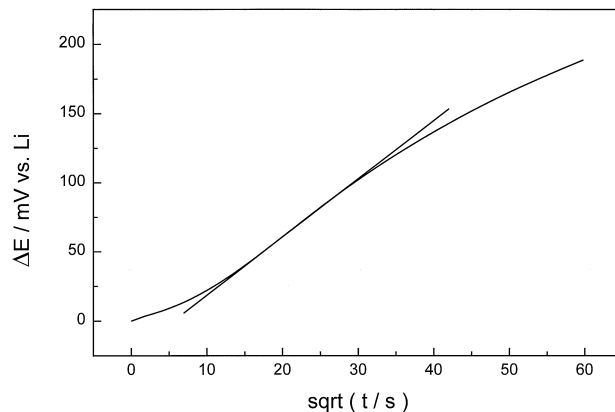


Fig. 2. Typical voltage response of cell (I) vs. the square root of time for a polarization experiment with a polycrystalline SnSb alloy ($E = 1.574 \text{ V}$, $I = 10 \mu\text{A}$, $T = 25^\circ\text{C}$); $k = 4.214 \text{ mV s}^{-1/2}$.

In the case of the nanocrystalline alloys, only thin films were available and therefore, a recently proposed method has been applied which is especially suitable for the determination of chemical diffusion coefficients with arbitrary electronic transport numbers [16,17]. Since the theory of galvanostatic processes in mixed conductors with arbitrary electronic transport numbers can be found elsewhere, only the relevant evaluation formulae for the determination of the chemical coefficient in compounds with predominant electronic conduction are given here.

The voltage response E of cell (I) due to a galvanostatic current step is related to the deviation of the lithium concentration from the equilibrium value $c_{\text{Li},0}$ at the surface of the sample Δc_{Li} [18]:

$$E = - \frac{jL}{\sigma} - \frac{t_e}{F} \frac{RT\vartheta}{c_{\text{Li},0}} \Delta c_{\text{Li}}, \quad (2)$$

with j , σ , t_e , F , R , T , and ϑ being the total current density, the total conductivity, the electronic transport number (in our case $t_e = 1$), the Faraday constant, the gas constant, the absolute temperature and the thermodynamic factor of the mobile neutral species ($\vartheta = d \ln a_{\text{Li}} / d \ln c_{\text{Li}}$ with a_{Li} denoting the activity of lithium), respectively. The deviation of the lithium concentration from its equilibrium value is found by solving Fick's second law of diffusion under adequate initial and boundary conditions [16,17].

The short-time approximation of the polarization voltage for times $t < 2L^2/3\tilde{D}\pi^2$ is given by:

$$E = - \frac{jL}{\sigma} - \frac{2jRT\vartheta\sqrt{t}}{F^2 c_{\text{Li},0} \sqrt{\pi\tilde{D}}}. \quad (3)$$

The long-time approximation of the polarization voltage for times $t \gg L^2/4\tilde{D}$ can be expressed as:

$$E = - \frac{jLRT\vartheta}{F^2 \tilde{D} c_{\text{Li},0}} \left(\frac{\tilde{D}t}{L^2} + \frac{1}{3} \right). \quad (4)$$

According to Eq. (3), the voltage response varies linearly with $t^{1/2}$ for short polarization times. A plot of E vs. $t^{1/2}$ is shown in Fig. 4. In this case, polarization experiments on cell (I) with a nanocrystalline 'SnSb'-alloy were performed at an emf of 1.160 V and a polarization current of 0.02 μA . The slope k of this straight line is given by:

$$k = - \frac{2jRT\vartheta}{F^2 c_{\text{Li},0} \sqrt{\pi \tilde{D}}} \quad (5)$$

An E vs. t plot is shown in Fig. 5. In accordance with Eq. (4), a linear behavior is observed at sufficiently long polarization times with the slope k' :

$$k' = - \frac{jRT\vartheta}{(zF)^2 L c_{\text{Li},0}} \quad (6)$$

The chemical diffusion coefficient is given by the ratio of the slopes k' and k :

$$\tilde{D} = \frac{4}{\pi} \left(\frac{k'L}{k} \right)^2 \quad (7)$$

3. Experimental

Polycrystalline samples of SnSb were prepared from the elements by solid-state reaction in evacuated quartz ampoules. Sn and Sb powders (99.99%, Johnson Matthey) were mixed in the required ratio. The material was ground, pressed into disk-shaped samples, annealed at 700°C for 30 min and cooled to room temperature. The material was ground, pressed again and kept at 400°C over night. For the investigations, a sample of 0.056 cm thickness and 1.00 cm diameter was used, which was fixed in a basket made of molybdenum wires.

Nanocrystalline 'SnSb' alloys (SnSb alloys with an excess of Sn as second phase) with particle sizes of 200–400 nm were deposited onto Cu substrates at a constant current density of 2 mA cm^{-2} from a solution of 30 g l^{-1} $\text{SnCl}_2 \cdot 2\text{H}_2\text{O}$ (Merck p.a.), 1.8 g l^{-1} SbCl_3 (Aldrich ACS 99 + %), 115 g l^{-1} $\text{Na}_4\text{P}_2\text{O}_7 \cdot 10\text{H}_2\text{O}$ (Aldrich ACS 99 + %), 7 g l^{-1} tartaric acid (Merck p.a.), 0.4 g l^{-1} gelatine (Fluka biochimica-medium gel strength) at 44°C, no stirring [3]. For the investigations, a sample with a mass of 1.104 mg, a thickness of 3.616 μm , and an area of 1.094 cm^2 was used. Chemical composition was checked with inductively coupled plasma-atomic emission spectroscopy (ICP-AES) and phase analysis performed by X-ray diffraction (XRD).

As electrolyte LiClO_4 (Merck battery grade) in PC (Aldrich 99%, distilled, stored over 4 Å molecular sieve) was used. The H_2O content of the electrolyte was below 20 ppm. Pure lithium (battery grade) served as reference electrode. The polarization current applied to cell (I) typically amounted to 10 μA for the polycrystalline alloys and

0.02 μA for the nanocrystalline alloy. The lithium content of the polycrystalline sample was modified in situ by performing coulometric titrations with typical currents in the range of 15–25 μA . In this case, two lithium electrodes were used as lithium sources and lithium was inserted from both surfaces into the disk-shaped sample. All experiments were carried out in a sealed glass cell. The cell voltage was measured with a high-impedance multimeter (Keithley Mod. 199). Precision current sources were used for the polarization experiments as well as coulometric titrations (Knick Mod. J152, Keithley Mod. 2400). With the polarization experiments, data points were collected every 2–6 s using a personal computer as a data acquisition system communicating with the multimeter via IEEE-interface.

4. Results and discussion

The coulometric titration curve of polycrystalline $\text{Li}_\delta\text{SnSb}$ at 25°C is shown in Fig. 1. Titration current densities were in the range of 6–15 $\mu\text{A cm}^{-2}$ and the sample was allowed to equilibrate for 2 days. At a cell potential of approximately 0.850 V vs. Li, the alloy $\text{Li}_\delta\text{SnSb}$ coexists with $\text{Li}_\delta\text{Sn}$ and $\text{Li}_{3-x}\text{Sn}_y\text{Sb}$ ($x, y \ll 1$) [19]. The range of homogeneity of $\text{Li}_\delta\text{SnSb}$ therefore amounts to $\delta \cong 0.09$ at 25°C.

Fig. 2 gives a typical voltage response of cell (I) vs. the square root of time for a polycrystalline SnSb alloy at a cell potential $E = 1.574$ V and a polarization current $I = 10$ μA . Fig. 2 confirms the linear behavior of the E vs. $t^{1/2}$ plot at sufficiently short times ($t < 2L^2/3\tilde{D}\pi^2$).

The chemical diffusion coefficient of polycrystalline $\text{Li}_\delta\text{SnSb}$ at 25°C, as determined by application of chronopotentiometry to cell (I) using Eq. (1) (with $V_m(\text{SnSb}) = 26.08$ $\text{cm}^3 \text{mol}^{-1}$), is plotted as a function of the nonstoichiometry parameter δ in Fig. 3. The composition has been varied using the coulometric titration technique and the equilibrium distribution of lithium in the

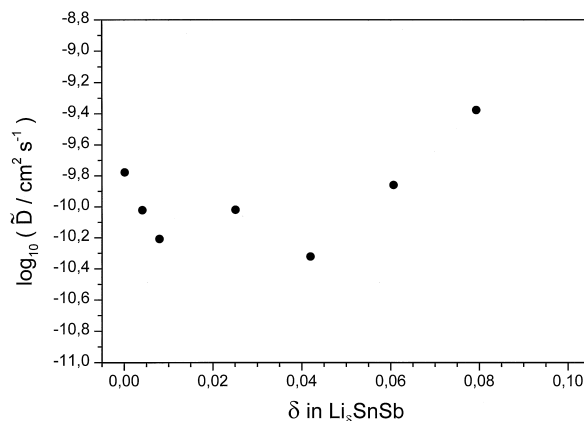


Fig. 3. Chemical diffusion coefficient \tilde{D} in polycrystalline $\text{Li}_\delta\text{SnSb}$ at various lithium compositions (25°C).

alloy is assumed after each titration step. With Fig. 3, it could be argued that the chemical diffusion coefficient \tilde{D} decreases slightly with increasing lithium content showing a minimum at $\delta = 0.02$ followed by an increase of \tilde{D} towards the phase boundary. As the slope of the coulometric titration curve is very high at δ -values below 0.01, an additional error regarding the determination of \tilde{D} may easily be introduced. We therefore do not want to emphasize this behavior but better interpret that the values of \tilde{D} are in the range of $10^{-10} \text{ cm}^2 \text{ s}^{-1}$ and are increasing slightly toward the phase boundary.

Fig. 4 shows the short-time voltage response of the polarization experiment on cell (I) with the square root of time for the nanocrystalline ‘SnSb’ alloy. The slope of this short-time approximation is given by Eq. (5) and amounts to $k = 0.4070 \text{ mV s}^{-1/2}$. The experimental data of Fig. 4 were obtained at an emf-value of 1.160 V vs. Li with a polarization current of 0.02 μA .

Fig. 5 shows the long-time voltage response of the polarization experiment for the nanocrystalline ‘SnSb’ alloy. The limiting slope from Fig. 5 is $k' = 0.00193 \text{ mV s}^{-1}$. The chemical diffusion coefficient of the nanocrystalline ‘SnSb’ alloy was obtained from k and k' using Eq. (7) and calculated to $\tilde{D} = 4 \times 10^{-12} \text{ cm}^2 \text{ s}^{-1}$. It must be mentioned that for the exact determination of \tilde{D} , the boundary condition $t \gg L^2/4\tilde{D}$ would have required longer polarization times than our data acquisition system allowed (which also may explain the ‘poor’ linearity of the long-time voltage response in Fig. 5). Taking into account this fact, an even smaller value of k' might have been observed, resulting in an even lower chemical diffusion coefficient according to Eq. (7).

The value of the chemical diffusion coefficient for the nanocrystalline alloy is distinctly smaller than $\tilde{D} = 10^{-10} \text{ cm}^2 \text{ s}^{-1}$ for the polycrystalline SnSb alloys. To explain this difference, we have performed diffusion experiments with pure polycrystalline Sn samples recently [20]. These experiments indicate that the chemical diffusion coefficient

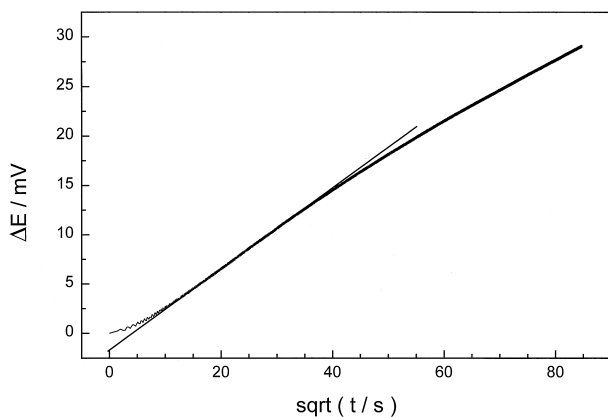


Fig. 4. Typical voltage response of cell (I) vs. square root of time for a polarization experiment with a nanocrystalline ‘SnSb’ alloy ($E = 1.160 \text{ V}$, $I = 0.02 \mu\text{A}$, $T = 25^\circ\text{C}$, $k = 0.4070 \text{ mV s}^{-1/2}$).

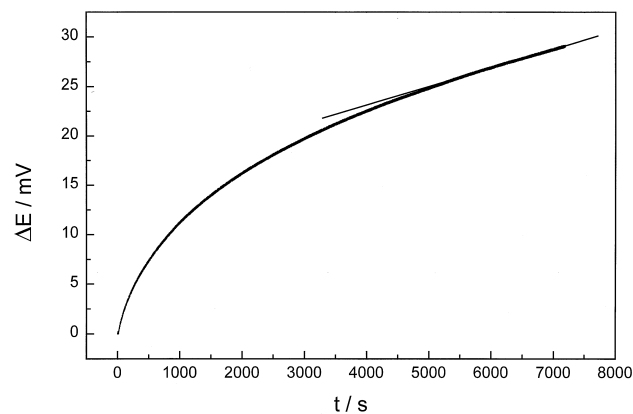


Fig. 5. Typical voltage response of cell (I) vs. time; same conditions as in Fig. 4; $k' = 0.00193 \text{ mV s}^{-1}$.

of Li_8Sn is significantly lower than that of the polycrystalline SnSb alloy. This fact supports the interpretation that the lower \tilde{D} -value of our nanocrystalline ‘SnSb’ alloys can be attributed to the presence of the excess Sn as well as the complex morphology of the nanocrystalline ‘SnSb’ alloy. The Sn host domains, being present as a second phase, are assumed to act as diffusion barriers and therefore, to increase the length of the diffusion paths for Li in the nanocrystalline electrode. Variation of the amount and size (morphology) of the nanocrystalline Sn domains should give further insight into the kinetic behavior of these nanocrystalline two-phase alloys. As far as the morphology of the porous, nanostructured ‘SnSb’ alloy is concerned, it has to be considered that, e.g., the actual length L is again not necessarily equal to the geometrical length (thickness) of the sample, and that also the contact areas between the single domains are restricted.

5. Conclusions

For the interpretation of the Li diffusion behavior of our nanostructured two-phase ‘SnSb’ alloy, the separate investigation of the Li insertion into polycrystalline SnSb turned out to be an indispensable prerequisite. Due to the different boundary conditions valid for the determination of the chemical diffusion processes in thin- and thick-film samples, we applied a combination of transient and steady-state methods for the disk-shaped polycrystalline samples and a combination of the short- and long-time approximation of the polarization voltage for the thin film nanocrystalline alloy. Whereas the molar volume must be known exactly in the case of the polycrystalline alloys, the thickness of the sample must be regarded as critical parameter for the nanocrystalline (two-phase) ‘SnSb’ alloy. In the latter case, the additional Sn domains are assumed to act as diffusion barriers and therefore, to increase the length of the diffusion paths for Li in the sample. Additionally, the lower values of the chemical diffusion coefficients of the nano-

structured alloys may be attributed to their complex but technologically important morphology.

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