

Tin and tin-based intermetallics as new anode materials for lithium-ion cells

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Abstract

The galvanostatic cycling behaviour of Sn/SnSb composite electrodes has been studied in 1 mol l⁻¹ LiClO₄/propylene carbonate (PC), 1 mol l⁻¹ LiPF₆/ethylene carbonate (EC)/diethyl carbonate (DEC) (1:1), and 1 mol l⁻¹ LiClO₄/PC saturated with *trans*-decalin (*t*-Dec). Capacities between 500 and 600 mA h g⁻¹ (with respect to the mass of active material) were obtained. Reasons for the irreversible capacities are given and film formation on lithium storage metals and alloys is discussed. The observed coulombic efficiencies were slightly higher for the EC-containing electrolyte than for the PC-based one. Alternatively, improved efficiencies and stand-time behaviour were obtained when the PC electrolyte was saturated with *t*-Dec, which acts as a surfactant. © 2001 Elsevier Science B.V. All rights reserved.

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1. Introduction

Lithium storage metals and alloys (intermetallics), such as Sn, Sb, Al, Si, SnSb . . . , show high theoretical charge densities and specific charges and have, therefore, been frequently proposed as alternatives to carbonaceous anode materials. What has hindered their breakthrough so far are the enormous volume changes which occur during cycling. In the case of compact and coarse morphology this immediately results in cracking and crumbling of the active material. It has been shown that these problems can to some part be resolved by using nano-crystalline, porous materials, by using multi- instead of single-component materials, and by including binary phases like SnSb, which due to their complex reaction mechanism help to relieve mechanical strain during charge and discharge of the material [1,2]. Alternatively, the cycling stability can be increased by limiting the cycling depth or by diluting the active material in an inactive matrix (e.g. the mixed-conductor matrix concept [3], Sn-oxide based materials [4,5], Sn₂Fe/SnFe₃C composites [6], etc.). However, in the latter cases the better cycling stability is achieved at the expense of capacity.

In contact with the electrolyte the anode in Li batteries is covered with a passivating film (the “solid electrolyte interphase”, SEI), which is formed by the reaction of the anode surface with the electrolyte during charge and which prevents further electrolyte decomposition (e.g. [7]). The protection of Li alloy anodes, which continuously undergo volume changes, by such a SEI will be quite demanding in view of the dynamic character of their surface. The SEI has to follow the changes of the surface and will, therefore, also experience large mechanical strain. Since film formation consumes charge and materials (Li, electrolyte, . . .) it strongly contributes to the irreversible capacity. Furthermore, it determines the electrode impedance during cycling and during stand-time. Hence, the interaction between the dynamic surface and the electrolyte plays an important role for the performance of the full Li-ion cell.

In this contribution, first results from a study of Sn/SnSb electrodes with various electrolytes and electrolyte additives are presented. Reasons for the irreversible capacity and a model for the filming of metallic host matrices are discussed.

2. Experimental

2.1. Sn/SnSb composite electrodes

Nano-crystalline Sn/SnSb, and Ni powders were precipitated with NaBH₄ from aqueous solutions of the respective

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chloride salts as described in detail in [1]. The BET surface areas were in the range of 15–50 m² g⁻¹, which corresponds to average particle diameters of around 15–60 nm (assuming ideal spherical shape of the particles and using the crystallographic densities for the calculation). Composite electrodes were prepared by pasting a slurry containing 82 wt.% Sn/SnSb (acting as active material), 10% Ni (electronically conductive additive), and 8% poly(vinylidene fluoride) (PVdF) (Aldrich, average $M_w = 534,000$) suspended in decane (Aldrich, $\geq 99\%$) onto both sides of a stainless steel mesh of wire diameter 25 μm and mesh width 67 μm (mesh 280), acting as current collector. 2.1–2.3 mg of composite material were brought up on an area of $2 \times 16 \text{ mm}^2$. Before usage, the composite electrodes were pressed and rigorously dried under fine vacuum.

2.2. Electroplated Sn/SnSb electrodes

Nano-crystalline, porous Sn/SnSb was electroplated onto a Cu-substrate from an aqueous solution containing 30 g l⁻¹ SnCl₂·2H₂O (Merck, p.a.), 1.8 g l⁻¹ SbCl₃ (Aldrich, $\geq 99\%$), 115 g l⁻¹ Na₄P₂O₇·10H₂O (Aldrich, 99%), 7 g l⁻¹ tartaric acid (Aldrich, 99%) and 0.4 g l⁻¹ gelatine (Fluka, medium gel strength, 180 bloom) at 2 mA cm⁻² and 44°C without stirring [8]. The electrodeposits covered a geometric area of 0.38 cm² and had a thickness of around 5.5 μm .

2.3. Galvanostatic cycling

Cycling experiments were performed in laboratory-type glass cells with the working electrode (Sn/SnSb composite electrode) placed between two Li counter electrodes and with a Li reference electrode at a fourth inlet. The electrodes were not closely packed in separator materials but loosely placed in the electrolyte without further support or protection. The electrolyte solutions were (i) 1 mol l⁻¹ LiClO₄ (Merck-Selectipur[®]) in propylene carbonate (PC) (Merck-Selectipur[®]), (ii) 1 mol l⁻¹ LiPF₆ in ethylene carbonate (EC)/diethyl carbonate (DEC) (1:1) (Mitsubishi Chemical Corp., Sol-Rite[®]), and (iii) 1 mol l⁻¹ LiClO₄ in PC saturated (~2 wt.%) with *trans*-decahydronaphthalene (*trans*-decalin) (*t*-Dec) (Aldrich, 99%). The applied current density was 0.5 mA cm⁻² (with respect to the geometric electrode area) which corresponds to specific currents between 84.8 and 92.9 mA g⁻¹ (with respect to the mass of active material). The cut-off potentials were 20 and 1200 mV versus Li/Li⁺, respectively.

2.4. Electrochemical impedance spectroscopy

Electrochemical impedance spectroscopy (EIS) was performed with electro-plated Sn/SnSb in electrolytes (i) and (iii), employing a Zahner IM6 station (Zahner Messtechnik, Kronach, Germany). A three-electrode set-up was used with Li-foil as working and counter-electrodes. The electrodes

were charged galvanostatically (0.2 mA cm⁻²) to 100 mV versus Li/Li⁺ and then kept at that potential. Potentiostatic impedance spectra were recorded between 10⁵ and 10⁻² Hz with an amplitude of 5 mV after the stand-times indicated in the figures. Then, the electrodes were discharged to 1200 mV and recharged to 100 mV, where further impedance spectra were recorded.

3. Results and discussion

Fig. 1 shows the results of full-capacity galvanostatic cycling tests with Sn/SnSb composite electrodes in 1 mol l⁻¹ LiClO₄/PC, 1 mol l⁻¹ LiPF₆/EC/DEC (1:1), and 1 mol l⁻¹ LiClO₄/PC saturated with *t*-Dec. Capacities between 500 and 600 mA h g⁻¹ (with respect to the mass of active material) and coulombic efficiencies of around 99% are observed (except for the first cycle). The differences in the capacities are within the range of reproducibility (small variations can be attributed to the preparation of

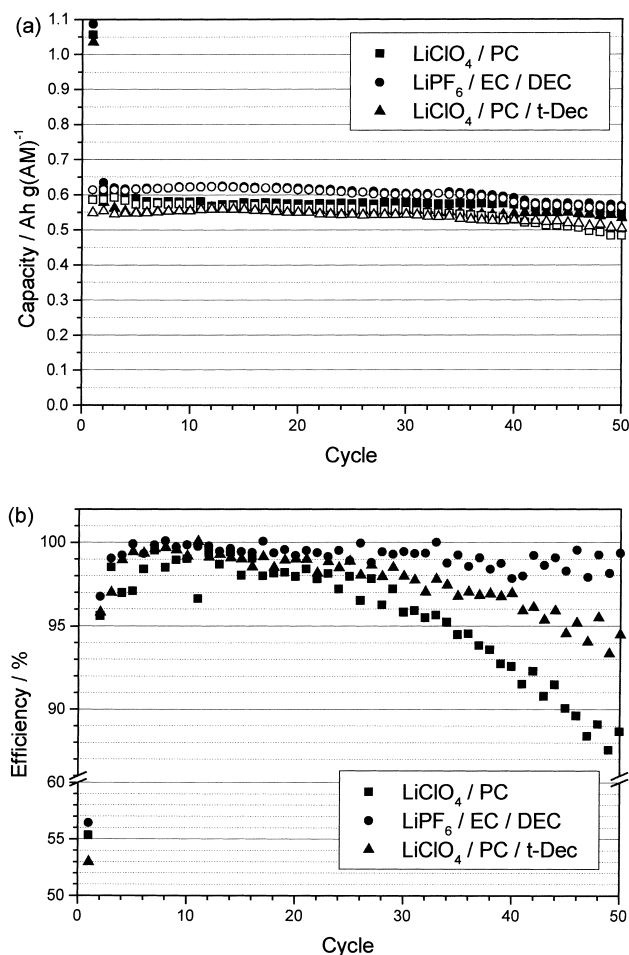


Fig. 1. Cycling behaviour of Sn/SnSb composite electrodes in various electrolytes. (a) Charge (solid symbols) and discharge (open symbols) capacities (with respect to the mass of active material (AM)) and (b) coulombic efficiencies.

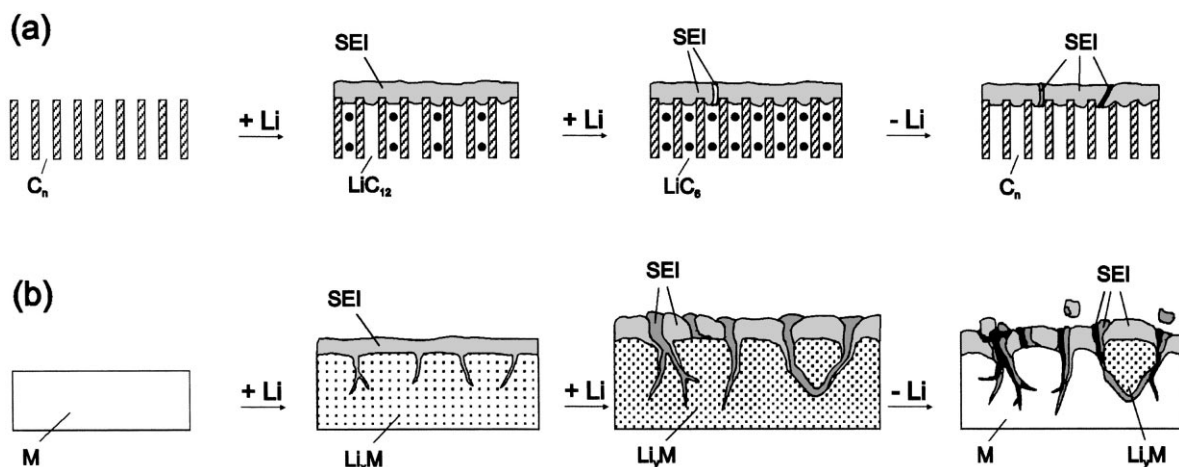


Fig. 2. Model for the film formation on (a) carbonaceous materials and (b) Li storage metals and alloys. SEI regions of different shadings refer to SEI formed at different times and not necessarily to different composition. See the text for details. (C_n = graphite, M = Li storage metal).

the composite electrode). The efficiencies are slightly higher for the $\text{LiPF}_6/\text{EC}/\text{DEC}$ and the $\text{LiClO}_4/\text{PC}/t\text{-Dec}$ electrolytes than for pure LiClO_4/PC , however, the differences are rather small and must not be over-interpreted. The decrease of the efficiency in the long run may be attributed to the use of Li metal as counter electrode, which due to dendritic deposition contaminates the electrolyte (e.g. [9]), to parts of the SEI which break off the electrodes or re-dissolve and accumulate in the electrolyte, and to swelling of the binder.

Several reasons can be made responsible for the irreversible capacity (i.e. for the efficiencies smaller than 100%):

1. *Reduction of oxide impurities.* Due to the preparation method the Sn/SnSb as well as the Ni(B) powder contain oxygen impurities, which will be irreversibly reduced to the respective metals and Li_2O . These reactions are mainly restricted to the first cycles.
2. *Electrolyte decomposition.* As in the case of carbon materials electrolyte reduction and hence the formation of a protective film (SEI) will occur.
3. *Loss of contact.* Due to the enormous volume changes during Li uptake and release, the active electrode material experiences large mechanical strain, which can lead to cracking, partial disconnection and full disconnection (Fig. 2b). In the latter case active material is lost. This effect should be less pronounced when nano-structured materials are used instead of coarse-grained or bulky ones, but it still occurs. Crack formation will be followed by filming when the new surface is exposed to the electrolyte.
4. *Trapping of lithium.* Due to kinetic and thermodynamic reasons not all of the inserted Li can be extracted again (at the employed time-scale). The capacity which can actually be cycled decreases.

One of the major problems of the Sn/SnSb material is so far the low coulombic efficiency in the first cycle. It may be explained with the fact that during the first charge the

formation of the active material occurs (first expansion, first filming, etc.) and shall not be further considered here. It has been proposed to compensate the low efficiency in the first cycle by blending the un lithiated metallic anode material with a lithiated material, such as $\text{Li}_{2.6}\text{C}_{0.4}\text{N}$ [10].

A closer inspection of Fig. 1a shows that the irreversible capacity (the difference between charge and discharge capacity) is generally much larger than the capacity fade (loss of discharge capacity, the difference between the discharge capacities of subsequent cycles). Whereas all four above-mentioned effects contribute to the irreversible capacity, in a first approximation only effects (3) and (4) are responsible for the capacity fade. Therefore, and considering that effect (1) is restricted to the first (few) cycle(s), the difference between the irreversible capacity and the capacity fade should be a rough measure for the electrolyte decomposition (film formation)¹.

In the case of carbon materials, which are almost dimensionally stable during Li uptake and release, the amount of filming will mainly be determined by the questions if a dense film can be formed, how long it takes until a dense film is formed, and if the film re-dissolves in the electrolyte (and how fast). A special case are graphitic carbons: they can only be cycled if the films prevent strong solvent co-intercalation, which is the case for EC-containing electrolytes but is not the case for pure PC-based electrolytes (e.g. [7]). However, the once formed film should experience only little mechanical strain, and thus be more or less mechanically stable (Fig. 2a). The situation is totally different for Li alloys. On the one hand, they do not suffer from the problems of solvent co-intercalation, and hence the use of PC-based electrolytes is possible. On the other hand, in addition to the effects mentioned above, the large volume changes of the film-substrate (the Li storage metal) have to be taken into account. Cracking of the film will occur, some parts of

¹ A detailed discussion of this model will be published in the near future.

the film may even break off, both during charge and discharge. Whenever fresh surface of active material gets into contact with the electrolyte new filming takes place and the cracked film is repaired (Fig. 2b). As a consequence, filming reactions will extend over a large number of cycles. In a way, the filming of Li alloys with their renewing surfaces resembles more the filming of secondary metallic Li, than that of carbon materials. The ideal film for Li alloys would be a flexible one, whose formation is associated with a minimum consumption of battery materials and charge.

EC is well-known to be a good filming agent. It rapidly forms dense films at high potentials and thus prevents solvent co-intercalation into graphitic carbons and provides high cycling efficiencies for metallic Li [7,9]. The better performance of the Sn/SnSb composite electrode in LiPF₆/EC/DEC than in LiClO₄/PC fits well into this scheme. By the fast formation of a dense and stable SEI, further filming can be kept low in the long run.

A contrary approach to minimize irreversible filming reactions is to use surfactant additives which reversibly adsorb at the electrode surface and thus prevent the approach

of the polar electrolyte molecules to the electrode surface. As a consequence, electrolyte decomposition should be retarded. Different classes of surfactant additives have been described in the literature, such as ionic surfactants [11,12], aromatic compounds [13], polymer surfactants [14], long-chain saturated hydrocarbons [15,16], and mono-cyclic and poly-cyclic saturated hydrocarbons [17,18]. Saturated hydrocarbons are chemically stable versus metallic Li or Li-rich alloys. In the case of linear saturated hydrocarbons the interfacial activity increases with the chain length. Unfortunately, the solubility in the polar electrolyte solvent parallelly decreases. On the other hand, a considerable surfactant concentration is necessary for an effective blocking of the electrode surface. This problem can be avoided when cyclic hydrocarbons are used [17]. For example, decalin shows a rather good solubility (approximately 2 wt.% in 1 mol l⁻¹ LiClO₄/PC) and a relatively high interfacial activity.

A strong effect of the addition of *t*-Dec to a 1 mol l⁻¹ LiClO₄/PC electrolyte is seen in the impedance spectra, whereas the improvement of the cycling efficiencies is only

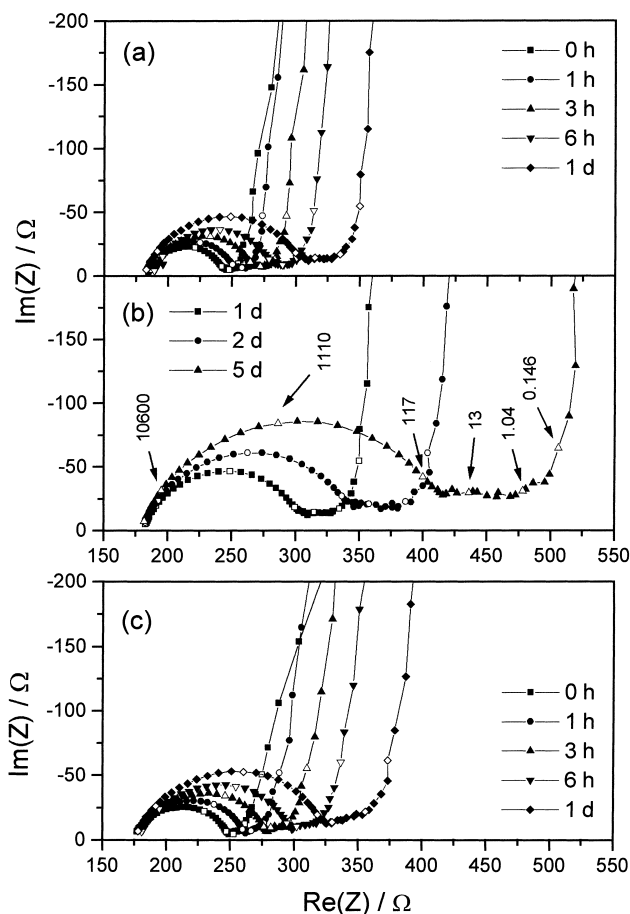


Fig. 3. Potentiostatic impedance spectra of electroplated Sn/SnSb in 1 mol l⁻¹ LiClO₄/PC at 100 mV vs. Li/Li⁺. (a,b) First charge; (c) second charge. The open symbols refer to selected frequencies which are explained for the "5 days" data-set in (b). The geometric electrode surface area was 0.38 cm².

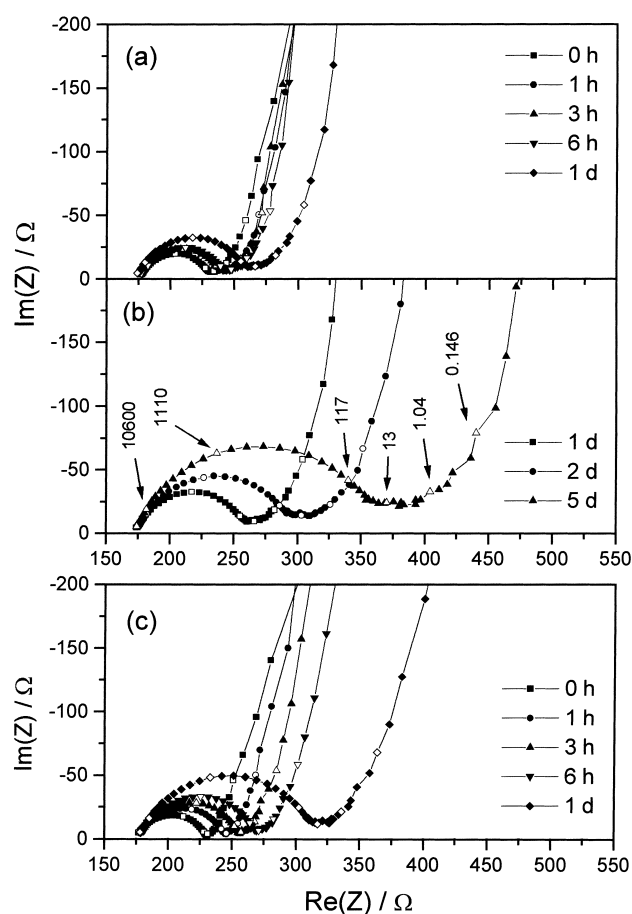


Fig. 4. Potentiostatic impedance spectra of electroplated Sn/SnSb in 1 mol l⁻¹ LiClO₄/PC saturated with *t*-Dec at 100 mV vs. Li/Li⁺. (a,b) First charge; (c) second charge. The open symbols refer to selected frequencies which are explained for the "5 days" data-set in (b). The geometric electrode surface area was 0.38 cm².

marginal. For both the LiClO_4/PC electrolyte and the $\text{LiClO}_4/\text{PC}/t\text{-Dec}$ electrolyte, a continuous increase of the film resistance with wet stand-time is observed (Figs. 3a,b and 4a,b). However, when current is passed through the cell, the large resistances break down again (cf. the second cycles in Figs. 3c and 4c). Similar results have been reported for other systems, e.g. a $\beta\text{-LiAl}$ alloy [15]. In the presence of $t\text{-Dec}$ the initial impedances are almost similar but the increase with stand-time (i.e. the film growth) proceeds much slower. Evidently $t\text{-Dec}$ provides a temporary protection of the electrode surface on a short time-scale and thus during charge and discharge when the electrode surface is dynamic. Filming cannot be prevented in the long run, but it can be retarded.

Beside the minimization of filming reactions surfactants show other positive effects. So, for example, during cycling of metallic Li a more uniform Li deposition and the suppression of dendrite formation can be observed [17]. Generally, the wetting behaviour of all components in the Li-ion cell (such as porous electrodes or separator materials) is improved, which renders the cell assembly easier.

4. Conclusions

The large volume changes of metallic and intermetallic Li storage materials, such as Sn/SnSb , during charge and discharge are a challenge for both the Li storage material itself and the SEI, which is formed at the interface and which influences the irreversible capacity during cycling. Filming reactions can be minimized by two contrary approaches: (i) by using filming agents, such as EC, which form dense and stable films with a minimum loss of charge and battery material and (ii) by using surfactant additives, such as $t\text{-Dec}$, which reversibly block the electrode surface and thus retard electrolyte decomposition. The positive effect of the surfactant additive is especially seen in the impedance spectra where a slower growth of the passivating film with wet stand-time is observed.

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