



ELSEVIER

Journal of Power Sources 97–98 (2001) 194–197

JOURNAL OF
POWER
SOURCES

www.elsevier.com/locate/jpowsour

Structural and mechanistic features of intermetallic materials for lithium batteries[☆]

J.T. Vaughey^a, C.S. Johnson^a, A.J. Kropf^a, R. Benedek^{a,b}, M.M. Thackeray^{a,*}, H. Tostmann^c, T. Sarakonsri^d, S. Hackney^d, L. Fransson^e, K. Edström^e, J.O. Thomas^e

^aElectrochemical Technology Program, Chemical Technology Division, Argonne National Laboratory, Argonne, IL 60439, USA

^bMaterials Science Division, Argonne National Laboratory, Argonne, IL 60439, USA

^cANL/MRCAT – Advanced Photon Source, University of Florida, Gainesville, FL 32611, USA

^dDepartment of Materials and Metallurgical Engineering, Michigan Technological University, Houghton, MI 49931, USA

^eInorganic Chemistry, Ångström Laboratory, Uppsala University, P.O. Box 538, SE-751 21 Uppsala, Sweden

Received 11 July 2000; received in revised form 7 December 2000; accepted 23 December 2000

Abstract

An anode system based on intermetallic phases with a zinc-blende-type structure (InSb, GaSb and AlSb) has been studied for lithium-ion batteries. The compound, InSb, in particular, cycles well between 1.2 and 0.5 V. After an initial “conditioning” cycle, a mechanism involving lithium insertion into an open framework structure followed by indium extrusion in the potential range 1.2–0.7 V, appears to dominate; between 0.7 and 0.5 V, a more complex mechanism occurs involving indium extrusion from a stable fcc Sb anion array and subsequent lithiation of the extruded indium. In situ X-ray diffraction and extended X-ray analysis fine structure (EXAFS) data were obtained over the voltage window 1.2–0.5 V, where a rechargeable capacity of 300 mAh/g is achievable. The results indicate that after the “conditioning” reaction a $\text{Li}_y\text{In}_{1-y}\text{Sb}$ zinc-blende framework, in which Li atoms partially substitute for In, is responsible for the good cycling behavior of the cells. Isostructural AlSb and GaSb electrodes provide inferior electrochemical capacities. © 2001 Elsevier Science B.V. All rights reserved.

Keywords: Lithium-ion battery; Intermetallic; Anode; Indium antimonide

1. Introduction

There is a significant amount of interest in the battery community in finding new anodes for lithium-ion cells [1–3]. This research is driven by both safety and cost considerations. In particular, the commonly used anode, lithiated graphite (LiC_6), provides a high cell voltage, but is susceptible to lithium plating if cells are overcharged. In the past, many intermetallic compounds were extensively investigated as negative electrodes for lithium cells [4,5]. There has recently been renewed interest in intermetallic electrodes since the announcement that tin-based compounds, particularly tin oxide, could operate effectively as alloying hosts for lithium [6,7]. In practice, these materials have the advantage of high capacity, acceptable rate capability, and a sufficiently low operating voltage versus

lithium. However, a number of materials issues prevent intermetallic compounds from replacing carbon, in particular, their relatively large volume expansion upon lithiation that results in mechanical disintegration of the electrode and consequent capacity fade. As an alternative approach, we embarked on a systematic search for intermetallic compounds that could accommodate lithium with relatively small volume change. We discovered that in the copper–tin system, lithium could react topotactically with Cu_6Sn_5 at approximately 400 mV (versus lithium) to yield a structure closely resembling Li_2CuSn ; this phase transition was accompanied by a volume expansion of 59% [8–10]. Further reaction with lithium at lower voltages results in a reversible displacement reaction during which copper is extruded from the “ Li_2CuSn ” structure to produce metallic copper and a lithium–tin composite alloy [8,11]. Of major significance to this study was the observation that the CuSn framework of Li_2CuSn had a zinc-blende-type structure that provided a three-dimensional interstitial space for lithium. The work on the copper–tin system, therefore, led us to consider the possibility of finding intermetallic electrodes with a stable

[☆] Published in the Proceedings of the 10th International Meeting on Lithium Batteries, Como, Italy, 28 May–2 June 2000.

* Corresponding author. Tel.: +1-630-252-9184; fax: +1-630-252-4176. E-mail address: thackeray@cmt.anl.gov (M.M. Thackeray).

zinc-blende-type structure that could act as a host for lithium. Our initial studies have been made on the family of antimonide compounds, notably the III–V semiconductors InSb, GaSb and AlSb. In this paper, we report the electrochemical and structural properties of these materials, notably InSb.

2. Experimental

Samples of InSb were synthesized by ball milling In and Sb in a stoichiometric ratio in the presence of a carbon solid lubricant. The elements were purchased from Aldrich and used as-received. The resulting black powder was determined to be single phase InSb by powder X-ray diffraction. The AlSb was synthesized in a similar manner to the InSb, while GaSb was purchased as a single crystal wafer from Wafer World Inc. (West Palm Beach, FL).

For the galvanostatically-controlled electrochemical evaluations, electrodes were laminated and cells constructed with metallic lithium counter electrodes using methods previously described [8]. The intermetallic electrodes (84 w/o) were blended with 8 w/o carbon and 8 w/o polyvinylidene fluoride (PVDF) binder. Coin cells of size 2032 were cycled in the voltage range of 1.2–0.5 V at a current density of 0.125 mA/cm².

The in situ X-ray diffraction analysis of InSb was performed in transmission mode using a STOE & CIE GmbH STADI powder diffractometer fitted with a position-sensitive detector (Cu K α ₁ radiation) at Uppsala University. Two-electrode “coffee-bag” cells, were constructed with an InSb working electrode, a lithium counter electrode and an electrolyte of 1 M LiPF₆ (Merck) in 2:1 by volume ethylene carbonate/dimethyl carbonate (EC/DMC) (Selectipur[®], Merck, Darmstadt, Germany). These cells were charged and discharged in potentiostatic mode on a MacPileII[™] with steps of 10 mV and a current density cut-off limit of <0.02 mA/cm². Before each diffraction pattern was recorded, the cell was allowed to equilibrate. Measurements were made at the following voltages: 2.73 V (open-circuit voltage); 1.01, 0.75 and 0.44 V during the first discharge; and 0.50, 0.71 and 1.55 V during the subsequent charge.

In situ EXAFS data of InSb electrodes were collected in transmission mode from two-electrode cells at the MRCAT Undulator (10-ID) beamline at the Advanced Photon Source (Argonne National Laboratory). A cryogenic Si(3 3 3) double crystal was used to monochromate the X-ray beam. The data were recorded from cells cycled between 1.2 and 0 V.

3. Results and discussion

In principle, the zinc-blende structure, as typified by InSb with its diamond-like framework, has several attributes that make it attractive as an electrode material for lithium batteries. The unit cell has cubic symmetry F $\bar{4}3m$ with two possible independent interstitial sites for lithium; moreover, a zinc-blende framework has a three-dimensional interstitial space that may allow lithium diffusion. The typical cycling profile of a Li/InSb is shown in Fig. 1a. After an initial “conditioning” reaction, the InSb electrode delivers a typical rechargeable capacity of 300 mAh/g that corresponds to a volumetric capacity of 1710 mAh/cm³ based on the density of InSb (5.7 g/cm³); these capacities correspond to the reaction of approximately 2.6 Li per InSb unit [12]. It is evident from Fig. 1a that several processes take place during the electrochemical discharge and charge reactions, which is consistent with the electrochemical reactions of lithium with InSb at 400°C observed by Sitte and Weppner [13]. Analyses of the lithiated InSb electrode by in situ X-ray diffraction (Fig. 2) and EXAFS (Fig. 3) confirmed our earlier report [12] that the reaction at the electrode during discharge occurs by lithium insertion and indium extrusion from a fixed cubic-close-packed Sb array. Although the reaction is complex, the X-ray diffraction and EXAFS data showed that the reaction can be described in the following general terms:

1. During the initial conditioning reaction to 500 mV, lithium is first inserted into some of the interstitial sites of the zinc-blende framework before a concomitant lithium insertion/indium extrusion process occurs; lithiation of the extruded indium occurs predominantly below \sim 700mV. The conditioning reaction yields a

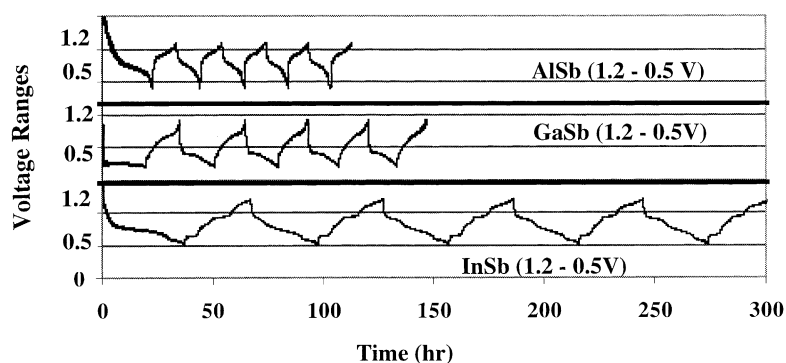


Fig. 1. The electrochemical voltage profiles of (a) Li/InSb, (b) Li/GaSb and (c) Li/AlSb cells, cycled between 1.2 and 0.5 V.

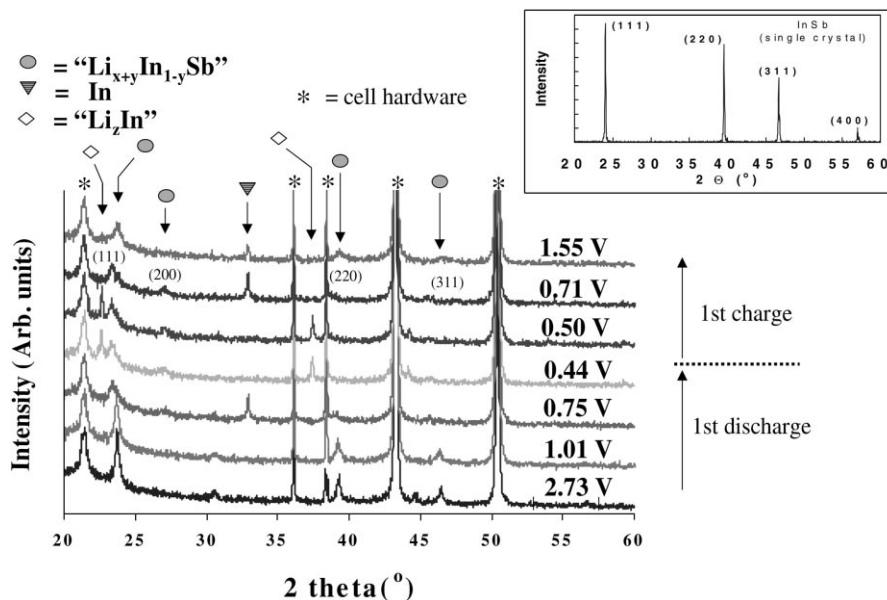


Fig. 2. In situ X-ray diffraction data of a Li/InSb cell with a ball-milled InSb electrode taken at various voltages during the initial discharge at 2.73 V (initial cell voltage), 1.01, 0.75 and 0.44 V and subsequent charge at 0.50, 0.71 and 1.55 V.

$\text{Li}_{x+y}\text{In}_{1-y}\text{Sb}$ product ($0 < x < 2$, $0 < y < 1$). At 500 mV, not all the In is extruded from the structure. We are not yet certain about the extent to which indium is displaced at the surface of the electrode particles or the extent to which lithium and indium diffuse through the bulk of the particles. In this respect, it is noteworthy that the diffusion of indium through antimony is among the fastest known for metal systems [14].

2. Not all the In is reincorporated back into the Sb array during charge; the excellent reversibility of the reaction after the conditioning cycle is, therefore, attributed to a modified $\text{Li}_y\text{In}_{1-y}\text{Sb}$ ($0 < y < 1$) zinc-blende framework; this hypothesis is consistent with the existence of compounds such as $\text{Li}_{1.5}\text{In}_{0.5}\text{Sb}$ and $\text{Li}_2\text{In}_{0.33}\text{Sb}$ that have been identified at 400°C by Sitte and Weppner [13]. At the top of charge, the EXAFS data indicate that

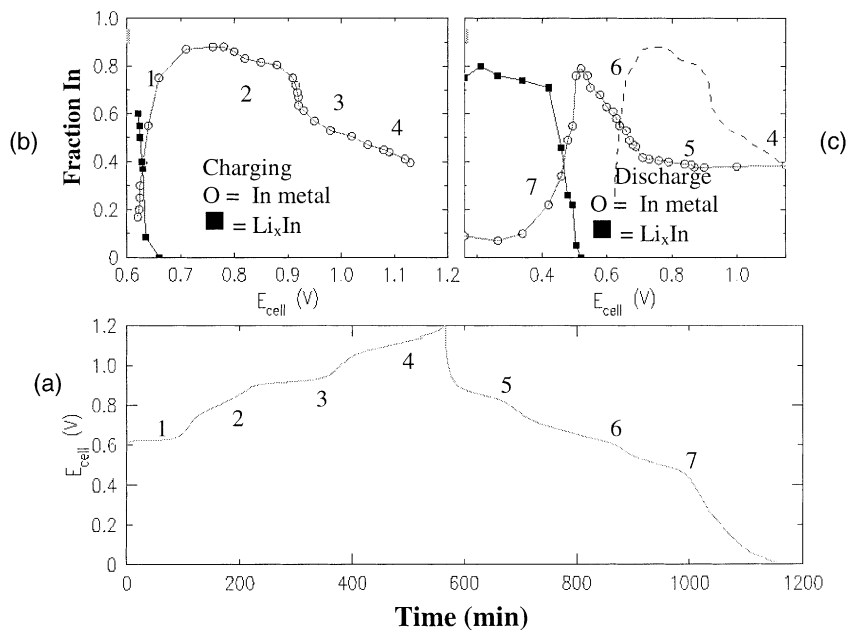


Fig. 3. In situ EXAFS data showing (a) the electrochemical profile of a conditioned Li/InSb cell cycled on charge between 0.5 and 1.2 V and subsequently discharged to 0.0 V; the fraction of In metal and lithiated In in the electrode as a function of (b) charge and (c) discharge. The large numbers in (b) and (c) correspond to the appropriate regions of the electrochemical charge and discharge profiles in (a).

as much as 40% of the indium may remain outside the zinc-blende framework; a small amount of residual lithium may also remain on the interstitial sites for charge compensation.

3. On the second discharge, lithium is inserted into the Sb array of the modified zinc-blende structure in a two-step process from 1.2 to 0.6 V; the first process corresponds predominantly to lithium insertion and the second to lithium insertion/indium extrusion. Lithiation of the extruded In starts to occur during a third step between 0.6 and 0.5 V.
4. If the discharge is taken below 0.5 V, then further lithiation of In occurs to form a series of Li_xIn phases in the range $0 < x < 4.33$. The Li_xIn products have not yet been unequivocally identified; it is most likely that they are related to known phases in the Li–In system, namely, LiIn , Li_5In_4 , Li_3In_2 , Li_2In and $\text{Li}_{13}\text{In}_3$ [15].
5. Experiments at elevated temperature (50°C) improve not only the rate capability of the cells, but also the extent to which In is reincorporated back into the fcc Sb lattice, thereby increasing the practical capacity of the Li/InSb cells [16].

The electrochemical performance of Li/GaSb and Li/AlSb cells when cycled between 1.2 and 0.5 V is compared with that of a Li/InSb cell in Fig. 1a–c. It is immediately obvious that both Li/GaSb and Li/AlSb cells provide significantly inferior capacities to the Li/InSb cell. Nevertheless, the electrochemical profiles of Li/GaSb and Li/AlSb cells are characteristic of a relatively simple electrochemical process that involves the reaction of approximately one lithium per GaSb and AlSb unit. These reactions show excellent reversibility. However, if the discharge reactions of these cells are taken below 0.5 V, then both cells lose capacity quickly. These data, therefore, suggest that GaSb and AlSb zinc-blende electrodes are less tolerant to lithium insertion/metal displacement reactions compared to InSb.

4. Conclusions

The family of metal–antimony compounds with a zinc-blende-type structure, notably InSb, exhibits interesting electrochemical properties in lithium cells. Lithium insertion and indium extrusion from the initial InSb electrode yield a modified $\text{Li}_y\text{In}_{1-y}\text{Sb}$ zinc-blende framework, which can undergo many electrochemical cycles while delivering a capacity of approximately 300 mAh/g. The excellent reversibility of this electrode is attributed, in part, to the fast diffusion of metallic indium in antimony.

Although our data on other materials with zinc-blende structures have not been presented in this paper, the family of antimony compounds appears to provide better cycling performance than zinc-blende materials containing other

Group V elements. The superior cycling behavior of Sb zinc-blende electrode structures, compared to zinc-blende structures containing As or P, appears to be related to the strong crystallographic relationship between the parent structure and its fully lithiated product. For example, Li_3Sb has a strong structural relationship to InSb; it can be considered as having a lithiated zinc-blende structure $\text{Li}_2(\text{LiSb})$ in which Li occupies all the interstitial sites of the zinc-blende structure as well as the In sites of InSb. Moreover, the volume of the cubic unit cells of pure Li_3Sb and InSb is almost identical, varying by only 4.4%. These close structural relationships do not appear to be the case for As- and P-based systems. Nevertheless, efforts are in progress to find such strong structural relationships in other non-antimony-based intermetallic insertion electrodes for lithium-ion batteries.

Acknowledgements

Support from the Office of Basic Energy Sciences, Division of Chemical Sciences, and from the Office of Advanced Automotive Technologies of the United States Department of Energy, under Contract No. W31-109-Eng-38 is gratefully acknowledged. The work was also supported in Sweden by grants from the Foundation for Environmental Strategic Research (MISTRA) and the Swedish Natural Research Council (NFR).

References

- [1] J. Wang, I. Raistrick, R. Huggins, *J. Electrochem. Soc.* 133 (1986) 457.
- [2] J. Besenhard, J. Yang, M. Winter, *J. Power Sources* 68 (1997) 87.
- [3] J. Yamaki, M. Egashira, S. Okada, *J. Electrochem. Soc.* 147 (2000) 460.
- [4] R.A. Huggins, Lithium alloy anodes, in: J.O. Besenhard (Ed.), *Handbook of Battery Materials*, Wiley, New York, 1999.
- [5] M. Winter, J.O. Besenhard, *Electrochim. Acta* 45 (1999) 31.
- [6] Y. Idota, T. Kubota, A. Matsufuji, Y. Maekawa, T. Miyasaka, *Science* 276 (1997) 570.
- [7] O. Mao, R. Dunlap, J. Dahn, *J. Electrochem. Soc.* 146 (1999) 405.
- [8] K. Kepler, J. Vaughey, M. Thackeray, *Electrochem. Solid State Lett.* 2 (1999) 307.
- [9] M.M. Thackeray, J.T. Vaughey, A.J. Kahaian, K. Kepler, R. Benedek, *Electrochem. Commun.* 1 (1999) 111.
- [10] M. Thackeray, C. Johnson, A. Kahaian, K. Kepler, J. Vaughey, *ITE Batt. Lett.* 1 (1999) 26.
- [11] D. Larcher, L. Beaulieu, D. MacNeil, J. Dahn, *J. Electrochem. Soc.* 147 (2000) 1658.
- [12] J.T. Vaughey, J. O'Hara, M.M. Thackeray, *Electrochem. Solid State Lett.* 3 (2000) 13.
- [13] W. Sitte, W. Weppner, *Z. Naturforsch.* 42a (1987) 1.
- [14] V. Kozlov, V. Agrigento, G. Mussati, L. Peraldo-Bicelli, *J. Alloys Comp.* 288 (1999) 255.
- [15] W.A. Alexander, I.D. Calvert, R.H. Gamble, K. Schinzel, *Can. J. Chem.* 54 (1976) 1052.
- [16] C.S. Johnson, personal communication.