ANL/CMT/CP-102060

First-principles calculations for Li insertion into InSb

R. Benedek [a], J. T. Vaughey [a], M. M. Thackeray [a], L. H. Yang [b], R. Prasad [c]

[a] Electrochemical Technology Program, Argonne National Laboratory, Argonne, Illinois 60439
[b] Condensed Matter Physics Division, Lawrence Livermore National Laboratory Livermore, CA 94551
[c] Physics Department, Indian Institute of Technology, Kanpur, India 208016

Abstract

First-principles calculations are presented for the zinc-blende-structure compound InSb, a candidate anode material for Li batteries. The atomic structure of InSb during Li insertion is discussed in the light of local density functional theory calculations based on plane-wave pseudopotential and linear muffin tin orbital methods.

Introduction

Electrochemical potentials a few hundred millivolts above that of Li metal would be desirable in an anode material, from the standpoint of operating safety. Since carbon-based anodes [1], which have electrochemical potentials for Li similar to Li metal, are otherwise favorable because their open structures readily accommodate Li, it seems worthwhile to investigate the suitability of non-carbon-bearing channeled structures. This contribution focuses on the zinc-blende-structure compound InSb [2], which may be viewed as channeled, although it is strongly bonded in three dimensions.

First-principles calculations are presented of the properties of Li in InSb and related materials. Experimental investigations [2-4] of the structural evolution of InSb during electrochemical cycling are still incomplete, and we therefore focus here only on the first discharge cycle, for which the broad outlines of the structural transformations are known.

DISCLAIMER

Portions of this document may be illegible in electronic image products. Images are produced from the best available original document.

Method

We refer to the compositions that arise during electrochemical cycling of InSb as $Li_{x+y}In_{1-y}Sb$. In this formula, x represents the amount of interstitial and y the amount of substitutional Li in the zinc-blende InSb framework structure. We consider both In- and Sb-coordinated tetrahedral interstices, denoted T_{In} and T_{Sb}, respectively [5], for Li interstitials in InSb. It would be desirable to treat small non-zero values of x and y, in view of the trace solubilities typical of Li in semiconductors, but the smallest value of x treated is 1/8.

We employ the plane-wave pseudopotential (PWP) method [6] in most of the calculations. Pseudopotentials were generated with the Troullier-Martins code, with the In and Sb 4d shells treated as valence electrons, and with a basis set cutoff energy of 80 Ry. To complement the PWP method, calculations have also been performed with the full-potential-linear-muffin-tin orbital (FLMTO) method [7], which yields highly precise results, but is restricted for computational reasons to smaller unit cells. Most of our calculations employed either the primitive unit cell (1 formula unit) or the conventional cubic unit cell (4 formula units). The equilibrium lattice constants predicted in our PWP and FLMTO calculations both differed by less than one percent from the experimental value, 6.47 Å, consistent with previous work [8, 9].

The limit x=2, y=1 corresponds to the compound Li_3Sb, in which both T_{Sb} and T_{In} interstitial sites are occupied, and Li is substituted on the In sublattice of the zinc blende structure. Our PWP calculations yield an equilibrium lattice parameter of 6.35 Å, about 3% lower than the experimental value.

Results and Discussion

A marked difference is observed between the electrochemical potential curves in the first discharge cycle and in subsequent cycles [2]. Apparently, the first discharge cycle serves to "condition" the electrode, after which relatively stable cycling behavior is established. From a phenomenological point of view, several types of structural changes come into consideration when Li is introduced into InSb.

a. Lithium intercalation into InSb

Our calculations indicate that the T_{In} sites are the preferred locations for Li in pristine InSb. Furthermore, interstitial Li is known to insert rapidly in InSb [10]. It is, therefore, reasonable to attribute the initial part of the first discharge cycle (apart from "transient" effects associated perhaps with surface oxides) to intercalation of Li into the zinc blende matrix. Our preliminary calculations yield an electrochemical potential (relative to Li metal) of 0.6 eV for insertion into T_{In} sites. This is lower than would be expected from the measured voltage profile for the first discharge cycle [2], but this value may be revised when calculations for smaller x are available.

One anticipates that only a relatively small amount of Li can be accommodated interstitially, in thermodynamic equilibrium. Interpolating between the FLMTO calculations for x=0 and x=1, we find that the approximate lattice constant expansion per unit Li concentration is

$$\Delta a/(a\Delta x) \sim 0.05$$

It has been observed empirically [11] that crystal lattices of compounds tend to amorphize when the lattice constant expands (as a result, for example, of hydrogenation or irradiation) by only about 1%. Applied to lithiated InSb, this criterion would correspond approximately to $x_{amorp}=0.2$, which is small compared with the full extent of the discharge [2], $x_{max}\sim 2\text{-}3$. There is no experimental evidence [2], however, of Li-induced amorphization.

b. Lithium intercalation accompanied by Li substitution: compensation

It may be favorable thermodynamically (although the precise kinetic path is unclear) to substitute a fraction of Li atoms on the In sublattice. A special case is the "line of compensation", x=2y, for which one-third of the Li atoms occupy substitutional sites. The electrons donated by interstitial Li atoms are then exactly compensated by Li acceptors on the In sublattice. Compensation may be favorable thermodynamically because bonding states are essentially filled, and antibonding states are essentially empty. Kinetic barriers to In diffusion, however, may prevent Li substitution from occurring, at relatively small x, in the absence of pre-existing In vacancies.

c. Formation of $Li_{3-\delta}In_{\delta}Sb$

A reaction to form the compound Li_3Sb, by extruding In metal during the insertion of Li, is considered. This reaction most likely limits the thermodynamic solubility of Li in InSb, as do analogous reactions in other zinc-blende compounds [12]. Our calculations predict an electrochemical potential for this reaction of 0.9 eV, relative to Li metal. Measured first-discharge potentials [3, 4], on the other hand, show a plateau at 0.75 eV for ball-milled specimens and 0.6 eV for single crystals. The results of extended X-ray absorption fine structure (EXAFS) measurements [4] suggest that the plateau is associated with the displacement of In from its sublattice in the zinc blende structure. Although local density functional theory calculations typically underestimate electrochemical potentials for Li batteries, our predicted voltage in this case is higher than experiment. The theoretical prediction corresponds to the ideal reaction $1/3[\,3Li + InSb \rightarrow Li_3Sb + In]$ in which the extruded component forms metallic In in its tetragonal crystal structure. The formation of metallic In, however, requires mass transport, and the measured electrochemical potential may correspond to local displacement of In to some intermediate state, before the mass transport can take place.

Summary

We have explored with local density functional theory some structures that arise when Li is inserted into zinc-blende InSb. The calculations predict that Li occupies the T_{In} sites initially.

We are unable to make a prediction of the solubility limit of Li in the framework lattice, but it is thought to be small. When this limit is exceeded, we believe that the extrusion of In occurs, with the formation of a ternary system with composition $Li_{3-\delta}In_{\delta}Sb$, similar to Li_3Sb. The extruded In eventually crystallizes in its usual metallic form, but this process may be delayed by the mass transport required for the In to reach the specimen surface or internal pores.

Acknowledgments

This work was supported at Argonne National Laboratory by the Chemical Sciences Division of the Office of Basic Energy Sciences of the U.S. Department of Energy, under contract no. W31-109-Eng-38. L. H. Yang was supported at Lawrence Livermore National Laboratory by the U. S. Department Energy under contract no. W-7405-Eng-48. Most of the computational work was performed at the National Energy Research Supercomputer Center.

References

1. J. Yamaki, M. Egashira, and S. Okada, J. Electrochem. Soc. **147** (2000) 460.
2. J. T. Vaughey, J. O'Hara, and M. M. Thackeray, Electrochem. and Solid-State Lett., **3** (2000) 13.
3. J. R. Kropf and H. Tostmann, unpublished work.
4. S. A. Hackney, unpublished work.
5. S. K. Estreicher, Materials Science Forum, **45** (1994) 349.
6. R. Benedek, M. M. Thackeray, and L. H. Yang, Phys. Rev. B **60** (1999) 6335.
7. We are indebted to J. M Wills for making his FLMTO code available to us.
8. S.H. Lee, J.H. Kang, and M. H. Kang, J. Korean Phys. Soc. **45** (1999) 31.
9. S. B. der Kellen and A. J. Freeman, Phys. Rev. B **54** (1996) 11187.
10. T. Takabatake, H. Ikari, and Y. Uyeda, Japan J. Appl. Phys. **5** (1966) 839.
11. P. R. Okamoto, N.Q. Lam and L. E. Rehn, "Physics of crystal-to-glass transformations" in *Solid State Physics*, vol. 52, pp. 1-135 (eds. H. Ehrenreich and F. Spaepen), Academic Press, New York (1999).
12. C. G. Van de Walle, D. B. Laks, G. F. Neumark, and S. T. Pantelides, Phys. Rev. B **47** (1993) 9425.