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ABSTRACT

The desired range of potentials for Li-battery anode materials is a few hundred millivolts relative to Li metal. The zinc-blende-structure compound InSb meets this criterion, and has relatively large capacity as well as ease of electrochemical reaction with Li. The structural transformations that occur in InSb during the initial reaction with Li and on subsequent electrochemical cycling, however, have not been established. The atomic structure of InSb during Li insertion is discussed in the light of first-principles calculations based on local density functional theory for $Li_{x+y}In_{1-y}Sb$, where x (y) is the concentration of interstitial (substitutional) Li.

INTRODUCTION

Carbon is a commonly used anode material for Li batteries[1]. Carbon-based electrodes are satisfactory in many respects, but the proximity of their electrochemical potentials for Li insertion to that of Li metal creates safety hazards. Electrochemical potentials a few hundred millivolts above that of Li metal would therefore be desirable in an anode material. The search for such a material has included semiconductors and metals as well as oxides. Attention has been given, for example, to metallic systems[2] such as Sn[3] and Al[2], each of which forms a series of intermetallic compounds with Li. The large volume expansion in the lithiated compounds is a significant drawback of these metals, however. Furthermore, Li insertion/extraction is sluggish.

As an alternative to metals that form Li compounds, one may consider channeled structures. Recent work at Argonne National Laboratory has focused on intermetallics and semiconductors that intercalate Li. In particular, the NiAs-structure η'–phase Cu_6Sn_5[4], and the zinc-blende-structure compound InSb[5] have been investigated. These materials may be viewed as channeled, although they are strongly bonded in three-dimensions, and are in this sense not analogous to the classic channeled systems exemplified by layered graphite and chalcogenides that have strong intralayer and weak interlayer bonding.

It was hoped that such materials would have relatively fast Li diffusion, low volume expansion, and high stability of the framework structure during Li insertion. Although the zinc-blende framework structure may undergo transformations during Li cycling, InSb exhibits some very attractive features, particularly high capacity[5]. The superior performance of InSb warrants further investigation to characterize the atomic and microstructural transformations that occur during Li cycling. In this contribution, we present first-principles calculations of the properties of Li in InSb and related materials. At the time of this writing, the existing body of both theoretical and experimental data is not sufficiently complete to support convincingly any particular model of the structural evolution of InSb, and the presentation of such a model must therefore be deferred to future work. The theoretical results presented here provide constraints on the form the eventual model of structural evolution model may take.

METHOD

First-principles calculations within local-density-functional theory (LDFT) were performed for InSb as a function of the concentration of inserted Li. In these calculations, periodic boundary conditions are employed, and disorder associated with the Li configuration, as well as that of the other components, is therefore not included. We refer to the compositions that arise during electrochemical cycling of InSb as $Li_{x+y}In_{1-y-z}Sb$. In this formula, x represents the amount of interstitial and y the amount of substitutional Li in the zinc-blende InSb framework structure. A concentration z of In vacancies may also be present after the first electrochemical cycle, however, calculations for vacancies have not yet been performed. Antisite Sb or In atoms are expected to be energetically unfavorable and are therefore not considered. Lithium-indium intermetallic compounds are possible by-products of electrochemical cycling of InSb, but are not addressed here.

In principle, both In- and Sb-coordinated tetrahedral interstices, denoted T_{In} and T_{Sb}respectively[6], are available for Li interstitials in InSb. Experiments on InP[7] have shown that Li substitutes for the group III component, and interstitial Li is coordinated with the group-V component in that compound. Interstitial and substitutional site preferences for Li in InSb have not been directly observed, but we assume substitution on the In sublattice is preferred, in view of the extrusion of this component. Our calculations address both the T_{In} and the T_{Sb} interstitial sites.

We employ the plane-wave pseudopotential (PWP) method[8] in most of the calculations. Pseudopotentials were generated with the Troullier-Martins code. It was found that a calculated equilibrium lattice constant for InSb close to the experimental value could be obtained by treating the In and Sb 4d shells as valence electrons, and pseudopotentials with valence 13 (15) for In (Sb) were therefore employed. To treat semicore states accurately, a relatively high basis set cutoff energy was selected, 80 Ry.

To complement the PWP method, calculations have also been performed with the full-potential-linear-muffin-tin orbital (FLMTO) method[9]. This method yields highly precise results, but is restricted for computational reasons to smaller unit cells than the pseudopotential approach. Most of our calculations employed either the primitive unit cell (1 formula unit) or the conventional cubic unit cell (4 formula units).

RESULTS

Calculations were performed for several compositions, each of which is specified by the pair of parameters (x,y). Most of the calculations correspond to y=0, for which only interstitial Li is present. There is also interest in the "line of compensation", x=2y, for which the n-type Li interstitials and the p-type Li substitutions exactly compensate each other. A selection of the results is presented below.

(x,y)=(0,0)

The equilibrium lattice constants predicted in our PWP and FLMTO calculations both differed by less that one percent from the experimental value, 6.47 Å. The bulk modulus calculated with FLMTO (48 Gpa) is also close to experiment, and is consistent with previous work [10,11]. The bulk modulus obtained in the PWP calculations was about 25% higher. The calculated band gap for the FLMTO calculation was 0.5 eV, about twice the experimental value, 0.23 eV. Spin-orbit interactions, not included in our calculations, are known to influence III-V bandgaps[10].

It would be desirable to treat small non-zero values of x and y, in view of the trace solubilities typical of Li in compound semiconductors[12]. The smallest value of x that we considered is 0.125, which corresponds to a primitive cell doubled along the three independent axes. The results are not complete, however, and will be presented elsewhere.

(x,y)=(0.25,0)

The PWP calculations for the configurations T_{In} and T_{Sb} showed the former to be lower in energy by 0.24 eV per Li atom. In these calculations, the unit-cell lattice constant was taken to be 6.51 Å, a value slightly larger than our PWP prediction for x=y=0, 6.48 Å. The internal coordinates were relaxed in the presence of the Li atom, but the lattice constant was held fixed. The In atoms that are nearest neighbors of the T_{In} Li relax outward by 0.06 Å, a significant distortion. Interpolating between PWP results for x= 0 and 1 (see below), the equilibrium lattice constant for x=0.25 should be about 6.53 Å, only slightly higher than the assumed value.

The preference of Li for the T_{In} sites is at first surprising, in view of the expected electrostatic attraction between Li and the formally anionic Sb. At least five III-V zinc blende compounds (GaAs, AlSb, GaSb, InSb, and InAs), however, show "anti-ionic" behavior, in which the effective charge of the trivalent species is negative[13]. Consistent with this picture, H in GaAs is found both experimentally and theoretically [6] to occupy T_{In} . On the other hand, Li in InP, which has "normal" ionic behavior, occupies T_P[7].

(x,y)=(0.5,0)

PWP calculations were performed, employing a cell lattice constant of 6.61 Å, in which two (out of a maximum of eight) tetrahedral interstitial sites in a conventional cubic unit cell were occupied by Li atoms. The internal coordinates were relaxed, and the lattice constants were held fixed. The energy difference between occupying T_{In} sites and T_{Sb} sites, $E(T_{in})-E(T_{Sb})=0.06$ eV per Li atom, and the site T_{In} is therefore preferred. Our results indicate that the Li site preference shifts from T_{In} sites to T_{Sb} sites between x=0.25 and x=0.5, the anti-ionic behavior mentioned above notwithstanding. This shift is perhaps a precursor to the Li-Sb bonding that occurs in the compound Li_3Sb, which corresponds to x=2 and y=1.

(x,y)=(0.0,0.25)

A single Li atom substitution on an In site in a conventional (zinc blende) cubic unit cell is considered. The energy cost of placing Li in a substitutional site, relative to a tetrahedral interstitial site, can be expressed as

$$\Delta E(S_{In},T_{In}) = E(S_{In}) - E(T_{In}) + \mu_{In},$$

where $E(S_{In})$ is the total energy of a cell in which a Li atom is substituted for an In atom, $E(T_{In})$ is the energy of a cell in which a Li atom is located on an Sb coordinated interstitial site, and μ_{In} is the chemical potential of In in In metal; (It is assumed in this process that In is extruded from InSb to form In metal, thereby vacating sites in the zinc-blende framework structure that are then available for Li substitution). Numerically, we find $\Delta E(S_{In},T_{In}) = 1.4$ eV. This result indicates that initially interstitial sites are strongly preferred energetically to substitutional sites.

(x,y)=(1.0,0)

At this composition, all T_{Sb} interstitial sites are filled. The total energy was calculated as a function of lattice constant. The PWP calculations yield an equilibrium lattice constant of 6.69 Å, whereas the FLMTO calculations give 6.85 Å. It is reasonable to attribute this discrepancy to the underestimation of atomic volumes characteristic of pseudopotential calculations for Li. The bulk modulus obtained from the FLMTO calculations is 25% smaller than that corresponding to InSb.

(x,y)=(2,1)

This composition corresponds to the compound Li_3Sb, which may be thought of as derived from InSb by filling all T_{Sb} and T_{In} interstitial sites, and substituting Li for In 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.

If the insertion of Li into InSb generates Li_3Sb and extruded In, the corresponding electrochemical potential, relative to Li metal would be

$$V(Li_3Sb) = -1/3\ [E(Li_3Sb) + \mu_{In} - E(InSb) - \mu_{Li}]$$

By inserting numerical values obtained from PWP calculations, we obtain $V(Li_3Sb) = 0.9$ eV. This result may be compared with the potential

$$V(T_{In}) \equiv -[E(T_{In}) - E(InSb) - \mu_{Li}] = 0.6 \text{ eV},$$

which corresponds to the insertion of Li into a T_{In} site.

DISCUSSION

The changes in atomic structure that accompany electrochemical cycling of InSb have not been precisely characterized, although experimental investigations with x-ray diffraction[5], extended x-ray fine structure (EXAFS)[14], and transmission electron microscopy[15], are either completed or in progress. A marked difference occurs between the electrochemical potential curves in the first discharge cycle and in subsequent cycles[5]. 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. In the following, we discuss some of these possibilities in the light of the calculations presented in the previous section.

Li intercalation in InSb

Our calculations indicate that the T_{In} interstitial sites are the preferred locations for Li in pristine InSb. Furthermore, experiments show that interstitial Li diffuses rapidly in InSb[16]. It is therefore reasonable to expect 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. We note that the calculated electrochemical potential (relative to Li metal) of 0.6 eV is lower than would be expected from the measured voltage profile for the first cycle[5]. The calculated value, obtained with the PWP method, is preliminary, however, and may increase when more precise and accurate calculations are available.

One anticipates that only a relatively small amount of Li can be accommodated interstitially, in thermodynamic equilibrium. This follows from the low solubilities of Li in zinc blende structure compounds [12], and the large predicted local distortions and lattice constant expansion induced by interstitial Li described in the previous section. Interpolating between the FLMTO calculations for x=0 and x=1, we find that the approximate lattice constant expansion per unit Li concentration is

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

In a recent review[17], it was observed empirically 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[5], $x_{max}\sim 2\text{-}3$. We are not aware, however, of any previous reports of Li-induced amorphization in zinc-blende semiconductors, and no evidence for amorphization of InSb has been observed[5]. One is therefore led to consider the possibility that a fraction of the Li enters the zinc blende framework substitutionally, which would reduce the lattice constant expansion that results from Li intercalation.

Li 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[6]. Preliminary calculations of the electrochemical potential for the line of compensation yield values slightly higher (order of 0.1 eV) than that for interstitial Li.

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

A reaction to form the known compound Li_3Sb, by extruding In metal during the insertion of Li, comes into consideration. This process corresponds to the terminal point of the line of compensation, for which x=2 and y=1. This reaction may limit the thermodynamic solubility of Li in InSb, as do analogous reactions in other zinc blende compounds[13]. Our calculations are not at this time sufficiently precise to predict the value of x at which this reaction occurs.

CONCLUSIONS

We have explored with local density functional theory some structures that arise when Li is inserted into zinc blende InSb. In the absence of a comprehensive model of the structural evolution of this system under electrochemical cycling, we confine our remarks to the first discharge cycle. The calculations suggest that Li occupies the T_{In} sites initially. Upon further lithiation, T_{Sb} sites become favorable. An important issue, on which we are unable to make a prediction at this time, is at what concentration Li can no longer be accommodated substitutionally in the framework lattice. At that point several transformations exist. One possibility is Li substitution for In, forming either a partially or fully "compensated" system (y>0), a special case of which is the compound Li_3Sb. A hypothetical possibility is Li-induced amorphization, which however has not been observed.

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REFERENCES

[1]J. Yamaki, M. Egashira, and S. Okada, "Potential and thermodynamics of graphite anodes in Li-ion cells," *J. Electrochem. Soc.* **147**, 460-465 (2000).

[2]R. A. Huggins, "Lithium alloy anodes," pp. 359-381, in *Handbook of Battery Materials*, edited by J. O. Besenhard, Wiley, New York (1999), and other articles in this volume.

[3]M. Winter and J. O. Besenhard, "Electrochemical lithiation of tin and tin-based intermetallics and composites," *Electrochimica Acta* **45**, 31-50 (1999).

[4]M. M. Thackeray, J. T. Vaughey, A. J. Kahaian, K. D. Kepler and R. Benedek, "Intermetallic insertion electrodes derived from NiAs, Ni_2In, and Li_2CuSn-type structures for lithium-ion batteries," *Electrochem. Commun.* **1**, 111-115 (1999).

[5]J. T. Vaughey, J. O'Hara, and M. M. Thackeray, "Intermetallic insertion electrodes with a zinc-blende-type structure for Li satteries: a study of Li_xInSb ($0<x<3$)," *Electrochemical and Solid-State Letters.* **3**, 13-16 (2000), and unpublished work.

[6]S. K. Estreicher, "Theoretical and μSR studies related to hydrogen in compound semiconductors, "*Materials Science Forum* **45**, 349-392 (1994).

[7] U. Wahl, H. Hofsaess, S. Jahn, S. Winter and E. Recknagel, ”Lattice sites of ion implanted Li in indium phosphide”, *Nucl. Instr. and Meth.* **64**, 221 (1992).

[8] R. Benedek, M. M. Thackeray, and L. H. Yang, “Atomic structure and electrochemical potential of $Li_{1+x}V_3O_8$,” *Phys. Rev.* B **60**, 6335-6342 (1999).

[9] We are greatly indebted to J. Wills of Los Alamos National Laboratory for making his FLMTO code available to us.

[10] S.H. Lee, J.H. Kang, and M. H. Kang, “Structural properties of semiconductors in the generalized gradient approximation,” *J. Korean Phys. Soc.* **45**, 31-50 (1999).

[11] S. B. der Kellen and A. J. Freeman, “Self-consistent relativistic full-potential Korringa-Kohn-Rostoker total-energy method and applications,” *Phys. Rev.* B **54**, 11187-11198 (1996).

[12] C. G. Van de Walle, D. B. Laks, G. F. Neumark, and S. T. Pantelides, “First-principles calculations of solubilities and doping limits: Li, Na, and N in ZnSe,” *Phys. Rev.* B **47**, 9425-9433 (1993).

[13] G.A. Wolff, “Bond characterization from crystal morphology”, pp. 167-189, in *Intermetallic Compounds*: Vol. 1, *Principles*, edited by J. H. Westbrook and R. L. Fleischer, Wiley, New York (1994).

[14] A. J. Kropf and H. Tostmann, unpublished work, 2000.

[15] S. R. Hackney, unpublished work, 2000.

[16] T. Takabatake, H. Ikari, and Y. Uyeda, “Diffusion of Li in InSb,” *Jpn. J. Appl. Phys.* **5**, 839-840 (1966).

[17] P. R. Okamoto, N.Q. Lam and L. E. Rehn, “Physics of crystal-to-glass transformations,” pp. 1-135, in *Solid State Physics*, vol. 52, edited by H. Ehrenreich and F. Spaepen, Academic Press, New York (1999).