Lithiation of InSb and Cu$_2$Sb : A Theoretical Investigation

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In this work, the mechanism of Li insertion/intercalation in the anode materials InSb and Cu$_2$Sb is investigated by means of the first-principles total-energy calculations. The electron localization function for the lithiated products of InSb are presented. Based on these results the change in the bonding character on lithiation is discussed. Further, the isomer shift for InSb and Cu$_2$Sb and there various lithiated products is reported. The average insertion/intercalation voltage and the volume expansion for transitions from InSb to Li$_x$Sb and Cu$_2$Sb to Li$_x$Sb are calculated and found to be in good agreement with the experimental values. These findings help to resolve the uncertainty regarding the lithiation mechanism in InSb.

I. INTRODUCTION

Intermetallic compounds present an attractive alternative to graphite as anode materials in Li ion insertion batteries due in particular to the high capacity, an acceptable rate capability and operating potentials well above the potential of metallic lithium. The work in this direction gained tempo after the announcement that tin-based compounds could operate effectively as alloying hosts for Li ions. In search of new anode materials one of the desirable qualities is that the structural and volumetric distortion of the host anode material on lithiation are small. This could be achieved if there existed a strong structural relation between the host and its lithiated products. Some of the compounds which show such structural relations are Cu$_x$Sn$_{0.57x}$, InSb$_{1.35x}$, MnSb$_{1.10x}$, Cu$_2$Sb$_{1.3}$, Ni$_4$Sb$_{1.1}$, GaSb$_{1.3}$ etc. These compounds can be divided into three main structure types, namely NiAs (Cu$_6$Sb$_5$, MnSb), ZnS (InSb, GaSb) and Cu$_2$Sb (Mn$_2$Sb). In these materials, one of the components (Cu, In, Mn, Ga) is less active and is extruded on lithiation, while the other component provides the structural skeleton for further lithiation. In a previous work the lithiation of Cu$_x$In$_{1-y}$Sb$_5$ was studied. In the present work, we investigate one representative compound from each of the other two structure types. These are InSb which belongs to the zinc blende structure and Cu$_2$Sb which is the prototype for the third class of materials.

Since it is desirable for an ideal anode material to reversibly insert/intercalate Li ions while maintaining the structural stability, the knowledge of the exact amount of Li accommodated within the structure before the extrusion of the less active component is extremely important. In this regard, recently the electrochemistry of the Li insertion in InSb was studied experimentally, and contradictory results were published: 1) Vaughan et al. initially proposed that 2 Li atoms could be incorporated within the InSb structure with very small volume expansion (5.6%) before In extrusion, resulting in excellent capacity 2) Johnson et al. subsequently reported that In extrusion occurred at an earlier stage according to a general reaction: $(x + y)\text{Li} + \text{InSb} \rightarrow \text{Li}_{x+y}\text{In}_{1-y}\text{Sb} (0 \leq x \leq 2; 0 \leq y \leq 1)$ in which a Li$_x$In$_{1-y}$Sb zinc-blende framework played an important role in the Li insertion/In extrusion process, but they could not determine the precise amount of Li that could be inserted before the onset of In extrusion; 3) On the other hand, Hewitt et al. claimed, that $x$ reached a maximum value of 0.27 before In atoms were extruded to immediately form Li$_x$Sb in a two-phase reaction, and that Li$_2$Sb could be generated on subsequent electrochemical cycling; 4) From in situ X-ray absorption measurements, Kroft et al. and Tostmann et al. provided supporting evidence that Li$_{x+y}$In$_{1-y}$Sb electrode compositions were generated during the initial discharge of Li/InSb cells and that 40% of the extruded In was not incorporated back into the Sb lattice during the subsequent charging of the cells. In the light of the uncertainty of the reaction process, there is a need to clarify the exact lithiation path. To this extent we perform total-energy calculations for studying the mechanism of Li insertion/intercalation in InSb. A similar pathway is also provided for Cu$_2$Sb. We also present the theoretically determined isomer shift (IS) for these materials and various lithiated products.

The change in the bonding character on lithiation is another important information that can be extracted from the first-principles calculations. Such analysis regarding battery materials, has been done in the past using the total or difference charge density. But it was noted by Bader et al. and Becke et al. that the information regarding the bonding in the molecular systems is not fully contained in the density ($\rho$) but rather in its Laplacian ($\nabla^2 \rho$) and in the kinetic energy density. These quantities are used to calculate the electron-localization-function (ELF), which varies between 0 and 1, with 1 corresponding to perfect localization and 1/2 corresponding to electron gas like behaviour. Thus ELF in a way quantifies the bonding between various atoms in a solid and hence is ideal for studying the change in the bonding nature as new bonds are formed and (or) old bonds are weakened or broken by the insertion of Li atoms. We present the ELF for some of the lithiated products of InSb in the present work.

The paper is arranged in the following manner. In Section II, we present the details of the calculations. Section IIIA deals with the energetics of lithiating InSb and...
Cu$_2$Sb. To facilitate the study of the change in the bonding character on the lithiation of these compounds the IS and the ELF are given in Section IIIB. Section IV provides a summary of our work.

II. METHODOLOGY

Total energy calculations are performed using the full potential linearized augmented plane wave (FLAPW) method. In this method, the unit cell is partitioned into non-overlapping muffin-tin spheres around the atomic sites and an interstitial region. In these two types of regions different basis sets are used. The scalar relativistic Kohn-Sham equations are solved in a self-consistent scheme. For the exchange-correlation potential we use the local density approximation (LDA). All the calculations are converged in terms of basis functions as well as in the size of the k-point mesh representing the Brillouin zone.

In order to compare the total energies, calculated from first principles, for any two structures one has to optimize the structural parameters. These parameters are the atomic positions and the unit cell volume, which are varied until the global energy minimum is found. Thereby the experimental crystalline data is used as a starting point. For all the energy differences reported in the present work these optimized crystal structures are used. For these calculations the existing WIEN2k code is used.

The details for the calculation of the IS of $^{121}$Sb have been presented before. In the present work, the same code is used. Calculation of ELF in a mixed basis like LAPW requires the kinetic energy density to be made smooth across the muffin-tin sphere. Thus these calculations are performed using super-LAPW, which requires the matching of the wave function and its first and second derivatives at the muffin-tin sphere boundary making calculations computationally more demanding but affordable because the size of the unit cells is relatively small.

III. RESULTS AND DISCUSSION

A. Lithiation of InSb and Cu$_2$Sb

InSb exists in the zinc blende structure with In atoms at (0,0,0) and the Sb atoms occupying four tetrahedral sites: (0.25,0.25,0.25), (0.75,0.25,0.75), (0.75,0.75,0.25) and (0.25,0.75,0.75). This kind of structural arrangement leaves four tetrahedral sites vacant namely (0.75,0.25,0.25), (0.25,0.25,0.75), (0.25,0.75,0.25) and (0.75,0.75,0.75). Along with this there is another void in the structure at (0.5,0.5,0.5). On lithiation of InSb (or other zinc blende compounds), there are two distinct probable processes: 1) The incoming Li ions go to one of these voids. 2) A substitutional reaction takes place, i.e., In (or the less active component) is extruded and is replaced by the incoming Li ions. In light of the existing controversy regarding these processes in InSb, we studied various possible lithiation paths. Using first-principles total-energy calculations we determine the formation energies for various lithiated products of InSb using the following formula:

$$y\text{Li} + \text{Li}_x\text{InSb} \rightarrow \text{Li}_{x+y}\text{In}_{1-y}\text{Sb} + y\text{In} \quad (1)$$

The formation energy for the compound $\text{Li}_{x+y}\text{In}_{1-y}\text{Sb}$ is given as

$$\Delta E = E_{\text{Li}_{x+y}\text{In}_{1-y}\text{Sb}} + yE_{\text{In}} - [E_{\text{Li}_x\text{InSb}} + yE_{\text{Li}}]. \quad (2)$$

Here $E_C$ is the total energy of the compound $C$ and $E_A^{\text{met}}$ is the energy per atom for metallic $A$. The formation energy defined this way reflects the relative stability of the compound $\text{Li}_{x+y}\text{In}_{1-y}\text{Sb}$ with respect to the reactants Li and $\text{Li}_y\text{InSb}$.

![FIG. 1: The formation energies in eV per formula unit. The compounds formed from the insertion/intercalation of Li atom in the previous compounds are represented by circles and compounds formed by the substitutional reaction are represented by triangles.](image-url)

These formation energies for InSb and its lithiated products are presented in Fig. 1. The compounds formed via the insertion/intercalation reaction of Li with the previous compound are shown as circles, while the compounds formed via the substitutional reaction are marked...
by triangles. As can be seen the formation energies of certain compounds are negative, i.e. these compounds are stable with respect to the reactants. A part of the Li-InSb phase diagram is shown in Fig. 2. Fig. 2(a) consists of the Gibb's triangle which consists of the energetically stable compounds in transition from InSb to Li$_3$Sb, which are shown in detail in Fig 2(b). We find that insertion of 1/2 Li atoms per InSb formula unit leads to a volume expansion of 5.3%. In atoms are extruded beyond this concentration of Li, leading to very little further volume expansion. These results show best agreement with the experimental findings of Tostmann et al. The maximum number of intercalated Li atoms before In extrusion as reported by Hewitt et al. is almost half the value obtained in the present work. According to the energetics, the compound Li$_2$InSb is unstable, but if formed leads to an enormous volume expansion of 15.4%. The total theoretical volume expansion on going from InSb to Li$_3$Sb is 5.6%, which is slightly more than the experimentally reported value of 4.4%. It can be noted from Fig. 1 that, like Hewitt et al., we find the formation of Li$_2$Sb during the first cycle to be energetically hindered. But we also note that the cubic phase of this compound is lower in energy than the hexagonal phase proposed earlier.

The initial incoming Li atoms have the freedom to occupy either the site (0.75,0.25,0.25) or (0.5,0.5,0.5) in the InSb framework to form Li$_{0.25}$InSb. We find that the probability for Li insertion at the position (0.75,0.25,0.25) is higher than at (0.5,0.5,0.5). The difference in energy between the two structures, Li$_{0.25}$InSb with Li at (0.75,0.25,0.25) and Li$_{0.25}$InSb with Li at (0.5,0.5,0.5), is 0.05 eV per formula unit. Our calculated average intercalation voltage (AIV) for a transition from InSb to Li$_3$Sb is 0.83V, which is higher than the experimental value of the plateau in the voltage profile (0.6V) and (0.7V).

Another important thing to be noted from Fig. 1 is the difference in the formation energies between the two consecutive compounds. After the formation of Li$_{3/4}$In$_{3/4}$Sb it is energetically less demanding for Li atoms to come in and (or) for In atoms to extrude from the structure. Also in the case of the reverse reaction it is energetically more demanding for In atoms to reincorporate in the structure beyond a concentration of 75%. This is in accordance with the experimental findings of Tostmann et al. that only about 60% of the In atoms go back into the structure on charging and that Li atoms are extracted more easily and rapidly from this In deficient phase of the kind Li$_{0.6}$In$_{0.4}$Sb leading to a good cycling capacity.

FIG. 2: (a) A part of Li-In-Sb phase diagram. (b) Close view of the energetically favourable InSb-Li$_3$Sb part of the phase diagram.

FIG. 3: The formation energies in eV per formula unit. The compounds formed from the insertion/intercalation of Li atom in the previous compounds are represented by circles, and compounds formed by the substitutional reaction are represented by triangles.

Cu$_2$Sb exists in a tetragonal structure with space group P4/nmm and 2 formulae units per unit cell. The Cu atoms occupy the sites (0.75,0.25,0.0), (0.25,0.75,0.0), (0.25,0.25,0.27) and (0.75,0.75,0.73) while the Sb atoms are situated at (0.25,0.25,0.70) and (0.75,0.75,0.3). There exist voids in the structure at (0.5,0.5,0.5), (0.25,0.75,0.5) and (0.75,0.25,0.5). The two reaction mechanisms investigated in the present are, 1) the insertion/intercalation of Li atoms, and 2) the substitution of Cu by Li atoms. The formation energies for these reaction paths are presented in Fig. 3. Similar to the previous case, the Cu atoms are extruded from the structure after insertion of 1/2 Li atoms per Cu$_2$Sb formula unit. The first incoming Li atoms occupies the site (0.25,0.75,0.5) in the unit cell. Further lithiation leads to replacement of the Cu atom at site (0.75,0.25,0.0) by a Li atom to form LiCu$_{3/2}$Sb.
FIG. 4: (a) A part of Li-Cu$_2$-Sb phase diagram. (b) Close up of the energetically favourable Cu$_2$Sb-Li$_3$Sb part of the phase diagram

A volume expansion of 18% per formula unit compared to Cu$_2$Sb. More incoming Li atoms lead to the formation of the Li$_2$CuSb and a free Cu atom. Li$_2$CuSb exists in a cubic structure with space group F43m. In this unit cell the Sb atoms are present at the origin, the face centers and four of the tetrahedral sites i.e. (0.75,0.75,0.75), (0.25,0.25,0.75) and (0.25,0.75,0.75) occupied by the Cu atoms. The Li atoms are located at the other four tetrahedral sites and at (0.5,0.5,0.5). The theoretically optimized structure of Li$_2$CuSb shows a volume expansion of 26.4% per formula unit compared to the initial compound Cu$_2$Sb. This is in good agreement with the experimental value of 25.2%.

Energetically favourable Cu$_2$Sb to Li$_3$Sb part of the phase diagram is shown in Fig. 4. The calculated value of the AIV for going from Cu$_2$Sb to Li$_3$Sb is 0.97 V, which is slightly higher than the experimental value of 0.82 V.

B. Isomer shift and electron localization function

An excellent method of studying the change in the local environment and symmetry is the Mössbauer IS. We have calculated the $^{121}$Sb IS of various lithiated products of InSb and the results are presented in Fig. 5. The calculated value for InSb is in good agreement with the experimental data of -8.6 mm/s. Insertion reaction of the Li atoms with the host makes the IS steadily more negative with a sudden increase when the In is extruded from the structure. The IS for the energetically hindered compounds LiInSb and Li$_2$InSb are -10.54 mm/s and -11.54 mm/s respectively. These values are largely negative as compared to the other lithiated products of InSb making them easily identifiable by Mössbauer spectroscopy.

It can be seen from Fig. 6, the IS for Cu$_2$Sb, like InSb, shows a decrease on lithiation via the insertion reaction and the continuous increase when the Cu extrusion starts. The IS has been shown to depend linearly on the partial number of $s$ electrons ($N_s$) and the variation of the IS with the Li concentration can be explained very well using this fact. As more Li atoms insert/intercalate in the host material, a part of the charge lost by them is gained by the Sb atoms. This causes an increase in $N_s$ and hence a more negative IS. On the other hand, on lithiation via the substitution reaction there is no excess charge. This causes the decrease in $N_s$ and hence the IS.
becomes less negative. Thus the change in the IS with the Li atom concentration is a good signature of the reaction mechanism and hence we suggest such experiments to be performed to shed more light on the reaction path and for the unambiguous clarification of whether compounds like LiInSb and Li₂InSb are formed or not.

The change in the bonding character on lithiation of the anode material can be studied using the charge density plots which have been used for Cu₆Sn₅₈ and Cu₂Sb₂₄. In the present work we use ELF for such an investigation of InSb. Fig. 8 shows the ELF for InSb, Li₀.₅InSb and Li₃Sb along the (111) direction. A covalent character of bonding between In atom at (0,0,0) and Sb atom at (1/4,1/4,1/4) can be seen as a strong localization of charge between the two atoms. Since only the valence electrons participate in the bond formation, the core charge has been ignored for all the atoms. The high value of ELF at the Li atom site is due the core states being taken into consideration as local orbitals. Lithiation of InSb to form Li₀.₅InSb leads to weakening of the bonding between In and Sb. This manifests itself by a lowering of the ELF from 0.9 to 0.79 between the two atoms. The bond between Li and Sb atoms is ionic in nature. This ionocity is retained all the way upto the formation of Li₃Sb. The presence of delocalized electrons between atoms is indicative of the metallic nature of the compound.

IV. SUMMARY

To summarize, the two prototype structures, InSb and Cu₂Sb, for the use as anode materials in Li-ion batteries are investigated in the present work. From first-principles total-energy calculations we conclude the following:

- On lithiation of InSb during discharge, the In atoms are extruded from the structure after insertion/intercalation of half a Li atom per InSb formula unit. The formation of Li₁/₂InSb leads to a volume expansion of 5.4%.

- It is much easier for In and Li atoms to come out of and go into the structure after formation of Li₅/₄In₃/₄Sb which supports the good cycling capacity.

- The formation of the compounds LiInSb, Li₂InSb and Li₃Sb is energetically hindered. In particular, the formation of LiInSb or Li₂InSb would lead to enormous volume expansions of 14.4% and 15.4%, respectively, which is much more than any experimental observation.

- Our calculated AIV for the transition from InSb to Li₃Sb is in agreement with the experimental value of the plateau in the measured voltage profile. These findings make our results closest to that of Tostmann et al.¹²

- In the case of Cu₂Sb, the Cu atoms are extruded after insertion of half a Li atom per Cu₂Sb formula unit.

- The trends in the IS with increasing Li concentration is an excellent signature of the lithiation reaction mechanism. The formation of compounds like LiInSb and Li₃InSb can be unambiguously determined using Mössbauer spectroscopy, since these compounds have large negative IS values compared to any other lithiated product of InSb.

- The ELF shows that lithiation of InSb results in the weakening of bonds between In and Sb atoms which would lead, upon further lithiation, to an extrusion of In atoms. The bonding changes from covalent for InSb to ionic in nature for Li₃Sb.

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