First-principle calculations on Li$_2$CuSb: A novel material for lithium-ion batteries

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Abstract
We investigate the Li$_2$CuSb full-Heusler alloy using the first-principles electronic structure calculations and propose the electrochemical lithiation in this alloy. Band structure calculations suggest the presence of metallic nature in this alloy contrary to half-metallic nature as predicted for most of the members of the full-Heusler alloy family. This alloy is found to be a promising anode material for high-capacity rechargeable batteries based on lithium-ion. We found a removal voltage of $\approx$ 2.48 V for lithium ions in the Li$_2$CuSb/Cu cell, which is in good agreement with the experimentally obtained result for a similar kind of material Cu$_3$Sb. During charge and discharge cycles of the Li$_2$CuSb/Cu cell, the formation of a non-stoichiometric compound (Li$_{2-y}$Cu$_{1+y}$Sb) having a similar structure as Li$_2$CuSb suggests a better performance as well as stability of this cell.

KEYWORDS
electrochemical properties, Heusler alloys

1 | INTRODUCTION

Rapidly growing demand, ever-increasing power costs, limited natural sources, environmental pollution, global warming, etc. are some of the global issues, on which almost every country is pumping in a huge amount of funding for research and development. Apart from energy generation, its storage and harnessing is also an equally important issue, and to fulfill the quest of a modern society filled with numerous kinds of gadgets and devices, a variety of novel materials are being explored for various applications such as rechargeable batteries. Various researchers around the globe are working very hard to design and develop low-cost new materials for compact, flexible rechargeable batteries. For the sake of better air quality in the cities and to lower the dependency on fossil fuels, the demand for electric vehicles is continuously increasing. The development of new materials will definitely open the possibility of more durability and higher capacity of batteries.

Many graphite-based materials have been extensively investigated and used as anode for lithium-based batteries, but the irreversible capacity loss due to electrolyte decomposition and structural change prohibits their applications. Several other types of compounds and composites based on tin and silicon have been extensively studied. The utilization of nanomaterials such as nanoparticles and nanowires to minimize the volume expansion has also been tried. During the lithiation process, the usage of transition metal oxides as an anode has also shown better cycling stability. Another versatile material, known as Heusler alloys, is mostly investigated for spintronics, thermoelectrics, catalysis, and many more interesting areas but very few people have tried to explore these alloys as a potential electrode material for lithium ion-based batteries. The better stability, robustness, sustainability, and a high value of theoretical gravimetric (specific) capacity make these materials a promising candidate for battery applications.
Heusler alloys are classified in mainly two categories: Half-Heusler alloys (XYZ, 1:1:1) and full-Heusler alloys (X₂YZ, 2:1:1), where the atoms X and Y are the transition metals, while Z is either a semiconductor or a non-magnetic metal and so far more than 1600 members in Heusler alloys family have been investigated. Apart from these, inverse Heusler alloys and quarternary Heusler alloys (XX'YZ) are also well explored. The unit cell consists of four interpenetrating \textit{fcc} sublattices, where the Wyckoff positions of the atoms are given by X: 4\textit{a} (0,0,0) & 4\textit{b} (0.5,0.5,0.5), Y: 4\textit{c} (0.25,0.25,0.25), and Z: 4\textit{d} (0.75,0.75,0.75). The absence of one atom from the X-site will create semi- or half-Heusler alloys.

Co₂MnSi Heusler alloy is one of the most investigated materials in the field of the spintronics industry and the same has also been investigated for lithium batteries as an anode material.\textsuperscript{30,31} In another alloy from this family, a discharge capacity of 220 mAh g\textsuperscript{-1} during the first charge cycle has been demonstrated through the formation of the lithiated Li₂CoSb phase in the Heusler alloys CoMnSb.\textsuperscript{32} Modern techniques such as machine learning are also being carried out in Heusler alloys to predict new materials with desired properties.\textsuperscript{33,34} On the other hand, very few theoretical investigations have been reported on Heusler alloys in order to make use of them as an electrode for high-capacity rechargeable batteries.\textsuperscript{35}

In this study, we report first-principle calculations on Li-based full-Heusler alloy Li₂CuSb (LCS) and investigate the bandstructure as well as density of states (DOS) for the optimized unit cell, and further propose the lithiation/delithiation processes in LCS/Cu electrochemical cell. A systematic study of the electronic properties of these alloys has already proven useful for various applications.

\section{Computational detail}

First principle calculations were performed on full-Heusler alloy LCS using two different codes for better structure optimization. We have used Green's function formalism-based full potential SPRKKR method for structural optimization.\textsuperscript{36} Various self-consistent calculations for different potentials have been carried out for a \textit{k}-grid of 22 × 22 × 22 and 30 energy points on the complex energy path. An initial value of lattice parameter of 6.28 Å was used. These calculations were carried out on LCS with \textit{fcc} structure (space group: 225, \textit{Fm\textbar3m}) where Li atoms are at (0.25,0.25,0.25) and (0.75, 0.75, 0.75); Cu atoms at (0, 0, 0), and Sb atoms at (0.50,0.50,0.50) atomic positions. For self-consistent calculations (SCF), the energy convergence criterion was set to be at 10⁻⁵ Ry.

\section{Results and Discussion}

First, SCF calculations have been performed on full-Heusler alloy (LCS) with a lattice parameter of 6.28 Å. After attaining the convergence criterion, volume optimization is done to obtain an optimized lattice parameter. For these calculations, the isotropic strain has been applied which maintains the unit cell geometry, and the formula unit cell volume has been varied in the range of ±10%. To estimate the actual volume per formula unit, total unit cell volume has been divided by 4. Figure 1 shows the variation of total energy (in Ry) with unit cell volume. The Murnaghan equation of state is used to obtain energy minimum and a minimum in unit cell volume is found to be at 432.47 au\textsuperscript{3} (au = atomic unit) and the corresponding equilibrium lattice parameter is 6.352 Å. After this, all further calculations have been done using this equilibrium lattice parameter.

First, to get the information about chemical bonding between different atoms, we have calculated the atom orbital projected local density of states (PDOS) and total density of states for LCS. Figures 2 to 5 show the total DOS as calculated for \textit{L21} ordered LCS Heusler alloy, and PDOS for Cu, Sb, and Li atoms, respectively. The total DOS is dominated by the PDOS of Cu-d and Sb-s states, wherever p states of the Li have very minimal contribution. Hence, the d orbitals of Cu and Sb atoms are strongly hybridized as compared with other atomic orbitals. To have a better idea about DOSs and PDOSs, the Y-axis has been zoomed in. These DOSs are extended from −4.0 eV to the Fermi energy (\(\varepsilon_F\)) and corresponding contributions are 37.4 electrons/eV for Cu-d, 0.18 electrons/eV for Cu-p states, 0.16 electrons/eV for Cu-s, 0.15...
0.94 electrons/eV for Sb-\(d\), 2.55 electrons/eV for Sb-\(s\), 0.14 electrons/eV for Li-\(p\), and 0.04 electrons/eV for Li-\(s\). This observation suggests that some of the electrons are transferred to the valence band and contribute to a weak covalent interaction between the same type of atoms.

Figure 6 shows the band structure plot for LCS Heusler alloy. A clear cross-over of a band (marked with black circles) suggests the metallic nature. The major occurrence of these bands near \(\epsilon_F\) results in the increased bandwidth which further pushes the conduction and valence bands towards lower and higher energies, respectively with respect to \(\epsilon_F\). It is also found that most of the hybridization between Sb-\(s\) and Cu-\(s/p\) states is occurring around energy ranging from \(-10.0\) to \(-5.0\) eV. On the other hand, the \(s\), \(p\), and \(d\) orbitals of Cu hybridize with \(p\) and \(d\) orbitals of Sb around the \(-5.0\) eV energy range. The bands corresponding to Li-\(s\) and Li-\(p\) states are found to be very broad. All of these strong electronic
correlations suggest the strong hybridization in this lithiated Heusler alloy.

In order to understand the mechanism for the lithiation/delithiation processes and electrochemical properties of this proposed LCS Heusler alloy, one of the possible interaction reactions can be written as:

\[
\text{Li}_2\text{CuSb} + \text{Cu} \rightarrow \text{Cu}_2\text{Sb} + 2\text{Li}^+ + 2\text{e}^-.
\]

(1)

Here, from the above reaction, we can see that there are two electrons that are involved in the LCS/Cu electrochemical cell process and a homogeneous insertion and extrusion of Cu and Li, respectively can occur. Another possibility could be the formation of Li$_3$Sb with a transfer of a single electron (for LCS/Li cell). In general, the above reaction can be written as:

\[
\text{Li}_2\text{CuSb} + x\text{Cu} \rightarrow \text{Li}_{2-x}\text{Cu}_{1+x}\text{Sb} + y\text{Li},
\]

(2)

with \(0 < x, y \leq 1\). From the total energy differences between reactants and products, we can get information about the average lithium removal voltage for the former case.

\[
V = \frac{1}{2F} \left[ \frac{E_{\text{total}}(\text{Li}_2\text{CuSb}) + E_{\text{total}}(\text{Cu})}{-E_{\text{total}}(\text{Cu}_2\text{Sb}) - 2E_{\text{total}}(\text{Li}^+)} \right]
\]

Here, \(E_{\text{total}}\) represents the total energy per formula unit, \(z\) is the electronic charge that is transported by lithium in the electrode, and \(F\) is the Faraday constant \((\approx 96485 \text{ A} \cdot \text{s/mol})\). By substituting all the required energies, we get a voltage of \(\approx 2.48 \text{ V}\) for the removal of lithium in Li$_2$CuSb/Cu, which is pretty close to the previously experimentally obtained value of 3.0 V for a similar kind of material Cu$_3$Sb.\(^3\) During the discharge cycle, the lattice volume can contract without any abrupt changes and we propose the following chemical reactions via which the insertion and removal of Li atoms in this electrochemical cell can occur by a solid-state solution:

\[
\text{Li}_2\text{CuSb} \rightarrow x\text{Li} + \text{Li}_{2-x}\text{CuSb}, \quad (3a)
\]

\[
\text{Li}_{2-x}\text{CuSb} + x\text{Li} \rightarrow \text{Li}_2\text{CuSb}. \quad (3b)
\]

Here, the first Reaction (3a) is for the first discharge while the second one (3b) is for the second charge. Both the charge and discharge cycle are accompanied by the formation of Lithium-Copper-Antimony alloy in the same crystal structure as for LCS. The stability of this intermediate The theoretical specific gravimetric capacity for LCS is \(\approx 269 \text{ mAh/g}\), so we can expect a high delivered rechargeable capacity of around 90% by considering a good utilization of this robust and dense alloy as an electrode. Based on the above proposal, we can expect some experimental work on this alloy could come up which will definitely trigger Heusler alloys to be used in this direction.

4 CONCLUSIONS

In this study, full Heusler alloy Li$_2$CuSb has been investigated using density functional theory and by applying the Murnaghan equation, unit cell volume is optimized. We have predicted that the Li$_2$CuSb full-Heusler should be a promising candidate for the electrode material to be used in high-capacity rechargeable lithium-ion batteries. The prediction of lithium removal voltage of \(\approx 2.48 \text{ V}\) in Li$_2$CuSb/Cu cell, is in good agreement with the experimental results of a similar kind of Cu$_3$Sb cell. Similar structural relationships with LCS and Lithium-Copper-Antimony (formed during charging and discharging cycle reactions) alloys, provide better stability for LCS/Cu cells. Hence, this alloy may be a possible candidate for its applications in the field of lithium-based batteries, but more investigation in the experimental direction is required.

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CONFLICT OF INTEREST

The authors declare no conflict of interests.

DATA AVAILABILITY STATEMENT

The data that support the findings of this study are available from the corresponding author upon reasonable request.

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