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# Electronic Structure of LiSi

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## ABSTRACT

Silicon is of special interest in lithium-ion batteries (LIBs) since it has large theoretical specific capacity or volumetric capacity. The crystal structure, charge distribution and density of states of LiSi as the Li-poorest side compound at the start of Li intercalation mechanism for Si anode in LIBs has been studied by using Density Functional Theory calculations. The triangular pyramids are formed by four Li atoms. Compared with the charge density of crystalline Si, the Si-Si covalent bonds in LiSi become weak due to Li intercalation. On the other hand, the electrons around the Li atoms in LiSi increase compared with metallic Li. The Li atoms in LiSi have negative charge of 0.830~0.843 compared with metallic Li. These electrons, which are transferred from  $p$  electrons in the Si atoms, are mainly made of  $p$  electrons of the Li atoms. When considering the lithium intercalation reaction from crystalline Si to LiSi, the average intercalation voltage is 0.4053 V.

## I. INTRODUCTION

Lithium-Ion Batteries (LIBs) are the most widely used secondary batteries due to higher energy density, higher operating voltages, and lower self-discharge [1,2]. Graphite has been commonly used as the anode material for LIBs by virtue of its low price, low and flat working voltage, and good cyclability. However, its theoretical specific capacity is limited to 372 mAh/g or volumetric capacity of 840 Ah/L[1]. Alternative anode materials with higher capacity are needed to increase the specific energy of LIBs.

Silicon is of special interest since it has large theoretical specific capacity of 4008mAh/g-Si (9339 Ah/L), which corresponds to a fully lithiated state of  $\text{Li}_{21}\text{Si}_5$  alloy, more than tenfold greater than that of graphite[3,4]. Due to these attributes, a great deal of attention has been given to using Si as a LIB anode material. However, crucial hurdles must still be overcome before this material can be used in commercial LIBs. The alloying process of Li with Si was found to be less reversible at room temperature[5-7]. During further cycling, rapid capacity fade was observed[8]. These reasons are commonly believed to be due to the big volume change during lithium intercalation/deintercalation,

which inevitably causes great stress in Si lattice and thus leads to cracking and crumbling of the Si particle. As a result, some of the particles may lose electric contact with the electrode, and capacity is lost.

During Li intercalation into Si in the first cycle, the voltage initially dropped quickly to about 0.2V versus Li/Li<sup>+</sup>, and then a slow decrease took place as seen in the long potential plateau. It is considered that this plateau is due to formation of Li–Si alloys. It is well known that the Li–Si phase diagram offers a rich variety of solid crystalline compounds[9]. Crystalline compounds exist with the compositions Li<sub>21</sub>Si<sub>5</sub>[10] which is generally called Li<sub>22</sub>Si<sub>5</sub>, Li<sub>13</sub>Si<sub>4</sub>[11], Li<sub>14</sub>Si<sub>6</sub>[12], Li<sub>12</sub>Si<sub>7</sub>[13,14], and LiSi[15,16]. To take advantage of the capacity available from Si and to overcome above problems, it is necessary to study Li–Si alloys from the perspective of the electronic structure in detail.

In this paper, we investigate LiSi as the Li-poorest side compound at the start of Li intercalation mechanism. We present the crystal structure, charge density distribution, and density of states (DOS) of LiSi by using density functional theory (DFT).

Next we calculate the average intercalation voltage. Recently, the average voltages of some metal oxides for LIB using the DFT calculations and basic thermodynamics are predicted[17,18]. The average intercalation voltage is derived from integrating the chemical potential difference in the anode and cathode, and related with the Gibbs free energy obtained by DFT calculations, that is, the Nernst equation. This voltage represents the equilibrium voltage (no load) and does not account for resistivity effects or over-potentials when current is drawn. In evaluation of the structures of intermediates during the electrochemical reaction, it is important to estimate this voltage since it approximately expresses the open circuit voltage (OCV) when a cathode is partially lithiated.

Assuming that a cathode is Li<sub>x</sub>Si and an anode is metallic Li, the lithium intercalation reaction during the discharge is expressed by



where  $y - x$  is the charge on the lithium ion in the electrolyte ( $y > x$ ).

By applying the method in Ref. 17 and 18 to the reaction (1), the average intercalation voltage,  $\bar{V}$  is given by

$$\bar{V} = -\frac{\Delta G_r}{(y - x)F} \quad (2)$$

where  $F$  is Faraday's constant and  $\Delta G_r$  is the Gibbs free energy change in the reaction (1).

Equation (2) allows one to compute the average voltage between Li<sub>x</sub>Si and Li<sub>y</sub>Si. Calculations can be significantly simplified by further approximating  $\Delta G_r = \Delta E_r + P\Delta V_r - T\Delta S_r$  by the change in internal energy ( $\Delta E_r$ ) at 0 K. The term  $P\Delta V_r$  is of the order of 10<sup>-5</sup> electron volts, whereas the term  $T\Delta S_r$  is of the order of the thermal energy[17,18]. Above approximation is good since  $\Delta E_r$  is of the order of 0.1 eV per molecule for Si materials.

## II. COMPUTATIONAL DETAILS

We used DFT calculations within the generalized gradient approximation (GGA) for the exchange-correlation functional using ultrasoft pseudopotentials[19,20] as implemented in the Vienna Ab Initio Simulation Package (VASP)[21-24]. The Perdew-Burke-Ernzerhof (PBE) functional[25,26] has been adopted for the GGA. The full-potential for the Li atom was used. An energy cutoff of 271.6 eV was used to expand the plane wave basis. The 16 Li atoms and 16 Si atoms are ordered in a unit cell for LiSi in consideration in the space group of LiSi,  $I4_1/a$ .

An  $11 \times 11 \times 11$  k-point mesh was used for calculations of LiSi and crystalline Si and a  $27 \times 27 \times 27$  k-point mesh was used for calculations of metallic Li. All structure relaxations are performed by conjugate-gradient (CG)[27,28] optimization for atomic coordinates to minimize the total energy. All the calculations performed here were non-spinpolarized.

## III. RESULTS AND DISCUSSIONS

We start our discussion by analyzing the structures of LiSi. The crystalline structure of LiSi is illustrated in FIG. 1. The Si atoms form a three dimensional network, and each Si atom is connected with three Si atoms by the Si-Si bond lengths of 2.42Å and 2.50Å. The triangular pyramids are formed by four Li-Li bonds of 2.94Å and two Li-Li bonds of 2.95Å. All of vertexes of the triangular pyramids are connected with vertexes of other four triangular pyramids by the Li-Li bonds of 2.69Å. Table 1 gives lattice constants  $a$  and  $c$ , volumes  $V$ , and fractional coordinates of LiSi. The “Calc” and “Expt” lines give the calculated parameters in this work and the experimental parameters determined by X-Ray Diffraction (XRD), respectively [15,16]. The calculated parameters are in good agreement with the experimental results. Table 2 shows interatomic distances and angles of LiSi. The “Calc” and “Expt” columns are of the same meaning as Table. 1. The interatomic distances and bond angles calculated are also in good agreement with the experimental results[17,18]. The shortest Li-Li bond length, the second shortest, and the third shortest are shorter than the calculated Li-Li bond length of 2.97Å in metallic Li. The formation of Li atoms into triangular pyramids within the Si cavities from their previous bcc structure in metallic Li has somehow shortened the Li-Li bonds in LiSi. On the other hand, the Si-Si bonds are longer than the calculated Si-Si bond length of 2.37Å in crystalline Si which suggests stretching of Si-Si bond upon Li intercalation into Si. This can be attributed to the cross linking of sheets of silicon atoms in LiSi [15].

Next, we calculate the Wigner Seitz radii of metallic Li and crystalline Si to estimate the ionic charges of Li and Si in LiSi. The Li atom in metallic Li should have 3 electrons ( $1s^2 2s^1$ ) within the spheres with the Wigner Seitz radius. Similarly, the Si atom in crystalline Si should have 4 electrons ( $3s^2 3p^2$ ) within the spheres. The Wigner Seitz radii is 1.814Å for metallic Li and 1.5765Å for

crystalline Si. Table 3 shows the numbers of electrons of Li in metallic Li, Si in crystalline Si, and Li and Si in LiSi. The number of electrons within the Li atom region was estimated as  $3.830 \sim 3.843$  electrons within the Wigner Seitz radius of  $1.814 \text{ \AA}$ . Therefore, we think that the Li atom in LiSi is an anion with an excess charge of  $0.830 \sim 0.843$ . Similarly, the number of electrons within the Si atom region was estimated as  $3.840 \sim 3.846$  electrons within the Wigner Seitz radius of  $1.5765 \text{ \AA}$ . Compared with the Li atom in LiSi, the Si atom is very weakly ionized. The ranges of the number of electrons of LiSi are due to the maximum and minimum electrons in all of Li atoms and Si atoms. There is no obvious change in  $s$  electrons of the Li atoms between metallic Li and LiSi. Similarly, there is no change in  $s$  electrons of the Si atoms between crystalline Si and LiSi. Compared with the numbers of electrons in the Li atoms of metallic Li and LiSi, increase of  $p$  electrons mainly contributes formation of Li anions in LiSi. In contrast, compared with the numbers of electrons in the Si atoms of crystalline Si and LiSi, decrease of  $p$  electrons mainly contributes decrease of electrons in Si. Both of Li and Si in LiSi contain slightly  $d$  electrons. The negatively charged Li atom also appeared from the DFT calculations of  $\text{Li}_6\text{Si}_5$ , which is one of subunits in crystalline  $\text{Li}_{12}\text{Si}_7$ , where the Li atom has an excess charge of 0.9 electrons[29]. Compared with the Si anodes and the graphite anodes in LIBs, the formation of Li anion in LiSi contrasts starkly with the DFT calculation results that the Li atom in the graphene loose 0.76 electrons[30].

The charge density distribution of metallic Li and the triangular pyramid of four Li atoms in LiSi are shown in Table 4. The first column starting from left is for metallic Li. The second column is for the triangular pyramid of four Li atoms in LiSi. The figures in the second line from the top indicate the body-centered cubic lattice of metallic Li and the triangular pyramids of four Li atoms. The symbols,  $a$ ,  $b$ ,  $c$ ,  $a_1$ ,  $b_1$ ,  $c_1$ , and  $d_1$  are locations of the Li atoms, and  $e_1$  is a location of the Si atom(See FIG. 1.) . Note that the triangles of  $b_1c_1d_1$ ,  $a_1b_1c_1$ ,  $a_1d_1c_1$ , and  $b_1a_1d_1$  are the congruence relations. The shaded portion in each figure indicates the plane to depict the charge density map. The third and fourth lines from the top indicate the ranges and intervals respectively. The maps in the fifth line from the top indicate the charge density distributions corresponding to the planes in the second line. First, we observe the charge density map of metallic Li. The electrons in metallic Li are mainly concentrated around the Li atom as characterized by its  $s$  orbital. Therefore, the charge density at the midpoint of the Li-Li bond is  $0.053 \text{ electrons/\AA}^3$ . We subsequently examine the charge density map of the triangular pyramid of four Li atoms in LiSi. The charge densities at the midpoints of three Li-Li bonds ( $b_1c_1$ ,  $c_1d_1$ , and  $d_1b_1$ ) are almost the same and higher than that for the Li-Li bond in metallic Li but  $0.074 \text{ electrons/\AA}^3$  when seeing the charge density map on plane formed by three Li atoms (triangle of  $b_1c_1d_1$ ). This increase of the charge density at the midpoint of the Li-Li bond supports the formation of the Li anions in LiSi. The charge density at the center of gravity of the triangular pyramid of four Li atoms is  $0.053 \text{ electrons/\AA}^3$ , and it is less than the minimum charge density on plane formed by three Li atoms,  $0.066 \text{ electrons/\AA}^3$ .

The charge density distribution of crystalline Si and the Si-Si bonds in LiSi are shown in Table 5. The first column starting from left is for crystalline Si, and the second column is for the Si-Si bonds in LiSi. The figures in the second line from the top indicate the diamond structure of crystalline Si and the Si-Si bonds in LiSi. The symbols, d, e, f, f<sub>1</sub>, and g<sub>1</sub> are locations of the Si atoms (See FIG. 1.). The other symbols are of the same meaning as Table 4. The view of figures of Table 5 are the same as Table 4. The charge density in crystalline Si is the highest at the bonding midpoints to form typical covalent bonds, and its value is 0.56 electrons/Å<sup>3</sup>. On the other hand, the maximum charge densities of the Si-Si bonds in LiSi are split into two, 0.47 electrons/Å<sup>3</sup> for the e<sub>1</sub>-f<sub>1</sub> bond and 0.49 electrons/Å<sup>3</sup> for the e<sub>1</sub>-g<sub>1</sub> bond. Hence, the charge densities at the bonding midpoints, where they are not maximum, are 0.43 electrons/Å<sup>3</sup> for the e<sub>1</sub>-f<sub>1</sub> bond and 0.47 electrons/Å<sup>3</sup> for the e<sub>1</sub>-g<sub>1</sub> bond. We think that two tops of charge density between the Si-Si bonds and the decrease of the charge densities at the midpoints of the Si-Si bonds in LiSi compared with crystalline Si are due to stretching of the Si-Si bonds upon Li intercalation into crystalline Si cavities.

The charge density distribution of the Li-Si bonds in LiSi is shown in Table 6. The view of the figures and the symbols of Table 6 are the same as Table 4. The two charge density distributions of the Li-Si bonds are shown because triangles of b<sub>1</sub>c<sub>1</sub>e<sub>1</sub>, c<sub>1</sub>d<sub>1</sub>e<sub>1</sub>, and d<sub>1</sub>b<sub>1</sub>e<sub>1</sub> are not the congruence relations. One is for the triangle of b<sub>1</sub>c<sub>1</sub>e<sub>1</sub>, and another is for d<sub>1</sub>b<sub>1</sub>e<sub>1</sub>. The charge densities are concentrated around the Si atoms when seeing the Li-Si bonds. Electrons are mainly located very close to the Si atoms due to electronegativity. The charge densities at the bonding midpoints of the Li-Si bonds are 0.27 electrons/Å<sup>3</sup> compared to 0.053/Å<sup>3</sup> in Li-Li bond in metallic Li. From the viewpoint of the Li atom, the Si atom-derived electrons come in proximity to the Li atoms. We think that these electrons are attributed to the formation of the Li anions.

The total DOS curve for LiSi is presented in FIG. 2. The energy scale is relative to the Fermi level ( $E_F$ ). Experiments have shown that LiSi has a narrow band gap of 0.057 eV[16]. The band gap of LiSi did not exist in the calculated total DOS. Discrepancies like these are not uncommon in DFT-based calculation as it is well known that it generally tends to underestimate the band gap. Figure 3 shows the element-partial DOS curve for LiSi and its decomposition into orbital momentum contribution in the top panel. The top panel in FIG. 3 is the DOS curve for Li, and the bottom is the DOS curve for Si. The element partial total DOS, its *s* component, and its *p* component of each element are depicted in full line, light line, and dashed line respectively. The energy scale is relative to  $E_F$ . The *d*-orbital momentum contributions in both panels are not shown since they are very small. It is found that both of Li and Si have no band gaps. For Li, the states are mainly made of *p* character from  $E_F$  to -3 eV, and a considerable mixing of *s* and *p* occurs from -3eV to -12 eV. On the other hand, for Si, the states are mainly made of *p* character from  $E_F$  to -5 eV, and intensity of *s* character reverses that of *p* character from -5 eV to -12 eV. We think that *p* electrons in the Si atoms transfer to *p* states in the Li atoms around below  $E_F$ .

Next, we calculate the average intercalation voltage. When considering the lithium intercalation reaction from crystalline Si to LiSi, we obtain the average intercalation voltage of 0.4053 V from the change in internal energies of metallic Li, crystalline Si, and LiSi by using Eq. (2).

C. J. Wen *et al.* obtained the equilibrium voltage of 0.332 V relative to pure liquid Li at 415°C by use of the coulometric titration technique on the assumption of coexistence of crystalline Si and  $\text{Li}_{12}\text{Si}_7$ [31]. On the other hand, P. Limthongkul *et al.* obtained the equilibrium voltage of 0.18 V relative to metallic Li at room temperature by use of the electrochemical test[32]. They advocated that Si sample lithiated to  $\text{Li}_{1.34}\text{Si}$  is not co-existence of the equilibrium crystalline phases Si and  $\text{Li}_{12}\text{Si}_7$ , the co-existence of an amorphous phase with crystalline Si by using X-ray diffraction and high resolution electron microscopy.

We investigated LiSi as earliest alloy during Li intercalation reaction, which is the Li-poorest alloy known experimentally. The calculated average intercalation voltage is close to the equilibrium voltage of 0.332 V. Therefore, we think that the intermediate during Li intercalation reaction in crystalline Si is not so much crystalline alloy like LiSi as amorphous alloy.

#### IV. CONCLUSIONS

The crystal structure, charge distribution and DOS of LiSi as the Li-poorest side compound at the start of Li intercalation mechanism for Si anode in LIBs has been studied by using DFT calculations. The crystal structure is in agreement with the experimental results. The triangular pyramids are formed by four Li atoms. Compared with the charge density of crystalline Si, the Si-Si covalent bonds in LiSi become weak due to Li intercalation. On the other hand, the electrons around the Li atoms in LiSi increase compared with metallic Li. The Li atoms in LiSi have negative charge of 0.830~0.843 compared with metallic Li. These electrons, which are transferred from  $p$  electrons in the Si atoms, are mainly made of  $p$  electrons of the Li atoms. We obtain the average intercalation voltage of 0.4053 V for the lithium intercalation reaction from crystalline Si to LiSi.

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## Caption

Figure 1 Crystal structure for LiSi. The white spheres are the Si atoms, and the gray spheres are the Li atoms. The top figure is full structure and the bottom is the structure of Li atoms and three Si atoms only. The Si atoms form a three dimensional network, and each Si atom is connected with three Si atoms by the Si-Si bond lengths of 2.42Å and 2.50Å. The triangular pyramid of  $a_1b_1c_1d_1$ , which is formed by four Li atoms, is geometrically identical with other triangular pyramids of  $a_2b_2c_2d_2$ ,  $a_3b_3c_3d_3$ , ..., and  $a_6b_6c_6d_6$ . The triangular pyramids of four Li atoms are formed by four Li-Li bonds of 2.94Å ( $= \overline{a_k b_k} = \overline{b_k c_k} = \overline{c_k d_k} = \overline{d_k a_k}$ ,  $k = 1, 2, 3, \dots, 6$ ) and two Li-Li bonds of 2.95Å ( $= \overline{a_k c_k} = \overline{b_k d_k}$ ,  $k = 1, 2, 3, \dots, 6$ ). All of vertexes of the triangular pyramids are connected with vertexes of other four triangular pyramids by the Li-Li bonds of 2.69 Å ( $= \overline{d_1 b_2} = \overline{d_2 b_3} = \overline{c_1 a_4} = \overline{c_2 a_5} = \overline{c_3 a_6}$ ). View along  $\sim [001]$ .

Figure 2 The total DOS curve for LiSi. The energy scale is relative to the Fermi level.

Figure 3 The element-partial DOS curve for LiSi and its decomposition into orbital momentum contribution in the top panel. The top panel is for Li, and the bottom is for Si. The element partial total DOS, its  $s$  component, and its  $p$  component of each element are depicted in full line, light line, and dashed line respectively. The energy scale is relative to the Fermi level. The  $d$ -orbital momentum contributions in both panels are not shown since they are very small.

Table 1 Lattice constants  $a$  and  $c$ , volumes  $V$ , and fractional coordinates of LiSi. The space group is  $I4_1/a$ .

\*It would appear that the fractional  $x$ -coordinate of Si, 0.0111(4), is an error of digit.

Table 2 Interatomic distances and angles of LiSi.

Table 3 Numbers of electrons of Li and Si in metallic Si, crystalline Si, and LiSi.

Table 4 The first column starting from left is for metallic Li. The second column is for the triangular pyramid of four Li atoms in LiSi. The figures in the second line from the top indicate the body-centered cubic lattice of metallic Li and the triangular pyramids of four Li atoms. The symbol,  $a$ ,  $b$ ,  $c$ ,  $a_1$ ,  $b_1$ ,  $c_1$ , and  $d_1$  are locations of the Li atoms, and  $e_1$  is a location of the Si atom(See FIG. 1.) . Note that the triangles of  $b_1c_1d_1$ ,  $a_1b_1c_1$ ,  $a_1d_1c_1$ , and  $b_1a_1d_1$  are the congruence relations. The shaded portion in each figure indicates the plane to depict the charge density map. The third and fourth lines from the top indicate the ranges and intervals respectively. The maps in the fifth line from the top

indicate the charge density distributions corresponding to the planes in the second line.

Table 5 The charge density distribution of crystalline Si and the Si-Si bonds in LiSi. The first column starting from left is for crystalline Si, and the second column is for the Si-Si bonds in LiSi. The figures in the second line from the top indicate the diamond structure of crystalline Si and the Si-Si bonds in LiSi. The symbols, d, e, f, f<sub>1</sub>, and g<sub>1</sub> are locations of the Si atoms(See FIG. 1.). The other symbols are the same meaning as Table 4. The view of the figures of this Table is the same as Table 4.

Table 6 The charge density distribution of the Li-Si bonds in LiSi is shown in Table 6. The view of the figures and the symbols of this Table are the same as Table 4.