Lithium insertion in Si electrodes studied by first principles method

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Abstract. Si has been considered as one of the most potential new-generation anode materials for high-capacity lithium-ion batteries. However, the lithiation and delithiation of lithium ions during the charge-discharge processes of the Si electrode would give rise to almost four-fold volume expansion, causing structural changes and cracks of the conductive network, limiting the application of Si-based anode material. In this paper, the lithium ions inserting into Si material at various positions and at different doping concentrations of lithium ions was studied by first-principles method. The stability of different insertion sites, the structural changes, band structures and density of States after Li insertion were analyzed. It has been found that the lithium ions doping is an interstitial doping rather than a substitutional one and the tetrahedral center (Td) site is the most stable insertion position. From the band structure analysis, it can be seen that the Si material with the insertion of lithium ions becomes metal-like, and as the concentration changes, silicon changes from an indirect gap semiconductor to a direct gap semiconductor. When the concentration reaches 12.5%, the structural expansion rate increases obviously. This work provides a strategy for the improvement of the Si based anode material used in high-capacity lithium-ion batteries.

1. Introduction
Environmental pollution and the decreasing availability of fossil fuels drive the demands for new clean energy and electric vehicles [1-3]. However, the development of electric vehicles is limited by the large-capacity energy storage technology [4]. Lithium-ion batteries are now the most important portable power sources for electronic devices such as cell phones and tablets, as well as electric vehicles.

At present, the commercial anode material widely used in lithium-ion batteries is graphite; however, its specific capacity has reached its physical limits (the theoretical capacity of graphite is 372 mAh/g), which is difficult to be further improved [3]. Si has been considered as the most promising anode materials for high-capacity lithium-ion batteries. Because Si has more than ten times the specific capacity as graphite (4200 mAh/g) [5-6]. Meanwhile, Si is the most common elements in the Earth's crust with a mass content of 26.4%, and has relatively low reactivity with the electrolyte.

However, the application of Si-based anode material is limited by its pulverization during the Li-Si alloying process, in which a four-fold volume expansion could take place, inducing cracks of the conductive network and a rapid degradation of electrochemical reversible capacity. Therefore, the investigation of dynamics of Li ions inserting into covalently bonded Si is critical for the resolution of...
the expansion problems [7-11].

In this paper, the first-principles method was used to investigate the insertion process of Li ions in bulk Si materials. Various doping positions and doping concentrations of Li ions are studied to elucidate the most stable insertion sites and the structure evolution of Li-Si system during Li-Si alloying process at various doping concentrations of Li ions.

2. Simulation methods
The density functional theory (DFT) calculations were carried out using the Vienna *ab initio* simulation package (VASP) in the Mede-A [11-12]. The pseudo-potential plane wave method based on spin-polarization DFT was used to describe the interaction between electrons and ion cores. The exchange correlation was Perdew-Burke-Ernzehof (PBE) functional [13] in generalized gradient approximation (GGA) [14], and the plane wave truncation energy $E_{\text{cut}}$ was taken as 400 eV [15], the structure of internal atomic coordinates and supercell shape was completely relaxed, and the self-consistent precision was set such that each atomic energy converges to $1 \times 10^{-5}$ eV·atom$^{-1}$. The internal stress convergence criterion of the crystal was 0.1 GPa [16]. In the structural optimization of the model, the Gaussian was adopted and the k-point of the first Brillouin zone was $7 \times 7 \times 7$. The bulk Si material structure was optimized firstly, and then Li was doped into the bulk Si material by substitution or interstitial doping, and finally structural relaxations were performed and relevant properties were obtained.

3. Results and discussion

3.1 Structural changes and binding energy analysis
In order to analyze the stability of different insertion sites, the binding energy, $E_b$, for all the
configurations listed above was calculated, which was defined as

\[ E_b = \frac{E_{Si} + n\mu_{Li} - E_{tot} - m\mu_{Si}}{n} \]  

(1)

Where \( E_{Si} \) is energy of bulk Si, \( E_{tot} \) is the total energy of the system, \( \mu_{Li}, \mu_{Si} \) are chemical potentials of Li ions and Si atoms. \( n \) represents the number of inserted Li ions. When \( m \) is 0, it is an interstitial doping; while when \( m \) is larger than 1, it is a substitutional doping. The obtained results for different configurations are shown in Table 1.

Table 1. Binding energies of Li dopant in bulk Si

| Doping form           | Single Atom binding Energy (eV) |
|-----------------------|---------------------------------|
| substitutional doping | -6.347                          |
| Hex site interstitial | 0.980                           |
| Td site interstitial  | 1.572                           |
| 2 Td sites interstitial doping | 1.540                        |
| 4 Td sites interstitial doping | 1.466                        |
| 8 Td sites interstitial doping | 1.360                        |

It is shown in Table 1 that \( E_b \) of the substitutional doping position is negative, which means that the impurity of Li ions at Si lattice site needs to absorb energy, and the system becomes less stable. While \( E_b \) of the interstitial doping results is positive, indicating that the systems become more stable with interstitial Li doping. Therefore, the Li ions doping is an interstitial doping rather than a substitutional one.

Table 2. Structural changes of crystalline Si structure after Li doping

| Cell parameters | Cell parameters | Volume | Expansion ratio |
|-----------------|-----------------|--------|----------------|
|                  | Lengths (Å)     | Angle  |                  |
| Without Li      | \( a=b=c=10.937 \) | \( a=\beta=\gamma=90 \) | 1308.18 | 1.9‰          |
| Td site         | \( a=b=c=10.948 \) | \( a=\beta=\gamma=90.08 \) | 1310.64 | 4.1‰          |
| Hex site        | \( a=b=c=10.946 \) | \( a=\beta=\gamma=90 \) | 1313.55 | 4.5‰          |
| 2 Td sites      | \( a= c=10.963 \) | \( b=10.978 \) |\( a=\beta=\gamma=90 \) | 1314.03 | 8.6‰          |
| 4 Td sites      | \( a= c=10.963 \) | \( b=10.978 \) |\( a=\beta=\gamma=90 \) | 1319.49 | 22.6‰         |
| 8 Td sites      | \( a=b=c=11.019 \) | \( a=\beta=\gamma=90 \) | 1337.75 | 22.6‰         |

For different interstitial insertion sites, \( E_b \) at various Td sites is about 0.59 eV larger than that at the Hex sites, indicating that the Td site is the most stable position compared with the Hex site. The structures of Si lattice with one Li ion inserted at the Td site and the Hex site are illustrated in Figure 2. It is found that when the Li dopant is inserted at the Td position, it has four nearest neighbor Si atoms and six second nearest neighbor Si atoms. After structural relaxation, all adjacent Si atoms around the inserted Li atom move outward, and the closest Si-Si bond lengths (\( L_1 \)) increase to 2.410 Å from 2.368 Å (without Li atom insertion). However, the second nearest Si-Si bond length (\( L_2 \)) does not change obviously. When Li atom is inserted in the Hex position, as shown in Fig. 2(b), it is adjacent to six equivalent Si atoms. The nearest Si-Si bond length has been extended to 2.448 Å, and the second nearest length is 2.370 Å, and all adjacent Si atoms around the inserted Li ion move outward, causing an increase of lattice constant, resulting in structural change and volume expansion. It also causes a change in angular structure.

In our study, the influence of Li ions doping concentrations is studied. As the increase of the number of Li ions inserted at Td site, that is, the doping concentration increases, the nearest Si-Si bond length does not change obviously, however, the second nearest Si-Si bond length increase more apparently about 2.407 Å (the increase ratio is 1.64%). When the doping concentration reached to 12.5%, the volume change trends to increase by 22.6‰.
Figure 2. Illustration of the structure of Si lattice with a Li ion inserted at the Td site (a) and the Hex site (b). The purple ball is the Li ion, the gray balls and bonds are its nearest Si atoms and Si–Si bonds, the yellow balls and bonds are its second nearest Si atoms and Si–Si bonds, and the remaining atoms are other Si atoms in the bulk.

3.2 Electronic structure analysis

Figure 3 shows the local band structure of the original and doped system. The Fermi level $E_F$ is 0 eV. The bulk Si has a band gap of 0.610 eV, which is an indirect bandgap semiconductor. After Li ion insertion, the band curve becomes dense and moves toward the deep energy level, and the conduction band is obviously narrowed. After a single Li ion doping, it is still an indirect bandgap semiconductor. Figure 3 (b) shows the band structure of the system with a Li ion inserted at the Td position. The Fermi level overlaps with the conduction band, and the band gap is 0.708 eV, a little larger than that of bulk Si. The band structure of the system with a Li ion inserted at the Hex position is shown in Figure 3 (c), from which we could see that its band gap value is 0.661 eV, and the Fermi level also overlaps with the conduction band. The energy band structures of the systems with different doping
concentrations are shown in Figure 3 (d), 3 (e) and 3 (f). It can be seen that the overlapping between the Fermi level and the conduction band becomes larger with the increase of. The band gap values are 0.707 eV, 0.667 eV, and 0.651 eV. As the increase of the Li ion doping concentrations, the structure becomes a direct bandgap semiconductor, and the band gap value becomes smaller, it means that the electron transition requires less energy, and the conductivity is better. This is due to the fact that the incorporated lithium ions provide more free electronic states.

The density of states (DOS) is an important factor in judging the conductivity. Figure 4 shows the total density of states and the density of the partial states under different doping conditions. 0 eV is the Fermi level. The top window shows the total DOS. And the middle and bottom windows show the PDOS of a Li dopant and its adjacent Si atoms, respectively. A low energy region located near -50 eV is Li 1s orbital, it was not displayed because it has less effects on the Li-Si interaction. It can be seen from Figure 4(a) that in the system, the density of states in the range of [-15, -5] eV is mainly provided by the Si-3s orbit. The density of states at the top of the conduction band in the range of [-5, 0] eV is provided by the Si-3p orbital. At the bottom of the valence band, the density of states is provided by the coupling of Si-3s, Si-3p and Si-3d. Figure 4(b), 4(c) shows the density of states for single-Li-doped system, the shape of DOS is almost the same as that of bulk Si, because the total DOS is mainly derived from Si atoms, and the main lattice hardly changes after Li doping. In particular, Li PDOS contains p and d orbits in a range almost identical to the p and d orbitals of Si atoms, and the p orbitals are larger than the s components. Therefore, it is apparent that the p, d orbital of the Li dopant is caused by the hybridization between the original Li 2s orbital and the Si 3s 3p orbital.

![Figure 4. (a) the DOS of supercell Si. The DOS of the supercell Si with Li occupying the (b) Td and (c) Hex sites. The dashed line here is the position of Fermi energy.](image)

4. Conclusion
In this paper, the first-principles method was used to investigate the insertion process of Li ions at various positions and at different Li doping concentrations in bulk Si materials. The binding energies for all configurations were discussed and the substitutional insertion of a Li ion by replacing one Si lattice site is also investigated. It was found that the Li ions doping is an interstitial doping rather than a substitutional one, the binding energy at Td site is much larger than that at Hex site, that is the Td site is the most stable insertion position. By analyzing the structural changes, band structures and density of states of different configurations, we found that after the Li ion dopant, the Si material with the insertion of Li ion becomes metal-like. However, the Li ion insertion will cause the expansion of the structure, and the Li-2p orbit will appear due to the hybrid of the embedded Li and Si. With the increase of Li doping concentration, the system turns to direct gap semiconductor. When the concentration reaches 12.5%, the expansion rate increases obviously (about 22.6‰).

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