



First-principles Study on Lithium Intercalation of Silicon Anode Materials in Supercapacitor

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The need for the higher specific capacity and relatively lower discharge voltage supercapacitor has become increasingly pressing. Although silicon is widely considered as the anode material, the factors affecting their actual are volume expansion and unstable SEI layer. Herein, it's relatively new to report on the mechanism investigation of crystalline silicon during lithium storage via DFT and first-principles calculation, and calculations are performed to electrochemical lithiation of the perfect crystalline silicon and flawed silicon. In addition, the mechanistic problems including binding energy and average embed voltage and PDOS and charge density and volume change based on geometry and electronic structure were calculated and forecast. Moreover, from the aspects of atomic and electronic structure, this paper aimed at silicon-based anode materials to explore the primary mechanism of lithium intercalation and volume expansion. Indicating that the silicon-based nodes as the ideal candidate for next generation anode materials rely heavily on the thickness of the SEI layer and stable structure, which can effectively inhibit large volume expansion and structural damage, thus to improve the reversible capacity of supercapacitor.

1. Introduction

Electrodes play a key role to electrochemical properties of supercapacitor, and silicon is widely considered as the successor to anode for Li-ion batteries given its highest theoretical capacity among known materials of 3579mAhg⁻¹(Zachary Favors et al., 2015). Silicon as anode materials always attracts the large amount of attention in the academic fields, which is also due to its own characteristics, such as its extremely high theoretical capacity (4200mAhg⁻¹)(Besenhard JO et al., 1997, S. Misra et al., 2012 and K. Kang et al., 2010) and relatively low negative electrochemical potential (Average operating voltage is only 0.4V, lower than 0.5V vs Li/Li⁺)(Huggins RA,1999, T. Nagaura,1990, D. C. Langreth et al.,1997 and R. M. Dreizler et al.,1990). Additionally, silicon has the advantage of abundant storage as a rock-forming element, and is favorable for environmental conservation, furthermore, it has the lower-cost than others. So that, Si-based anode materials are regarded as next generation anode materials, the need for the higher specify capacity and more stable cycling performance has become increasingly pressing, but the reports are almost less.

However, silicon's ability to intercalate large amount of lithium leads to volume expansion, which can make the electrode material undergo structure and the morphology change, thus to pulverize the active material, and arouse capacity attention. Studies have shown that these phenomena should seriously suffer from the bad stability of lithium intercalation and reduce the cycle life of Si-based anode materials. Although, Si nano material can improve the electrode chemical properties. Li et al.(1999) showed that scaling of Si nanostructure can not only control the volume expansion of Si(Wu H. et al., 2012, Ge,M et al., 2012 and 2013), but also improve the electrical conductivity because of the greater specific, in this case, the devices should stores much more than the embedded lithium.

Generally, the excellent electrochemical performance combined with the high degree of stable capacity and cycle, which makes Si-based anode materials an ideal candidate for supercapacitor. Recently, it has been found that the lithium intercalation process possesses a much improved as the anode material for supercapacitor(Ramasahayam et al., 2015,Oh Ilgeun et al., 2015 and Ma, Mingze et al., 2015). Focused on

the material choice, they achieved phased progress in the experiment, however little is known about the lithiation/delithiation process. In the recent 30 years, quantum chemical calculations were carried out into these issues of lithium intercalation. Based on first-principle calculation with density functional theory (DFT), and molecular dynamics, the essential in formation of dramatic volume expansion in Si electrodes can be provided at the atomic level (G. A et al., 2012, M. K. Y. Chan et al., 2012, W. H. Wan et al., 2010 and K. Doll et al., 1999). The most significant function to Si-based anode is that the geometric and electronic structures can be more intuitive calculations, which means that the lithium intercalation behavior in bulk silicon and silicon composite anode materials can be given further guide to design the next generation electrode materials.

It's worth noting that the average potential of electrode materials can give a good prediction (Benedek R et al., 1999, Tang P et al., 2003 and Sigala C et al., 1995), and analysis the primary factors lead to the distortion of Si-based anodes (Ceder G, 2010 and Meng Y S et al., 2009) by first-principles calculation coupled with molecular dynamics, so as to provide the fundamental basic for the design of the next generation electrodes.

So far, the reports of Si-based anode materials in supercapacitor are less than others, and research achievements are relatively relative lack. This paper reviewed the band structure, density of states and energy based on the first-principles and density functional theory, in addition, studied Li-ion diffusion behaviors in different topical Li-Si alloy and calculated the Li migration in vacancy, and electrical structures and lithium storage properties of Si-based anode materials have been calculated by means of PWP (Plane Wave Pseudopotential method), in order to make the precision of calculation and guarantee the accuracy of the calculation results, the results such as lattice constants and band structures are in good agreement with experimental data. Further analyzed the mechanism of silicon and lithium storage to provide theoretical and experimental guidance for the design of Si-based anode materials, which were implemented in the simulation package (CASTEP).

2. Experimental Details

First-principles calculations was performed the electrochemical lithiation and delithiation of the pure silicon and flawed silicon with DFT (Density Functional Theory), the necessary work was to test the convergence of a few important parameters, and to be truncated to point sampling $E_{cut-off}$ (Cut-off Energy) and k-point. The exchange-correlation part was described with GGA (Generalized Gradient Approximation) (Perdew J P et al., 1993) by PW91 (Perdew and Wang) (L. A. Stearns et al., 2003). The Monkhorst-Pack scheme k-point sampling with $6 \times 6 \times 6$ (for unitcell cases) and $2 \times 2 \times 2$ supercell U has been used for the integration of the Brillouin zone. $E_{cut-off}$ for the plane waves was chosen to be 650eV, and the parameter increases gradually from 300eV to 750eV with 50eV step, finally, $E_{cut-off}$ converged to 650eV in Figure 1. The lattice parameters and the atomic position are fully relaxed, and the final forces on all relaxed atoms are less than $10e^{-5}$ eV/atom.

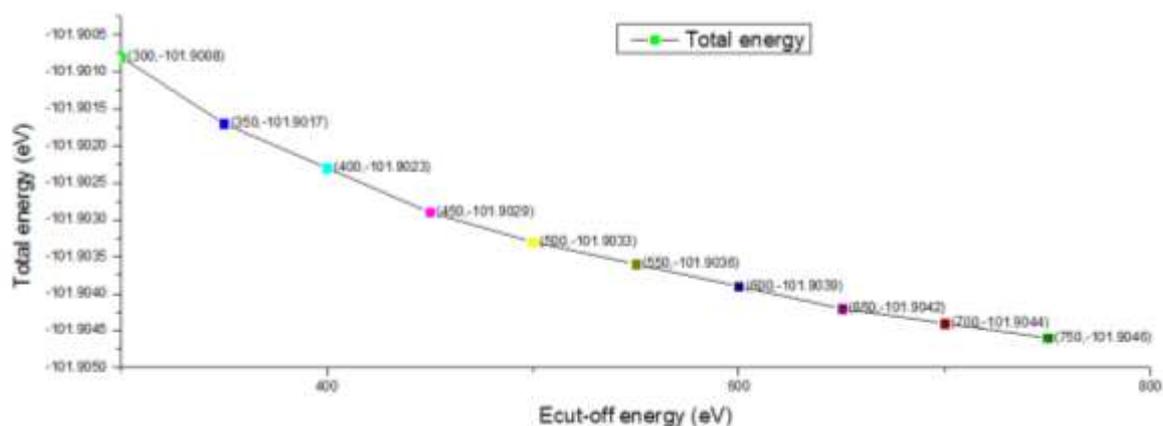


Figure 1: Convergence test of $E_{cut-off}$

3. Results and Discussion

Crystalline silicon the typical structure with diamond, and its space group is the Fd-3M, as shown in Figure 2a, so it can be simplified as two sets of face-centered cubic lattice. One consists of face centered cube silicon and silicon atom at a cube corner, another set of face-centered cubic lattice is be composed of silicon atom in the position of body diagonal, and move them a quarter of the displacement along diagonal direction, then have access to get the crystalline structure, in addition, the silicon atoms can occur orbital hybridization

between 3s and 3p orbital during forming a covalent bonds. The calculation contains eight silicon atoms in the unit cell adopting periodic boundary conditions, and this system is marked as Si_8 , moreover, energy calculation in reciprocal space.

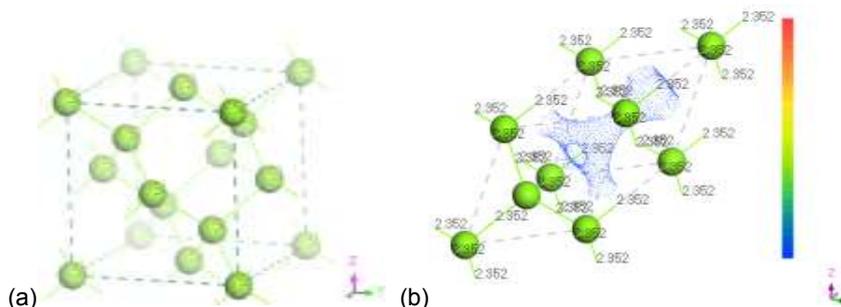


Figure 2: Crystalline structure of silicon (a-typical structure,b-structure optimization)

Crystal geometry optimization results were shown as Figure 2b, it had a stable structure. Namely, the bond length changed from 2.341Å to 2.352Å, and the bond angle remained unchanged, which was useful for lithiation to further study. For above reasons, the supercell structure was optimized, and the calculation results were shown in Table 1.

Table 1: Crystal structure parameters for Si_8

	a(Å)	b(Å)	c(Å)	α	β	γ	Si-Si bond length
Exp(D.M.Toebbens et al.,1974)	5.432	5.432	5.432	90	90	90	2.341
Calculation	5.4307	5.4307	5.4307	90	90	90	2.352

Silicon primitive cell formed energy band structure at the Fermi level as shown in Figure 3, in which the dotted line is the Fermi level position, and occupied orbitals locates below the Fermi level, that is the position of the valence band. Moreover, the space above the horizontal dashed line is the forbidden band which refers to the band gap. In addition, the band gap is 0.622eV according to Figure 3, the results are smaller than the experimental value (about 1.16eV) (P. E. Blochl et al., 1994). The reason for this phenomenon is due to the use of the density functional theory to calculate the band gap underestimated. Although it has also been reported in other literature(Mallia G et al., 2007), but the results are still comparable. While scissors takes 0.4, the band gap of the crystalline silicon near the Fermi level is about 1.132eV, which consistent with experimental values and the energy gap crystal, and it can be seen in a crystal structure of a metal from the total density of states, silicon is a good semiconductor. So it's to say that the selection of pseudopotential and calculation method is appropriate.

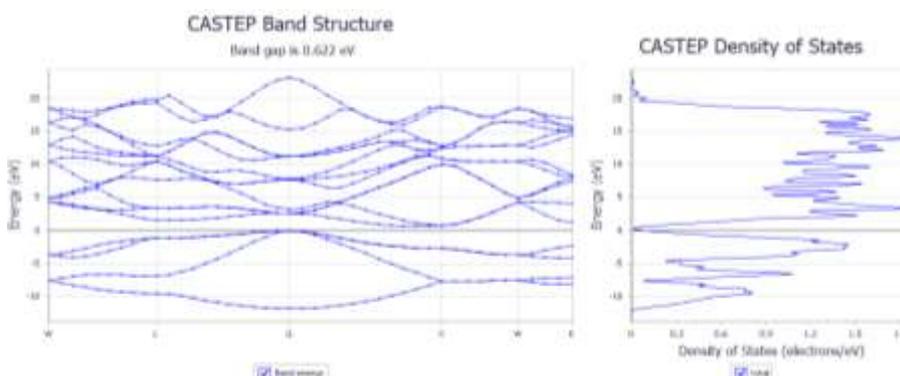


Figure 3: Band structure and density of states of crystalline silicon

The Figure 4 shows the PDOS (Partial Density of States) of crystalline silicon, energy band structure of the Fermi level passes through the valence band, indicating that the material is a conductor(Reshak AH et al., 2011). In terms of total density of states, s and p orbital track can be clearly distinguish from the partial-wave

of crystalline silicon in the valence electrons, and the Figure shows energy distribution area of the s-track is consistent with three energy distribution area of px, py and pz, and the peak position appears in the same position, so s-orbital and p-orbitals of crystalline silicon are hybridized, and sp³ hybridization occurs in the 3s and 3p orbital track.

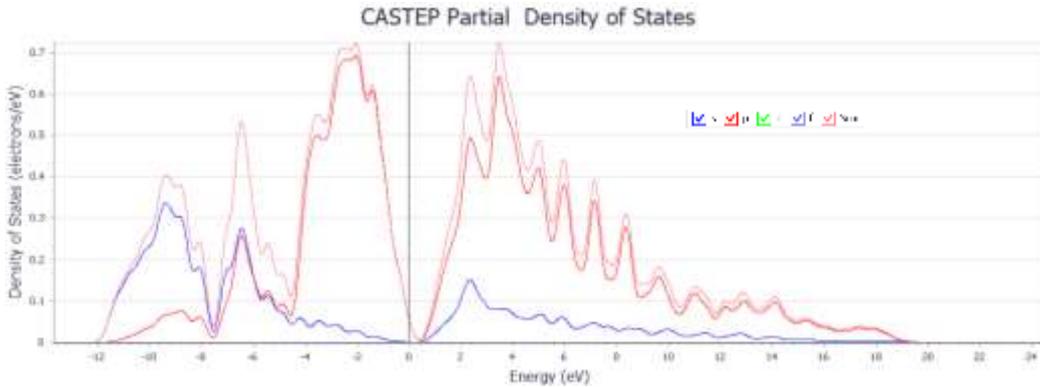


Figure 4: Partial density of states of crystalline silicon

Lithiation is characterized by not directly embedding into iso-crystalline silicon, and the interaction between lithium silicon is rather weak, so Si_xLi_y alloy system is easy to form and up to be concerned as lithium storage materials. Generally, the experiment has become a crystalline silicon lithium storage material, it is precisely because the lithium insertion process. Study: lithiation relies heavily on vacancy early (L.A. Stearns et al., 2003). In contrast to the Si₈ system, lithium was firstly embedded in the vacancy of Si₈Vac structure, namely, to place one lithium at the central location of the unit cell. At present, embed voltage is -1.225eV, the result means that lithium can't be directly embedded into crystal silicon, however, the experiment observed Si₇Li₁ alloy phase. So Si₇Li₁ structure (use one lithium to instead of one silicon at center position of the unit cell, as shown in Figure 5a), and the average embed voltage is -0.094eV. Furthermore, Si₇Li₁ rendered metal according to the PDOS of Figure 5c. It was successfully to observe charges localized in silicon atoms around, and the distribution of charges around the lithium showed a trend of enhanced tendency. Indicating that the interaction between silicon atoms has been weakened, and Si-Li role has been enhanced, as shown in Figure 5a and 5b. It's clear that the defect structure is more beneficial to embed lithium, but the average embedded voltage remains negative along with increasing alternative to lithium.

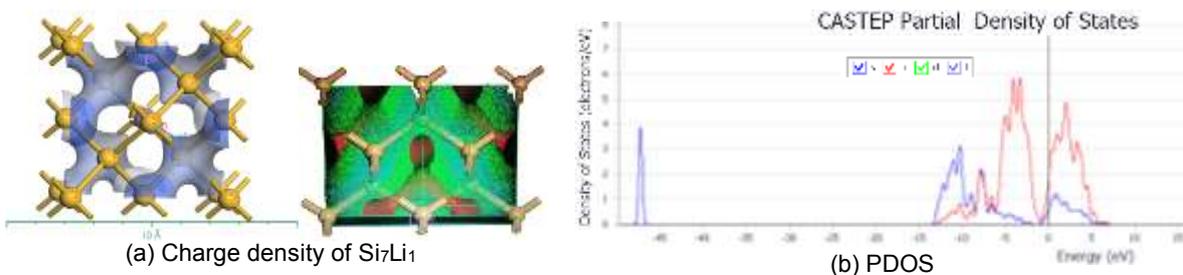


Figure 5: Charge density distribution and partial density of states of Si₇Li₁ structure

In term of PDOS, some charges appear on both the top of the valence band and the bottom of conduction band near Fermi level in Figure 5c, herein bring out metallic conductivity properties. In addition, alloy phase electrons exist a highly localized phenomenon among -13.5-7.0eV, which illustrates the lower orbit interaction within the energy range, corresponding to find the electron density of states composed of s-orbitals at Li near -50eV deep level valence band. To prove the function of defect structure during embedding lithium, the crystal silicon was transformed into 2×2×2 supercell, then to position one Li in the center of the Si₆₄ instead of one Si atom, and marked it as Si₆₃Li₁. It is worth noting that binding energy of lithium and silicon is 3.026eV, and higher than the energy of lithium metal. Additionally, interaction between lithium and silicon has been strengthened because of positive intercalation potential. When the examine replaced Li to form new Si_xLi_y (x+y=64) structure in Figure 6, the study found that the average embedded voltage becomes positive, which attributes the higher binding energy than Li metal, obviously, lithium can be smoothly embedded in crystalline silicon.

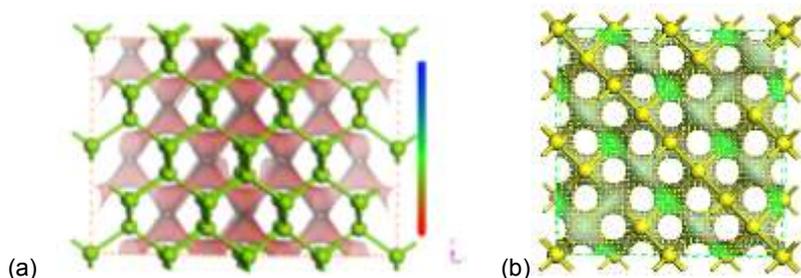


Figure 6: Structure and charge density distribution of lithiation (a- $\text{Si}_{63}\text{Li}_1$, b- $\text{Si}_{56}\text{Li}_8$)

Furthermore, Figure 6 shows that conductive properties of alloy phase increase along with increasing concentrations of lithium, and the charges were mainly distributed in the center of the supercell around Li according to the dept of color, which helps improve conductivity and cycle properties of materials. For comparison, the higher conductivity was accompanied the serious volume expansion in some ways of the change in geometry, and large volume expansion is useless for the negative electrode materials, so far as to generate seriously affecting on the cycle life of the electrode, the problem arises in part from taking electrode powder off. Generally, faced a pair of mutually contradictory constraints factors, researchers need to find a balance or choose the most critical factor to improve the cycle performance of Si-based anode materials.

4. Conclusions

In conclusion, the work has demonstrated the first-principles calculation predict that flawed structure of silicon is useful for lithiation of crystalline silicon as anode materials in supercapacitor, and can make silicon-based anode rather excellent electrochemical performance. Namely, alloy phase electrons exists highly localized phenomenon among -13.5 - 7.0eV due to the lower orbit interaction within the energy range, and the results of DOS identified the following characteristics of electron density of states composed of s-orbitals at Li near -50eV deep level valence band. It is obvious that the flawed structure of silicon is helpful to impose the stringent restrictions on volume expansion and make SEI layer be more stable. What is more, the theoretical calculation indicates that the silicon-based nodes can be as the next generation anode materials under the precondition of improving the reversible capacity of supercapacitor. Obviously, this theoretically explore for lithiation of crystalline silicon as anode materials is can also provide guidance and reference to design new silicon material on the experiments.

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