



# Ab initio and kinetic Monte Carlo simulation study of lithiation in crystalline and amorphous silicon



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## HIGHLIGHTS

- DFT and KMC study of energetics and kinetics of c-Si and a-Si under Li insertion.
- Phase transformation of c-Si to a-Si under Li insertion via Si–Si bond breaking.
- Li diffusion in a-Si predicted by environment dependent KMC method.
- KMC shows larger Li diffusivity in a-Si than c-Si at room temperature.

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## ABSTRACT

Energetics and kinetics of Li insertion into c-Si and a-Si systems are investigated using the density functional (DFT) theory calculations and kinetic Monte Carlo (KMC) simulations. DFT formation energies show the mechanism of phase separation between crystalline silicon and amorphous lithium silicide. Both crystalline and amorphous Si show similar trends in volume expansion and phase transition under lithiation, and kinetics of Li diffusion in bulk silicon (from DFT and KMC) shows a big difference between c-Si and a-Si. The Li migration barrier is 0.6 eV in c-Si, and quickly decreases to 0.4 eV under increasing Li concentration or Si volume expansion. To simulate Li diffusion in amorphous silicon using KMC, we have developed a formulation for environment dependent migration energy barriers of Li in a-Si using a volume dependent function. KMC simulations are performed for Li diffusion in both c-Si and a-Si, and the diffusion coefficient of Li in a-Si is an order of magnitude larger than in c-Si. These studies help to understand mechanisms of lithiation with atomic scale details and elucidate the phase separation between c-Si and lithium silicide.

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## 1. Introduction

The lithiation of silicon has attracted a lot of research interest due to the possible application of nano-structured silicon as a high capacity anode material for Li-ion batteries. [1] Compared to graphite (372 mAh g<sup>-1</sup>), silicon has a large theoretical charge capacity (4200 mAh g<sup>-1</sup>) which is more than 10 times higher than that of graphite. However the lithiation and delithiation characteristics of Si are qualitatively different from those of graphitic

carbon anode. In contrast to intercalation compounds (graphite anode and transition metal oxide cathode materials), Si anode undergoes phase transformation involving Si–Si bond breaking as the Li concentration increases in Li<sub>x</sub>Si. For  $x \geq 1$ , diverse crystalline phases (LiSi, Li<sub>12</sub>Si<sub>7</sub>, Li<sub>7</sub>Si<sub>3</sub>, Li<sub>13</sub>Si<sub>4</sub>, Li<sub>15</sub>Si<sub>4</sub>, Li<sub>22</sub>Si<sub>5</sub>) are known to be thermodynamically stable. However, room temperature lithiation and delithiation studies have shown a crystalline-to-amorphous phase transition that takes place during the first charge cycle of crystalline Si anode. [2–4] Furthermore, the nonconventional phase change characteristics of the lithiation of Si introduces a volume changes up to 400%, an elastic softening, and a phase separation during insertion of Li [5–8].

The lithiation of Si results in substantial atomic structure changes, in contrast to transition metal oxides or graphite electrode materials where Li ion intercalates into existing layers with limited

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structural distortions. Specifically, Si transforms into various crystalline  $\text{Li}_x\text{Si}$  phases at high temperature (400 °C), but amorphous lithium silicides ( $\text{Li}_x\text{Si}$ ) are formed during lithiation at room temperature. [9–11] The formation of crystalline or amorphous phases during the lithiation of Si is known to be associated with capacity fade. [5,11,12] Previous studies have attempted to explain the performance degradation of Si anode resulting from the complex phase change during lithiation. The strong coupling between diffusion and large mechanical deformation would induce the corresponding mechanical stress, [13–16] crack formation [11,17], and mechanical weakness due to the formation of weak Li–Si bonds. [18–20] Even though these previous studies have explained certain aspects of Si anode degradation mechanisms, quantitative nature of atomic structure evolution during the lithiation of Si is not well understood yet. Specifically, the initial lithiation of crystalline silicon is known to produce amorphous  $\text{Li}_x\text{Si}$  compound, but the detailed nature of amorphous phase formation is not understood yet. Furthermore, how Li diffuses in a- $\text{Li}_x\text{Si}$  is not well understood, either.

In recent studies, [21,22] many investigations on failure mechanism of Si anode have focused on the issues of phase separation and diffusion kinetics of Li because they significantly affect the stress state at interfaces or lithiated domains during lithiation cycles (Fig. 1). Fig. 1b schematically shows a phase separation between  $\text{Li}_x\text{Si}$  and Si, and large interfacial stresses are expected to induce mechanical failure modes. Furthermore, the Li diffusion is a key parameter in determining how fast a battery can be cycled (i.e., power density). [2,9,15,23–25] Current experimental and theoretical reports on the failure mechanisms of Li–Si systems are not fully consistent with each other. Specifically, several DFT-based studies of Li–Si systems have been reported, focusing on Li behavior studies in bulk or nanostructure, atomic and electronic properties of Li–Si structure based on high temperature crystalline compounds, or aspects of amorphous model structure generated by ab-initio molecular dynamic (AIMD) simulation.

Two-phase (Si and  $\text{Li}_x\text{Si}$ ) separation (shown in Fig. 1b) is generally known as the key failure mechanism of Si anode which arises from a thermodynamic driving force, diffusion induced Li accumulation, and a high activation energy of phase transition on the Si– $\text{Li}_x\text{Si}$  interface. [26] However, a quantitative theoretical basis to explain the phase separation phenomenon is yet to be developed even though many authors have reported different aspect of it. It has been reported in experimental studies that the thermodynamic driving force of two-phase separation and activation energy of phase transition is high, but previous theoretical studies are not consistent with these finding. [27,28] Consequently, it is necessary to develop more detailed theoretical understanding based on DFT and kinetic Monte Carlo (KMC) simulation studies to elucidate the phase separation between c-Si and a- $\text{Li}_x\text{Si}$ . Current DFT and KMC studies in this paper show complex phenomena of initial phase instability and Li accumulation due to slow Li diffusion in c-Si as we discuss later.

Kang et al. have experimentally shown that crystalline LiSi phases are present during battery operation cycles, although primarily amorphous  $\text{Li}_x\text{Si}$  states are present for most Li composition during charging and discharging. [29] The maximum capacity of Si anode at room temperature has been attributed to the crystalline  $\text{Li}_{15}\text{Si}_4$  phase. [30,31] In this work, we focus on initial stage of Li insertion into c-Si before the occurrence of crystalline  $\text{Li}_x\text{Si}$  (i.e.,  $x < 1$  in  $\text{Li}_x\text{Si}$ ) and investigate the energetics and kinetics of initial lithiation.

## 2. Methodology

### 2.1. Computational methods

The ab initio calculations are performed using Vienna ab initio simulation package (VASP) for the density functional theory (DFT) study of  $\text{Li}_x\text{Si}$  model systems within the local density approximation. [32–34] The projector augmented wave method is chosen to describe the interaction between ion core and valence electrons. [35] For Li atom, the Li-sv pseudo-potential treated the semi-core 1s states as valence electrons for accurate description of  $\text{Li}^+$  ionic states. A k-point mesh in the Monkhorst-Pack scheme is set by  $3 \times 3 \times 3$  for  $2 \times 2 \times 2$  supercell of Si. The plane wave basis cut off energy is 500 eV. The structures are fully relaxed for both internal atomic coordinates and supercell shapes. The geometry optimizations are carried out until the forces on each atom become smaller than  $0.01 \text{ eV \AA}^{-1}$ . For ab initio molecular dynamics simulation, the k-point is sampled only at the gamma point. To build amorphous structures, the MD simulations are performed at 1200 K to randomize their initial crystalline configurations. A time step of 3.0 fs and overall simulation steps of 2000 are used. Insertion of Li atoms is done in such a way to achieve a homogenous distribution. At least five samples are generated at each Li concentration ( $x$ ) in  $\text{Li}_x\text{Si}$  models. The Delaunay triangulation method (previously used to generate amorphous Li–Si bulk) is chosen for Li insertion. [36] To study Li kinetics in Si environment, diffusion pathways and barriers were determined using the climbing-image nudged elastic band (NEB) method. Macroscopic diffusion coefficients of Li in c-Si and a-Si are obtained using Arrhenius equation and kinetic Monte Carlo (KMC) simulations.

The detailed KMC algorithm for simulating the time evolution follows the conventional procedure [37,38]. Results of the KMC simulations are statistically averaged to obtain macroscopic behavior. In this study, the standard KMC algorithm is used to simulate an activated random-walk process of Li interstitial defects in Si. Movements of the Li defects have followed the general KMC procedures: (i) Identify all possible events from the current atomic configuration. In this study, we consider first-nearest-neighbor ( $< 3.5 \text{ \AA}$ ) Li sites from sites of tetrahedral Si. (ii) Determine a list of the rates ( $k_i$ ) of all possible transition events in the system. The rates are proportional to  $\exp(-E_m/kT)$ , where the migration energy ( $E_m$ ) is obtained from the ab-initio calculation and generalized to a-

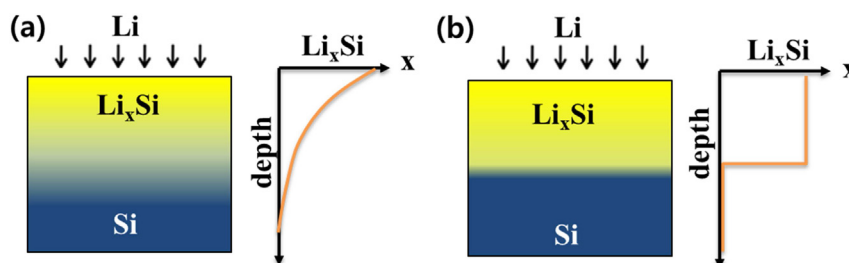


Fig. 1. Schematic of Li diffusivity migration and stress distribution in Si: (a) one-phase diffusion, (b) two-phase diffusion.

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