On the origin of the significant difference in lithiation behavior between silicon and germanium

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HIGHLIGHTS

- We examine and compare the lithiation behavior of Si and Ge using DFT calculations.
- Li diffusivity is greater and less concentration-dependent in Ge as compared to Si.
- Li diffusion is subject to Li–host interaction and host lattice rigidity/dynamics.
- We reveal the origin of the superior rate performance of Ge-based anodes.
- High performance anodes can be designed via fine-tuning of Si–Ge alloys.

GRAPHICAL ABSTRACT
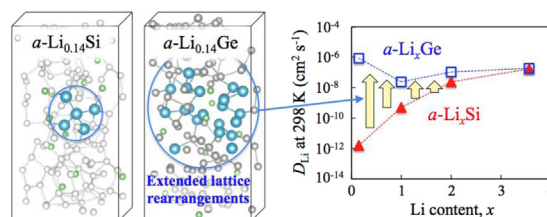
ABSTRACT

Silicon and germanium are both recognized as a promising anode material for high-energy lithium-ion batteries. Si is best known for its superior energy storage capacity, while Ge exhibits better rate capability and cycleability. To better understand the underlying reasons behind their lithiation behavior differences, particularly the enhanced Li transport in Ge, we examine and compare Li-host lattice interactions and dynamics using density functional theory calculations. At the onset of lithiation, an isolated Li interstitial is found to form polar covalent bonds with four nearest host atoms, while the degree of covalency is noticeably greater for Li–Si than Li–Ge bonds. The relatively stronger Li–Si interaction, along with the stiffer Si lattice tend to be responsible for the suppressed Li mobility ($D_{Li} = 10^{-13}$ cm^2 s^{-1}) in c-Si, as compared to the c-Ge case ($D_{Li} = 10^{-11}$ cm^2 s^{-1}). With continued lithiation, D_{Li} in a-Li$_x$Si increases significantly from 10^{-12} to 10^{-7} cm^2 s^{-1} ($x = 0.14$–3.57); contrarily, D_{Li} in a-Li$_x$Ge is around 10^{-7} cm^2 s^{-1} and less concentration dependent. Our analysis shows that the rapid Li diffusion in a-Li$_x$Ge is directly related to the facile atomic rearrangements of host Ge atoms even at the early stages of lithiation.

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1. Introduction

Li-ion batteries (LIBs) have received tremendous attention as they power a wide range of applications from portable devices, electric vehicles to various renewable energy systems [1–3]. Currently, the most adopted anode material is graphite, which has good cycleability but the dendrite formation raises safety concerns

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and the capacity is rather limited (372 mAh g^{-1}) especially at high charge/discharge rates. Therefore, in order to satisfy the ever-increasing energy density/power capability requirements and stringent safety standards, there is an imminent need to find new electrode materials with superior lithiation properties. Among the alternatives considered, Si stands out the most because of its impressive capacity (4200 mAh g^{-1} for Li$_{22}$Si$_5$ [4,5]), safe thermodynamic potential and abundance. Second only to Si, Ge has a relatively high theoretical capacity of 1624 mAh g^{-1} (Li$_{22}$Ge$_5$ [6]), a higher electrical conductivity compared to Si [7], and a superior rate capability, up to 1000 C (full lithiation in 1/1000 h) [6]. However, the understanding and development of Ge-based anodes have gained much less attention likely because of its higher price relative to Si.

Being in the same column in the periodic table, Si and Ge share many similarities, including the disadvantages of undergoing large structural changes and volume expansion upon lithiation, which can consequently lead to early capacity fading. To overcome this drawback, many ongoing studies have focused on utilizing Si and Ge of different forms, such as thin films [8–12], nanoparticles [13,14], nanowires [15–18], and alloys/composites with active/inactive elements [19–22]. In both Si and Ge cases, nanostructuring seems to have positive impacts on enhancing the rate capability and reducing/preventing electrode pulverization, thereby improving the cycleability. In comparison to Si, Ge of comparable nano-architecture is able to withstand much faster charging rates with noticeably less crack formation [23,24]. Furthermore, there appears to be subtle differences in their responses to electrochemical lithiation/delithiation, as demonstrated by recent in-situ characterization [24]. On the theoretical side, there have been many studies employing density functional theory (DFT) to examine Li incorporation in Si (crystalline/amorphous bulks [25–27] and nanowires [28,29]) and a few on Ge [30–32]. Nonetheless, the fundamental understanding regarding the nature and origin of their dissimilar responses to lithiation is still limited; to the best of our knowledge, no atomistic study has been reported to investigate the likely overlooked differences between Si and Ge as anode material, especially regarding their lithiation dynamics.

In this paper, on the basis of DFT calculations, we examine how Li diffusion is affected by its interaction with the pure Si and Ge matrices, analyze the dynamic behaviors of Li as well as the host lattice atoms, and look into the impacts of Ge-alloying on anode performance. The fundamental findings explain the origin of the lithiation behavior differences between Si and Ge, particularly the significantly enhanced Li transport in Ge, and thus assist the rational design of the next-generation high performance Si- and Ge-based anodes.

2. Computational methods

The calculations reported herein were performed on the basis of density functional theory (DFT) within the generalized gradient approximation (GGA-PW91) [33], as implemented in the Vienna Ab-initio Simulation Package (VASP) [34–36]. Spin polarization of the Li–Si (Ge) system was also examined, but appears to be unimportant. The projector augmented wave (PAW) method with a planewave basis set was employed to describe the interaction between ion cores and valence electrons. The PAW method is, in principle, an all-electron frozen-core approach that considers exact valence wave functions. Valence configurations employed are as follows: $1s^2 2s^1$ for Li, $3s^2 3p^2$ for Si and $4s^2 4p^2$ for Ge. An energy cutoff of 350 eV was applied for the planewave expansion of the electronic eigenfunctions. The crystalline Si (Ge) host was modeled using a 216-atom supercell with a fixed lattice constant of 5.457 (5.777) Å; the effect of volume relaxation was also checked, and

turns out to be unimportant as the 216-atom supercell is large enough to accommodate one Li atom with no significant volume change (less than 1%). For geometry optimization, all atoms were fully relaxed using the conjugate gradient method until residual forces on constituent atoms become smaller than 5×10^{-2} eV Å^{-1}, and a $(2 \times 2 \times 2)$ k-point mesh in the scheme of Monkhorst–Pack was used for the Brillouin zone sampling [37]. Diffusion pathways and barriers were determined using the climbing-image nudged elastic band method with eight intermediate images for each hopping step.

The model structures of amorphous a-Li$_x$M alloys (M = Ge and Si$_{1-y}$Ge$_y$) were created using ab initio molecular dynamics (AIMD) simulations based on the atomic configurations of a-Li$_x$Si alloys that were previously generated using the combined modified embedded atom method (MEAM) and AIMD simulations (see Refs. [31,38] for detailed computational methods). The interaction between Li and Ge is very similar to that with Si, and their lithiated phases tend to share many structural similarities [31,40,41]; therefore, the a-Li$_x$Si structure is likely a good starting configuration for the a-Li$_x$M structure. The Si atoms (in a-Li$_x$Si) were replaced by Ge atoms accordingly to achieve desired composition ratios; the replacement sites were carefully chosen to ensure homogeneous atomic mixing. The model structures, each containing 128 atoms, were then annealed at 300 K for 1.5 ps with a time step of 1 fs to allow sufficient atomic rearrangement (the annealing temperature was controlled via velocity rescaling), followed by geometry optimization using a $(2 \times 2 \times 1)$ k-point mesh. Periodic boundary conditions were employed in all three directions, and for each composition three independent samples were considered. This approach can provide reasonable Li–M amorphous structures at significantly reduced computational burden compared to starting with crystalline initial configurations. Finally, for diffusivity calculations, AIMD simulations of 8 ps duration with a time step of 1 fs were carried out at appropriate temperatures controlled via Nose–Hoover thermostat.

3. Results and discussion

We first examined how the room-temperature diffusivity of Li varies with Li content (x) in a-Li$_x$Si alloys using AIMD simulations
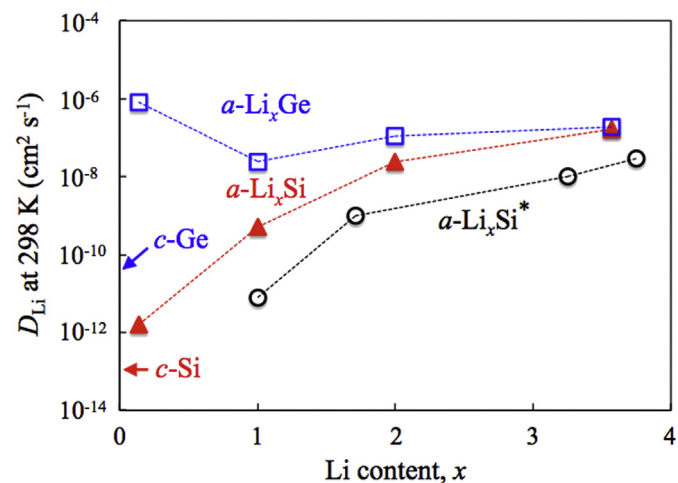
Fig. 1. Predicted diffusivity of Li (D_{Li}) in a-Li$_x$Si and a-Li$_x$Ge using AIMD simulations at 298 K. The predicted D_{Li} values for single Li diffusion in c-Si [42] and c-Ge [31] are indicated by red and blue arrows, respectively. For comparison, D_{Li} values calculated by MD simulations with an embedded atom method interatomic potential are indicated by * [45]. (For interpretation of the references to color in this figure legend, the reader is referred to the web version of this article.)