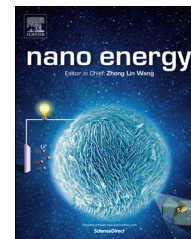




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RAPID COMMUNICATION

# Effects of stress on lithium transport in amorphous silicon electrodes for lithium-ion batteries



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## Abstract

Silicon, as a promising electrode material for high energy density lithium ion batteries, experiences large strains and stresses during lithiation and delithiation. The coupling effect between stress and lithium diffusion leads to a grand challenge to optimizing the design of Si electrodes with high capacity and high rate capability, particularly considering the amorphization of Si during initial cycles. In this study, we established a relationship between stress and the diffusion coefficients of Li in amorphous Si by *ab initio* molecular dynamics calculations (AIMD). The prediction from AIMD was validated by the potentiostatic intermittent titration measurements. Our results showed that two Li diffusion mechanisms can operate depending on the stress state. Specifically, the stress can increase Li diffusion either through increasing free volume under tension or by changing local structure under compression. However, within the range of stress generated during the lithiation and delithiation process, diffusion coefficients are expected to vary by only one order of magnitude.

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## Introduction

In recent years, silicon (Si) has received much interest as a promising negative electrode material for lithium ion batteries (LIBs) because of its high specific capacity, low discharge voltage, and low cost [1–4]. However, these merits come with

a range of problems: large volume expansion upon cycling ( $\sim 300\%$ ), cracking, and structural changes [5,6], leading to severe capacity degradation and short cycle life. Furthermore, lithium (Li) transport in  $\text{Li}_x\text{Si}$  electrodes is slow with a diffusion coefficient approximately between  $10^{-10}$  and  $10^{-14}$   $\text{cm}^2 \text{s}^{-1}$  [7-10]. The performance of LIBs at high charge/discharge rates (i.e., high current densities) critically depends on the Li transport properties in electrodes. To limit the impact of these challenges, nano-structured Si systems (e.g., nanowires [11-15], nanotubes [16,17], nanoparticles [18,19], and patterned nanostructures [20]) have been proposed to meet the demands for high performance batteries. In these electrode structures, improved rate-performance is made by reducing the effective diffusion distance that Li must travel. These improvements are achieved at the cost of (1) severe solid electrolyte interphase (SEI) formation due to large surface area and (2) relatively low energy density. In order to design Si electrodes with required performance and durability, careful engineering is needed to balance the intrinsic properties of Si and nanostructuring. Thus, it is necessary, in the context of charge/discharge rate, to understand the detailed mechanism of Li diffusion in Si electrodes.

On the other hand, the coupling effect of Li diffusion and its induced stress makes the understanding of Li transport more difficult, since stress can impact Li diffusion and *vice versa*. Although several publications have reported Li diffusion coefficients in Si [7-10], the effect of stress on diffusion behavior has not been reported. Large stresses on the order of a few GPa [21,22] have been observed during lithiation and delithiation of Si. In most cases, Si electrodes are amorphous. Unfortunately, there is no universal rule which can describe the effects of hydrostatic stress on diffusion [23] in amorphous alloys. In some amorphous systems, the hydrostatic compressive stress would increase the diffusion coefficient (e.g., the viscosity decreased with pressure in  $\text{NaAlSi}_2\text{O}_6$  melts [24], and enhanced interdiffusion in amorphous Si/Ge multilayers [25]), while in some other amorphous systems the effects of pressure on diffusion are absent (e.g.,  $^{57}\text{Co}$  diffusion in  $\text{Co}_{81}\text{Zr}_{19}$  [26]). In addition, it was found that a compressive stress could decrease the diffusion rates in some metallic glasses (e.g.,  $^{95}\text{Zr}$  diffusion in  $\text{Co}_{92}\text{Zr}_8$  [27]). The fact that Si experiences both compressive and tensile stresses during electrode cycling raised additional complexities. Therefore, it is necessary to study the detailed kinetics and structural changes under hydrostatic tension and compression in order to understand Li transport in amorphous Si.

In this paper, we present a study integrating both calculations and experiments to investigate the effect of stress on Li diffusion in Si electrodes. Explicit *ab initio* molecular dynamics (AIMD) simulations based on density functional theory (DFT) were performed to study the changes in structure, diffusion rates, and transport mechanisms in stressed LiSi systems. Our calculations found that Li diffusion coefficients vary within one order of magnitude under the stresses encountered in Si electrodes, in agreement with experimental observations of Li diffusion coefficients in lithiated Si. The results of this work provide a better understanding at the atomic level of Li diffusion behavior in amorphous Si, which can also be helpful to the understanding of diffusion in other similar inorganic amorphous systems.

## Methodology

### Computational details

*Ab initio* Molecular Dynamics simulations, which provide fundamental information about diffusion at the atomic scale, were performed using the Vienna *ab initio* Simulation Package (VASP) [28,29]. The exchange and correlation function was approximated at the level of the generalized gradient approximation (GGA) in the Perdew-Burke-Ernzerhof (PBE) flavor [30]. In addition, the ionic cores were modeled with projector-augmented-wave (PAW) potentials [31]. The Brillouin zone was sampled at the  $\Gamma$  point, which represented about  $3.3 \times 10^{-4} \text{ \AA}^{-3}$  k-points for the selected box size. The energy cutoff for the planewave expansion of the electronic eigenfunctions was 350 eV. These parameters were selected based on convergence tests of calculated total energy, and were comparable with the parameters used in previous calculations [32].

In the present calculations, we focus on amorphous LiSi (atomic ratio 1:1) composition as an example of a range of amorphous  $\text{Li}_x\text{Si}$  materials relevant to Si based LIB electrodes. Amorphous LiSi alloy structures were prepared by AIMD within VASP [28,29]. The systems were first created as crystals, typically containing 192 atoms (96 atoms for each species). These structures were then heated up to a temperature above the melting temperature [33] (e.g., 1700 K). At this temperature, systems were equilibrated for 8000 MD steps with a 0.5 fs time step. To obtain amorphous structures relevant at lower temperatures, the systems were then quenched to a temperature of interest to perform structural studies and diffusion calculations (e.g., 1200 K and 900 K) with a rapid cooling rate: 200 K per 2000 time steps (1000 fs), similar to the cooling rates used in previous calculations [34,32]. To prepare systems with different stresses at a specific temperature, we performed AIMD simulations at various volumes by adjusting the simulation box size from above to below the equilibrium volume of the stress-free state. A total of 2000 time steps (0.5 fs/step) was used to equilibrate the volume controlled system. The potential energy of each system converged to a stable value (the differences in potential energy were within  $10^{-4}$  eV/atom) after 2000 time steps, signalling the end of the equilibration phase of the AIMD simulations at a given volume. After that, the potential energy of another 2000 time steps were averaged and the energy values of different volumes were fitted to a third order polynomial with respect to the box volume  $V$ . (See Supporting Information for details.)

The hydrostatic stress in the simulation box is determined as

$$\sigma_{T,N} = \left. \frac{\partial \langle E(V, T, N) \rangle}{\partial V} \right|_{T,N}, \quad (1)$$

where  $\langle E(V, T, N) \rangle$  is the equilibrated potential energy represented by the third order polynomial which is a function of the volume,  $V$ , of the simulation boxes, the temperature,  $T$ , and the number of atoms,  $N$ . The equilibrium volume (stress-free volume) at different temperatures corresponds to the volume  $V_{\text{equi}}$  at which

$$\frac{\partial \langle E \rangle}{\partial V} = \frac{1}{3a_0^2} \frac{\partial \langle E \rangle}{\partial a_0} = 0, \quad (2)$$

where  $a_0$  is the supercell lattice constant. The equilibrated simulation box volumes corresponding to each stress state of interest (e.g., 2, 1, -1, and -2 GPa) were calculated from

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