



Full paper

Stress effects on lithiation in silicon

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ARTICLE INFO

Keywords:

External stress effect
Lithiation kinetics
Phase boundary
Reaction and diffusion
Lithium-ion battery
Atomistic simulations

ABSTRACT

Recent experiments have revealed that external bending breaks the symmetry of lithiation in germanium nanowires. However, the effects of external stress on lithiation in silicon and the associated underlying mechanisms remain unclear. Here, we have performed a series of large-scale atomistic simulations based on a newly developed reactive force field (ReaxFF) to investigate the effects of external stress on the interfacial reactions and diffusion (two dominant processes during lithiation) of silicon anodes. The simulation results quantitatively show the variations in the migration velocity of the phase boundary (i.e., the reaction front during lithiation) and the diffusivity of lithium (in crystalline and amorphous lithiated silicon) as a function of the external stress and indicate that the tensile stress accelerates the lithiation rate while the compressive stress retards it. Furthermore, comparing the large-scale ReaxFF-based simulations and previous *ab initio* molecular dynamics (AIMD) simulations indicated that large samples and long duration times are crucially important and indispensable for accurately calculating the diffusivity of amorphous lithiated silicon under external stress. These results not only provide a fundamental understanding of the intimate coupling between mechanical stress and lithiation kinetics but also open avenues for optimizing batteries to control/alter the lithiation rate of silicon anodes by applying external mechanical stresses.

1. Introduction

Due to its high capacity, high energy density, and low cost, silicon has been considered as a promising next-generation anode material for lithium-ion batteries [1]. However, Si anodes undergo large volume changes due to electrochemical lithiation/delithiation during charge/discharge, which mechanically degrades, fractures and even pulverizes the anodes [2–10], hindering their use in commercial applications. To elucidate lithiation/delithiation-induced mechanical degradation/fracture of Si anodes, several experimental, computational and theoretical studies [11–21] have recently focused on the complicated coupling or interplay between their mechanical stresses and chemical reactions (i.e., lithiation/delithiation). An *in situ* wafer curvature technique [7,11] has been used to measure the generation and evolution of stress in Si thin film electrodes during lithiation/delithiation. Upon lithium insertion, a portion of the crystalline Si phases was transformed into amorphous Li-Si alloys, leading to the formation of an atomically sharp phase boundary (representing the reaction front), which separated the amorphous lithiated phases from the unreacted phases [7]. During lithiation,

compressive stress was produced in the film, and the maximum value reached the order of 1.0 GPa [7], enabling plastic deformation of the lithiated Si. Upon lithium removal, the stress became tensile and gradually increased. Thus, the film first underwent elastic unloading, followed by elastic loading and then tensile plastic flow. When the tensile stress exceeded 1.5 GPa, multiple cracks formed in amorphous phases, leading to fragmentation of the electrodes [7]. *In situ* experiments inside a transmission electron microscope (TEM) [4–6] have indicated that lithiation induces high localized tensile stress at the surfaces of crystalline Si nanoparticles and nanowires, which initiates cracking and eventual catastrophic fracturing. Similarly, lithiation-induced stress can lead to the delamination of Si film electrodes from current collectors due to interfacial sliding [12]. Lithiation/delithiation induces mechanical stresses in Si that, in turn, regulate the lithiation/delithiation kinetics. For crystalline Si nanoparticles and nanowires, recent *in situ* TEM observations revealed a self-limiting lithiation front, i.e., the movement of the reaction front usually slowed as it progressed into the interior of the electrodes [13,14]. The self-limiting lithiation phenomenon has been attributed to the retardation effect of the lithiation-induced stress,

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i.e., the varying mechanical stress at the reaction front alters the driving force (chemical potential) of the reaction or diffusion [13,14]. This retardation effect has been corroborated with continuum-level chemo-mechanical models [16,17].

Notably, the mechanical stress induced by lithiation/delithiation, as mentioned above, is essentially an internal stress. The internal stress is self-generated due to inhomogeneous deformation of the Si anodes [20]. Similar to the internal stress, the external stress also influences the lithiation kinetics. To date, few studies regarding this issue have been conducted. During a recently published in situ TEM experiment, after prebending an individual Ge nanowire, the lithiation rate at the tensile side was much faster than that at the compressive side, resulting in asymmetric lithiation at the cross section of the nanowires [15]. Atomistic simulations for the lithiation of Si nanowires have shown that as the bi-axial pressures on nanowires increase, the lithiation rate significantly decreases [18]. In a thin-film-based device with two identical lithiated Si electrodes, the external bending stresses generated a chemical potential difference, driving the Li ion flux from the compressed electrode to its stretched partner to generate an electrical current [21]. These studies demonstrate some of the significant effects of external stress on lithiation kinetics. However, the influence of external stress on lithiation kinetics, such as the interfacial reactions and diffusion, and the associated underlying mechanisms remain unclear. In this paper, we first mimic bending-induced asymmetric lithiation using large-scale atomistic simulations. Then, we quantitatively characterize the lithiation rates in crystalline Si under different external bi-axial stresses by describing the number of reacted Si sites and the average velocity of the phase boundary during the initial lithiation process. Finally, we calculate the diffusivity and activation energy barrier for Li diffusion in both crystalline and amorphous Li-Si phases.

2. Method

Atomistic simulations were carried out using large-scale atomic/molecular massively parallel simulator (LAMMPS) [22]. During the simulations, a ReaxFF [23] force field is used to describe the interatomic interactions. This force field is capable of accurately predicting the mechanical properties of various Li-Si mixtures and capturing their bonding/de-bonding behaviors [23]. The time step for integration is taken as 0.2 fs. Similar to previous atomistic simulations [18,24], all simulations are performed at 900 K, which is just below the melting temperature of Li-Si alloys [25], to accelerate the lithiation and to reduce the simulation time. We first mimic bending-induced asymmetric lithiation in crystalline Si. Previous experimental studies [3,26] have demonstrated that the lithiation is anisotropic in crystalline Si, i.e., lithiation depends on the crystallographic orientation, which is distinct from the isotropic lithiation in crystalline Ge [15]. Therefore, the simulated sample is square-shaped at the cross section and has the same orientation on both bending sides to ensure the same initial conditions for lithiation. The simulated sample has a size of $50.0 \times 5.0 \times 5.0 \text{ nm}^3$ and contains 72,570 atoms. The sample is oriented in [111], $[\bar{1}\bar{1}2]$ and $[1\bar{1}0]$ along the x , y and z directions, respectively. The sample is bent into an arc with specific central angles of $\varphi = 30^\circ$, 60° , and 90° by mapping atoms to a deformed configuration corresponding to pure bending in the x - y plane, as shown in Fig. 1a. The bent sample is first equilibrated for 10 ps at 900 K and then incorporated in an amorphous Li reservoir with a size of $50.0 \times 30.0 \times 5.0 \text{ nm}^3$, as shown in Fig. 1a. Before incorporation, the Li reservoir is equilibrated for 20 ps at 900 K. The overall simulated system includes approximately 550,000 atoms. The temperature is maintained at 900 K via a Berendsen thermostat. For simulated samples with different bending angles, the inserted vertical heights (h) are identical, as illustrated in Fig. 1a. A periodic boundary condition is imposed in the z direction. Throughout the simulations, both ends of the samples are fixed.

3. Results and discussion

After the sample is bent to a certain central angle, its left side undergoes tensile stress, while the right side undergoes compressive stress (Fig. 1a). Fig. 1b-d show the atomic configurations of the lithiated samples with different prebending angles at $t = 60 \text{ ps}$. For clarity, the Li atoms are represented as transparent, while the Si atoms are colored according to their potential energies, in Fig. 1b-d. The Si atoms with high potential energies had reacted with the Li atoms and were used to indicate the lithiation thickness. Note that the lithiation thickness is nonuniform along the length direction of the sample. Therefore, the maximum lithiated thicknesses at each 10 ps are recorded and then normalized by the initial thickness. Fig. 1e presents the plots of the time-dependent normalized lithiation thickness curves. As lithiation proceeds, the lithiation thickness curve gradually becomes saturated, indicating strong lithiation retardation due to self-generated internal stress. This trend is similar to previously reported experimental observations regarding the lithiation of prebent Ge nanowires [15]. For samples with a given bending angle, the lithiation thickness at the tensile side at any time step is always larger than that at the compressive side, indicating asymmetric lithiation (Fig. 1b-d). At a given time, as the prebending angle increases, the lithiation thickness at the tensile side increases dramatically, while that at the compressive side decreases slightly. These results are qualitatively consistent with those from previous experiments on the lithiation of prebent Ge nanowires [15]. Supplementary Fig. 1 shows the hoop stress contours of prebent samples with different bending angles. Although there exist some stress fluctuations, an apparent stress gradient is observed in the thickness direction of the samples. Such stress gradient is on the order of 1 GPa/nm, which significantly influences the lithiation process. The stress gradient increases with increasing bending angle, which provides a rational explanation for the observed effect of the bending angle on lithiation thickness in Fig. 1e. Fig. 1f presents two typical snapshots of the breaking bonds during lithiation of the prebent samples. The Si-Si bonds break when the Li atoms diffuse preferentially along the [110] direction, leading to layer-by-layer peeling of the {111} atomic facets and further formation of amorphous Li-Si alloys. This mechanism is consistent with previously reported TEM observations during the lithiation of stress-free crystalline Si [27].

Prebending induces different stress states and contact areas in both the tensile and compressive sides. Therefore, the asymmetric lithiation observed in Fig. 1b-d involves the influences of both the stress state and contact area. To verify the influence of the contact area, we conducted molecular dynamics (MD) simulations for the lithiation of straight stress-free samples with the same size as the prebent samples. These samples are incorporated in a Li reservoir at different inclined angles of $\theta = 30^\circ$, 60° , and 90° , as shown in Fig. 1g. Fig. 1h-j depict the atomic configurations of the lithiated samples with different inclined angles at $t = 60 \text{ ps}$. For samples with $\theta = 30^\circ$ and 60° , the contact area on the left is larger than that on the right; hence, the left lithiated layer is thicker than the right one. In the case of $\theta = 90^\circ$, the lithiation on the left and right sides is nearly perfectly symmetrical due to the identical contact areas. The lithiation thickness curve of the stress-free sample with $\theta = 90^\circ$ is included in Fig. 1e and is located between the curves of the tensile and compressive cases.

The initial stress in the prebent sample exhibits a gradient variation along the thickness direction. As the lithiation advances from the surface to the interior, the stress gradually weakens. Quantitatively characterizing the influence of such varying stress on the lithiation process is complicated. Hence, we subsequently focus on a simple but general case of the effect of external stress on lithiation. The simulated system includes a crystalline Si block with a volume of $9.41 \times 7.10 \times 2.30 \text{ nm}^3$. The Si block is oriented in [111], $[\bar{1}\bar{1}2]$ and $[1\bar{1}0]$ along the x , y , and z directions, respectively, and its (111) surface is exposed to a Li reservoir with a volume of $28.23 \times 7.10 \times 2.30 \text{ nm}^3$, as illustrated in Fig. 2a. The overall system contains 7680 Si atoms and 18,027 Li

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