



# Microscopic model for fracture of crystalline Si nanopillars during lithiation



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## HIGHLIGHTS

- We model lithiation in crystalline Si anode based on discrete phase boundary motion.
- Anisotropic phase boundary motion is taken into account.
- Microscopic model is derived to explain size-dependent fracture during lithiation.
- We estimate the work of fracture of lithiated Si.

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## ABSTRACT

Silicon (Si) nanostructures are attractive candidates for electrodes for Li-ion batteries because they provide both large specific charging capacity and less constraint on the volume changes that occur during Li charging. Recent experiments show that crystalline Si anodes expand highly anisotropically through the motion of a sharp phase boundary between the crystalline Si core and the lithiated amorphous Si shell. Here, we present a microscopic model to describe the size-dependent fracture of crystalline Si nanopillars (NPs) during lithiation. We derive a traction–separation law based on the plastic growth of voids, which, in turn, is used in a cohesive zone-finite element model. The model allows for both the initiation of cracking and crack growth. The initial size and spacing of the nanovoids, assumed to be responsible for the fracture, together with the computed fracture toughness, are chosen to conform to recent experiments which showed the critical diameter of Si NPs to be 300–400 nm. The anisotropy of the expansion is taken into account and that leads naturally to the observed anisotropy of fracture. The computed work of fracture shows good agreement with recent experimental results and it may be possible to use it to describe the failure for other loading and geometries.

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## 1. Introduction

High-capacity lithium-ion batteries (LIBs) have attracted much attention as a key element for portable electronic devices and electric vehicles [1,2]. The search for anode materials with high charging capacity has identified silicon (Si) as one of the most promising candidates, because it has an exceptionally high specific charging capacity of 4200 mAh g<sup>-1</sup> [3]. However, the associated huge volume expansion during lithiation, can cause pulverization and capacity loss [4,5], thus impeding the development of Si anodes. To avoid the mechanical degradation due to lithiation-induced stresses, various nanostructures have been suggested as possible electrodes for improved cycling performance and fracture

resistance. Examples include nanowires [6], thin films [7,8], core–shell structures [9], and hollow structures [10,11].

Recent experiments have shown that lithiation of crystalline Si differs from that for amorphous Si: the lithiation process for crystalline Si involves a two-phase reaction, with an atomistically sharp phase boundary existing between the amorphous Li<sub>x</sub>Si shell and the pristine crystalline Si core [12,13]. Moreover, the phase boundary moves faster in the <110> direction of crystalline Si than other directions [12,14,15]. These phenomena differ from the lithiation of amorphous Si, where lithiation is governed mainly by diffusion.

In an effort to understand the lithiation process for crystalline Si, and especially to understand the stress evolution and fracture, several authors have analyzed the stress evolution and deformation associated with interface reaction-controlled lithiation. Zhao et al. [16] developed an analytical model for concurrent interface

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reaction and plasticity in nano-spheres. Pharr et al. [17] developed a kinetics-based model for anisotropic motion of phase boundaries by specifying phase boundary motion and computing morphology changes associated with lithiation, similar to those found experimentally [18]. By adjusting the diffusivity of lithium ions to simulate a sharp boundary, Yang et al. [19] also developed a model to show the anisotropic shape changes. In addition, McDowell et al. [20] have suggested a kinetics model to account for the effect of stress on the interface reaction rate.

In the present study, we have developed a microscopic model to explore size-dependent fracture of crystalline Si nanopillars (NPs) during lithiation. As a first approximation, we model the phase boundary motion by specifying a temperature field, using the analogy between thermal expansion and lithiation-induced swelling. Using this model, we can simulate the anisotropic expansion and accompanying stress evolution during the lithiation of crystalline Si NPs with various crystallographic orientations.

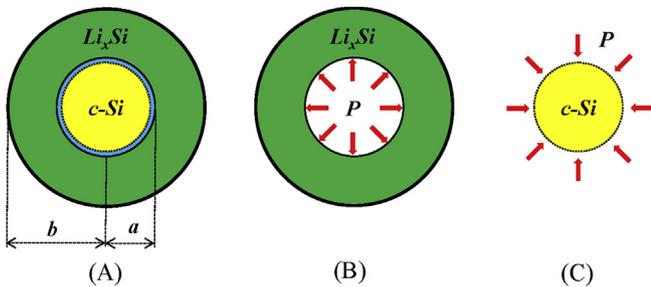
To model the crack initiation and propagation, we first derive a traction–separation law based on a microscopic description of the plastic growth of voids. From the traction–separation law, the work of fracture ( $G_c$ ) is estimated by taking the initial size and spacing of the nanovoids such that a critical diameter of Si NPs of 300–400 nm is predicted, consistent with experiment.

We also performed experiments to determine the critical diameter for fracture of Si NPs during lithiation for different crystallographic orientations. We used the scanning electron microscope (SEM) to observe the shapes of individual pillars after lithiation, as done previously [18]. These experiments are then directly compared with the modeling results and the comparison leads to a good agreement on the size effect on fracture. This characterization method determines a critical diameter for fracture and also serves as a standard to judge the validity of our modeling.

## 2. Stress evolution during lithiation

### 2.1. Isotropic expansion model

Recent transmission electron microscopy (TEM) studies showed that a sharp phase boundary exists between crystalline Si and amorphous  $\text{Li}_x\text{Si}$ , thus creating a core–shell structure during lithiation of a crystalline Si NP [13,21,22]. As a first approximation, we start with the isotropic expansion model. To derive an approximate analytical solution for the stresses during lithiation, we divide the domain between the crystalline Si core and the amorphous  $\text{Li}_x\text{Si}$  shell, as shown in Fig. 1A. In this model, crystalline Si and the amorphous  $\text{Li}_x\text{Si}$  are assumed to be elastic and elastic–plastic, respectively. When the phase boundary moves during lithiation,



**Fig. 1.** Schematic of lithiation of a crystalline Si nanopillar (A) At a given time, pristine silicon core and  $\text{Li}_x\text{Si}$  alloy shell. The thin layer (blue color) stands for the atomistically sharp phase boundary only where lithiation occur at the given time duration. (B) Stress state of the lithiated Si alloy shell. (C) Stress state of pristine Si core. (For interpretation of the references to color in this figure legend, the reader is referred to the web version of this article.)

the interface reaction involving the breaking of Si–Si bonds and the forming of Li–Si bonds is assumed to occur only in an atomistically thin layer (blue color in Fig. 1A). Due to the volume expansion of the thin layer between the core and shell, the surrounding  $\text{Li}_x\text{Si}$  shell can be considered to be in the same stress state as a pressurized cylindrical tube, with the core being subjected to a uniform radial pressure, as shown in Fig. 1B and C. [16,19,23]. Following Hill's treatment of a pressurized tube with the Tresca yield criterion [24], the stresses in the  $\text{Li}_x\text{Si}$  shell would then be

$$\left(\frac{\sigma_{rr}}{Y}\right)_{\text{Li}_x\text{Si}} = -\ln\left(\frac{b}{r}\right), \quad \left(\frac{\sigma_{\theta\theta}}{Y}\right)_{\text{Li}_x\text{Si}} = 1 - \ln\left(\frac{b}{r}\right), \quad (1a,b)$$

after assuming that the tube deforms fully plastically due to the large volume expansion.  $\sigma_{rr}$ ,  $\sigma_{\theta\theta}$  and  $Y$  are radial, tangential and yield stress, respectively.  $b$  is the outer radius of tube and  $r$  is the distance from the center. The corresponding stresses in the Si core would be

$$\left(\frac{\sigma_{rr}}{Y}\right)_{\text{Si}} = \left(\frac{\sigma_{\theta\theta}}{Y}\right)_{\text{Si}} = -\ln\left(\frac{b}{a}\right), \quad (2a,b)$$

where  $a$  is the radius of the Si core. From this analytical solution for the hoop stress, we can see that a tensile stress should develop at the surface.

To account for the stress state in the interfacial layer, we use a finite element package, ABAQUS (2010 version), for lithiation-induced swelling with plasticity. In this model, we adopt an isotropic elastic and perfectly plastic model, using the mechanical properties shown in Table 1. Using the analogy between diffusion-induced swelling and thermal expansion, we model the phase boundary by specifying the temperature field. The total strain rate at any point is composed of the elastic ( $\dot{\epsilon}^e$ ), and plastic ( $\dot{\epsilon}^p$ ) strain rates as well as the transformation strain rate ( $\dot{\epsilon}^t$ ) due to lithiation. Elastic properties are assumed to be isotropic, obeying Hooke's law, and the conventional J-2 flow rule, without hardening, is used for plastic strain calculations. The amorphous  $\text{Li}_x\text{Si}$  shell expands isotropically according to the specified temperature distribution with a linear transformation strain of 0.4, which leads to about a 300% volume expansion. The reaction front thickness is taken to be much smaller than the radius. For the out-of plane deformation, we assume a plane strain condition.

With the numerical model described above, stresses have been computed for the lithiation of a Si NP with a diameter of 100 nm. The hoop stresses are plotted in Fig. 2. It shows tensile stress developed easily at the surface due to huge volume expansion at the interfacial boundary, which provides a clear explanation for why cracking is initiated at the surface of the NPs during lithiation of crystalline Si [25], rather than from the center.

### 2.2. Anisotropic expansion model

Our recent experimental study revealed that lithiation of crystalline Si occurs faster in the  $\langle 110 \rangle$  direction than other directions [18,26]. To model the anisotropic phase boundary motion, we

**Table 1**  
Material properties and operating parameters.

Material	Description	Symbol [dimension]	Value	References
Crystalline Si	Young's modulus	$E$ [GPa]	185	[36]
	Yield point	$y$ [GPa]	7	[37]
	Poisson's ratio	$\nu$	0.28	[36]
$\text{Li}_x\text{Si}$ alloy	Young's modulus	$E$ [GPa]	35	[38]
	Yield point	$y$ [GPa]	1	[39]
	Poisson's ratio	$\nu$	0.22	[40]

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