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Stress-modulated driving force for lithiation reaction in hollow nano-anodes



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HIGHLIGHTS

- We determine the effect of mechanical stress on driving force for lithiation reaction.
- We consider concurrent lithiation reaction and deformation with a sharp reaction front.
- We reveal a hollow silicon nanowire is easier to be fully lithiated than a solid one.

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ABSTRACT

Lithiation of a crystalline silicon anode proceeds by the movement of an atomically sharp reaction front that separates a pristine crystalline phase and a fully-lithiated amorphous phase. The velocity of the reaction front is limited rather by the reaction rate at the lithiation front than by the diffusivity of lithium ions in the amorphous lithiated phase. Experiments on solid nanoparticle/nanowire silicon anodes show an initial rapid advancing of reaction front at the initial stage of lithiation, followed by an apparent slowing or even halting of the reaction front propagation. Lithiation-induced stresses during lithiation are attributed to alter the driving force of lithiation and thus result in the observed slowing of reaction front. Recent experiments on lithiation of hollow silicon nanowires reveals similar slowing of reaction front, however, quantitative study of the effect of lithiation-associated stress on the driving force of lithiation still lacks so far. Here, through chemo-mechanical modeling and theoretical formulation, we present a comprehensive study on lithiation-induced stress field and its contribution to the driving force of lithiation reaction in hollow silicon nanowire anodes. We show that hollow silicon nano-anodes could be fully lithiated with lower stress-induced energy barrier than solid silicon nano-anodes. As a result, it is expected that the hollow nanowires and nanoparticles may serve as an optimal structural design for high-performance anodes of lithium-ion batteries. Results from the present study shed light on a number of open questions of lithiation kinetics of silicon-based anodes in recent literature and offer insight on developing silicon-based anodes with high charging capacity and high charging rate.

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1. Introduction

There has been a surge of interests in developing next-generation lithium-ion batteries with high specific capacity [1–5]. Silicon is emerging as the most promising anode (i.e., negative electrode¹) material due to its high specific capacity which is about ten times that of current graphite-based anodes [6,7]. The high

theoretical capacity of silicon stems from the fact that one silicon atom can host up to 3.75 lithium atoms upon fully lithiation [8]. However, on the other hand, insertion of large amount of lithium atoms causes excessive volume change (~300%) and large mechanical stresses, which may eventually fracture the silicon anodes and lead to huge irreversible capacity fading [9–11]. Therefore, mechanical failures induced by the large volumetric expansion during lithiation are the key issue that hinders the mass application of silicon as anodes for next-generation lithium-ion batteries. To mitigate the mechanical failures of silicon-based anodes, intensive research efforts have been focused on developing nanostructured anodes including nanowires [9,12], nano-sized thin film [13], nanoporous structures [14,15], nano-sized beaded-string structure

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¹ The term of “anode” here corresponds to the discharging half-cycle in electrochemistry. Silicon indeed serves as the cathode during the charging half-cycle. In either half-cycle, silicon is the negative electrode.

[16], nano-walls [17] and nano-islands [18,19]. Lithiation-induced stress, deformation and mechanical failure in these novel silicon nanostructures are widely studied through experimental characterization [20–22] and chemo-mechanical modeling [23–30]. As shown in these studies, shape optimization, mechanical constraint and size control help release excessive lithiation-induced stresses and thus avoid pulverization of anodes and active materials in nano-structured silicon anodes [16,23,24,31].

Lithiation kinetics in such silicon nanostructured anodes has also been studied recently [25,32,33]. Experimental evidences have accumulated that the lithiation of crystalline silicon advances by the movement of an atomically-sharp reaction front [12,27,33,34], which separates an unlithiated pristine silicon phase and a fully lithiated silicon phase (as shown by the schematics of Fig. 1(b)). Therefore, the lithiation of silicon is a two-phase reaction [35,36] and it indicates that the lithiation process is controlled by the reaction between lithium and silicon at the reaction front, rather than the diffusion of lithium through the lithiated silicon phase [25,27]. Experimental measurements of reaction velocity in solid silicon particles reveal that the reaction front usually slows down as it progresses into the solid particles [32]. Existing studies have shown that lithiation-induced stress field could affect the driving force of lithiation [21,22,28,37,38]. A theoretical model is recently developed to account for simultaneous lithiation and the associated stress field evolution [25,31]. Interestingly, the model predicts that the evolving stress field across the reaction front acts as an energy barrier and retards the lithiation reaction. Therefore, it is expected that the contribution of stresses to the driving force for Li–Si reaction results in the observed slowing of reaction front in solid particle silicon anodes [25,32].

Recently, hollow silicon nano-anodes attract attentions since they have more free space to accommodate the large volume expansion due to lithium insertion and thus possess excellent cycling performance [15,39–43]. It is noteworthy that lithiation of hollow silicon nanowires also shows similar slowing or even halting of the reaction front [16]. Although the observed slowing or halting of reaction front in hollow silicon anodes can also be attributed to the negative contribution of lithiation-induced stress, a quantitative understanding is still lacking to fully decipher the lithiation-induced stress field and its influence on reaction rate in hollow silicon nano-anodes. What remain elusive include, e.g., how does the hollow nature of silicon anodes alter the role of mechanical stresses in retarding lithiation reaction? How does the

slowing of reaction front in hollow silicon anodes differ from that in solid ones? Is hollow nanostructure a good anode design from lithiation kinetics standpoints? Quantitative answers to these questions are crucial for advancing the design of high-performance silicon-based hollow anodes.

In this paper, we present a finite element based chemo-mechanical modeling method as well as a theoretical model to quantitatively determine the stress field in hollow silicon nanowire anodes as the lithiation reaction proceeds. The driving force for the movement of the sharp lithiation reaction front is then identified based on the stress distribution across the sharp reaction front. The lithiation process is fully specified by the current position of the lithiation front and the lithiation-induced volume expansion of the fully lithiated silicon. Our calculation reveals that, compared with solid silicon anodes, hollow silicon anodes suffer less stress-induced reduction of driving force for lithiation, therefore could act as a better anode structural design for next-generation high performance lithium-ion batteries. Moreover, our calculation results can help answer a number of open questions of lithiation kinetics of silicon-based anodes in perspective of the experimental results in recent literature.

2. Lithiation-induced stress field in a hollow nanowire

We consider the lithiation process of a hollow cylindrical amorphous silicon nanowire anode with an inner radius R_i and outer radius R_o at the pristine reference state, whose cross-section view is illustrated in Fig. 1(a). Recent experiments indicate that the reaction rate of amorphous silicon at the lithiation front is isotropic, without obvious preferential directions [16]. Therefore, as lithiation advances, velocity of the reaction front is the same everywhere along the front and thus the lithiation front sweeps through the hollow silicon nanowire with a cylindrical shape of radius $A(t)$ (Fig. 1(a)). Here, $A(t)$ decreases with time as the reaction front propagates from the outer surface of silicon nanowire to its inner surface. During this process, lithiated silicon expands in volume to accommodate the lithium insertion. Therefore, a material element characterized by initial radius R in the reference state is deformed and moves to a new position with radius $r(t)$ after this material element is lithiated. In particular, the outer surface with a radius R_o in the reference state is pushed out to be the current outer surface with a radius r_o . During the lithiation process, stress field arises and evolves in response to the volume change caused by lithium insertion.

To solve the lithiation-induced stress field in the silicon nanowire, the concurrent lithiation reaction and deformation of the silicon nanowire along its cross-section are simulated using finite element code ABAQUS. In order to mimic the inward movement of the reaction front, the cross section of the silicon nanowire is evenly divided into N (an integer) annuluses and these annuluses are lithiated one by one from outer surface toward inner core of the silicon nanowire. Experimental evidence has accumulated that the reaction front is atomically sharp with thickness of ~ 1 nm [34]. In the simulation, the thickness of the reaction front is defined by the thickness of each annulus, which is set to be 2 nm to compromise between simulation expense and modeling fidelity. The lithiation of each annulus is modeled by prescribing a volume change of 400% (i.e., fully lithiated). The pristine silicon is modeled to be linearly elastic with a Young's modulus of 160 GPa and a Poisson's ratio of 0.24 [27]. The fully lithiated silicon phase is taken to be elastic-perfectly plastic with a Young's modulus of 40 GPa, a Poisson's ratio of 0.22 and a yielding stress of 1.5 GPa [27,44]. Recent experiments reveal that a hollow cylindrical silicon anode with the deformation of its inner surface largely constrained demonstrates a better durability during lithiation compared with its counterpart

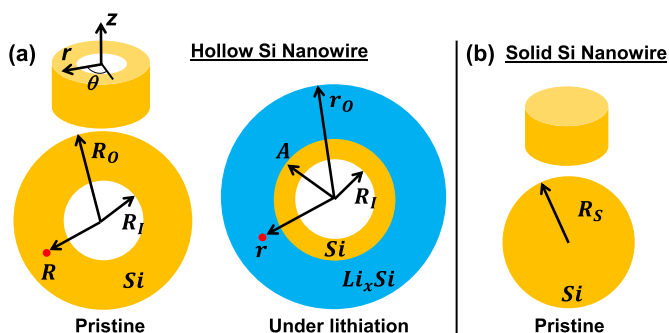


Fig. 1. (a) Left: cross-section of a pristine hollow cylindrical silicon nanowire with an initial inner radius R_i and an initial outer radius R_o is considered to be the reference state. A material point (labeled by the red dot) is at a radius R . Right: in the lithiation state at time t , the lithiation front is located at a radius of $A(t)$, the outer surface is now at a radius $r_o(t)$, and the material point labeled by R in the reference state moves to a new location at a radius $r(t)$. (b) Cross-section of a pristine solid cylindrical silicon nanowire of a radius R_s , with the same volume of the hollow silicon nanowire defined in (a). (For interpretation of the references to color in this figure legend, the reader is referred to the web version of this article.)

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