



First-principles simulations of lithiation–deformation behavior in silicon nanotube electrodes



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ABSTRACT

The lithiation mechanisms that occur in silicon nanotube lithium-ion battery electrodes are not well understood at the atomic level. In this study, first-principles calculations were carried out to investigate the mechanism responsible for the insertion of lithium in armchair and zigzag nanotubes. The size dependence of the formation energy and the Young's modulus was investigated for the placement of a single Li atom. Our simulations showed that the elastic softening of a zigzag nanotube will occur when a single Li atom was placed, and that the lithiated configuration will transform from a crystalline structure to an amorphous structure with increasing Li concentration for both armchair and zigzag nanotubes. Formation energy and voltage analyses also demonstrated that zigzag nanotubes exhibit a much steeper descending trend compared with armchair nanotubes. It was found that, under uniaxial tension, the corresponding fracture strength of a silicon nanotube will decrease with increasing Li concentration, and that the ductility of such a nanotube will be improved greatly with increasing Li concentration, meaning that plastic deformation will occur relatively easily. This understanding of the lithiation mechanisms will provide useful guidelines for the designing of silicon nanotube electrodes in lithium-ion batteries.

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1. Introduction

Lithium-ion batteries are ubiquitous in electronics and are promising power sources for electric vehicles [1]. However, the limited capacity of the lithium-ion battery materials, especially the anode materials [2], has limited the development of this technology for the renewable energy sources. Much research efforts have therefore been dedicated to improving the capacity of anode materials [3–6]. Recently, silicon has attracted much attention as a potential anode material because of its large capacity of 4200 mAh/g (for $\text{Li}_{4.4}\text{Si}$) [7], which is almost 10 times that of graphite [8]. However, lithium will diffuse into the electrode during charging cycles, leading to a mechanical deformation and a large stress [9]. In practice, this mechanical deformation with lithium causes significant volume expansion, and may result in failure of the electrode [10–13], followed by irreversible capacity and poor cyclability during lithiation. In an attempt to solve this problem, a large number of studies [14–18] have applied the mechanical modeling of lithium-ion batteries using volume-averaged methods to

analyze the mechanical failure in the electrode. Recently, we have analyzed the effects of the dislocation and bending of nano-scaled electrodes on the stress or strain energy, and proposed fracture criteria for electrodes because of the lithium ion insertion [19–22].

Lithiation-induced fracturing not only limits the lifetime of lithium-ion batteries but also seriously restricts the development of larger capacities. One way to overcome this problem is to mitigate the mechanical damage via the use of nanostructures, such as nanowires [8], nanotubes [23] and nanoparticles [24], which can relieve the effects of diffusion induced stress. A number of experimental and theoretical analyses [25–28] to clarify the mechanism have been reported. For example, Sethuraman et al. [29] analyzed the stress evolution in Si thin films, using in situ measurements to detect the plastic deformation of lithiated Si. Lithium insertion and diffusion in bulk crystalline Si [30], thin films [31], nanowires [32], and the crystalline Li_xSi phases [33] have also been analyzed. In addition, the structural evolution process and the electronic properties of armchair silicon nanotubes had been discussed [34]. Although the experimental observations and the simulations of silicon lithiation based on density functional theory (DFT) [33–37] have provided an understanding of the ambitious mechanical properties, the plastic behavior at atomic-scale level in lithiation remains poorly understood.

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In the above-mentioned work, the researchers investigated the electronic properties, surface effects, and phonon modes in different types of Si anodes using theoretical models. In general, lithium ions which reside within the crystal structure of the electrodes carry current between the anode and cathode when the lithium ion batteries are in operation. During charging, lithium ions move from the cathode to the anode. Recently, Zhao et al. [38] reported a study of the deformation mechanism in lithiated Si materials at relatively low Li concentrations, and found that the lithium insertion may lead to the breaking of Si–Si bonds. In addition, the density functional studies had been performed to investigate the formations of boron-doped and nitrogen-doped models of silicon nanotubes [39] and the properties of armchair and zigzag models of silicon nanotube [40]. There is great interest in understanding the deformation mechanism, such as understanding and improving the physical properties of Si nanotube electrodes. Here we propose a method for the simulation of the lithiation of different types of Si nanotubes and their electronic properties. Large stresses and volume changes occur during lithiation, which will greatly limit the lifetime of the electrode. The first-principles computational method proposed here gives insights into the structural and mechanical behavior of the lithium-ion battery electrode materials during lithiation. The atomistic structures of the lithiated Li_xSi were presented and analyzed during the simulation process, and the formation energies and Young's modulus of Si nanotubes with different types and diameters were then investigated. It was found that Si nanotubes with different diameters will introduce the different formation energies, and different types of Si nanotubes produced different Young's modulus values. In the end, the strain-stress relationship for the lithiation electrodes material was derived for different Li concentrations.

2. Computational methods

2.1. Density functional theory calculations

The First-principles calculations reported herein were performed based on DFT within the local-density approximation (LDA), as implemented in the Cambridge Serial Total Energy Package (CASTEP) [41]. Single-walled carbon nanotubes are typically indexed using two integers (n, m) to characterize their helicity. Here, we have considered two types of Si nanotubes, which are armchair and zigzag. The two types of pure Si nanotube structure were modeled as a $1 \times 1 \times 2$ supercell of the conventional cell containing twenty atoms, with periodic boundary conditions. A small supercell was chosen because we studied a large number of possible configurations of pure Si nanotube structures, as well as the plastic behavior of the equilibrium structures during lithiation, for various Li concentrations.

The kinetic energy cutoffs were set at 350 eV for the plane wave basis set [42–44] and the k -point mesh of $2 \times 2 \times 3$, with a convergence criterion of 1 meV/cell for ionic relaxation. It was important to develop techniques that can simulate the insertion of Li into Si nanotubes that initially display a well-defined structure. In all calculations, the cell dimensions were relaxed, and optimized results have made the usual convergence checks. Furthermore, in energy optimization calculations, both the atomic coordinates and supercell shape were relaxed. What's more, the energy optimization was considered to be completed using the conjugate gradient method when the magnitude of the force on each atom was smaller than $0.04 \text{ eV } \text{Å}^{-1}$, convergence of energy change per atom was smaller than $2 \times 10^{-6} \text{ eV}$, the residual force was smaller than $0.01 \text{ eV } \text{Å}^{-1}$, the stress was smaller than 0.02 GPa and the displacement of atoms was smaller than 0.001 Å.

2.2. Silicon nanotube model

It was first necessary to investigate the presence of Li atoms in the Si nanotube and the mechanism responsible for that presence. Different nonequivalent sites of Li atoms have been discussed in the literature [32,38]. Tetrahedral interstitial positions $(1/2, 1/2, 1/2)$ are the lowest-energy sites for the insertion of Li into bulk Si [45], and we therefore began our study by investigating the tetrahedral site for the Li atom placement. Before adding the lithium atoms to the Si nanotubes, the pristine silicon nanotubes will be optimized and the optimized results have made the usual convergence checks in the calculations. Many studies show that the lowest-energy sites can be assumed as the center positions in the nanotube. In our study, we determined the center positions $(1/2, 1/2, 1/2)$ of a single lithium atom in two types of Si nanotubes. Supercells were created to examine the size dependence of the relaxation. A single Li atom was placed into the supercell at a center site, as shown in Fig. 1. It was noted that Fig. 1 showed the original two types of nanotubes when a single Li atom was placed into the supercell at a center site in order to better show the tetrahedral site $(1/2, 1/2, 1/2)$ for the Li atom placement. Based on the optimized geometry, the physical process of lithiation broke the crystalline Si lattice. When the structures relaxed due to Li intercalation, the nanotube structures are expanded in the horizontal directions and the lattice constant changed. Fig. 2 shows views of the initial and optimized structures of the armchair and zigzag Si nanotubes, respectively ((5,5) and (5,0) NTs are shown as illustrative representations). Firstly, we discuss how the different diameters can affect the mechanical properties when a single lithium atom was inserted into the nanotubes, such as Young's modulus. Then, a history-dependent approach was necessary for the simulation of the lithiation process. To find Li_xSi configurations that were connected to the initially crystalline Si through the mechanistic insertion of Li, Chevrier and Dahn [46,47] used a step-by-step Li insertion procedure, starting from amorphous Si, in which Li was inserted into the largest void within the computational cell at each step. Thus, our simulations were performed using a step-by-step insertion of Li into the Si nanotube.

3. Results and discussion

3.1. Effect of the nanotube diameter during lithiation

Two types of Si nanotubes were built; the two types were the armchair (n, n), and zigzag ($n, 0$), with the type depending on the rolling direction [48]. Because many studies had reported the lithium materials will pulverize when the silicon nanowires diameter is over about 200 nm during lithiation [49]. Therefore, to analyze the effects of changes in the tube diameter, armchair nanotubes (ANTs)/zigzag nanotubes (ZNTs) were built with different diameters, from (5,5)/(5,0) to (12,12)/(18,0). A single Li atom was placed into the supercell at the tetrahedral site. The formation energies were calculated based on the optimized geometry at each step of the lithiation routine, that is,

$$\Delta E_x = (E_{\text{Li}_x\text{Si}} - xE_{\text{Li}} - E_{\text{Si}})/N \quad (1)$$

where $E_{\text{Li}_x\text{Si}}$ denotes the energy of a lithiated structure (Li_xSi), E_{Si} is the lowest-energy without Li insertion, and N is the number of Si atoms where lithiation is allowed. Fig. 3 shows the size dependence of the formation energy for a fully relaxed Si nanotube when a single Li atom was placed into the supercell. It is obvious that the size dependence was evident for both types of tubes. The value of formation energy decreased monotonically with increasing diameter, for both types of nanotubes. These results showed that tubes with a smaller diameter tube had stronger formation energies. By

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