A systematic investigation of cycle number, temperature and electric field strength effects on Si anode

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HIGHLIGHTS

- Deformation behavior and microstructure evolution of Si anode are analyzed by MD simulations.
- Effects of cycling number, crystal orientation, temperature and electric field strength are explored.
- Considering surface stress, analytical modeling of diffusion-induced stress is established.
- Number and radius of nanovoid depend upon cycling number, temperature and electric field strength.
- Surface morphology of Si electrode relies on cycling number and temperature as well as electric field strength.

GRAPHICAL ABSTRACT
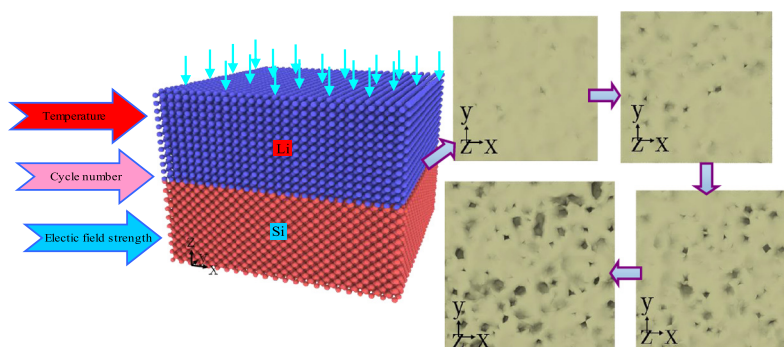
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ABSTRACT

Cycling number, crystal orientation, temperature and electric field strength play key roles in affecting the capacity and cycling ability of Li-ion battery. However, the detailed dynamic and continuous process of capacity decline mechanism from above factors need to be further understood at nanoscale. Herein, we report deformation behavior and microstructure evolution of Si anode under electric field using molecular dynamics simulations. The results show larger cycling number and electric field strength cause larger volume expansion of Si electrode, leading to the capacity loss and the reducing cycling ability as well as the decreasing structural stability. The phase transformation from diamond cubic structure to body-centred tetragonal structure and the amorphous formation depend on lithiated and delithiated depths. The crystal orientation [100] Si anode produces the volume expansion owing to a large number of nanoscale void. The various temperatures strongly affect the number and radius of nanovoid. The associated transition in the nanovoid nucleation due to the involuntary diffusion process is driven by larger cycling number or electric field strength, resulting in the irreversible capacity loss of Li-ion battery. An established analytical model suggests that diffusion-induced stress not only relies on the position of Si anode but depends upon the cycling time.

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1. Introduction

Li-ion batteries have attracted extensive research interest in recent years due to reports of high energy density and excellent operating voltage, which have gotten broad applications in mobile electronic devices and electric vehicles [1–3]. In most cases, Li-ion batteries have superior rate capability but at the expense of capacity and cyclic performance [4,5], which considerably limits the life and practical utility of Li-ion battery. The failure mechanism of Li-ion battery depends on the dominant aging modes [6–10], such as extremely high gradient stress [6,7], formation and growth of solid-electrolyte interphase (SEI) [8,9], and cracking [10]. More intriguingly, the electrochemical and mechanical properties of Li-ion battery would be influenced when the amorphous Si electrodes undergo the large plastic deformation [11–13]. Therefore, it is strongly suggested that further study on the failure mechanisms during cycling are of great necessity and finally achieve the purpose of prolonging the Li-ion battery life by reducing and controlling the its plastic behavior.

Some experiments [14,15] show that the loss of structural integrity to reduce the electrical conductance results in the fading of the capacity of Li-ion battery during cycling. Some theoretical modelings show the elastic-plasticity behavior of Li_xSi alloys described by the continuum mechanics theories, and reveal the stress-gradient effects during the Li-ion diffusion process [16,17]. Diffusion-induced stress computed by the analytical expression is investigated for nanowire [18], cylindrical modeling [19], plate modeling [20], and spherical modeling [21,22]. The deformation behavior of amorphous LixSi alloys has been well explained by some atomic simulations, such as density functional theory (DFT) calculations and molecular dynamics (MD) simulations [23–25]. Using the reactive-force-field (ReaxFF) potential, Ostadhossein et al. [24] studied the lithiation process of the crystal Si nanowires. They found that Li insertion into interlayer spacing between two adjacent (111) planes results in the amorphization, which is in good agreement with experimental observations. By the modified embedded atomic method (MEAM), Cui et al. [25] predicted the mechanical properties of crystal and amorphous Li_xSi alloys, such as Young's modulus, yield strength and Poisson's ratio. However, all the studies are concentrated on the plastic deformation mechanisms of Si electrode, no systematic research has been dedicated to the effects of crystal orientation, cycling number, temperature and electric field strength on the nanoscale deformation behavior in the Si anode during cycling.

The manuscript is organized as follows: Section 2 contains the details of MD simulations of lithiation and delithiation. Section 3 discusses the MD results, which are compared with previous experimental observations and atomic simulation results. The effects of crystal orientation, cycling number, temperature, and electric field strength on deformation behavior and structural stability of Si anode are investigated with the aid of MD simulation. In addition, the analytical model on the diffusion-induced stress is established. Our conclusions are shown in Section 3.6. Our work would be able to provide a plastic deformation and structural stability during the charge-and-discharge cycle. Although the Li-ion battery failure does not originate from a single reason, the current studies help us further understand the nanoscale failure mechanism of Si anode and improve the Li-ion battery life.

2. Simulation details

Using large-scale atomic/molecular massively parallel simulator (LAMMPS) [26], the Si anode and Li electrode under electric field are performed by MD simulations, which are used to study solute diffusion driven by the electric field [27,28], as shown in Fig. 1a. The MD model is build by the single-crystal Li electrode and single-crystal Si anode. The every Li-ion has a unit positive charge [28], and the every Si atom maintains neutral. The dimension of Si electrode consisting of 43,560 Si atoms is $12.2 \times 12.2 \times 5$ nm^3, and that of Li electrode consisting of 42,875 Li-ions is $12.2 \times 12.2 \times 5$ nm^3. The red and blue spherical

particles represent Li-ions and Si atoms, respectively. The crystal orientations of the Li and Si electrodes are [100] along x direction, [010] along y direction, and [001] along z direction. The lithiation is performed under a constant electric-field strength, while the delithiation is performed under a same constant electric-field strength with opposite direction. According to the work [29], the electric current density I and electric field strength E can be expressed by $E = I/\sigma$, where σ is the electrical conductivity. During the charging and discharging of Li-ion battery, the electric current density is $J = 0.5$ mA/cm^2 [30]. The electrical conductivity of Si is $\sigma = 4 \times 10^{-5}$ S/cm [31]. Hence, the electric field can be calculated $E = 1.25$ V/cm. In order to improve the calculation efficiency combined with the reasonable computation time, a higher electric field $E = 1$ V/Å is used to achieve the charging and discharging process in Li-ion battery. Periodic boundary conditions are imposed in both the x and y directions, and the free surface is used to the z direction [28]. The MEAM potential is used to describe the atomic interactions [25,28], which can be capable of accurately predicting the mechanical properties of Li-ion battery over nanometer scales [7,25,28]. In addition, the electrostatic interactions between the intercalated Li-ions account for the Coulomb interactions for the MD simulation system.

According to the Maxwell-Boltzmann distribution, the velocities of all Li-ions and Si atoms are randomly given. The temperature is maintained at target temperatures, such as 100, 200, 300, 500 and 800 K, via Nose-Hoover thermostat [28]. In the all simulation cases, the time step is set to 1 fs, and the isobaric-isothermal canonical ensemble (NPT) dynamics is performed. During the first charging-and-discharging cycle, the simulations are divided into three stages as followed: firstly, at the relaxation stage, the system is kept at target temperature for 100 ps to achieve an equilibrium state; secondly, at lithiation stage Li-ion begins to insert into Si electrode under the given electric field along the negative z-axis direction until initial Li-ions reach the end of Si electrode. To conduct the every step of lithiation process, the electric field is applied in every 10 fs, and then the system is relaxed to an equilibrium state for 100 ps; finally, at delithiation stage Li-ion begins to extract into Si electrode under the given electric field along the z-axis inverse direction until all Li-ions leave the upper surface of Si electrode. To conduct the every step of the delithiation process, the electric field with inverse direction is applied in every 10 fs, and then the system is relaxed to an equilibrium state for 100 ps. For next charging-and-discharging cycle, a similar way related to the electric field acts on the electrodes. Although the massive MD calculations successfully offer important insights into the relationship between microstructure and properties based on the high-performance computing, notwithstanding the fact that the time scale of MD simulation on large-scale systems is typically <1000 ps. Hence, the current simulated cycling of Li-ion battery at a very short time period is mainly focused on the microstructure-dominated electrochemical performance, to reveal the deformation and failure mechanism during cycling. Moreover, this study could gain further understanding of real cycling behavior to guide the design and optimize the structure in Li-ion battery.

In this simulation, the open visualization tool (OVITO) software is used to visualize the LAMMPS output data for the charging-and-discharging process [32]. The evolution and distribution of the possible phases during cycling are discussed in terms of coordination number (CN) and radial distribution function (RDF).

3. Results and discussion

3.1. Lithiation and delithiation phenomenon

The Li-ion diffusion processes in the Si anode have been carefully studied by experiments, theoretical models and simulations [16–22,33–38]. However, most of these experiential, theoretical and simulated results are focused on the structure and mechanical properties of the final status of Li_xSi alloys [36–38], which could not model diffusion-induced strain upon electrochemical lithiation and delithiation.