



# Multi-scale analysis of an electrochemical model including coupled diffusion, stress, and nonideal solution in a silicon thin film anode



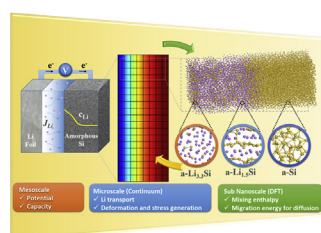
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## HIGHLIGHTS

- Multi-scale model for electrochemical and mechanical characterization of a-Si film.
- Stress-dependent migration barrier and molar excess Gibbs free energy by DFT.
- Atomic-scale effects strongly influence nonlinear distribution of Li concentration.
- Predicted potential-capacity hysteresis of a-Si anode matches the experiments well.

## GRAPHICAL ABSTRACT



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## ABSTRACT

The electrochemical performance of Li-ion batteries strongly depends on the interaction between atomic scale and micro scale phenomena in high capacity electrode materials such as silicon and sulfur. Local thermodynamic interactions between host and guest species on atomic-scale significantly influence transfer kinetics and deformation kinematics on the micro-scale. We propose a multi-scale model to characterize the electrochemical and mechanical response of an amorphous silicon thin film during discharge/charge cycling. In the atomic-scale simulation, the stress-dependent energy barrier for the migration of lithium and the molar excess Gibbs free energy were calculated using density functional theory. These atomic-scale effects account for the nonlinear lithium diffusion behavior in the continuum simulation. In the continuum simulation, we considered the coupled diffusion and large deformation model on the cell-scale to determine the non-equilibrium cell potential as a function of the surface lithium concentration using Butler-Volmer kinetics. We clearly show that Li macroscopic kinetics is significantly affected by the stress induced by the volumetric strain associated with diffusion and the mixing formation energy of  $\text{Li}_x\text{Si}$ . Our simulation results demonstrate that the multi-scale model is consistent with experimental observations at different C-rates.

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## 1. Introduction

Silicon has attracted much attention in the development of high-energy-density Li-ion batteries (LIBs) for use in energy storage

systems (ESS) and electric vehicles (EV) [1,2]. Compared to the conventional carbon-based anode, amorphous silicon (a-Si) shows a remarkable ability to absorb Li ( $3580 \text{ mAh g}^{-1}$ ), forming  $\text{Li}_{3.75}\text{Si}$  [3,4]. This high absorption capacity, however, causes undesirable volume expansion that results in the mechanical pulverization of electrodes [5,6]. As a consequence, electrodes can induce fracture, triggering electrical contact loss and the formation of a solid

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electrolyte interface (SEI) on the fractured surface. This result eventually leads to a significant irreversible capacity loss [7,8]. This loss is one of the main drawbacks for the commercial use of Si as an anode material in LIBs. Many strategies have been proposed to reduce this large electrochemically related stress so that the cycle performance of the Si anode can be improved. In particular, nano-structured Si materials such as nanowires, nanotubes, nanofilms and porous structures have been studied to enhance the mechanical stability of Si anodes by managing deformation patterns through geometric restrictions and shape optimizations [9–11].

In addition to experimental studies, theoretical work has been carried out to understand the kinematics of large deformations during lithiation/delithiation [12–15]. Zhao et al. [16] proposed a reactive flow model that considers the concurrent non-equilibrium process of the Li insertion reaction and the plastic flow of electrodes. Recently, Bower et al. [17] proposed a theory involving finite deformation, diffusion, plastic flow, and electrochemical reactions. First-principles calculations were conducted to gain a better understanding of the electrochemical kinetics and deformation from a fundamental perspective. The kinetics of Li insertion into a-Si has been investigated by Moon et al. [18,19]. Moon et al. reported the concentration-dependent diffusivity of Li in  $\text{Li}_x\text{Si}$  compounds. Shenoy et al. calculated mechanical properties such as the Young's modulus, shear modulus, and Poisson's ratio that show elastic softening during lithiation. Shenoy et al. explained that elastic softening occurs due to structural evolution that causes the formation of weak Li–Si bonds from strong Si–Si covalent bonds [20]. Several other models have been developed for which various aspects of Li-ion cell behavior [21–24]. Mostly previous battery cell models employed the classic Fick's second law to describe Li transport in battery systems. Fick's second law for a Li diffusion is a reasonable approximation to fit experimental observations of potential versus capacity [25]. Potential profiles of high charge rate (C-rate) conditions, however, have shown large discrepancies between model predictions and experimental data because existing models simply fail to describe accurately the physical phenomena that actually occur. Jagannathan et al. incorporated charge rate-dependent diffusion coefficients in the classic Fick's law model in an attempt to overcome these issues. This model, however, is not a physics-based model, and neglects important physical phenomena such as diffusion-induced stress, concentration-dependent material parameters, and Li–Si mixing enthalpy. These properties must be taken into account to describe the variation of potential hysteresis [26]. For this reason, multi-scale physical modeling techniques need be considered to provide a deeper insight into a physics-based battery model that properly describes electrochemo-mechanical behavior. The continuum theory of diffusion-induced stress should be extended to an atomic-scale analysis in which the local thermodynamic interactions between Li and Si influence macroscopic mechanical behavior.

Therefore, the objective of this study is to propose a multi-scale model to characterize the electrochemical and mechanical response of a-Si thin film. In a multi-scale framework, the diffusion induced stress (DIS) model [27] on a cell-scale includes atomic-scale effects of internal stress on the migration energy barrier, and concentration-dependent mixing enthalpy. These effects contribute significantly to the nonlinear distribution of Li concentration. In order to investigate these atomic-scale physical and chemical effects on the overall Li diffusion and discharge/charge potential hysteresis, we split the multi-scale model into four different models: (1) diffusion induced stress (DIS) model, (2) DIS coupled with stress-dependent migration energy barrier, (3) DIS coupled with concentration-dependent mixing enthalpy, and (4) DIS coupled with all of these effects. Each of these models was analyzed for individual atomic-scale effects. We then demonstrated

that our multi-scale analysis is quantitatively consistent with the experimental observations of a Si thin film at different C-rates. The results shows that the macroscopic kinetics of silicon anode materials in Li ion batteries are highly affected by the stress induced by lithiation/delithiation, and the mixing formation energy of  $\text{Li}_x\text{Si}$ .

## 2. Methodology

### 2.1. Multi-scale modeling of Li batteries

The electrochemical performance of Si-based materials depends on the interaction between atomic-scale and micro-scale phenomena that occur at the electrodes [28]. The electrochemical reaction of Li with Si occurs on a nanometer-scale. This reaction, of course, depends on the molar fraction of each reactant and their mixing energies. Li transfer and the mechanical deformation of the host material, however, depends on the physical properties of each material. The mechanisms for the manifestation of these are strongly and nonlinearly coupled over the nano and micro scales, which affects the macroscopic behavior of LIBs [29].

Fig. 1 shows a multi-scale model of a LIB. In the atomic-scale simulation (sub nanoscale diagram), the migration energy barrier to the lithium diffusion and the excess molar Gibbs free energy representing deviation from an ideal solution were calculated using density functional theory (DFT). We incorporated the results of the atomic-scale simulation into the continuum model (micro-scale model) that accounts for the diffusion-coupled elastic-plastic deformation in the cell-scale (meso-scale). In the meso-scale model, we determined the non-equilibrium cell potential as a function of surface lithium concentration using Butler-Volmer kinetics.

### 2.2. Atomic-scale simulation of Li in Si

Ab-initio calculations were performed using the DFT method with generalized gradient approximation (GGA) [30,31]. We used the projector augmented wave (PAW) method with a plane wave basis set as implemented in the Vienna Ab-initio Simulation Package (VASP) [32]. The valence configuration for Li ( $1s^2 2s^1$ ) and Si ( $3s^2 3p^2$ ) were employed. The energy cutoff for the plane wave basis set was kept fixed at a constant value of 500 eV. A k-point mesh in the Monkhorst-Pack scheme was set to  $3 \times 3 \times 3$ . The amorphous Si structure contained 64 Si atoms with periodic boundary conditions. The geometries of  $\text{Li}_x\text{Si}$  ( $0 \leq x \leq 4$ ) were optimized using the conjugated gradient method until the residual forces on constituent atoms become smaller than 0.01 eV/Å. For the ab initio molecular dynamics simulation, the k-point was only sampled at the gamma point. Amorphous structures of  $\text{Li}_x\text{Si}$  were made using the ab initio MD (AIMD) simulation avoiding crystalline configurations at 2200 K. A time step of 3.0 fs, and overall simulation steps of 2000 were used. To study Li kinetics in a Si environment, diffusion pathways and barriers were determined using the climbing-image nudged elastic band (NEB) method [33].

#### 2.2.1. Stress-dependent migration energy barrier for diffusion

Diffusivity  $D$  is related to mobility according to Eq. (1).

$$D = MRT \quad (1)$$

where  $M$  is the mobility of the diffusion component, and  $R$  and  $T$  are the universal gas constant and the absolute temperature, respectively.

Here we consider the effect of the internal stress field on the migration energy barrier of diffusion, as follows. On the atomic-scale, the diffusion of a solute particle in an atomic lattice is

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