



# Modeling diffusion-induced stress on two-phase lithiation in lithium-ion batteries

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## ABSTRACT

Capacity fade induced by chemo-mechanical degradation during charge-discharge cycles is the bottleneck in the design of high-performance batteries, especially high-capacity electrode materials. In this paper, a flexible sigmoid function is used to create the two-phase electrochemical lithiation profile, describing a sharp phase boundary that separates the pristine core from the lithiated shell of an electrode particle. According to such a phase transition, an analytical solution of the stress evolution is obtained by introducing an electrochemical reaction layer into the plastic model. Finally, based on the theory of diffusion-induced stress and the energy principle, we determine the critical thickness of radius of a lithiated layer, at which fracture occurs.

## 1. Introduction

Lithium-ion batteries (LIBs) have been widely used as power devices for portable electronics (Mukhopadhyay and Sheldon, 2014; Nam et al., 2006; Van Noorden, 2014). Silicon (Si) is emerging as the most promising anode material, given its theoretical capacity ten times high as that of conventional graphite-based anodes (Chen et al., 2014; Yao et al., 2011). As is known, a large volume swelling of ~300% during Li insertion (or extraction) may result in fracture of active Si anodes and irreversible capacity fading (Jia and Li, 2016). However, there is still not a good understanding on its intrinsic mechanism.

Recently, experimental observations have shown the formation of a core-shell structure in a partially lithiated Si nanoparticle, which consists of a two-phase boundary that separates an inner core of crystalline Si from an outer shell of amorphous  $\text{Li}_x\text{Si}$  ( $x = 3.75$ ) (Liu et al., 2012; McDowell et al., 2012). A sharp phase boundary implies that the Li-poor and Li-rich phases do not transform continuously (McDowell et al., 2013). An abrupt change of Li concentration across the amorphous-crystalline interface promotes a drastic volume strain inhomogeneity, which is significantly different from that of single-phase lithiation (Wang et al., 2013). Thus, it is necessary to investigate the diffusion-induced stress, deformation and fracture on the basis of a two-phase electrochemical reaction lithiation process. In consideration of the analogy between diffusion and heat flow, diffusion-induced stress can be modeled as thermal stress (Lee et al., 2000; Prussin, 1961; Song

et al., 2012; Yang, 2013; Yao et al., 2011). It is shown that there is a hoop compression stress in the surface layer and a tension stress in the center where fracture appears. However, this contrasts with *in situ* transmission electron microscopy observations of fracture initiation on the particle surface (Liu et al., 2012; McDowell et al., 2012).

During lithiation and delithiation processes, the lithiation-induced large deformation of Si electrodes is accommodated by plastic flow when stress exceeds the yield strength (Chon et al., 2011; Sethuraman et al., 2010). This makes it possible for Si anodes with small size to maintain a high capacity after many cycles, such as thin films (Takamura et al., 2004), nanowires (Chan et al., 2008), and porous structures (Wada et al., 2014). Sethuraman et al. (2010) measured the diffusion-induced stress as a function of the state of charge (SOC) in an amorphous Si thin film and found a pronounced hysteresis, indicating plastic deformation of lithiated Si. The microscopic mechanism was elucidated for the onset of large plastic deformation in lithiated crystalline Si (*c*-Si) and amorphous Si (*a*-Si) (Zhao et al., 2011), and captured the dramatic brittle-to-ductile transition of *a*-Si at a relatively low Li concentration by first-principles computational methods. A new stress-dependent chemical potential was reported for solid state diffusion under multiple driving forces (Cui et al., 2012), and also discovered that when plastic deformation occurs, the hoop stress is tensile on the particle surface.

On the other hand, the two-phase electrochemical reaction lithiation plays an important role in the stress evolution. A two-phase model

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was presented with the diffusivity dependence on Li concentration to describe the evolving core-shell structure with a sharp interface between Li-poor core and Li-rich shell (Liu et al., 2012). Also, anisotropic swelling and fracture of Si nanowires during lithiation were studied (Yang et al., 2012). An analytical solution of the co-evolving reaction and rigid-plasticity was exhibited in a spherical particle to explain the stress evolution (Zhao et al., 2012b). The kinetic model and finite element simulation were applied to obtain solutions of the Li-ion concentration distribution, the moving velocity of phase interface and the stress evolution (Pharr et al., 2012; Xie et al., 2016). A mechanics foundation was proposed for a direct physical understanding of stress generation during lithiation of high-capacity electrode materials with curved geometries (Huang et al., 2013).

In spite of the plastic flow and two-phase electrochemical lithiation, there is a strong size dependence of fracture, which means that, over a critical diameter, particles initially crack on surfaces and then fracture due to lithiation-induced swelling (Haftbaradaran and Gao, 2012; Liu et al., 2011, 2012; Zhao et al., 2010, 2012a). Using the theory of diffusion-induced stress and the energy principle, relations between the critical concentration of solute atoms and average damage size can be established for insertion-induced cracking and buckling in an elastic film (Yang, 2011). From the perspective of strain energy release rate, the critical size of various Si nanostructures can be also determined (Ma et al., 2013). Taking fracture and debonding of hollow core-shell nanostructures into account, the critical size was investigated relating to the core radius, the shell thickness, and SOC for a hollow structure (Ma et al., 2015; Zhao et al., 2012a).

In this paper, we aim to build up an analytical solution of diffusion-induced stress based on a two-phase lithiation process. The paper is organized as follows. In Section 2, a sigmoid function is set to be the analytical solution of concentration. Further, by introducing an elastic transition layer in an elastic-plastic model, the analytical relation between stress and radius of the elastic transition layer is obtained. In Section 3, the Li concentration profile, lithiated shell thickness, diffusion-induced stress field, and the size-dependent fracture are discussed. Finally, the concluding remarks are given in Section 4.

## 2. Theoretical model

### 2.1. Concentration

As illustrated in Fig. 1, the crystalline core (c-Si) is surrounded by an amorphous shell (a-Li<sub>x</sub>Si) in a core-shell Si electrode. Initially, the electrochemical charge-transfer reaction at electrode-electrolyte interfaces causes Li-ions to be reduced with intercalation of Li in electrodes. Then, Li atoms diffuse through lithiated Si, and react with crystalline Si to form an amorphous phase at the reaction front. Here, migration of Li-ions in electrolyte is controlled by the Li diffusion through Li<sub>x</sub>Si and the reaction of Li and Si at interface between Li<sub>x</sub>Si and Si. According to previous studies (Xie et al., 2016; Zhao et al., 2012b), the relative rate of diffusion and reaction can be characterized as  $\beta = D/kR$ , where  $D$  is the diffusivity of Li in the lithiated Si,  $k$  is the velocity of the reaction front, and  $R$  is the particle size. If  $\beta$  is large, the diffusion of Li is fast,

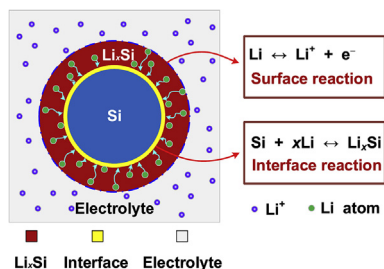


Fig. 1. Schematic illustration of the two-phase mechanism for Li-ion diffusion.

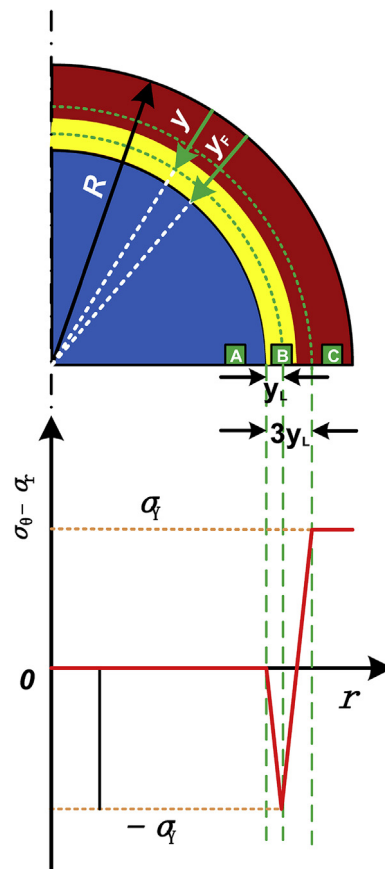


Fig. 2. Illustration of the stress state of a core-shell structure in a partially lithiated electrode particle.

and lithiation is limited by the electrochemical reaction. For the migration of phase boundaries, we adopt a flexible sigmoid (or generalized logistic (Huang et al., 2013)) function to describe the Li-ion concentration,  $c(r)$  along the radius,  $r$ , that is

$$\frac{c(r)}{c_0} = \frac{1}{1 + \exp\left[-\beta \frac{r-(R-y)}{R}\right]} \quad (1)$$

where  $y$  is the center position between the two-phase boundary ( $c = 0.5$ ) and surface. Such a logistic function in Eq. (1) has two asymptotic limits of  $c = 0$  and  $1$ , representing the pristine Si core and Li<sub>3.75</sub>Si shell, respectively. To move the phase boundary from the particle surface ( $y = 0$ ) to its center ( $y = R$ ), we can prescribe different time laws. As illustrated in Fig. 2, the transition layer thickness can be written as,  $2y_L = 2(y_F - y)$ , where  $y_F$  is the thickness of lithiation layer. Then, the SOC is deduced as

$$\text{SOC} = \frac{\int_0^R c(r)r^2 dr}{\int_0^R r^2 dr} \approx \frac{R^3 - (R-y)^3}{R^3} = 1 - \left(1 - \frac{y}{R}\right)^3 \quad (2)$$

### 2.2. Stress

In the case of a symmetrical spherical particle, the stress state can be represented by  $(\sigma_r, \sigma_\theta, \sigma_\theta)$ , with  $\sigma_r$  and  $\sigma_\theta$  the radial and hoop stresses, respectively. As shown in Fig. 2, the crystalline core is under homogeneous hydrostatic compression, so the stress state of element A is  $\sigma_\theta - \sigma_r = 0$ . On the two-phase boundary, as the reaction front sweeps through element B, a large lithiation strain creates at zone B. Owing to the constraint of surrounding materials, local compressive stresses reach to the yield stress  $\sigma_y$ , viz.  $\sigma_\theta - \sigma_r = -\sigma_y$ . The material element C is pushed outward by newly lithiated Si, causing further displacement

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