



# Phase field modeling of silicon nanowire based lithium ion battery composite electrode



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## ABSTRACT

A phase field model is developed to investigate the silicon nanowire behaviors in lithium-ion battery electrode during its lithiation process. The coupling effect among lithium ion diffusion/insertion process, structure deformation and local stress/strain evolution are established. Modeling demonstrates that such coupling effect can significantly influence electrochemical performance of silicon composite electrode. On a 2D silicon nanowire geometry, Cahn-Hilliard equation and Ginzberg-Landau equations are developed and solved by finite element method. The developed model has nearly the same prediction on volumetric expansion ratio of silicon NW in comparison with the published experimental observation and can capture the  $a - Li_{\eta}Si/c - Si$  phase boundary during lithiation. Numerical results show that large local stress exists in the outer region of silicon NW and could negatively influence the fast charging performance of silicon composite electrode. Results also show that small lithium mobility can limit the lithiation depth of silicon electrode during the charging process, and can result in reduced charge capacity of silicon composite electrode. By simulating different silicon NW structures, it is found that silicon NW structure can significantly influence the local stress distribution and evolution in silicon composite electrode. It is also found that porous silicon NW has potential structure degradation around the core region during its lithiation process. These obtained results can provide insights into the dynamic process of silicon electrode degradation and can assist in developing applicable high performance silicon electrode for future lithium ion batteries.

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## 1. Introduction

Lithium ion batteries (LIBs) have been widely used as the primary energy storage devices on portable electronics, power tools and in recent years on electric vehicles (EVs) [1,2]. The rapid development of modern electric vehicles technologies requires high performance LIBs with large charge capacity and high energy density [2]. In response, the silicon based electrode has been developed and widely recognized as a potential alternative to current commercial graphite electrode due to its high Li accommodation capacity [3]. However, numerous experiments have shown that silicon electrode typically cannot retain its capacity over a long battery charge-discharge cycles, and its charge capacity can be quickly decreased below 50% of its initial capacity after first a few cycles [4]. This is found as a result of the large volume change during the lithium ion intercalation and de-

intercalation process [5]. To address this issue, silicon nano-wires (NW) based composite electrodes are proposed in recent years, which can improve the electrode electrochemical performance by reducing the diffusion distances for lithium atoms and enables facile strain relaxation [6]. Although the silicon NW composite electrodes have shown much better cycling stability in experimentation than bulk silicon electrodes, their phase transformation during charging and discharging operation is quite large and a large stress can be generated on their nanostructure, which can induce unpredictable debonding and fracture. Moreover, the local structure deformation can cause continuous generation of solid electrolyte interface (SEI) products that can fill up the pores in the silicon composite electrode. This will dramatically hinder lithium diffusion process, and eventually lead to a strongly heterogeneous lithiation of the electrode and rapid capacity fade of LIBs [7].

With recent advancement in 3D imaging and *in situ* technologies [8], the behaviors of LIB electrodes on their original position can be observed and linked to the battery electrochemical responses. Different from current commercial electrodes, i.e. graphite, lithium manganese spinel (LMO) [9,10], lithium-nickel-

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## Nomenclature

$c$	Lithium concentration;
$c_m$	Maximum local lithium concentration;
$E$	Young's modulus;
$F$	Faraday's constant;
$h(\theta)$	Double-well free energy function;
$H$	Total free energy;
$i$	Current density;
$J_{Li}$	Mass flux of lithium ions;
$k$	Lithiation reaction rate of
$M$	Effective mobility of lithium in silicon;
$M_0$	Molecular mobility of lithium in silicon;
$N_A$	Avogadro's number;
$q$	Elementary charge;
$R$	Gas constant, $8.314 \text{ J K}^{-1}\text{mol}^{-1}$ ;
$T$	Temperature;
$u$	Elastic strain;
$u_i$	Displacement on $i$ direction;
$\nu$	Poisson's ratio;
$z$	Charge number;
$\varepsilon_{ij}$	Strain tensor component;
$\xi_s$	Local elastic strain energy density;
$\sigma$	Hydrostatic stress;
$\sigma_{ij}$	Stress tensor component;
$\Omega$	Partial molar volume;
$\Omega_{Li_\eta Si}$	Atomic volume of $Li_\eta Si$ phase;
$\theta$	Phase field parameter;
$\kappa_i$	Gradient energy coefficient;
$\phi$	Electrostatic potential;
$\mu_0$	Standard chemical potential;
$\eta$	Number of lithium in $Li_\eta Si$ phase;
$\zeta$	Relaxation constant of phase change

cobalt-aluminum (NCA) [11,12], etc., which all have less than 15% volume change, the silicon electrodes are reported with up to 300% expansion during lithiation [3]. The coupled electrochemical-mechanical effect has been recognized as the major reason leading to its capacity fading and failure. Because it is difficult for current experimental tools to investigate the inhomogeneous lithium distribution under a variety of physical effects, capturing the related structure evolution and the stress generation of silicon electrode can only be accomplished by modeling analysis. Based on the electrochemistry of lithium insertion, plenty of modeling works have already been proposed in literatures: Christensen et al. [13] developed a mathematical model to simulate the fracture and stress generation on a spherical electrode particle induced by lithium ion intercalation, where the lithium concentration and stress profiles were studied during the particle volume change. Bucci et al. [14] numerically investigated the mechanical and electrochemical response of thin film amorphous silicon electrode during cyclic lithiation, and compared their model predictions with the experimental measurements. Siladitya et al. [15] also studied the amorphous silicon thin film anode by developing a mathematical modeling, where they focused on the electrochemical cycling induced film delamination. Sikha et al. [16,17] proposed a two dimensional silicon nanowire model to study the electrochemical lithium insertion process. They simulated three different core-shell structures of silicon nanowire, and studied the radial and tangential stresses generation induced by lithium diffusion. Yang et al. [18] also proposed a chemo-mechanical model to investigate the deformation of silicon nanowire during lithiation

where they investigated the stress generation at different angular sites of silicon nanowires. Those modeling works have successfully simulated the sharp electrode/particle interface evolution during lithiation by assuming a regular simple interface structure. However, when complex interface topologies exist, e.g. porous silicon composite electrode, the difficulties of this type numerical modeling and the needed computational efforts would be increased enormously due to the nonlinear nature of microstructure evolution [19]. Therefore, a more general and continuous model is required for high capacity electrodes to study their electrochemical-mechanical behavior.

Phase field model (PFM), the so-called interface-diffuse model, employs continuous order parameters between two adjacent phases to avoid tracking the sharp interface through a step function [19]. The modeled properties can vary smoothly across the region that separates the compositional or structural domains. Through straightforward numerical solution of equations, it makes the simulation of complex microstructure evolution of high capacity electrodes under coupled stress, electrical, temperature and other fields become feasible. To date, a bunch of phase field models have been proposed to study the electrochemical processes inside the LIBs, including the electro-deposition process [20], electrolysis process [21], electrical double layer and charge separation [22,23], and even the SEI film growth effect [24], but only several of them have studied the mechanical behaviors of battery electrode: Huttin et al. [25] proposed a phase field model to study the stress generation in a sphere  $Li_xMn_2O_4$  particles. They indicated that even at very low charge-discharge rate, particles can fracture leading to battery capacity fade. Chen et al. [26] developed a phase field model to study the evolution of phase and stress in a free silicon nanowire, where they focused on the effect of lithium concentration on the silicon elasto-plastic deformation. Zuo et al. [27] also proposed a phase field model by coupling the lithium diffusion with stress evolution in a thin bulk silicon electrode, where they aim to simulate the possible crack propagation process. However, these PFM works for silicon either simplified the lithium ions transport by only considering diffusion process in solid phase or neglected the complicated interaction among lithium ions intercalation, silicon deformation and local stress/strain variation. Moreover, none PFM work has been developed to study the structure effect of silicon NWs during the complicated dynamic lithiation process and to understand their degradation mechanisms behind the rapid capacity fading.

In this study, we propose a phase field model to investigate the coupled electrochemical and mechanical behaviors of silicon NWs in lithium ion battery composite electrode. The coupling among lithium ion transport, silicon lithiation/deformation and stress/strain evolution is established, and we apply a core-shell structure silicon NW as a physical base. The system total free energy is determined by lithium concentration, elastic strain and structure deformation, with Cahn-Hilliard equation and Ginzberg-Landau equations developed for those control parameters. Finite element method is applied to solve the coupled equations under different lithiation conditions. On different NW structures, our PFM model well proves its capability on simulating the coupled lithiation and deformation under a variety of physical effects. The modeling results can be used to assist the design of high performance silicon NW composite electrode in future work.

## 2. Phase field modeling

The lithiation and de-lithiation process of silicon material have been extensively investigated in literature both experimentally and numerically. In general, the crystal silicon ( $c-Si$ ) can be electro-chemically lithiated to a metastable amorphous phase  $a-$

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