



## Mathematical model for silicon electrode – Part I. 2-d model



Godfrey Sikha<sup>a,\*</sup>, Sumitava De<sup>b</sup>, Joseph Gordon<sup>a</sup>

<sup>a</sup> Applied Materials Inc., 3225 Oakmead Village Drive, Santa Clara, CA 95054, USA

<sup>b</sup> Department of Energy, Environmental and Chemical Engineering, Washington University, St. Louis, MO 63130, USA

### HIGHLIGHTS

- A 2-d transient mathematical model to simulate the electrochemical lithiation in silicon nano-wire structure is developed.
- The model geometry is an axisymmetric cylindrical silicon nanowire electrode anchored to a copper current collector substrate.
- Model physics include diffusive transport of lithium, volume expansion, and diffusion induced stresses.
- Larger radius of the nanowire, and faster lithiation rates lead to increased radial and tangential stresses in the nanowire.

### ARTICLE INFO

#### Article history:

Received 17 February 2014

Accepted 8 March 2014

Available online 21 March 2014

#### Keywords:

Li-ion battery

Silicon anodes

Intercalation induced stress generation

Mathematical model

### ABSTRACT

This paper presents a 2-dimensional transient numerical model to simulate the electrochemical lithium insertion in a silicon nanowire (Si NW) electrode. The model geometry is a cylindrical Si NW electrode anchored to a copper current collector (Cu CC) substrate. The model solves for diffusion of lithium in Si NW, stress generation in the Si NW due to chemical and elastic strains, stress generation in the Cu CC due to elastic strain, and volume expansion in the Si NW and Cu CC geometries. The evolution of stress components, i.e., radial, axial and tangential stresses in different regions in the Si NW are presented and discussed. The effect of radius of Si NW and lithiation rate, on the maximum stresses developed in the Si NW are also discussed.

© 2014 Elsevier B.V. All rights reserved.

### 1. Introduction

Silicon electrode is pursued as a potential negative electrode for lithium-ion batteries owing to its high gravimetric ( $\text{mAh g}^{-1}$ ) and volumetric capacity ( $\text{mAh L}^{-1}$ ) compared to the existing state of the art graphite electrode [1]. One of the critical challenges in the commercialization of Si electrode is to minimize particle fracture developed during lithiation and delithiation of the Si electrode [2,3]. Recent experimental studies have demonstrated the use of nano-size Si structures as electrodes. These electrode structures exhibited minimal particle fracture and also enabled repeated cycling [4–6]. While different mechanisms have been proposed for this behavior, a detailed physics based analysis combining the electrochemical and structural aspects of lithium insertion in such nanostructures have not been undertaken. A variety of detailed phenomenological models exists in the literature for lithium intercalation in porous electrodes, which treat the transport of

electrolyte due to diffusion and migration, reaction kinetics at interfaces, and transport of Li and electrons in solid phase [7–13]. The general modeling framework presented in these papers cannot be directly used to simulate advanced high capacity electrodes, specifically the alloy type electrodes such as Si, Sn etc., because (a) the stresses developed during lithium insertion/deinsertion and (b) volume change associated with lithium insertion/deinsertion are not considered. So to accurately model such type of high capacity electrodes which undergo substantial volume changes, particle level expansion/contraction and electrode level displacement along with build up of stresses have to be captured. Early research by Prussin [14] demonstrated that the diffusion induced stresses generated by concentration distributions are of similar nature to the thermal stresses developed in an elastic medium. Modeling of diffusion induced stresses was also studied in detail by other researchers [15–18] for different geometries such as hollow cylinders, plates etc. Similar approaches were extended to battery electrode chemistries on a particle level to calculate intercalation induced stresses assuming no volume changes. Zhang et al. [19] presented a numerical model to calculate diffusion induced stresses for spherical and ellipsoidal shaped  $\text{LiMn}_2\text{O}_4$  single particle. Also, the work by Cheng and Verbrugge [20,21] derived analytical expressions

DOI of original article: <http://dx.doi.org/10.1016/j.jpowsour.2014.03.130>.

\* Corresponding author.

E-mail addresses: [Godfrey\\_Sikha@amat.com](mailto:Godfrey_Sikha@amat.com), [Sikha.Godfrey@gmail.com](mailto:Sikha.Godfrey@gmail.com) (G. Sikha).

(assuming negligible pressure induced diffusion and no volume change) to calculate stresses that arise from concentration gradients for a spherical particle. This modeling framework was also incorporated into a porous electrode framework [22]. All the above referenced models in addition to other published work [23–25] were developed assuming dilute solution theory for diffusion within particle, with no moving boundaries (negligible volume change) and for low expansion materials.

Christensen et al. [26] presented a more rigorous mathematical framework based on concentrated solution theory, which incorporates volume expansion and stress build up in a single spherical particle electrode and case studies for lithiation in a spherical carbon particle (8% volume expansion) were discussed. The same framework was also used to calculate the stresses in  $\text{LiMn}_2\text{O}_4$  single spherical particle electrode [27] and was also later extended to porous electrodes [28] containing graphitic mesophase-carbon-microbead (MCMB) anode and lithium manganese oxide spinel cathode. The author also emphasizes the importance of thermodynamic factor, pressure driven diffusion and extent of volume change in determining the cell potential profiles and initiation of fracture. However most of the above mentioned work was based on electrodes which undergo volume change in the order of 10%. To model large volume expansion in electrodes, Chandrasekaran et al. [29] modeled a single particle Si electrode under galvanostatic and potentiodynamic control of lithiation of Si to  $\text{Li}_{3.75}\text{Si}$  associated with a 270% volume change. In a later paper [30], the same approach was extended to a porous electrode to describe how particle level expansion affects the porosity of the electrode. The authors ignored stress calculations based on the assumption that the nano sized particles would not build appreciable concentration gradients to generate diffusion induced stresses. Gao et al. [31] modeled stress build up due to concentration gradients for a 1-d (radial) cylindrical geometry for a nano sized Si electrode for a dilute solid solution with constant density. The authors also discuss the strong coupling between stress enhanced diffusion and diffusion induced stresses for electrodes associated with large volume expansion.

In this paper (Part I), we present a model to describe diffusion and stress build up in a 2-d silicon nanowire (Si NW) geometry

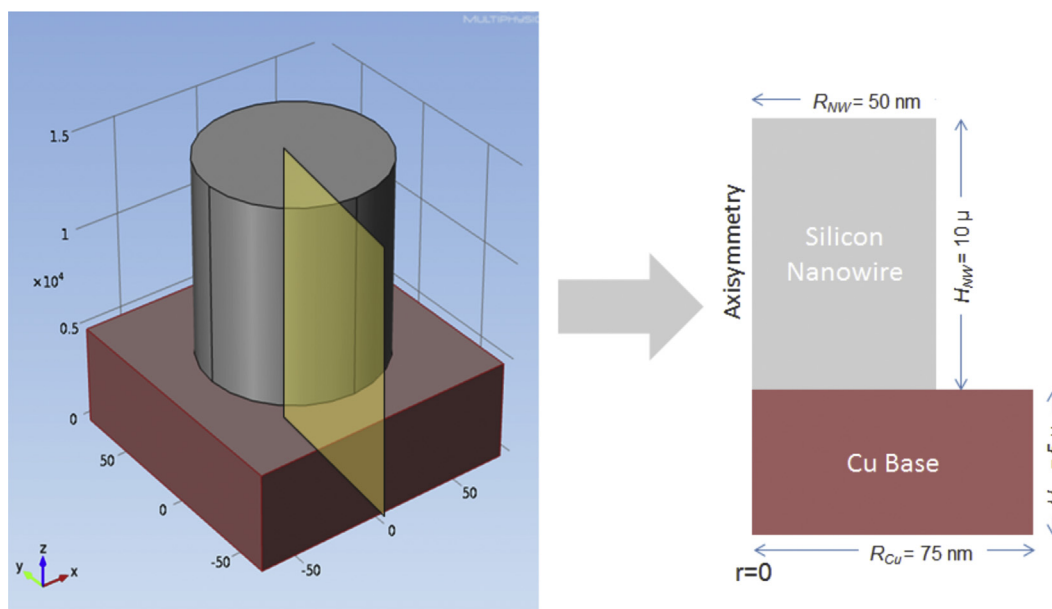
anchored to a Cu substrate under galvanostatic conditions. The model in general follows the framework described in reference [26] but applied to Si electrode with a maximum lithiation to  $\text{Li}_{3.75}\text{Si}$  associated with a 270% volume change. Case studies related to lithiation rate & nanowire radius are presented. In the second part of the paper (Part II), a dimensionally reduced 1-d model (in the radial co-ordinate) is presented and the predictions between the 1-d and 2-d model are compared. The concentration and stress profiles predicted by the 1-d model compares well with the 2-d model at regions far away from the Cu substrate. Consequently, the 1-d model was used to analyze different geometries - nanotube & core/shell structures and the evolution of stresses in these geometries are compared to the nanowire geometry.

## 2. Model development

### 2.1. Assumptions

The geometry of the Si NW anchored to the Cu CC substrate is shown in Fig. 1 (left); the initial unexpanded radius and the length of the Si NW are  $R_{\text{NW}} = 50 \text{ nm}$  and  $H_{\text{NW}} = 10 \mu$  respectively. The model geometry consists of a 2-d axisymmetric cut from the overall geometry as shown in Fig. 1 (right), wherein the dependence of the variables in the  $\theta$  direction was ignored. Other key assumptions in the model were

- The charge storage mechanism in the Si electrode is modeled by considering the electrochemical reaction of Li at the surface of the Si NW followed by transport of Li into the Si NW. The lithiated Si mixture is represented as a solid solution, therefore phase transitions are ignored.
- The transport of the host silicon is solely due to the convective flux, where as the transport of lithium is due to the combined effect of gradients in concentration and pressure, and convective flux.
- Lithium diffusion into Cu CC substrate is ignored and therefore the Si NW/Cu CC interface acts as a Li blocking interface.
- Stress strain relationship was assumed to obey Hooke's law (linear) in the entire lithiation regime. For particles of nanometer radii, the stress generated due to insertion is typically less



**Fig. 1.** Schematic of the Si NW anchored to the Cu CC substrate (left). 2-d axisymmetric slice of Si NW anchored to Cu CC base substrate used as the geometry for the 2-d model (right).

Download English Version:

<https://daneshyari.com/en/article/7736723>

Download Persian Version:

<https://daneshyari.com/article/7736723>

[Daneshyari.com](https://daneshyari.com)