Investigation of the Chemo-Mechanical Coupling in Lithiation/Delithiation of Amorphous Si
Through Simulations of Si Thin Films and Si Nanospheres

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Abstract

A strong asymmetric rate behavior between lithiation and delithiation has been observed in amorphous Si (a-Si) anode in the form of thin films, but not in other geometries, such as Si nanospheres. This work investigated the rate behavior of the two geometries through numerical simulations. The results reveal that the rate behavior is affected by the geometry and the constraint of the electrode, the chemo-mechanical coupling, and the prior process. A substrate-constrained film has a relatively low surface/volume ratio and a constant surface area. Its lithiation has a great tendency to be hindered by surface limitation. The chemo-mechanical coupling also plays an important role. The stress profiles differ in the two geometries but both affect the lithiation process more than the delithiation process. The overall delithiation capacity is affected very little by the chemo-mechanical coupling. In cyclic loading, the delithiation capacity is reduced at the same rate as the lithiation capacity because of the low initial state of charge in the electrode. The asymmetric rate behavior was absent under cyclic loading. On the other hand, a slow charging process resulted in a better retained delithiation capacity and an asymmetric rate behavior at higher rates.

Keywords: Chemo-mechanical coupling; Lithiation and delithiation; Asymmetric rate performance, Finite Element Analysis, Amorphous Silicon thin films and nanospheres.

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1. Introduction

Lithium-ion battery (LIB) has been widely used in electronics because of its high gravimetric and volumetric energy density comparing to existing battery technologies. However, the energy density of the current LIBs is still far from meeting the requirements of large electrical applications such as hybrid and electrical vehicles [1]. Si is one of the promising high capacity anode materials for LIB. Si has a theoretical specific energy density over 4000 mAh/g, which is ten times more than the graphite anode (~ 372 mAh/g) used in the first generation of LIBs. A major challenge in using Si anode is the large volume expansion/contraction (up to 400 %) of Si during lithiation cycles. The large volume variation of Si during lithiation/delithiation cycles can induce high stresses. This presents a great challenge to the structural integrity of LIBs. The high stresses and large volume variation have been cited as a primary cause for rapid capacity fading of LIBs with Si anode. Therefore, understanding the lithiation process, stress evolution and its effect on Si lithiation is of great importance for Si electrode design.

The stress evolution has been measured *in situ* during lithiation/delithiation for amorphous Si (a-Si) thin films[2–5]. The measured stress can reach as high as 1.5 GPa in both compression and tension. The stress also influences the lithiation process[6,7]. It was reported that, after the crystalline Si (c-Si) nanosphere had been lithiated for some time, the growth rate of lithiated thickness (thickness of Li_xSi shell in the first lithiation) reduced significantly [6]. The phenomenon was primarily attributed to the high compressive stress at the reaction front that

eventually prohibited Li from further insertion. However, the mechanism of how the stress interacts with Si lithiation is not clear.

In literature, two categories of chemical-mechanical coupling theories have been proposed for the stress effect on Li diffusion into Si: (I) by influencing Li diffusivity, and (II) by influencing the chemical potential of Li in Si.

In category (I), it assumes that the Li diffusivity is modulated by the stress induced activation free energy barrier shift [8–10]. The rate of reaction depends on the activation energy (i.e. free energy between the ground state and transition state). So far, the relationship is qualitative only. The activation energy is adjusted by either hydrostatic stress [8,11] or biaxial stress (in thin film) [12] with a coefficient which varies in a wide range.

In category (II), it postulates that the chemical potential of Li in Si changes because the free energy difference between Si and Li_xSi is altered by stress [5,13–17]. This effect is still quite argumentative given different treatments in literature [5,9,15,18–22]. For example, some proposed that only the hydrostatic stress influenced the chemical potential for ideal solution [18,23] or non-ideal solution [9] whereas others casted the chemical potential as a function of both hydrostatic stress and deviatoric stress components [5,16].

The chemical-mechanical coupling has two facets: 1) the diffusion induced deformation and stress; 2) the stress effect on diffusion process. Because the co-existence of these two facets for any given geometry, it is difficult to determine the coupling relationship with a single geometry. In this work, two geometries will be investigated: a-Si thin film and a-Si nanosphere. In experiments with a-Si thin film, Li et al. [24] has observed a strong asymmetric rate behavior such that the lithiation capacity reduced much faster than that of delithiation with increasing the charging/discharging rates, i.e. the C rates. So far, the asymmetric rate behavior has only been

reported for a-Si anodes in the form of thin films, but not for other geometries such as anodes with nanoparticles [25]. Since the stress state developed in a substrate-constrained thin film would be very different from that of a weakly constrained sphere during lithiation/delithiation, these two cases provide a unique opportunity for the investigation of chemical-mechanical coupling. A model with a correct coupling relationship would predict the rate behaviors of both geometries.

It should be noted that, although the abovementioned chemical-mechanical coupling theories have been formulated using both the small strain [5,21,22] and large strain [15,23] frameworks, the Li transport is commonly considered with the normalized Li concentration calculated using the dimension of unlithiated Si. As a result, the analytical/simulation results could not be compared directly to the dimension/shape changes observed in experiments. In our previous work, a model that considers the lithiation/delithiation of Si with its accompanied volume change has been developed and used to determine the Li diffusivity in a-Si [26]. The current work extends the model to include chemo-mechanical coupling by considering the stress effect on chemical potential [27].

2. Model Setup

The physical phenomena involved inside a-Si electrodes are the diffusion of Li, diffusion induced deformations and stresses, and the coupling among them. This section presents the problem formulations, their implementation in the model, and the model parameters.

2.1 Mass Transport

Once entered the Si host, the movement of Li is governed by diffusion. In our previous work [26], the stress effect on diffusion was ignored and the mass transport of Li in Si was considered by Fick's second law

$$\frac{\partial c}{\partial t} + \nabla \cdot (-D \nabla c) = 0 \quad \text{Eq. 1}$$

where D is the diffusivity and c is the concentration of Li in Si.

In this work, the chemo-mechanical coupling is considered by incorporating the stress effect to the chemical potential. In Eq.1, the Li diffusion driving force is the concentration gradient ∇c . Replacing it with the gradient of chemical potential $\nabla \mu_{Li}(\boldsymbol{\sigma})$, we have [27]

$$\frac{\partial c}{\partial t} + \nabla \cdot \left(-\frac{D_{Li}}{RT} c \nabla \mu_{Li}(\boldsymbol{\sigma}) \right) = 0 \quad \text{Eq. 2}$$

The chemical potential under stress $\mu_{Li}(\boldsymbol{\sigma})$ is defined as [27,28]

$$\mu_{Li}(\boldsymbol{\sigma}) = \mu_{Li} + \Delta \mu_{Li}(\boldsymbol{\sigma}) \quad \text{Eq. 3}$$

where μ_{Li} is the Li chemical potential in Si under zero stress, and $\Delta \mu_{Li}(\boldsymbol{\sigma})$ is the change in chemical potential due to stress. μ_{Li} can be mathematically determined under various assumptions, such as the ideal solution assumption [18,29–32], where the driving force for Li-Si mixing is the entropy with zero enthalpy so that it allows components miscibility in all proportions; the regular solution assumption [33–35], which includes both the entropic and enthalpic contributions to Li-Si mixing; and the non-ideal solid solution assumption [5,19,20,36], where Li occupies the interstitial or substitutional lattice sites with a saturation limit in the host material.

As this work focuses on the stress effect on Si lithiation rather than Li-Si mixing theories, as the first step, the ideal solution assumption was adopted. With this assumption, Eq.3 becomes [18,30,37]

$$\mu_{Li}(\boldsymbol{\sigma}) = \mu_{Li}^0 + RT \ln \chi_{Li} + \Delta \mu_{Li}(\boldsymbol{\sigma}) \quad \text{Eq.4}$$

where χ_{Li} is the mole fraction of Li in Li_xSi , and μ_{Li}^0 is a constant corresponding to the chemical potential of Li in Si at its standard state. The value of μ_{Li}^0 is unknown. Since the interests here are the change of chemical potential $\mu_{Li}(\boldsymbol{\sigma}) - \mu_{Li}^0$, and the gradient $\nabla\mu_{Li}(\boldsymbol{\sigma})$, the exact value of μ_{Li}^0 is not needed.

As the first step, a simple form of chemo-mechanical coupling relationship was adopted based on [18,19,38]

$$\Delta\mu_{Li}(\boldsymbol{\sigma}) = \alpha\Omega\sigma_h \quad \text{Eq. 5}$$

where σ_h is the hydrostatic stress, i.e., the average of principal stresses $\sigma_h = (\sigma_1 + \sigma_2 + \sigma_3)/3$; α is a coefficient for the influence of hydrostatic stress on chemical potential; Ω is the partial molar volume of Li defining the volume change due to one mole of guest atom insertion into the host material. For Li in Si, $\Omega = 9 \times 10^{-6} \text{m}^3/\text{mol}$ [39].

2.2 Large Deformation and Stress Evolution

2.2.1 Deformation of Si

To model the large deformation of Si electrode, the finite deformation theory [31], also called finite strain theory, was used. Similar approaches have been used for lithiation of Si in other works [5,14,15,17,30,41,42]. The deformation of a-Si anode during battery cycling includes the deformation due to mechanical constraint and those induced by Li concentration and temperature variations [43–46]. At this stage, the heat generation and the thermal effect were not considered and hence the thermal deformation was neglected.

The deformation gradient $\mathbf{F}$ can be calculated as [15]

$$\mathbf{F} = (\mathbf{I} + \nabla \mathbf{u}) \quad \text{Eq. 6}$$

where $\mathbf{I}$ is the identity matrix, $\mathbf{u}$ is the displacement vector.

The deformation gradient is composed of an elastic deformation gradient $\mathbf{F}_{el}$ and an inelastic deformation gradient $\mathbf{F}_{inel}$. In a Si anode, the inelastic deformation includes the plastic deformation gradient $\mathbf{F}_p$ and the Li concentration induced deformation gradient $\mathbf{F}_c$ such that[30,42]

$$\mathbf{F} = \mathbf{F}_{el}\mathbf{F}_{inel} = \mathbf{F}_{el}\mathbf{F}_p\mathbf{F}_c \quad \text{Eq. 7}$$

Li insertion causes Si anode to increase its volume. The ratio of the current volume V to the initial volume V_0 is proportional to the change in Li concentration[17]. In a stress-free Si network

$$\frac{V}{V_0} = \det(\mathbf{F}_c) = 1 + \Omega\Delta c \quad \text{Eq. 8}$$

where Δc is the lithium concentration increment calculated by using the initial volume V_0 .

To describe the large deformation, the stretch ratio λ instead of strain is often used. It is defined as[40,47]

$$\lambda = \frac{\text{length in current state}}{\text{length in reference state}} = \frac{l}{L} \quad \text{Eq. 9}$$

For a-Si, the deformation is isotropic. The lithiation induced stretches λ_1 , λ_2 and λ_3 , therefore, are assumed to be equal[17]

$$\det(\mathbf{F}_c) = 1 + \Omega\Delta c = \lambda_1\lambda_2\lambda_3 \stackrel{\text{isotropic}}{=} \lambda^3 \quad \text{Eq. 10}$$

The lithiation induced deformation is determined through the deformation gradient as

$$F_{c,ij} = \sqrt[3]{1 + \Omega\Delta c}\delta_{ij} \quad \text{Eq. 11}$$

where δ_{ij} is the Kronecker delta.

2.2.2 Stress Generation

The Cauchy stress tensor $\boldsymbol{\sigma}$ is related to the elastic strains in Si by Eq. 12 to 14[48,49]

$$\boldsymbol{\sigma} = J^{-1} \mathbf{F} \mathbf{S} \mathbf{F}^T \quad \text{Eq. 12}$$

where $\mathbf{F}$ is the deformation gradient tensor, J is the determinant of $\mathbf{F}$, $\mathbf{S}$ is the second Piola-Kirchhoff stress tensor which can be derived from the relation[48,49]

$$\mathbf{S} = \mathbf{S}_0 + 2 \frac{\partial W_s}{\partial \mathbf{C}} \quad \text{Eq. 13}$$

where $\mathbf{C}$ is the elastic right Cauchy-Green deformation tensor, $\mathbf{C} = \mathbf{F}_{el}^T \mathbf{F}_{el}$. The Cauchy stresses refer to the current configuration, whereas the second Piola-Kirchhoff stresses refer to the reference configuration. W_s is the strain energy density calculated based on the elastic Lagrange strain tensor $\mathbf{E}$ as[48,49]

$$W_s = \Lambda \text{tr}(\mathbf{E})^2 + M \text{tr}(\mathbf{E}^2) \quad \text{Eq. 14}$$

where $\mathbf{E} = (\mathbf{C} - \mathbf{I})/2$; The Λ and M are the Lamé constants which are giving in terms of Young's

modulus E and Poisson's ratio ν , $\Lambda = \frac{\nu E}{(1+\nu)(1-2\nu)}$, $M = \frac{E}{2(1+\nu)}$.

The non-homogeneous volume expansion in a solid results in stresses. The high stress may lead to the yielding of the Si anode. The yield function f is defined as

$$f = \sigma_{VM} - \sigma_Y \quad \text{Eq. 15}$$

where σ_{VM} is the Von Mises stress; σ_Y is the yield stress, which is a function of the Li concentration. The post yielding response was assumed to be perfect plastic.

2.3 Model Implementation

In this work, a commercial finite element (FE) package COMSOL Multiphysics[®] was used as the solver. The diffusion equation was solved using the General Form PDE (partial differential equation) module whereas the diffusion induced expansion was computed with the Solid Mechanics (SM) module. To account for the large volume expansion of the Si electrode, the

geometry nonlinearity was activated. The two modules were solved in a staggered fashion as described below.

The volume expansion of Si during lithiation was computed in SM module through the thermal-mass diffusion analogy. The thermal strain is calculated as[50]

$$\varepsilon_{ij}^T = \beta \Delta T \delta_{ij} \quad \text{Eq. 16}$$

where ΔT is the temperature increment, which is equivalent to the effective concentration increment Δc_{eff} ; β is the thermal expansion coefficient. Comparing Eq. 16 to Eq. 11, the mass expansion coefficient for the analogy is derived as

$$\beta(c_{eff}) = \frac{\sqrt[3]{1 + \Omega \Delta c} - 1}{\Delta c_{eff}} \quad \text{Eq. 17}$$

where c_{eff} is the effective Li concentration calculated based on the current Li_xSi volume V . It should be noted that c_{eff} differs from the Li concentration c calculated with the unlithiated Si volume V_0 , $c_{eff}/c = V_0/V$, as discussed in [26]. Therefore, the state of charge (SOC) is determined by

$$\text{SOC} = \frac{cV_0}{c_{theory}V_0} = \frac{c_{eff}V}{c_{theory}V_0} \quad \text{Eq. 18}$$

where c_{theory} is the theoretical maximum Li concentration in V_0 , which is about $3.11 \times 10^5 \text{ mol/m}^3$ [32].

In this work, the Li diffusion equation was formulated in PDE module in spatial coordinate system. The large deformation of Li_xSi was considered in SM module in material coordinate system. In simulations, the Li transport was bi-directionally coupled with Li_xSi large deformation through the Thermal Expansion node within the SM module (i.e. through the time derivative of the Li concentration that depends on the deformation). However, the mass conservation was not

automatically satisfied[51]. In simulations in spatial coordinates, the Li flux applied at the Si boundary does not account for its dependency on the deformation. Therefore, a constant flux would result in an increase in the total number of Li entering the Si host if the surface area increases. To account for this effect, a mass correction coefficient m_c was introduced at the boundary with Li source such that $m_c = V/V_0$ [26].

2.4 Model Parameters

2.4.1 Li Diffusivity in a-Si

In our previous study[26], Eq. 1 was used in the study of Li diffusivity in Si through correlations of FE based numerical simulations with the *in-situ* lithiation experiments of Si nanospheres by McDowell et al.[52]. The value of D was estimated in the range of 2.0×10^{-17} m²/s for Li poor phase in the first two-phase lithiation, and 2.0×10^{-15} m²/s for Li rich phase in the first lithiation and the subsequent cycles.

The coefficient of D_{Li} in Eq. 2 is not exactly the same as D in Eq. 1. When the stress contribution is not considered ($\Delta\mu_{Li}(\boldsymbol{\sigma}) = 0$), and with $\chi_{Li} = c/(c + c_{Si})$ (c_{Si} is Si concentration in V_0), Eq. 4 becomes

$$\mu_{Li}(\boldsymbol{\sigma}) = \mu_{Li} = \mu_{Li}^0 + \left(RT \ln \frac{c}{c + c_{Si}} \right) \quad \text{Eq. 19}$$

Substitute Eq. 19 into Eq. 2, when $c \ll c_{Si}$, $c/(c + c_{Si}) \approx c/c_{Si}$, we have

$$\frac{\partial c}{\partial t} + \nabla \cdot \left(-\frac{D_{Li}}{RT} c \nabla (RT \ln c - RT \ln c_{Si}) \right) = \frac{\partial c}{\partial t} + \nabla \cdot (-D_{Li} \nabla c) = 0 \quad \text{Eq. 20}$$

Comparing Eq. 20 to Eq. 1, D_{Li} equals to D only when $c \ll c_{Si}$. However, in Li_xSi , x can reach to a maximum value of 3.75. Therefore, D_{Li} was re-estimated using the same correlation

procedure as in [26] but with Eq. 2. The D_{Li} value was found in the range of $1.8 \times 10^{-15} \text{ m}^2/\text{s}$ for single-phase lithiation/delithiation after the first lithiation. Since the stress in Si nanosphere is relatively low (showed in later discussion), the stress effect was neglected when determining D_{Li} . The D_{Li} obtained in this way is an averaged value without the consideration of Li concentration-dependency and stress effect. This value was used in the investigations of the stress effect on Li_xSi reported thereafter.

2.4.2 Mechanical Properties

The mechanical properties of lithiated Si, including the elastic modulus, the Poisson's ratio and the yield stress, were described as functions of SOC based on literature reported data. The elastic modulus [53] and Poisson's ratio of Li_xSi [54] were based on the first-principles calculations. For the yield stress, there was a significant discrepancy between the computed values [3] and the experimental results [2,5]. Therefore, the yield stress was estimated based on the range and trend reported in literature. All three functions were the same as in [26]. Table 1 presents a summary of the parameters used in the current model.

Table 1. Parameters in the model for Li diffusion, volume expansion and stress generation.

Parameter	Symbol	Unit	Value
Theoretical maximum Li concentration	c_{theory}	mol/m^3	3.11×10^5
Gas constant	R	$\text{J}/(\text{K mol})$	8.314
Temperature	T	K	298
Li diffusivity	D_{Li}	m^2/s	1.8×10^{-15}
Partial molar volume	Ω	m^3/mol	9×10^{-6} [39]
Poisson's ratio	ν		Linear function of SOC [54] $\nu = -0.042 \times \text{SOC} + 0.283$
Yield stress	σ_Y	GPa	Linear function of SOC [2] $\sigma_Y = -0.89 \times \text{SOC} + 1.59$
Young's modulus	E	GPa	Function of SOC [53], presented in [26]

				SOC	E (GPa)	
				0.00	101.53	
				0.03	63.70	
				0.06	34.86	
				0.11	18.51	
				0.23	17.62	
				0.45	14.76	
				1.00	14.76	

3. FE Models and Simulation Conditions

Two experiments with distinct geometries were selected to study the stress effect on Si lithiation: the first was the cycling experiment of a-Si thin film conducted by Li et al.[24]; the second was that of Si nanospheres by Liu et al.[25].

These two experiments were carried out galvanostatically but with two different conditions. In [24], the thin film was evaluated independently for single-phase lithiation and delithiation, i.e., a slow lithiation/delithiation at C/10 was performed to reach the same SOC before each delithiation/lithiation measurement at the desired rate. In [25], the anode with nanospheres was lithiated and delithiated under the same rate for at least ten cycles before moving to the next rate. These are simulated as Condition 1 and Condition 2 as shown in Table 2. Simulations for the two geometries were performed with both conditions.

Table 2. Two conditions used in simulations.

Condition 1	A slow lithiation/delithiation at C/10 is conducted before each delithiation/lithiation measurement at the desired rate
Condition 2	The lithiation/delithiation measurement is conducted following a delithiation/lithiation at the same rate

3.1 Amorphous Si Thin Film Model

Li et al.[24]galvanostatically cycled the a-Si thin film of 70 nm thickness in a Li-ion cell over a wide range of rates between 0.05 V and 2.0 V. The rate performance was evaluated following Condition 1. The cells were cycled a few times in advance to minimize the effect of solid-electrolyte interface (SEI)[24]. Their results are reproduced in Fig. 1, which shows that the reduction of capacity with C rate was much faster in lithiationthan in delithiation. This was referred as the asymmetric rate behavior. It was attributed to the voltage shift introduced by the electrode Ohmic resistance at higher C rates, as the capacity is highly dependent on the voltage at the end of lithiationbut not so much at the end of delithiation. Although the authors suspected that the stress may be a contributing factor, it effect was not investigated in [24].

Figure 1. Asymmetric rate performance of 70nm a-Si thin film observed in experiment[24].

To simulate this experiment, a two-dimensional (2D) plane strain FE model was built, as shown schematically in Fig. 2. Since the experimental setup was not elaborated in detail in [24], the boundary conditions for the model were defined based on other Si thin film cycling experiments[2,55]. The Si thin film is usually deposited on a rigid substrate which restricts the

in-plane expansion of the thin film. This boundary condition is often referred as substrate-constrained in literature. In the FE model, this boundary condition was simulated by constraining all degrees of freedom of the nodes at the bottom of the film. The thickness of the film was 70nm, the same as in [24]. In experiments, the width of the thin film is usually in the range of micrometers, which results in a large aspect ratio (width/thickness) of several hundreds. In the FE model, the large aspect ratio was simulated with a film with a width/thickness ratio of 10 constrained by a symmetric (roller) boundary condition at the left and right hand sides. The upper surface of the film was allowed to expand freely. The Li flux was applied to the upper surface according to the C rate used in [24]. The thin film was meshed with 5400 quadrilateral elements with an average size about 3 nm. The mesh is shown in Fig. 2.

Figure 2. Schematic illustration of the 2D model for a-Si thin film with boundary conditions (BCs), and the FE mesh. The schematic is not drawn to scale.

The model for the thin film was first verified with the experiment of Sethuraman et al.[2], which measured the curvature change of substrate-constrained Si thin film during lithiation and delithiation. The *in-situ* stress variation was then determined using the Stoney equation[56,57]. The results were reported in terms of biaxial stress σ_b , which equals to the averaged in-plane stress in isotropic Li_xSi such that $\sigma_b = \sigma_{xx}^{ave} = \sigma_{yy}^{ave}$. Fig. 3(a) compares the model prediction with

the experimental result for biaxial stress variation during cycling of a film of 250 nm thickness under C/4 rate. The chemo-mechanical coupling effect was not considered in the model because of the low rate. As seen, the film undergoes compression (up to -1.5 GPa) during lithiation, and reverses to tension (up to 1.5 GPa) upon delithiation. The predicted stress was in good agreement with the experiment both in the trend and the range. The stress profiles in thin film at various SOC under lithiation were showed in Fig. 3(b). This showed that, as the cycling rate was small, the Li concentration variation through the thickness was small and the stress distribution was almost uniform in the film.

Figure 3. Biaxial stress in thin film during cycling of a-Si thin film of 250 nm thickness under C/4 rate were plotted, (a) the stress history vs. SOC was compared with the experimental result was from Sethuraman et al[2]. In simulations, the lithiation started with a residual stress from delithiation at the same rate; (b) the stress profiles inside the thin film showed that the stress distribution was almost uniform in the film during lithiation.

3.2 Si NanosphereModel

Besides a-Si thin films, the asymmetric rate behavior has not been reported in Si anodes of other geometries, like Si nanosphere[25], hollowed sphere[58], and nanotube[59].

The experiment with Si nanospheres by Liu et al.[25] was investigated here. In [25], the spheres were encapsulated inside graphite shells. The graphite shells were then bonded with alginate binder to form the anode, as shown in Fig.4(a). Since Si was not in direct contact with an electrolyte, there was no SEI formation on Si surface. The cell with this anode was galvanostatically lithiated and delithiated under the same rate ranging from C/10 to 4C, i.e. following Condition 2. The measured lithiation and delithiation capacities were almost the same, i.e. symmetric (Fig. 4(b)), although the cycling capacity decreased about 80% from C/10 to 4C due to the poor ionic conductivity of the alginate binder[25].

(a)

(b)

(c)

Figure 4. (a) The anode with Si nanospheres encapsulated inside graphite shells[25] and (b) its capacity measured under various cycling rates, reproduced from Figure S8 in [25]. (c) The FE model and its boundary conditions used in simulations.

In [25], the average diameter of the spheres was around 100 nm. The void between Si sphere and graphite shell allowed enough room for Si expansion. The *in-situ* transmission electron microscopy (TEM) characterization [25] suggested that the constraint of the graphite shell to the spheres was negligible. The spheres behaved as freestanding structures and grew as having a uniform Li supply at their surface.

Liu's experiment can be simplified as a free-standing single Si nanosphere. The 100 nm sphere was simulated using a 3D model. The sphere was meshed with nearly 20000 elements (for half sphere), with a mix of both hexahedral and tetrahedral elements. The average element size was about 3nm. Fig. 4(c) presents a 2D cross section of the 3D model with the boundary conditions and local meshes. A constant current for the corresponding rate was applied at the particle surface. The sphere was allowed to freely expand upon lithiation/delithiation. In [25], the initial nanosphere was c-Si but the measurement was performed over a wide range of rates from 0.1C to 4C with more than 10 cycles at each rate. Since c-Si will turn into amorphous phase after the first few cycles[52], the responses in Fig.4(b) can be considered as that of a-Si. Therefore, the Si sphere was modeled as the same material as for the a-Si thin film.

4. Results and Discussion

4.1 The Rate Behaviors

The simulations for Si thin film and nanosphere were carried out for charging and discharging at C rate between C/10 to 100C under the two conditions. The chemo-mechanical coupling was

investigated by varying the coefficient α in Eq.5: $\alpha=0$ for the case of without the stress effect; and $\alpha=0.01$ for with the stress effect. To mimic the cut-off voltage in galvanostatic cycling experiment, the lithiation was terminated when the SOC at the geometry surface reached to about 0.83 in lithiation and 0 in delithiation.

To compare with the experimental trends, the predicted specific capacities were plotted vs. C rate for the thin film and nanosphere in Fig. 5. In these plots, the solid lines are for the results with $\alpha=0$, and the dashed lines are that with $\alpha=0.01$. The lithiation and delithiation are represented by triangle and round symbols, respectively. Table 3 provides a summary of the remaining capacities at 100C under various conditions in respect to the capacity at 0.1C. In this investigation, 100% capacity is equivalent to SOC=0.83.

(a)

(b)

(c)

(d)

Figure 5. The predicted specific capacities vs. C rate for both 70nm a-Si thin film and a single a-Si nanosphere with ($\alpha=0.01$) and without ($\alpha=0$) the stress effect (a) thin film under Condition 1; (b) thin film under Condition 2; (c) nanosphere under Condition 1 and (d) nanosphere under Condition 2.

Table 3. The specific lithiation/delithiation capacity at 100C in respect of the capacity at 0.1C for the thin film and nanosphere under Conditions 1 and 2.

	α	100C Lithiation		100C Delithiation	
		Condition 1	Condition 2	Condition 1	Condition 2
Thin film	0	76.4%	74.6%	96.1%	74.6%
	0.01	49.5%	47.8%	94.4%	47.3%
Sphere	0	99.7%	99.1%	99.7%	99.1%
	0.01	90.7%	90.2%	99.0%	89.9%

Fig. 5 reveals that the asymmetric rate behavior occurs only under Condition 1. For the thin film, the asymmetric rate behavior was pronounced. Over the range of 0.1C to 100C, when $\alpha=0$, the decrease in capacity was about 23.6% for lithiation and 3.9% for delithiation. With $\alpha=0.01$, the decrease was 50.5% for lithiation and 5.6% for delithiation. Under Condition 2, both the lithiation and delithiation capacities reduced at a similar pace which resulted in a symmetric rate behavior.

The Si nanosphere displayed a symmetric rate behavior under Condition 1 and under Condition 2 when $\alpha=0$. However, it showed a small asymmetric rate behavior under Condition 1 with $\alpha=0.01$. The capacity decreased about 9.3% for lithiation and 1.0% for delithiation.

For Si nanosphere, the predicted decrease in capacity is not as dramatic as that in the experiment as shown in Fig. 4(b). This is due to the fact that only one Si nanosphere was simulated and the effect of the binder was not included.

The simulations with chemical-mechanical coupling correctly captured the trends of the rate behavior of these two geometries. To understand why the two geometries displayed distinctly different rate behaviors, the simulation results were analyzed further. Three aspects were investigated: the electrode geometry, the chemo-mechanical coupling and the effect of the prior process.

4.2 Electrode Geometry

Under Condition 1, with $\alpha=0$, the asymmetric rate behavior was observed in the thin film but not in the nanosphere. This result is not related to the chemo-mechanical coupling. A close inspection indicates that the surface limitation associated with the electrode geometry and its boundary constraint is a likely cause.

Let us compare a substrate-constrained thin film with a free-standing sphere. In lithiation, the surface area would remain the same for the thin film but increase to $(r/r_0)^2$ times for the sphere (r and r_0 correspond to the radius of the deformed sphere and the original sphere). Under galvanostatic charging, the rate of Li insertion into the electrode remains a constant. Furthermore, a sphere has the highest surface/volume ratio among all geometries. As a result, the Li concentration at the surface layer of the nanosphere is much lower than that in the thin film. The

lithiation terminates when Li reaching the maximum concentration at the surface layer. This will happen at a much lower charging rate in a thin film than that in a nanosphere if the thickness and the radius of the two are comparable.

4.3 Chemo-Mechanical Coupling

Under Condition 1, with $\alpha=0.01$, the asymmetric rate behavior was much pronounced in the thin film. A small asymmetry was also observed in nanosphere. The results indicate that the chemo-mechanical coupling played a role in the rate behavior.

To understand this process, the profiles of Li concentration (c_{eff}), hydrostatic stress and the Li flux obtained with $\alpha=0$ and $\alpha=0.01$ are compared. Fig. 6 and 7 present the results at 100°C during lithiation/delithiation for the thin film and nanosphere, respectively. For the thin film, the profiles were plotted against the instantaneous thickness measured from the substrate to the top surface of the film at selected time intervals. For the sphere, they were plotted against the instantaneous radial distance from the center to the surface. The solid lines are for $\alpha=0$ and the dash lines for $\alpha=0.01$. The Li flux was calculated according to Fick's first law as $\mathbf{N} = -D_{Li}c\nabla\mu_{Li}(\boldsymbol{\sigma})/RT$.

4.3.1 Thin film

During lithiation, the hydrostatic stress in the thin film changed quickly from a tensile residual stress resulted from the prior slow delithiation to a large compressive stress, as in Fig. 6(c). The Li concentration profiles at different time had similar shapes and the curves moved up steadily with time (Fig. 6(a)). The compressive stress suppressed the Li diffusion. With the stress effect, the driving force for Li diffusion and the flux reduced, the Li concentration gradient increased. With the progress of lithiation, the difference between $\alpha=0$ and $\alpha=0.01$ increased. The process terminated when the maximum SOC was reached at the surface of the film. The predicted

termination time was 27.5s and 17.8s, corresponding to a capacity retention of 76.4% and 49.5% for $\alpha=0$ and $\alpha=0.01$, respectively.

In delithiation, the hydrostatic stress changed from compression to tension, in Fig. 6(d). Unlike in lithiation where the stress transition took less than 2s, the transition in delithiation took about 10s and 15s to propagate through the thickness of the film for $\alpha=0$ and $\alpha=0.01$, respectively. With $\alpha=0.01$, the stress profiles had a steeper slope, and the Li flux had a steep step over the transition region. A stress profile that was tensile at the surface and compressive at interior resulted in a large Li concentration gradient in the film. When the stress in the film fully converted to tensile, the Li concentration gradient reduced, as seen in Fig. 6(b). Towards the end of delithiation, the Li concentration profiles for the two cases were very close. The process terminated at 34.6s and 34.0s, corresponding to a capacity retention of 96.1% and 94.4% for $\alpha=0$ and $\alpha=0.01$, respectively. The results show that although the profiles differed significantly, the chemo-mechanical coupling had a relatively small effect on the overall delithiation capacity.

(a)

(b)

Figure 6. Profiles of Li concentration, hydrostatic stress and Li flux vs. the distance to the bottom of the thin film at 100C under Condition 1. Solid line for without ($\alpha=0$) and dash line for with the stress effect ($\alpha=0.01$). (a) and (b) plot the Li concentration; (c) and (d) plot the hydrostatic stress; (e) and (f) plot the Li flux N_z . (a)(c)(e) are under 100C lithiation and (b)(d)(f) are under 100C delithiation.

4.3.2 Nanosphere

The Li concentration, hydrostatic stress and Li flux profiles in the nanosphere were quite different from those in the thin film. The tensile and compressive hydrostatic stress always co-existed in the sphere. During lithiation, it was compression at the surface and gradually changed to tensile at the core (Fig. 7(c)). It was vice versa for delithiation (Fig. 7(d)). The stress profile in

lithiation suppresses the Li transport at the surface layer but enhances it in the core area. It is vice versa in delithiation. As a result, the Li distribution was much more uniform across the sphere as compared to that in thin film, as in Fig. 7(a) and (b). Furthermore, the Li flux at the surface of the sphere was not a constant. It reduced with lithiation and increased with delithiation as the surface area varied, as discussed in section 4.2 and presented in Fig. 7(e) and (f).

Comparing the cases of $\alpha=0$ and $\alpha=0.01$, the stress and Li flux profiles differed but the Li concentration profiles were almost identical with the exception towards the end of lithiation and at the beginning of delithiation where the profiles for $\alpha=0.01$ were steeper. As shown in the case of thin film, a steeper Li distribution towards the end of a process reduced the capacity. The lithiation capacity was affected. The value was 99.7% and 90.7% for $\alpha=0$ and $\alpha=0.01$, respectively. The delithiation capacity was almost unaffected. The values were 99.7% and 99%, respectively.

(a)

(b)

(c)

(d)

(e)

(f)

Figure 7. Profiles of Li concentration, hydrostatic stress and Li flux vs. the radial distance for the sphere at 100C under Condition 1. Solid line for without ($\alpha=0$) and dash line for with the stress effect ($\alpha=0.01$). (a) and (b) plot the Li concentration; (c) and (d) plot the hydrostatic stress; (e) and (f) plot the Li flux N_z . (a)(c)(e) are under 100C lithiation and (b)(d)(f) are under 100C delithiation.

The above results show that the stress profiles in the two geometries play an important role in their rate behavior. During lithiation, a compressive hydrostatic stress exists throughout the thin film. In a sphere, it is only in the surface layer. Although Li transport was suppressed at the surface for both cases, the stress profile in the sphere promoted a more uniform Li distribution.

The stress profile together with the electrode geometry discussed in section 4.2 provided a better lithiation capacity for a Si nanosphere than that for a Si thin film.

During delithiation, the stress profiles were vice versa to that of lithiation. A tensile hydrostatic stress promotes the Li transport. As shown in Fig. 6 and 7, under Condition 1, the chemo-mechanical coupling had a very small effect on the delithiation capacity of the two geometries. Again, the stress profile in the sphere favored a more uniform Li distribution. The condition that resulted in a larger nonuniform Li distribution towards the end of the process reduced the overall capacity.

4.4 Effect of Prior Process

The asymmetric rate behavior occurred only under Condition 1. The results indicate that the prior process has an effect on the capacity of the electrode in the next step. It was suspected that the residual stress from the prior process might have played a role. To investigate this effect, the Li concentration and the hydrostatic stress profiles for the thin film at 100°C with $\alpha=0.01$ under the two conditions were compared in Fig. 8.

As seen from the profiles at $t=0$ s, Condition 1, a slow process, resulted in a nearly uniform Li distribution, whereas Condition 2, a fast process, resulted in a nonuniform Li distribution through the thickness of the thin film.

For lithiation, the stress profiles at $t=0$ s by the two conditions were very close, both were tensile and had a uniform distribution. During lithiation, although the stress gradient for Condition 2 was higher initially, the stress profiles of the two conditions became indistinguishable after 5s. As the lithiation progressed, the Li profiles of the two conditions became closer. As discussed above, the Li profile toward the end of a process appears to

determine the lithiation capacity. The retaining capacity was 49.5% and 47.8% for Conditions 1 and 2, respectively.

For delithiation, the stress profiles of the two conditions differed significantly. At $t=0$ s, although both were compressive, the one for Condition 1 was uniform whereas the other had a gradient. At later time intervals, the shapes of the profiles between the two conditions had some similarity but the curves remained apart. Nevertheless, a closer inspection reveals that the difference in the delithiation capacity between the two conditions was originated from their initial SOC, rather than the residual stress. The Condition 1 resulted in a complete charged state (SOC=0.83) whereas Condition 2 resulted in a partially charged electrode (SOC=0.41), corresponding to 100% and 47.8% of the capacity, respectively. The delithiation capacities for the two conditions were 94.4% and 47.3%. These values correlated well with the amount of Li initially in the electrodes. The same phenomenon was observed for the nanosphere. The delithiation capacity 89.9% at 100C under Condition 2 can be traced back to its initial SOC which was at 90.2% of the capacity.

Based on these results, we conclude that the reduction in delithiation capacity under cyclic charge/discharge is related to the lower SOC in the electrode.

(a)

(b)

(c)

(d)

Figure 8. Profiles of Li concentration and hydrostatic stress vs. the distance to the bottom of the thin film at 100C with $\alpha=0.01$ under Condition 1 (dashed line) and Condition 2 (solid line). (a) and (b) are Li concentration; (c) and (d) are hydrostatic stress. (a) and (c) are under 100C lithiation; (b) and (d) under 100C delithiation.

Besides the voltage shift introduced by the Ohmic resistance, Li et al.[24] pointed out that the stress may also contribute to the asymmetric rate behavior of the thin film by affecting the Li diffusivity. The current study confirms that the stress is indeed an important factor contributing to the asymmetric rate behavior. In future work, the chemo-mechanical coupling will be incorporated into a multiphysics battery model to consider other effects such as electrochemistry, kinetics, temperature, charge transport in other battery components, and etc. [44–46]. Furthermore, this model can be modified to consider the anisotropic behavior of crystalline Si in the first lithiation and in amorphized state in later cycles [52]. The model can also be adapted to study other high capacity electrodes, such as sulfur cathode and tin anode, etc.

5. Conclusion

The chemo-mechanical coupling of Si lithiation was investigated using finite element analysis with a model that incorporates the stress effect into the diffusion equation through influencing the