Study of Lithium Diffusivity in Amorphous Silicon

via Finite Element Analysis

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Abstract

As an anode active material, Si experiences large deformations during battery cycling, which has been cited as a primary cause for the electrode fracture and thus capacity fading. The problems caused by the electrode deformations can be remedied through electrode design, and the numerical models will greatly facilitate this design process. However, the lack of key material properties for Si/Li_xSi, especially the Li diffusivity in Si, has prevented the efficient use of such numerical tools in the design of lithium-ion batteries with Si anodes. In this work, finite element (FE) analysis was used to study the Li diffusivity in amorphous Si (a-Si) anodes. To simulate the large deformation, a large strain based formulation for the concentration induced volume expansion was proposed. The Li diffusion and volume expansion were coupled and solved in COMSOL Multiphysics[®]. By comparing with the lithiation experimental observations for the a-Si nanospheres, the Li diffusivity was estimated to be on the order of $2.0 \times 10^{-15} \text{ m}^2/\text{s}$ for the Li-rich phase and $2.0 \times 10^{-17} \text{ m}^2/\text{s}$ for the Li-poor phase. These values were further validated by comparing the thickness growth of the Li-rich phase and the lithiation time.

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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, which affects the structural integrity of LIBs and results in rapid capacity fading. It has been shown that the cycle life of Si anode can be improved significantly through various novel electrode designs [2–13]. So far, such work is conducted through experiments.

Numerical simulations have the potentials for design optimization of LIBs [14–21]. In our previous work [17], a microstructure-resolved multiphysics model (MRMM) have been developed for LIBs with graphite anode. To simulate Si anode is far more challenging. The major obstacles are the large deformation of the Si anode and the uncertainty in material properties. For example, the Li diffusivity in Si is a key parameter determining the lithiation time and Li concentration gradient, the latter in turns influences the intercalation stresses. The reported Li diffusivity values, however, vary a great deal, ranging from $10^{-13} m^2/s$ to $10^{-19} m^2/s$

[22–29]. Furthermore, the experimentally measured diffusivity is based on the initial Si volume. Such values cannot be used directly in analysis with large volume variations.

This study investigates the possible range of the Li diffusivity in a-Si through correlations of numerical simulations with the in-situ lithiation experiments by McDowell et al. [30]. To simulate the large deformation of Si, a large strain based formulation for the concentration induced volume expansion is proposed. The problem is solved using COMSOL Multiphysics®.

2. Model Development and Implementation

In literature, McDowell et al. [30] investigated the lithiation of a-Si nanospheres in-situ in a transmission electron microscope (TEM). The experimental setup is shown in Fig. 1(a). Li was supplied to a-Si spheres through crystalline silicon (c-Si) pillars. Potentiostatic charge and discharge under 3V were carried out. The images and video clips showed that during lithiation and delithiation, the a-Si spheres expanded and contracted radially and remained a spherical shape. During the first lithiation, a boundary between Li-rich and Li-poor regions (named as reaction front) was clearly visible, Fig. 1(b). This phenomenon is known as the two-phase lithiation.

The experiment by McDowell et al. [30] provides a good study case. The spherical growth pattern suggests that the constraint of the Si pillar to the spheres was negligible, the spheres behaved as free-standing structures; and the sphere grew as having a uniform Li supply at its surface. In addition, since the spheres were not in contact with the electrolyte, there were no solid-electrolyte interface (SEI) layer on the particle surface.

The a-Si sphere was modeled as 2D axisymmetric. Fig. 1(c) presents the schematic of the model along with the boundary condition. The potentiostatic charge was simulated by a constant Li concentration boundary condition. The Li concentration corresponding to $\text{Li}_{3.75}\text{Si}$ was applied

during lithiation. To ensure the stability of the simulations, it was introduced with a ramp of 3s. The sphere was allowed to expand freely during lithiation.

In a MRMM battery model [17], the Butler-Volmer equation would be used to consider the electrochemical reaction at the electrode/electrolyte interface. In the experiment [30], however, the a-Si spheres were not in direct contact with the electrolyte and they were lithiated with excess Li supply. Therefore, a simple Li concentration boundary condition was sufficient to approximate the experimental setup.

The physical phenomena involved inside the a-Si sphere are Li diffusion, the diffusion induced elastic-plastic deformation and Li intercalation induced stresses. The problem formulations and their implementation in the model are presented next.

2.1 Mass Transport

Once entered the Si host, the movement of Li is governed by diffusion. In the current work, the stress effect on diffusion was ignored. 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 of Li in Si. Its order will be determined in this work. This value will serve as a baseline for further investigation on lithiation of Si with stress influence.

2.2 Large Deformation

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 [29,32–37]. The deformation induced inside a Si anode during battery cycling includes the deformation due to mechanical constraint and the deformation induced by lithiation and

temperature [17,18,21,38]. 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 [34]

$$\mathbf{F} = (\mathbf{I} + \nabla \mathbf{u}) \quad \text{Eq. 2}$$

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 lithiation/delithiation induced deformation gradient $\mathbf{F}_c$ such that [32,36]

$$\mathbf{F} = \mathbf{F}_{el} \mathbf{F}_{inel} = \mathbf{F}_{el} \mathbf{F}_p \mathbf{F}_c \quad \text{Eq. 3}$$

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 the Li concentration [35]. In a stress-free Si network

$$\frac{V}{V_0} = \det(\mathbf{F}_c) = 1 + \Omega \Delta c \quad \text{Eq. 4}$$

where Δc is the lithium concentration increment in the initial volume V_0 . Ω is the partial molar volume, which defines the volume increase due to one mole of guest atom insertion in the host material. For Li in Si, $\Omega = 9 \times 10^{-6} \text{ m}^3/\text{mol}$ [39].

To describe large deformation, the stretch ratio instead of strain is often used. The stretch ratio is defined as [31,40]

$$\lambda = \frac{\text{length in current state}}{\text{length in reference state}} = \frac{l}{L} \quad \text{Eq. 5}$$

For a-Si, the deformation is isotropic. The lithiation induced stretches λ_1 , λ_2 and λ_3 , therefore, are assumed to be equal [35]

$$\det(\mathbf{F}_c) = 1 + \Omega \Delta c = \lambda_1 \lambda_2 \lambda_3 \stackrel{\text{isotropic}}{=} \lambda^3 \quad \text{Eq. 6}$$

The lithiation induced deformation is determined through the deformation gradient as

$$F_{c,ij} = \sqrt[3]{1 + \Omega \Delta c} \delta_{ij} \quad \text{Eq. 7}$$

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. 8 and 9

$$\boldsymbol{\sigma} = J^{-1} \mathbf{F} \mathbf{S} \mathbf{F}^T \quad \text{Eq. 8}$$

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

$$\mathbf{S} = \mathbf{S}_0 + \mathbf{C} : \boldsymbol{\varepsilon}_{el} = \mathbf{S}_0 + \mathbf{C} : (\boldsymbol{\varepsilon} - \boldsymbol{\varepsilon}_{inel}) \quad \text{Eq. 9}$$

where $\mathbf{C}$ is elastic right Cauchy-Green tensor. The Cauchy stresses refer to the current configuration, whereas the second Piola-Kirchhoff stresses refer to the reference configuration.

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

$$f = \sigma_{VM} - \sigma_Y \quad \text{Eq. 10}$$

where σ_{VM} is the Von Mises stress; σ_Y is the yielding stress, which is a function of the Li concentration. Perfect plasticity is used for post yielding in the current model.

2.3 Model Implementation

In this work, 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 volume expansion of Si during lithiation was computed in SM module through thermal-mass diffusion analogy. The thermal strain is calculated as

$$\varepsilon_{ij}^T = \beta \Delta T \delta_{ij} \quad \text{Eq. 11}$$

where ΔT is the temperature increment, which is equivalent to the effective concentration increment Δc_{eff} ; β is the thermal expansion coefficient. Comparing Eq. 11 to Eq. 7, the mass expansion coefficient for the analogy is derived as

$$\beta(c_{eff}) = \frac{(\sqrt[3]{(1 + \Omega \Delta c)} - 1)}{\Delta c_{eff}} \quad \text{Eq. 12}$$

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 based on the initial Si volume V_0 , $c_{eff} / c = \frac{1}{V/V_0}$, as shown in Fig. 2.

In simulations, the PDE and SM modules are solved together iteratively. However, the software has a limitation in passing coupling parameters. Although the concentration computed by PDE is passed to SM in every iteration, the deformation computed by SM is passed back to PDE only at each time step. In other words, PDE and SM are coupled one way within each time step. As discussed below, this solution method resulted in error in mass conservation.

The PDE and SM are coupled as follows. At step i , the Li concentration c_i is determined in PDE based on V_{i-1} , the volume determined in the previous step. The total mass of Li at the end of step i is $M = \int c_i dV_{i-1}$. At each iteration, the FE model with c_i is solved in SM module to obtain

V_i , the updated volume. V_i obtained at the end of step i is used at step $i+1$ in PDE as the initial condition. In another word, at the beginning of step $i+1$, the total mass is $M^* = \int c_i dV_i$, instead of M . The mass increasing rate $\frac{dM^*}{dt} \neq \frac{dM}{dt}$. This small difference occurs in each time step.

Cumulatively, the error can be significant, $(dM^*/dt) / (dM/dt) = V/V_0$.

To correct this error, a mass correction coefficient m_c was introduced, $m_c = V/V_0$. The diffusion equation of Eq. 1 is modified such that

$$m_c \frac{\partial c_{eff}}{\partial t} + \nabla \cdot (-D \nabla c_{eff}) = 0 \quad \text{Eq. 13}$$

The mass conservation in the coupled analysis was examined using two electrodes, a sphere (Fig. 3(a)) and a thin film on a substrate (Fig. 3(b)). The simulations were carried first using $m_c = 1$, i.e. without the correction. Fig. 3(c) plots the mass rate ratio between the mass increasing rate of Li inside the Si calculated with $\frac{dM^*}{dt} = \frac{d(\int c dV)}{dt}$ to that entered the Si electrode through the surface. The results showed that $m_c = V/V_0$ was valid for the two examined cases with a variety of model representations. Simulations were then carried out for both thin film and sphere geometries with correction $m_c = V/V_0$ with a Li diffusivity, $D = 5.0 \times 10^{-16} \text{ m}^2/\text{s}$. The error in mass conservation was within 3%, Fig. 3(d).

2.4 Model Parameters

2.4.1 Li diffusivity in a-Si

The literature data on Li diffusivity in Si varies over a wide range [22–29]. Table 1 provides a summary of reported values for a-Si. For comparison, the representative values for Li in c-Si are also listed in the first three rows. As shown, the Li diffusivity is about one to two orders higher in a-Si than that in c-Si. Furthermore, the values estimated by ab initio molecular dynamics (MD) simulations [22] and potential step chronoamperometry (PSCA) [24], where chemical diffusion took place, appears to be much higher than the values determined by electrochemical experiments such as the cyclic voltammetry (CV) [28], electrochemical impedance spectroscopy (EIS) [27], galvanostatic intermittent titration technique (GITT) [22], and potentiostatic intermittent titration technique (PITT) [26,29].

The large variation in diffusivity measurement is attributed to the complex physics involved in lithiation of Si. The diffusivity measured with electrochemical experiments may include the effect of interface reaction, stress-diffusion interaction, the contribution of SEI layer, and etc. For instance, Bucci et al. [29] considered the stress-diffusion interaction and chemical interaction of Li with Si host and determined an intrinsic diffusivity of $10^{-19} m^2/s$ based on PITT experiment. Li et al. [26] reported that their samples were cycled four times between 1.0 to 0.3V to form a stable SEI layer before measurement. **SEI layer is reported to act as a Li-ion diffusion barrier, limiting Li-ion transport with a high resistivity** [29,41]. Furthermore, the diffusivity determined by experiments is an averaged value across the electrode over one or multiple cycles, and may be a function of potential or state-of-charge (SOC) [23,27]. Results may be strongly dependent on Si geometry and size [25]. Finally, the experimentally determined diffusivity is based on the initial volume. Such values cannot be used directly in analysis considering volume changes.

To estimate the order of Li diffusivity in Si with volume change, a numerical parameter study was conducted for the experiment in Fig. 1. Both the two-phase lithiation observed in the first lithiation and the single-phase lithiation observed in the subsequent cycles were investigated.

The two-phase phenomenon in the first lithiation is related to a lower Li diffusivity in pristine Si. In general, the diffusivity in Li-poor phase is about an order lower than that in Li-rich phase. In the current investigation, for the first lithiation, the diffusivity values were assigned separately for the Li-poor core and the Li-rich shell with a rapid increase of Li diffusivity at reaction front, as shown in Fig. 4. The exact composition of the metastable α - Li_xSi at the reaction front was difficult to determine [42,43]. Based on literature discussions [44–46], the composition was assumed as Li_2Si in the current study. Within each phase, the diffusivity was assigned as a constant and the Li composition dependency was not considered. The diffusivity determined for Li-rich phase was then used in simulations of single-phase lithiation. Considering the uncertainty in Li diffusivity, the stress effect to the diffusivity was ignored in this work.

Table 2 presents the initial six test cases for diffusivity study. The Li diffusivity in Li-poor and Li-rich phases were denoted as D_1 and D_2 , respectively. The tests were divided into two sets. The first set (Tests 1 to 3) was used to investigate D_2 , where D_1 was kept constant while D_2 varied from $1.0 \times 10^{-15} \text{ m}^2/\text{s}$ to $1.0 \times 10^{-14} \text{ m}^2/\text{s}$. The second set (Tests 3 to 5) was used to investigate the D_1 , where D_2 was kept constant while D_1 varied from $1.0 \times 10^{-18} \text{ m}^2/\text{s}$ to $1.0 \times 10^{-16} \text{ m}^2/\text{s}$. Test 6 was added based on the results of Tests 1-5. Results will be discussed in later session.

2.4.2 Mechanical Properties

The mechanical properties of lithiated Si, including the elastic modulus, the Poisson's ratio and the yielding stress, were described with three piecewise linear relationships vs. SOC as shown in Fig. 5. The elastic modulus was from the first principle calculation of Li_xSi subjected to a uniaxial tension reported by Zhao et al. [47]. The Poisson's ratio was calculated by Shenoy et al. [48]. For the yielding stress, there was a significant discrepancy between the computed values [49] and the experimental results [29,50]. Based on the range reported in literature, a simple linear yielding function verses SOC was used in the current model based on experiments by Sethuraman et al.[50].

3. Results and Discussion

3.1 Two-phase lithiation

TEM images from McDowell et al. [30] showed the lithiation process of an a-Si sphere with diameter about 570 nm at several time frames, as presented in the first row in Table 3. An a-Si sphere of the same size was simulated according to the six tests in Table 2. The simulation results were compiled in Table 3, which compares the Li concentration distributions and the reaction front in the sphere with the experimental result. The scaled bar was normalized to the maximum achieved c_{eff} (81884 mol/m³).

In the first set simulations (Tests 1 to 3), the results showed that when $D_2 \leq 1.0 \times 10^{-15} \text{ m}^2/\text{s}$, the two-phase lithiation was still in progress at 129s, which was much longer than the time for Li-poor phase to disappear observed in the experiment. On the other hand, when $D_2 \geq 1.0 \times 10^{-14} \text{ m}^2/\text{s}$, the Li-poor phase disappeared at about 60s, which was much shorter than the time in the experiment. Test 3, with $D_2 = 2.5 \times 10^{-15} \text{ m}^2/\text{s}$, matched the experiment reasonably well.

The results in the second set simulations (Tests 3 to 5) showed that D_1 , the diffusivity in Li-poor phase, had a significant influence on the lithiation time. When D_1 was small (Test 4), the lithiation time greatly increased. When D_1 was large (Test 5), the lithiation time reduced but the reaction front was diffused.

The effect of D_1 was further examined by comparing the concentration profiles obtained from simulation (Fig. 6(b)) with the experimental results (Fig. 6(a)). The experimental profiles were established according to the light intensity in TEM images [30]. It should be noted that the light intensity may not have a linear relationship with the Li concentration. The profiles generated this way, therefore, were only qualitative indications. As shown in Fig. 6(b), Test 3 and 4 resulted in Li concentration oscillations in the Li-poor phase near the reaction front. This was caused by a convergency problem in computation related to the relatively steep diffusivity gradient at the reaction front. The smaller D_1 in Test 4 resulted in an oscillation of larger amplitude. Reducing the FE mesh size reduced the amplitude of the oscillation. The concentration profiles at the reaction front, however, remain to be steep. Diffusivity values in both tests were rejected because the predicted profiles did not match the shape of the experimental profiles in Fig. 6(a). On the other hand, Test 5 resulted in a much diffused reaction. Therefore, a new test case, Test 6, was added. The concentration profiles in Test 6 had a distinguishable reaction front at 48s and 61s, resembling those depicted in experiments. Among all test cases, Test 6 appeared to provide the best correlation between simulation and experiment. This yielded the diffusivity values of $D_1 = 2.0 \times 10^{-17} \text{ m}^2/\text{s}$ and $D_2 = 2.0 \times 10^{-15} \text{ m}^2/\text{s}$.

Comparing with the diffusivity values in Table 1, the value of $D_2 = 2.0 \times 10^{-15} \text{ m}^2/\text{s}$ is one to two orders higher than that measured by electrochemical experiments [26–28] but two orders

lower than the value determined by chemical diffusion [22,24]. The electrochemical experiments include the effect of SEI layer, and the Li diffusivity is determined with the dimension of undeformed Si electrode. Taking these factors into consideration, $D_2 = 2.0 \times 10^{-15} \text{ m}^2/\text{s}$ is in a reasonable range.

McDowell [30] also plotted the thickness of the Li-rich phase (lithiated-thickness) versus time, as showed in Fig. 7(a). The results showed the thickness increased linearly with time. However, the slopes of these curves varied over a wide range, which may be caused by differences in experimental conditions, such as the particle sizes and quality of electrical/Li⁺ pathway connection. The thickness plot was used to examine the Li diffusivity values established in Test 6. The specific information on the range of sphere sizes was not provided in Ref. [30]. To compare the results, simulations were carried out for spheres with diameter of 570 nm and 400 nm, because these two sizes were mentioned in Ref. [30]. As shown in Fig. 7(a), the lithiated thickness growth curves of both spheres obtained from simulations fell within the experimental range. The lithiated thickness increased almost linearly during the two-phase lithiation, as seen in the experiment. These results further confirmed that the Li diffusivity values in Test 6 were reasonable estimations. Finally, in simulations, the slope of the curves reduced to nearly zero when the Li-poor phase was consumed. Further lithiation proceeded in Li-rich phase as the sphere continued to grow.

3.2 Single-phase lithiation

As reported [30], Si undergoes two-phase lithiation only in the first lithiation. The subsequent delithiation and lithiation display as a single-phase process without a visible reaction front. Furthermore, the time for lithiation is greatly reduced. For a-Si sphere of 400 nm, the lithiation time was 122 seconds and 31 seconds for the first and second lithiation, respectively.

The disappearance of the two-phase lithiation is likely due to the further amorphization of a-Si. a-Si may have some short range order in local areas. Li insertion disturbed the ordered structure as in the amorphization of c-Si [45]. Diffusion proceeds fast in amorphous host. Therefore the subsequent lithiation is similar to that in Li-rich phase.

The single-phase lithiation was simulated for a-Si sphere of 400 nm with $D = 2.0 \times 10^{-15} \text{ m}^2/\text{s}$, the value for the Li-rich phase in two-phase lithiation. In single-phase lithiation, the reaction front was assumed at Li_2Si , the same as in two-phase lithiation. The location of the reaction front was determined from concentration profile plots at different time intervals. Fig. 7(b) showed that the single-phase lithiation of the sphere took about 30 seconds while the two-phase lithiation took more than 70 seconds. The simulation results agreed with the experimental observations quite well, confirming that $D = 2.0 \times 10^{-15} \text{ m}^2/\text{s}$ is a reasonable estimation for a-Si single-phase lithiation.

3.3 Concentration Dependency of Diffusivity

Li diffusivity may be a function of Li concentration. Metastable $\text{a-Li}_x\text{Si}$ phases form during lithiation before a-Si becomes fully lithiated. Therefore, the Li diffusivity may vary when Li_xSi composition and the network structural change. The concentration dependency of the diffusivity, however, is unclear.

To investigate the effect of the concentration dependency of the diffusivity, additional simulations were performed with a relationship proposed by Berla et al. [51]

$$D = \left(1 - c / c_{\max}\right)^3 D_1 + \left(c / c_{\max}\right)^3 D_2 \quad \text{Eq. 14}$$

Two new tests were performed using a diffusivity described by Eq. 14. In Test 7, the values used in Ref. [51], $D_1 = 1.0 \times 10^{-17} \text{ m}^2/\text{s}$ and $D_2 = 1.0 \times 10^{-16} \text{ m}^2/\text{s}$, were adopted. In Test 8, the values established in the current work, $D_1 = 2.0 \times 10^{-17} \text{ m}^2/\text{s}$ and $D_2 = 2.0 \times 10^{-15} \text{ m}^2/\text{s}$, were used. As shown

in Fig. 8(a), Eq. 14 described a smooth curve instead of a sharp change. As a result, the reaction front between Li-poor and Li-rich was not maintained in Test 7 and 8. As shown in Fig. 8(b), the lithiated thickness growth curves predicted by Test 7 and 8 deviated from the nearly linear growth trend observed in experiments. In comparison, the simulation with a simple approximation of constant diffusivity values in Test 6 matched the experimental trend closer.

4. Conclusion

The Li diffusivity in the two-phase lithiation and the subsequent single-phase lithiation of a-Si was investigated by simulating the in-situ TEM experiments of a-Si nanospheres [30]. To simulate the large deformation of Si, a large strain based formulation for the concentration induced volume expansion was used. The coupled diffusion and deformation problem was solved in COMSOL Multiphysics[®]. The diffusivity of Li in a-Li_xSi was approximated with two distinct diffusivity values for the Li-poor phase and Li-rich phase, respectively. Simulations with Li diffusivity values ranging from $1.0 \times 10^{-18} \text{ m}^2/\text{s}$ to $1.0 \times 10^{-14} \text{ m}^2/\text{s}$ were carried out and the results were compared with experiments for the movement of the reaction front, the lithiated-thickness growth, and the lithiation time. The Li diffusivity was found at the order of $2.0 \times 10^{-15} \text{ m}^2/\text{s}$ for Li-rich phase and $2.0 \times 10^{-17} \text{ m}^2/\text{s}$ for Li-poor phase in the two-phase lithiation. The single-phase lithiation of a-Si after the first cycle was simulated with a Li diffusivity of $2.0 \times 10^{-15} \text{ m}^2/\text{s}$. The computed lithiation time agreed well with the experimental results.

The Li diffusivity for single-phase lithiation determined in this work is two orders lower than that determined by chemical diffusion process but one to two orders higher than that established in electrochemical experiments. The value reported here is in a reasonable range taking into account that the Li diffusivity is calculated for deformed Li_xSi volume and the analysis is for a case without the **limiting effect on Li-ion transport from SEI layer**.

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Table 1 Literature data on Li diffusivity in Si.

Method	Li Diffusivity in Si (m^2/s)	Material	Current density
ab initio MD [22]	$1.67 \times 10^{-14} \sim 4.88 \times 10^{-13}$	c-Si slab	chemical diffusion
CV, EIS, GITT [23]	1×10^{-16}	nano c-Si	$0.2 \text{ mA}/\text{cm}^2$
PSCA [24]	2×10^{-15}	single crystal wafer	chemical diffusion
ab initio MD [22]	$1.25 \times 10^{-13} \sim 3.69 \times 10^{-12}$	a-Si slab	chemical diffusion
PSCA [24]	1×10^{-13}	a-Si thin film	chemical diffusion
PITT [26]	$7.7 \times 10^{-18} \sim 1.0 \times 10^{-17}$	100nm and 1000nm a-Si film	$0.07 \text{ mA}/\text{cm}^2$
EIS [27]	$3 \times 10^{-17} \sim 3 \times 10^{-16}$	a-Si thin film	0.4 V , $0.0025 \text{ mA}/\text{cm}^2$
CV [28]	1.9×10^{-17}	120nm a-Si thin film	$0.1 \text{ mA}/\text{cm}^2$
PITT [29]	1×10^{-19}	104nm a-Si thin film	discharge, 0.395 to 0.39V, Intrinsic value

Table 2 Diffusivity study test cases.

Test label	Li-poor Diffusivity D_1 (m ² /s)	Li-rich Diffusivity D_2 (m ² /s)
Test 1	1.0×10^{-17}	1.0×10^{-15}
Test 2	1.0×10^{-17}	1.0×10^{-14}
Test 3	1.0×10^{-17}	2.5×10^{-15}
Test 4	1.0×10^{-18}	2.5×10^{-15}
Test 5	1.0×10^{-16}	2.5×10^{-15}
Test 6	2.0×10^{-17}	2.0×10^{-15}

Table 3 Comparison of simulations with experimental results of two-phase lithiation.

Test label	48s	61s	129s	Comments
Experiment – first lithiation of a-Si [30]				<p>Scale bar for Li concentration in simulatons.</p>
Test 1				$D_2 \leq 1.0 \times 10^{-15} \text{ m}^2/\text{s}$, the time for two-phase lithiation was much longer than that in the experiment.
Test 2				$D_2 \geq 1.0 \times 10^{-14} \text{ m}^2/\text{s}$, the Li- poor phase disappeared before 50s, which was much shorter than the time in the experiment.
Test 3				$D_2 = 2.5 \times 10^{-15} \text{ m}^2/\text{s}$, matched the experiment reasonably well.
Test 4				$D_1 \leq 1.0 \times 10^{-18} \text{ m}^2/\text{s}$, lithiation time increased greatly.

Test 5				$D_1 \geq 1.0 \times 10^{-16} \text{ m}^2/\text{s}$ resulted in a diffused reaction front.
Test 6				Best correlation with experimental results.

Figure 1

Figure 2

Figure 3

Figure 4

(a)

(b)

(c)

Figure 5

(a)

(b)

Figure 6

(a)

(b)

Figure 7

(a)

(b)

Figure 8

Figure Captions

Figure 1. Axisymmetric model for modeling lithiation of a-Si nanoparticle. (a) Experimental setup by McDowell et al. [30]; (b) two-phase lithiation in the first lithiation observed in experiment [30]; and (c) simulating two-phase lithiation of a-Si nanospheres using an axisymmetric 2D model.

Figure 2. The ratio of the effective Li concentration c_{eff} to the apparent Li concentration c as functions of volume ratio V/V_0 .

Figure 3. Verification of the mass correction coefficient with (a) a free expanding Si sphere and (b) a constrained thin film Si on a substrate, expanding only in the through thickness direction. (c) The mass rate ratio as a function of volume ratio V/V_0 . The results showed that the mass correction coefficient follows the relation of $m_c = V/V_0$. (d) The mass conservation was maintained for both thin film and sphere geometries when Eq. 13 was used.

Figure 4. Constant diffusivity was assigned separately for Li-rich and Li-poor phases with a small transition at around Li_2Si .

Figure 5. Mechanical properties of Li_xSi used: (a) elastic modulus, (b) Poisson's ratio, and (c) yielding stress.

Figure 6. Concentration profile comparison: (a) The image intensity during lithiation of the 570 nm diameter sphere during lithiation in experiments [30]. Red circles label the concentration drop at reaction front. (b) Lithiation of Si in Tests 3 to 6 in simulations: concentration profile vs. distance to particle center.

Figure 7. Lithiated thickness as a function of time during lithiation of a-Si spheres, including: (a) Two-phase lithiation comparison between results from experiments and simulations. Experimental curves (black) #1-#4 are from McDowell et al. [30] out of 26 nanospheres with unspecified diameter range. Simulation curves (red) are a-Si spheres of 400 nm and 570 nm. (b) Comparing lithiation speed between single-phase lithiation and two-phase lithiation.

Figure 8. Simulations of lithiation of Si sphere of 570 nm diameter with a concentration dependent diffusivity. (a) Diffusivity functions; (b) Lithiated-thickness versus time, comparing to experimental data reported in Ref. [30] as shown in Fig. 7(a).