Effect of Li Concentration-Dependent Material Properties on Diffusion Induced Stresses of Sn Anode

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ABSTRACT
Sn is one of the promising Li ion battery anode with high theoretical capacity and mechanical properties that allow for effective relaxation of Li diffusion-induced stresses. Sn is a low melting point metal with low modulus, strength and has the ability to relax stresses via plasticity and creep deformations. In this study, concentration-dependent material properties are used in numerical simulations to model the Li diffusion-induced stress evolution in Sn micropillars. Simulation results using lower modulus and high diffusivity with increasing Li content resulted in a completely different failure mode in comparison to that of concentration-independent simulation results. Tensile hoop stress needed for crack propagation was analyzed to be at the core for concentration independent material properties that switched to tensile hoop stress being at the surface for the case of concentration independent simulation results. In addition, by incorporating these maximum tensile DIS results, critical size for failure of Sn micropillar was determined to be 5.3 μm for C/10 charging rate. This was then correlated to experimental observations, where fracture occurred in Sn micropillars with sizes larger than 6 μm while 4.4 μm sized Sn micropillar survived the lithiation cycle.
Key words: Li ion battery, creep relaxations, diffusion-induced stresses, numerical simulations, Li concentration

1. Introduction

Due to its light weight, high operating voltage (>4V) and high energy density, Li ion batteries (LIBs) have become a potential candidate for power sources ranging from many portable consumer applications to high power applications such as electric and hybrid electric vehicles. In the quest for high performance LIBs, the anode materials that alloy with Li i.e. Li_xM (M=Si, Sn, Ge and SiO_x) have attracted great attention due to their higher charging capacities as compared to commercialized graphite. However, the Li alloying process with these materials typically results in an extreme volume expansion by up to 300-400 % \(^1\). In practice, lithiation leads to inhomogeneous Li concentration gradient in the active material which in turn causes undesired diffusion-induced stresses (DIS) \(^2\). Morphological changes and structural degradation caused by repeated, anisotropic volume changes during multiple charging/discharging cycles lead to crack initiation and propagation within the anode and corresponding loss in capacity \(^3\). The key for enhanced stability and reliability of the LIB anode is in understanding the evolution of the DIS and designing a material/structure that can minimize fracture in the active materials.

Host anode materials that alloy with Li will experience significant changes in their material properties during lithiation. With rising concentration of Li in the anode, the material parameters including the Li diffusion coefficient as well as Young’s modulus, Poisson’s ratio, yield strength are rehabilitated. Due to the dramatic changes in these material properties, DIS of Li_xM electrodes can deviate significantly as compared to DIS with constant material parameters. For instance, DFT studies showed that Li insertion in the host materials such as Si, Sn, SiO_x causes significant softening, where the Young’s modulus decreases by an order of magnitude\(^5\)-\(^7\). On the other hand, Li_xC compounds (Li-graphite) result in stiffening where threefold increase in the Young’s modulus of the graphite electrode is reported upon lithiation\(^8\). In order to accurately analyze the DIS using numerical modeling methods, it is therefore essential to incorporate these material properties.

Previous studies have investigated the effect of Li concentration dependent properties such as elastic modulus and Poisson’s ratio on DIS, but there are only few studies focusing on the effect of increasing diffusivity on the change of stress distribution. In the work by Deshpande et al., Li diffusivity was taken to be independent of Li concentration when exploring the effect of Li concentration-dependent Young’s modulus on DIS of battery electrode, and a decrease in the elastic modulus upon lithiation was reported that in turn lowered DIS\(^10\). Guo et al. have calculated the effects
of hydrostatic stresses that arise due to volume expansion with incorporation of the concentration-dependent elastic modulus on DIS and concluded that the change in elastic modulus has a significant effect on the distribution of hoop and radial stresses\textsuperscript{11}. Chang et al. has conducted a multiscale analysis for Si electrode and concluded that the nature and magnitude of DIS in elastic deformation are relaxed when taking the Li concentration-dependent modulus and diffusivity\textsuperscript{12}. In these studies, coupling between mechanics and Li diffusion was investigated while considering the Li concentration-dependent material properties including the Young’s modulus, Poisson’s ratio and diffusivity\textsuperscript{11,13-14}. However, for the case of Sn anode, in which diffusion controlled lithiation occurs, the effect of increased diffusivity on DIS and moreover the incorporation of plasticity and creep-based relaxation on DIS have not been investigated. Therefore, in order to get more realistic mapping of DIS on Sn anode on LIBs, varying the diffusivity values should be incorporated in numerical modeling of working electrodes.

Among anode materials, Sn is considered as a promising choice owing to a relatively high theoretical capacity of ~994 mAh\textsuperscript{-1} as well as being abundant, inexpensive and also being able to effectively relax the DIS due to its favorable mechanical properties such as low modulus and strength. In addition, since Sn is ductile in nature and known to have low melting point ($T_m = 505$K) to induce the creep deformations even at room temperature, stress relaxations through plasticity is expected during lithiation. Although Si with a higher capacity of ~4200 mAh\textsuperscript{-1} has been studied more extensively\textsuperscript{15-17}, reports on the analysis of DIS in Sn anode is limited. Previous report on DIS of Sn anode indicates a promising mechanical stability during lithiation, where Sn micropillar with 1 $\mu$m in diameter at 1C charging rate condition during lithiation showed the maximum elastic tensile hoop DIS reducing from 1 GPa to 200 MPa upon allowing for plasticity and then relaxed further to about 0.45 MPa with creep relaxations\textsuperscript{19}. However, no studies have been reported so far to the authors’ knowledge that examined the effect of the concentration dependent material properties on DIS. During lithiation, different phases of Li$_x$Sn alloys (i.e. LiSn, Li$_2$Sn$_3$, Li$_3$Sn$_2$, Li$_7$Sn$_2$, and Li$_{12}$Sn$_5$) form and thus are expected to cause significant changes in intrinsic material properties such as diffusivity, elastic properties that can in turn change the numerically calculated DIS. Therefore, in this study, a numerical analysis is utilized to understand the effect of Li concentration-dependent material properties including the Young’s modulus, Poisson's ratio and diffusivity on DIS of Sn micropillars.

2. Experimental Section
2.1 Theory and Numerical Modeling

For an axisymmetric analysis, this study utilized a numerical analysis using COMSOL Multiphysics to illustrate the effect of concentration-dependent material properties on the corresponding DIS during Li diffusion into Sn micropillars. Transport of Li into host can be defined by Fick's second law, where the concentration gradient is the driving force for Li diffusion\textsuperscript{20-21}. Li atoms diffuse from the surface to the center of Sn micropillar along the radial direction. An axisymmetric model is used for analysis where the radial diffusion of Li atoms can be described by the Fick’s second law in axisymmetric cylindrical coordinates, i.e.

\[
\frac{\partial c}{\partial t} = D \nabla^2 c = D \left[ \frac{\partial^2 c}{\partial r^2} + \frac{1}{r} \frac{\partial c}{\partial r} \right],
\]  

where \(c\) is the concentration of Li and \(D\) is the diffusivity of Li in Sn anode.

For a given charging rate, Li atoms will be provided at a constant flux on the surface of the Sn micropillar that will result in an initially Li free surface to increase in concentration over time. Therefore, the initial and boundary conditions can be described as

\[
c(r, t = 0) = 0
\]  

(2)

\[
D \nabla c(r = 0, t) = 0
\]  

(3)

\[
D \nabla c(r = R, t) = J_s
\]  

(4)

where \(R\) is the radius of a micropillar.

To analyze the DIS of Sn micropillar, perfectly elastic and elasto-plastic plasticity and creep deformation models were incorporated. The total strain variation induced by lithiation, \(d\varepsilon_{ij}^L\), is thus defined by the sum of the three contributions as given by,

\[
d\varepsilon_{ij}^L = d\varepsilon_{ij}^{EL} + d\varepsilon_{ij}^{EP} + d\varepsilon_{ij}^{CP}
\]  

(5)

where \(i\) and \(j\) represent directions and the increase of lithiation-induced strain, \(d\varepsilon_{ij}^L\), is proportional to concentration variation of Li, i.e. \(d\varepsilon_{ij}^L = \beta d\varepsilon_{ij} = \beta(c - c_0)\), where the \(\beta\) is the expansion coefficient. Moreover, the increment of elastic strain is governed by the Hooke’s law,

\[
d\varepsilon_{ij}^{EL} = \frac{1}{E} \left[ (1 + \nu) \sigma_{ij} - \nu \sigma_{kk} \delta_{ij} \right]
\]  

(6)

where \(\nu\), \(\sigma_{ij}\), and \(E\) are the Poisson's ratio, stress components and Young's modulus, respectively and \(\delta_{ij}\) is the Kronecker delta.
For the perfectly-elastic deformation model, i.e., \( \text{d} \varepsilon_{ij} = 0 \), in analogy to thermal expansion, the constitutive relation between stress and strain tensors can be denoted as follows:

\[
\varepsilon_{rr} = \frac{\sigma_{rr} - \nu (\sigma_{\theta\theta} + \sigma_{zz})}{E} + \beta (c - c_0) \tag{7}
\]

\[
\varepsilon_{\theta\theta} = \frac{\sigma_{\theta\theta} - \nu (\sigma_{rr} + \sigma_{zz})}{E} + \beta (c - c_0) \tag{8}
\]

\[
\varepsilon_{zz} = \frac{\sigma_{zz} - \nu (\sigma_{rr} + \sigma_{\theta\theta})}{E} + \beta (c - c_0) \tag{9}
\]

To solve this problem, deformation model should satisfy the force balance and strain compatibility condition. Sum of stress in all directions \( (x_j) \) at equilibrium state should always satisfy following condition at all times.

\[
\frac{\partial \sigma_{ij}}{\partial x_i} = 0 \tag{10}
\]

Furthermore, strain tensor is related to displacement field \( (u_i) \) according to direction component \( (x_j, x_j) \) can be described as follows:

\[
\varepsilon_{ij} = \frac{1}{2} \left( \frac{\partial u_i}{\partial x_j} + \frac{\partial u_j}{\partial x_i} \right) \tag{11}
\]

For modeling the plastic deformations, the \( J_2 \)-flow rule is assumed that gives

\[
\text{d} \varepsilon_{ij} = \begin{cases} 
0, & \sigma_e < \sigma_y \\
\lambda S_{ij}, & \sigma_e = \sigma_y \\
d \sigma_e = d \sigma_y, & \sigma_e = \sigma_y \end{cases} \tag{12}
\]

where \( S_{ij} = \sigma_{ij} - \sigma_{kk} \delta_{ij}/3 \) is the deviatoric stress, \( \sigma_e = \sqrt{3} S_{ij} S_{ij}/2 \) the equivalent stress and \( \sigma_y \) is the yield strength of Sn pillar. In addition, creep parameters obtained from our previous work were utilized to include creep behavior of Sn pillar in our simulation model\(^{19,33} \). The strain variation by creep is governed by power law formulation, given by

\[
\dot{\varepsilon} = A \sigma^n \tag{13}
\]

As Li concentration increases in the Sn anode, phase transformations occur as Sn transforms to \( \text{Li}_2\text{Sn}_3 \), \( \text{LiSn} \) (tetragonal), \( \text{Li}_2\text{Sn}_3 \) (monoclinic), \( \text{Li}_3\text{Sn}_2 \) (trigonal), \( \text{Li}_4\text{Sn}_2 \) (orthorhombic) and then becomes \( \text{Li}_{12}\text{Sn}_5 \) (diamond cubic) in the fully lithiated state\(^{25} \). As a result, material properties including diffusivity, Young’s modulus, and Poisson’s ratio are altered with phase transformations during lithiation. Material properties of lithiated Sn phases such as the elastic modulus, Poisson’s ratio and diffusivity were first explored in a few DFT studies\(^7 \). Since lithiation results in
the filling of antibonding p orbital by electron donations of Li ions, the Sn-Sn bonds become weaker, leading to lower Young’s modulus ($E_c$) and Poisson’s ratio ($\nu_c$)\textsuperscript{6,22}. Furthermore, an experimental study was also carried out that confirmed increasing diffusivity of Li in Li$_x$Sn alloy with increasing SOC\textsuperscript{23}. During charging, Li ions diffuse into the host that changes the lattice constants which in turn can be assumed as to vary linearly with volume of the inserted Li ions\textsuperscript{29-30}. To determine the diffusivity of Li in Sn thin film electrode, coulometric titration and electrochemical impedance spectroscopy (EIS) techniques were utilized. Diffusivity of Li in Sn anode was determined from Warburg constant ($W = \frac{|dE/dc|}{F\sqrt{2D}}$) of optimal equivalent circuit\textsuperscript{24}. Other experimental studies also revealed the diffusivity in Sn electrode by other techniques such as galvanostatic intermittent titration technique and potentiostatic intermittent titration technique\textsuperscript{25,27-28}.

During charging at a constant current density, there is a constant flux of Li ions arriving on the surface of electrode. In other words, flux of Li is defined as $J_s = \frac{i}{F}$ where $i$ is applied current density during charging process and $F$ is Faradaic constant. Li diffuses from the surface of Sn pillar towards the center where the concentration gradient is the driving force for the diffusion and DIS is calculated by using hygroscopic swelling approach which calculate the strain from the difference between Li concentrations of current and initial states. Given no anisotropic expansion in Sn anode, the small strain model was used\textsuperscript{31-32}. Since the volume expansion is a linear function of SOC or lithiation time ($t$), the DFT calculated values of $E_c$, $\nu_c$ and $D_c$ for each intermetallic compound are linearly interpolated in COMSOL. The top end of pillar was free to deform axially while fixing the bottom end of the pillar, thus making a generalized plane-strain condition along the z-axis. Also, lithiation kinetics of Sn is controlled by diffusion of Li, unlike the reaction controlled lithiation in Si, so the diffusion controlled lithiation model which does not show sharp phase boundary in host materials was utilized in simulation. Moreover, to model the DIS evolutions along with plastic deformations, elastic-perfectly plastic governing behavior was assumed.

The underlying effect of Li concentration-dependent material properties on the evolution of DIS was studied on Sn micropillars with a diameter of 1 μm and c-rate of C/10. To illustrate the DIS along the radial direction of Sn pillar, a dimensionless radial position was defined as $r/R$, where $r$ = position along the radial direction, at the halfway of pillar’s height and $R$ = total radius of Sn micropillar. The simulation domain was carefully meshed to guarantee numerical stability and to ensure the convergence the relative and absolute tolerances were set to $10^{-10}$ and $10^{-4}$, respectively. For the DIS modeling, $E_c$ and $\nu_c$ were taken from the work by Shenoy’s group\textsuperscript{22}. The material properties
for pure Sn (Li = 0) for fully lithiated states (Li = 4.4) used in the simulations are stated in Table 1. Yield strength ($\sigma_y$) of 150 MPa and creep parameters (i.e. $n = 1.5$, $A = 2.3 \times 10^{-8}$\textsuperscript{33}, $\beta = 2.0522 \times 10^{-6}$ m$^3$ mol$^{-1}$ and $C_{\text{max}} = 2.155 \times 10^{5}$ mol m$^{-3}$ were taken as simulation conditions\textsuperscript{38}.

**Table 1** List of parameters used in this simulation to analyze the stress of Sn anode during lithiation

<table>
<thead>
<tr>
<th>Phase</th>
<th>Diffusivity ($m^2/s$)</th>
<th>Young’s modulus (GPa)</th>
<th>Poisson’s ratio</th>
</tr>
</thead>
<tbody>
<tr>
<td>Sn</td>
<td>$1.1 \times 10^{-17}$</td>
<td>50</td>
<td>0.33</td>
</tr>
<tr>
<td>LiSn</td>
<td>$4.5 \times 10^{-17}$</td>
<td>41.1</td>
<td>0.2419</td>
</tr>
<tr>
<td>Li$_2$Sn$_3$</td>
<td>$4.3 \times 10^{-17}$</td>
<td>31.29</td>
<td>0.1791</td>
</tr>
<tr>
<td>Li$_2$Sn$_2$</td>
<td>$5.1 \times 10^{-17}$</td>
<td>30.73</td>
<td>0.1721</td>
</tr>
<tr>
<td>Li$_3$Sn$_2$</td>
<td>$1.6 \times 10^{-16}$</td>
<td>29.75</td>
<td>0.1617</td>
</tr>
<tr>
<td>Li$_{22}$Sn$_5$</td>
<td>$3.4 \times 10^{-16}$</td>
<td>28.08</td>
<td>0.1538</td>
</tr>
</tbody>
</table>

**Other parameters**

- Maximum Li concentration: $2.155 \times 10^5$ mol/m$^3$
- Yield strength: 150 MPa
- Expansion coefficient: $2.0522 \times 10^{-6}$
- Creep exponent: 1.5
- Creep coefficient: $2.3 \times 10^{-8}$
2.2 Preparation of Sn micropillar anode

Sn electrode with thickness of ~15 μm was prepared on top of a nickel substrate by electrodeposition from a bath containing 0.044M of tin dichloride, 0.22 M of tri-ammonium citrate, and 0.05M of thiourea. Constant current density of 8 mA cm\(^{-2}\) was applied with a VMP3 potentiostat (BioLogic) at room temperature for 2 hours using Sn plate (99.9% purity) as the counter electrode. Sn micropillars with different diameter sizes (0.97 μm, 2.4 μm, 3.5 μm, 4.4 μm and 6.0 μm) were prepared via Focused Ion Beam (FIB, Helios Nanolab 450, FEI company) milling with a fixed diameter to height aspect ratio of 1:3.

2.3 Characterization

Galvanostatic cycling of Sn micropillar anode was carried with 2032 stainless steel coin cell in a half-cell configuration, which was assembled in an argon glove box. The electroplated Sn electrode served as the working electrode and Li metal served as the counter electrode. A monolayer polypropylene separator (Celgard® 2400) was used as the separator and a 1M LiPF\(_6\) in 1:1 volume ratio mixture of ethylene carbonate (EC) and dimethyl carbonate (DMC) was used as the electrolyte. Each micropillar containing Sn electrode was galvanostatically lithiated/delithiated at C/10 rate. Five complete lithiation/delithiation cycles were conducted and after the sixth lithiation, the cell was disassembled in an argon glove box and the electrode was rinsed in DMC to remove residual Li salts and dried in the argon glove box prior to characterization.

After complete lithiation, X-ray diffraction characterization (XRD, D/MAX-2500, RIGAKU) was performed to confirm Li to Sn ratio of 4.4:1 and the formation of the fully lithiated Li\(_{22}\)Sn\(_5\) phase (ICDD card number: 01-081-656911). Furthermore, scanning electron microscope (SEM, JSM-7610F, JEOL) observations were carried out on the Sn micropillars before and after lithiation/delithiation cycles to provide insight into changes in morphology due to volume expansion/contraction.

3. Results and Discussions

3.1 Effect of concentration-dependent \(D_c\), \(E_c\), \(\nu\) on elastic DIS

In order to investigate the effect of using concentration dependent material properties on Sn micropillar,
concentration profile was first analyzed for the case of constant, concentration independent properties first and then compared against that of concentration dependent properties. Since the size of the micropillar is fixed to a diameter of 1 μm for all results in this study, the concentration profile then depends on the c-rate and diffusivity of Li in Sn. Concentration profile of Sn pillar is first investigated at 0.1C for both concentration-independent and dependent diffusivity cases and the resulting Li concentration in Sn (c) is normalized with maximum theoretical capacity ($C_{\text{max}}$) of Sn at Li$_{4.4}$Sn as a function of radial position r normalized by outer radius R (r/R) as shown in Fig. 1. For pure Sn case (no Li insertion), c = 0, c = 1 denotes when Sn anode surface reaches its full capacity of $C_{\text{max}}$. The concentration of Li at surface is determined by the charging rate, and Li starts to diffuse towards the center of the pillar, and the steep concentration gradient starts to gradually relax with further lithiation for the case of constant diffusivity.

Next, concentration dependent $D_c$ is incorporated in the numerical modeling. $D_c$ for Li-rich phases increases by ~2 orders of magnitude, hence resulting in Li ions diffusing towards the center of Sn micropillar faster. As a result, the steady state concentration profile for concentration dependent $D_c$ shown in Fig. 1b differs from the case for constant diffusivity shown in Fig. 1a, where a more homogeneous, or less steep concentration gradients are observed at varying SOC for the case with concentration dependent $D_c$. Difference in the concentration profiles for the concentration independent and dependent cases are clearly shown in the comparison in Fig. 1c.

![Fig. 1](image-url) Distribution of Li ions along the radial direction of Sn pillar of 1 μm at c-rate of C/10 as a function of SOC for (a) constant diffusivity ($D$) and (b) Li concentration-dependent diffusivity ($D_c$). (c) Comparison of concentration profile along the radial direction between concentration independent and dependent diffusivity cases.

The elastic stress distributions for the case of concentration independent properties were then investigated as shown in Fig. 2. As the concentration gradient is formed, the strain mismatch in the volume of the lithiated shell and unlithiated core results in DIS. Traction in radial direction by concentration gradient in Sn pillar results in tensile radial stresses with max value at the core and the radial stress is rapidly decreased by zero at traction-free surface.
(Fig. 2a) As for the hoop stresses, expanded shell causes compressive hoop stresses to develop near the surface and tensile hoop stresses form in the core region. In the early stages of lithiation (~SOC < 5.5 %), there is a steep increase in the hoop stresses, where the maximum tensile hoop DIS at center of micropillar increases from ~750 MPa to ~1280 MPa. The DIS reaches a steady state at ~SOC = 22.5 % with maximum tensile stress ~1280 MPa and no observable changes in hoop stresses are observed up to ~SOC = 100 % as shown in Fig. 2a.

![Fig. 2](image)

**Fig. 2**: Evolution of elastic (a) radial and (b) hoop DIS of Sn micropillar with constant material properties.

The concentration dependent mechanical properties ($E_c$ and $\nu_c$) in addition to using concentration-dependent $D_c$ were then incorporated in the elastic DIS analysis. Fig. 3 shows the evolution of radial and hoop DIS as a function of SOC when the Li concentration-dependent mechanical properties are incorporated in the numerical calculations. As previously explained, the concentration dependent $D_c$ results in relatively homogeneous concentration gradients due to faster diffusion of Li in lithiated region, and hence lower radial and hoop stresses are generated (Fig. 3). Although initial value of hoop stress is similar with that of Sn micropillar, concentration of core increase faster than that of surface region leading to much lower DIS. In the early stages of lithiation with SOC < 5.5%, both tensile radial and hoop DIS at center of Sn pillar reach to its maximum value of ~750 MPa. However, for SOC > 5.5%, the effect of Li concentration-dependent parameters on DIS starts to emerge and, thereby, the tensile radial and hoop DIS decrease to ~150 MPa when SOC reaches to ~58% (comparable to Li$_2$Sn$_2$ phase). Interestingly, the faster diffusivity and lower modulus together have therefore enhanced the durability of Sn pillars during lithiation. Tensile radial and hoop DIS at center drop to ~20 MPa at ~SOC=100% (at Li$_{22}$Sn$_5$). It is evident from these results that effect of material
parameters on DIS is significant.

![Graph](image_url)

**Fig. 3** Effect of Li concentration-dependent material properties during evolution of elastic (a) radial and (b) hoop DIS as a function of SOC

### 3.3 Elastoplastic and creep deformations for lithiated Sn pillars

Sn has low yield strength and creeps even at room temperature that allows for relaxation of stresses via plastic deformations and creep. To investigate the effects of plasticity and creep, yield strength and power law based creep behavior ($\dot{\varepsilon} = A\sigma^n$) are included to simulation model. All values for simulations including the yield strength and creep parameters were taken from our previous experimentally measured values\cite{19,33}. As the DIS first increase with lithiation to a point where von Mises stresses exceed the yield strength, plasticity starts to occur that relaxes both the radial and hoop stresses. In case of Sn micropillar, unlike Si, since the yield strength is low (~150 MPa), plasticity can occur easily in Sn anode, and thus the overall magnitudes of DIS have lowered significantly in both concentration independent and dependent case as shown in Fig. 4a, c. Furthermore, when creep deformation is included in simulation model, maximum tensile hoop stress becomes drastically lowered more than only elastoplastic deformation due to vigorous creep behavior of Sn micropillar (Fig. 4b, d). However, most importantly, it is noteworthy that the hoop stress at the surface is transformed from compressive to tensile stress in plastic deformation. This interesting phenomenon is due to the increasing diffusivity according to concentration instead of decrease in Young’s modulus and Poisson’s ratio by SOC. (Fig. S2)
Fig. 4 DIS evolution along with plasticity and creep deformations. Hoop stresses of Sn micropillar with (a) constant material properties (c) concentration-dependent material properties as a function of SOC in elastoplastic deformation. Hoop stresses of Sn micropillar with (b) constant material properties and (d) concentration-dependent material properties as a function of SOC in elastoplastic and creep deformation.

To analyze the stress transition of Sn micropillar in more detail, the expansion rate in hoop direction of Sn micropillar by Li insertion and mechanical strains caused by expansion are investigated. From Fig. 5, stress transition phenomenon is ascribed to two factors, which are expansion rate and plastic strain. Fig. 5a, d is the lithiation-induced strain rate profile according to time in Sn pillar with concentration independent and dependent case respectively, which can be described as $\frac{\partial e^{Li}}{\partial t} = \beta \frac{\partial c}{\partial t}$ by lithiation-induced strain ($e^{Li} = \beta c$). In Sn micropillar with concentration independent material properties, expansion rate of outer region is always higher than that of core region. Therefore, compressive hoop stress always occurs at outer region during lithiation and this compressive stress gradually increases...
with SOC (Fig. 2b). However, in concentration dependent case, Li can reach the core faster due to increase in diffusivity and, thereby, more rapid expansion of core occurs. In Fig. 5d, strain rate of core region drastically increases from $t=1000s$ to $1500s$ and consequently strain rate of core region is higher than outer region near the surface due to the increase in diffusivity with Li content. Therefore, the strain mismatch between core and surface of Sn micropillar is alleviated leading to gradual relaxation of compressive hoop stress at the surface of Sn micropillar (Fig. 3b).

Next, the plastic strain distribution of Sn micropillar with concentration independent and dependent material properties, respectively, is shown in Fig. 5c, f. Plastic strain relaxation occurs in the regions of which applied stress is higher than its yield point (150MPa), and higher plastic strain relaxation appears to show high values at the surface of Sn micropillar in both concentration dependent and independent case until $t=3000s$. In other words, expansion of only outer region is partially relaxed by plastic strain in initial charging process. Comprehensively, in the case of Sn micropillar with constant material properties, surface strain by expansion is decreased by plastic strain (Fig. 5c). However, lithiation-induced strain rate of core is always lower than that of outer region (Fig. 5a). Therefore, expansion of core is not enough to overcome the expansion of outer region. As a result, elastic strain of inner region is tensile and, reversely, that of surface is compressive. However, in the case of Sn micropillar with concentration-dependent diffusivity, lithiation-induced strain rate of core region is dramatically increased by its higher diffusivity with SOC and plastic strain at surface is much higher than core region (Fig. 5d, f, up to $t=3000s$). After $t=3000s$, elastic strain of outer region transforms from compressive to tensile (Fig. 5c) causing tensile hoop stress to develop at surface of Sn micropillar (Fig. 3c). Furthermore, at SOC ~5.5% ($t=1980s$), hoop stress at the surface is already transformed from compressive to tensile by creep relaxation (Fig. 4c, d). Results of this study is consistent with prior study by Chao et al., who revealed that cracks of Sn micro-particles are propagated from surface to center gradually by transmission X-ray microscopy that is indicative of tensile hoop stress at the surface of the particles$^{36}$. 
Fig. 5 Comparison of strain rate and strain variation of Sn micropillars in elastoplastic deformation. (a) Lithiation-induced strain rate, (b) elastic strain, and (c) plastic strain of Sn micropillar with constant material properties. And (d) Lithiation-induced strain rate, (e) elastic strain, and (f) plastic strain of Sn micropillar with concentration-dependent material properties.

3.4 Critical Size to prevent the fracture

The failure of the Li-Sn alloy is dependent on the tensile DIS which leads to the crack propagation. The critical size for fracture of Sn micropillar was determined from incorporating the numerical simulation results of maximum tensile hoop stress locating at the center of the Sn micropillar. Therefore, stress intensity factor ($K_I$) was calculated from the maximum tensile hoop stress determined previously from COMSOL and then J-integral method of ABAQUS FEM simulations was used to incorporate the Sn elastic material properties. If $K_I$ exceeded the fracture toughness of Sn micropillar ($K_{IC}$), then the failure occurs leading to crack propagation. In addition, since different c-rates results in different tensile DIS, in order to determine the critical size at a particular c-rate, $K_I$ values with different Sn micropillar sizes were calculated and determined. The critical diameter of Sn micropillar for a c-rate of C/10 was determined to be ~ 5.3 μm, which is much larger than that of Si (~300 nm) at the same c-rate.

To support the simulation results experimentally, Sn pillars of varying diameters were etched using the FIB from electroplated Sn film of ~15 μm in thickness. Lithiation was performed galvanostatically with a c-rate of C/10.
6th lithiation process, after 5 cycles of full lithiation/delithiation process, samples were extracted, and rinsed in dimethyl carbonate and brought to SEM. As shown in the figure below, after lithiation, Sn micropillar with 0.97 μm, 2.4 μm, 3.5 μm, 4.4 μm and 6.0 μm in diameter expanded to 1.9 μm, 3.3 μm, 5.9 μm, and 6.9 μm and 11.4 μm respectively. This is equivalent to 195%, 138%, 169%, and 164% and 190% volume expansion respectively. However, as shown in Fig. 6e and 6j, micropillar with diameter size greater than 6.0 μm did not survive the volume expansion as there were no signs of the micropillar after the lithiation. Therefore, with a c-rate of C/10, the critical diameter of Sn micropillar was found to be around 4.4 μm, analogous to the simulation result. The experimental observations therefore confirmed that the critical size for fracture of Li-Sn alloy is many orders of magnitude larger than that of Si, which is ~300 nm, hence, proving the merit of using Sn as an anode material.

![Fig. 6](image-url) Pre-lithiation (a-e) SEM images of Sn micropillars and post-lithiation pillars (f-j) SEM images of Sn micropillars
4. Conclusions

In this study, the effect of using Li concentration-dependent properties on stress evolution on Sn pillars in numerical simulations was explored. Among different parameters for concentration dependent properties, which are elastic modulus, poisson’s ratio and diffusivity for different phases of Li-Sn alloy, diffusivity was found to be the most important parameter that affects the DIS in Sn micropillar. Diffusivity of Li in Sn increases as lithiation proceeds, and this caused more homogeneous concentration profile and thus results in less steep concentration gradients. As a result, the DIS in Sn pillar reduced significantly if only elastic deformations are considered. However, if the Sn pillar was allow to deform through plasticity and creep, push-out effect on the outer surface occurred due to faster expansion rate of core by increase of diffusivity and higher plastic strain of outer surface of the pillar. Consequently, as a result of the push-out effect, the compressive hoop stresses transformed into tension. In addition, fractures on surface of Sn pillars was observed by SEM upon lithiation/delithiation, which indicated that tensile hoop stress was generated on the surface of Sn pillar during lithiation. However, the critical size of Sn pillar anode for fracture was 4.4 μm,
which is significantly larger than that of Si, hence confirming potential of Sn anode in providing more reliable electrochemical cyclic lifetime. To summarize, this work has clearly shown that DIS in Sn pillar during lithiation is severely affected by Li concentration-dependent material properties. Therefore, for anodes in which the lithiation reaction occurs via alloying that causes phase transformations, it is critical to incorporate the Li concentration-dependent properties in numerical simulations to accurately analyze the DIS for the purpose of designing of mechanically robust anode.

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References