Supplementary Information

For

Alloying with Ge and hollowing reduces lithiation-induced stresses in Si nanopillar anodes

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Figure S1. In-situ atomic-scale image of electrochemical lithiation of Si from the experimental study by Liu et al. [1]. Reproduced with permission. Copyright 2012, Macmillan Publishers Limited.
Figure S2. The variation in lithium diffusivity with lithium concentration for different values of $\alpha$, which controls the thickness of the reaction interphase. The corresponding reaction interphases are shown.
Figure S3. R-θ plot for the spatial variation in \( D_0(\theta) \) across the cross-section of the nanopillars for different materials.

1. Lithiation induced elasto-plastic deformation

In the finite-strain plasticity framework, deformation is characterized by the elastic and plastic stretch rates (denoted by \( d^e \) and \( d^p \), respectively) and spin rates (denoted by \( W^e \) and \( W^p \), respectively). Subsequently, the total stretch rate tensor, \( D \), during lithiation can be decomposed into three additive parts: \( D = d^e + d^p + d^c \), where \( d^e \), \( d^p \) and \( d^c \) are the elastic, plastic and chemical stretch rates, respectively [2–4]. The constitutive response of the lithiated phase can be described by the elastic and perfectly plastic model, which relates the stretch rate \( (d^e) \) and stress rate \( (\tau^P) \) by \( \tau^P = \frac{E_I}{1 + v_I} \left[ d^e + \frac{v_I}{1 - 2v_I}\text{tr}(d^e)I \right] \), where “tr()” operator denotes the
trace of a tensor and $\tau$ is the Kirchhoff stress. The superscript in $\tau^\nabla$ denotes the Jaumann rate of $\tau$, that accounts for the spin of a material point. Note that the Kirchhoff stress is related to the Cauchy stress $\tau = J\sigma$, where $J$ characterizes the volume expansion [2]. $E_i$ and $v_i$ are the concentration dependent Young’s modulus and the Poisson’s ratio which are adopted form the literature and are shown in Figure S4 [5–8]. The plastic stretch rate, $(d^p)$, obeys the associated J2-flow rule. Primarily, plastic yielding is hypothesized to occur when the equivalent stress, $\tau_{eq} = \sqrt{3s:s}/2$, reaches the yield strength, $\tau_y$, which is taken to be 1.5 Gpa [9]. Here, $s = \tau - tr(\tau)I/3$ is the deviatoric stress tensor. In the J2-flow theory, the plastic stretch rate is given by $d^p = 3sd^p_{eq}/2\tau_{eq}$, where $d^p_{eq} = \sqrt{2d^p:d^p}/3$ is the equivalent plastic stretch rate.

The lithiated phase is modelled as an isotropic elastic and perfectly plastic material. However, perfect plasticity often leads to numerical instability in simulations. To circumvent this difficulty, we use the Cowper–Symonds overstress power law with appropriately chosen parameters to approximate the perfectly plastic limit, as $d^p_{eq} = m(\tau_{eq}/\tau_y - 1)^n$ where $m$ and $n$ are the reference stretch rate and the rate sensitivity exponent taken as $m=1000$ and $n=1$ in our simulations. In the interphase, an abrupt change of Li concentration causes large chemical strains [3,4]. We assume that the lithiation-induced electrochemical deformation rate is dilational without spin and the electrochemical stretch rate $(d^c)$ is proportional to the increment of the Li concentration, $d^c = \beta I \dot{c}$, where $\beta$ is the lithiation expansion coefficient and $I$ is the identity tensor. We take $\beta = 0.6$ for Si corresponding to the observed 300% volume expansion at the full lithiation [9,10]. Similarly $\beta = 0.52$ is chosen for the Ge corresponding to the 260% volume expansion at full lithiation [11]. We take $\beta = 0.56$ as the average value for the Si$_{0.5}$Ge$_{0.5}$ alloy.
Figure S4. The material properties, Young’s modulus ($E_l$) and Poisson’s ratio ($\nu_l$) for Si, Ge and Si$_{0.5}$Ge$_{0.5}$ alloys as a function of Li concentration ($c$).

Table S1. Yield stress and parameters in Cowper Symond law ($m$ and $n$)

| Yield stress (GPa) | $m$ | $n$ |
|-------------------|-----|-----|
| 30                |     |     |
| 50                |     |     |
| 70                |     |     |
| 90                |     |     |
| 110               |     |     |
| 130               |     |     |
| 150               |     |     |
| 170               |     |     |
2. Validation

We validate the model with the previous study of Hui Yang et al. [9]. Our results of stress profiles are compared with their results at different degree of Li concentration as shown in Figure S5.

![Figure S5](image)

Figure S5. The validation of model with the previous study of Hui Yang et al. [9]. Our computed stress profiles are plotted along with theirs at different degree of Li concentration ($C_{Li}$).

3. Additional Results:

3.1. Solid Nanowires:

In the Figure 2 (of the main manuscript), we analysed the stress profiles at a particular degree of lithiation. These profiles depict the stress distribution in the cross-section of the nanowire along with the deformation. One can identify the points of stress accumulation and predict
regions prone to fracture. In order to understand the continual variation in the stresses during lithiation, we plot the stress evolution in the nanowire. The maximum stresses indicate only the point of fracture, not the overall stresses in the material. Hence, we plot volumetric average stresses as a function of the volume of the nanowire. The volumetric average stress is computed as $\int \sigma \, dv / \int dv$, where $\sigma$ is the Hoop’s stress inside an infinitesimal element and $dv$ is the corresponding volume. The variation is shown in Figure S6. It can be seen that near full lithiation, the volumetric average stress is minimum in Si. This is because in Si, most of the material has either compressive stress or no stress at all and only few points have high tensile stress. This suggests that in Si, stresses accumulate at some localized zones and are not distributed over the entire material. Whereas, in Ge and Si$_{0.5}$Ge$_{0.5}$ alloy, stresses are distributed over the entire material that makes the average volumetric stress higher. Because of the stress being distributed over the entire material, the possibility of cracking is reduced. Apart from the average volumetric stresses, Figure S6 also shows that at full lithiation Si has the highest volume compared to the other materials.

Figure S6. Average Hoop’s stress vs Volume for different materials: Si, Ge, Si$_{0.5}$Ge$_{0.5}$ Alloy and Si Core Ge shell.
3.2. Nanotubes (No lithiation form the inner surface):

Here, we plot the evolution of the average volumetric stresses against volume in Figure S7. Similar to the previous section, the stresses are lower for pure Si and Si-Ge core-shell as compared to the pure Ge and Si$_{0.5}$Ge$_{0.5}$ alloy. Due to the distribution of stresses in pure Ge and Si$_{0.5}$Ge$_{0.5}$ alloy, there are less chances of cracking for these materials compared to the pure Si and Si-Ge core-shell materials.

![Figure S7. Average Hoop’s stress vs Volume for different materials: Si, Ge, Si$_{0.5}$Ge$_{0.5}$ Alloy and Si Core Ge shell.](image)

The value of stress inside the Si nanotube for lithiation (only from the outer surface) is found to be minimum at $R_{\text{in}}/R_{\text{out}}=0.4$ as shown in Figure 4 (of the main paper). The concentration and stress profiles for this structure are shown for different materials in Figure S8 when y-intercept of the Li-front $y_{\text{Li-front}} = R_{\text{in}}+(R_{\text{out}}-R_{\text{in}})/2$. 

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Figure S8. Li concentration ($C_{Li}$) and Hoop’s stress profiles ($\sigma_{oo}$) along the cross section of (100) oriented nanotubes. The outer radius of the nanotube, $R_{out}=10.911$ nm and inner radius $R_{in}=4.36$ nm ($R_{in}/R_{out}=0.4$). The $y$-intercept of Li-front, $y_{Li-front} = R_{in} + (R_{out}-R_{in})/2$. Four material configurations are considered: (i) Si, (ii) Si-Ge Core-Shell (iii) Si$_{0.5}$Ge$_{0.5}$ alloy (iv) Ge.

3.3. Additional shapes:

3.3.1. Square:

To study the effect of shape on stresses developed, we model lithiation in square nanorods. The square nanorods allow for extra material at the points where stresses are known to accumulate
(from the results associated with the circular cross-section). For effective comparison, the square nanorods are considered with the same amount of material as that of the circular nanowire (with side $2a=17.72$ nm). The Li concentration and stress profiles are shown in Figure S9. Initial stresses developed when the Li front reaches $x=a/2$ (as shown in Figure S9(a)) are higher in all cases when compared with the case of circular cylindrical nanowires (Figure 2(a) in the main manuscript). The stresses in Si and Si-Ge core-shell nanorod at near full lithiation (Figure S9 (b,i,ii)) are less than those developed in circular nanowire case (Figure 2 (b,i,ii)) due to predominant anisotropy in Li diffusion. However, the stresses in Si$_{0.5}$Ge$_{0.5}$ alloy and in pure Ge nanorod at near full lithiation (Figure S9 (b,iii,iv)) are higher than the case of circular nanowire (Figure 2 (b,iii,iv)) due to predominant isotropic nature of Li diffusion. So, square nanorods help in reducing the stresses developed due to the anisotropic effect of Li diffusion by providing more material volume near the plausible fracture points. Here also, Si$_{0.5}$Ge$_{0.5}$ alloy and pure Ge nanorods show lower stresses compared to the pure Si and Si-Ge core-shell nanorods.
Li concentration and stress profiles at various positions of lithiation front

(a) $x_{\text{Li-front}} = a/2$

(b) $x_{\text{Li-front}} = a/5$

(i) Si

(ii) Si-Ge core-shell

(iii) Si$_{0.5}$Ge$_{0.5}$ alloy

(iv) Ge

Figure S9. Li concentration ($C_{\text{Li}}$) and stress profiles ($\sigma$) (maximum in-plane principal) at different penetrations of Li front. The side of the square, $2a=17.72$ nm. (a) Position of Li front along the x axis, $x_{\text{Li-front}} = a/2$. (b) Position of Li front along the x axis, $x_{\text{Li-front}} = a/5$. Four material configurations are considered: (i) Si, (ii) Si-Ge Core-Shell (iii) Si$_{0.5}$Ge$_{0.5}$ alloy (iv) Ge.

Here, we plot the evolution of the average volumetric stresses with the volume in Figure S10. Similar to the previous sections, the stresses are lower for the pure Si and Si-Ge core-shell as compared to the pure Ge and Si$_{0.5}$Ge$_{0.5}$ alloy. The stress in Si are accumulated at a point and are negligible at other places. This makes the average volumetric stress inside the Si lower compared to the other cases. Similar to the case of nanowires and nanotubes, stresses inside
pure Ge and Si0.5Ge0.5 alloy are more distributed. Therefore, the average stresses are higher. Therefore, the possibility of fracture in Ge and Si0.5Ge0.5 alloy is less compared to Si and Si-Ge core-shell materials.

Figure S10. Volumetric average stresses in square nanorods with respect to the volume for different materials: Si, Ge, Si0.5Ge0.5 Alloy and Si Core Ge shell.

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