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To cite this article: Abhishek Bansal *et al* 2020 *J. Electrochem. Soc.* **167** 013542

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Alloying with Ge and Hollowing Reduces Lithiation-Induced Stresses in Si Nanopillar Anodes

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High energy-density batteries are crucial to energy storage solutions. In lithium-ion batteries (LIBs), Si nanopillars are promising anodes due to their highest theoretical specific capacity. However, volume expansion and fracture during cycling inhibit its widespread adaptation. Ge, which is isomorphous with Si, shows better fracture resistance and higher cycle life but has higher molecular weight and cost. Alloying Si with Ge offers a trade-off in optimizing stresses, weight and cost. Here, we computationally evaluate the effect of alloying Si with Ge in reducing stresses generated during lithiation. Hollowing, which creates additional free surface for expansion is also considered. First, we model the stress evolution in nanopillars of Si, Ge, Si-Ge core-shell and Si_{0.5}Ge_{0.5} alloy. Alloying Si with Ge uniformly, reduces the maximum circumferential stress by around 17%, however, the Si core-Ge shell structure shows stress reduction only when lithiation is confined only to the Ge. Stresses in Si/Ge alloyed nanotubes considering lithiation from the outer boundary as well as from both boundaries are considered. We find a non-monotonous change in lithiation stress with varying radius ratio (R_{in}/R_{out}) and $R_{in}/R_{out} = 0.4$ leads to the least maximum Hoop stress. The stress reduction in Si-nanotubes in such configuration is found to be 16%.

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Manuscript submitted September 30, 2019; revised manuscript received December 1, 2019. Published January 17, 2020. *This paper is part of the JES Focus Issue on Mathematical Modeling of Electrochemical Systems at Multiple Scales in Honor of Richard Alkire.*

Supplementary material for this article is available [online](#)

Lithium-ion batteries (LIBs) are extensively used as energy storage devices in portable electronic systems and are being implemented to power electric vehicles.¹ Traditionally, LIBs use carbon, in the form of graphite, as the anode material. While graphite has a relatively low theoretical capacity (372 mAh g⁻¹), it exhibits excellent cyclic behaviour (lithiation/delithiation), which is the main reason for its widespread adoption.² With the ever-increasing demand for energy and power densities, other elements from the same group such as Si, Ge and Sn have drawn attention as a viable replacement for graphite due to their higher theoretical capacities, which are 3579 mAh g⁻¹, 1600 mAh g⁻¹, 994 mAh g⁻¹, respectively.³⁻⁵ However, Si anode undergoes huge volume change during lithiation/delithiation (300% expansion by volume due to Li insertion),⁶ due to which large anisotropic stresses develop.⁷ These lithiation-induced stresses are responsible for fracture and fast degradation of such anodes.⁸⁻¹⁰ Hence, for Si anodes, higher capacity can be achieved only at the cost of unacceptably poor cycle life.

Although Ge has a lower gravimetric capacity (due to its higher molecular mass) than Si, it is a softer material.¹¹ Moreover, Li transport is isotropic in Ge unlike in Si, leading to non-localization of stresses.¹² It is observed that Ge develops lower maximum stress compared to Si for the same degree of lithiation and offers a better cycle life.¹³ The above observations provide clues of an effective design strategy for LIB-anodes by involving both Si and Ge leading to a trade-off between the capacity and fracture-propensity. A previous experimental study indeed revealed that alloying Si with Ge lowers the stresses resulting in a significant improvement in capacity retention.¹⁴ It was also shown that a Si-Ge core-shell anode can extend the effective limit of discharge capacity.¹⁵

High capacity anode materials from group 14 in the periodic table are often synthesized as nanostructures to increase the reactive interfacial area and to overcome the issue of quick structural degradation. It is found that nanoparticle-based electrodes can

facilitate higher stress relaxation and have a higher surface-to-volume ratio upon Li-insertion.^{16,17} Recent experiments conducted on nanoparticle-based Li-ion battery electrode¹⁸ gave real-time information on stress evolution, diffusion paths and fracture evolution.^{19,20} The developed stresses, in turn, also affect the electrochemical potential of the battery.²¹ Shi et al. fabricated (100)-oriented single-crystal Si nanopillars using photolithography.²² They showed the mechanism of crack propagation and deflection during the fracture of Si nanopillars lead to attrition of the material, thereby drastically reducing capacity. Computational studies have been conducted to elucidate the lithiation behaviour and associated mechanical performance of silicon-based electrodes.²³ Yang et al. have modelled the coupled stress-diffusion in the Si electrode and have validated their model against experimental results.^{6,8,12,24} The model predicts the stress evolution in nanopillars during lithiation and the results compare reasonably well with the experimental studies of fracture in Si and Ge anodes. The model can be considered to study different configurations of the nanopillars for optimization towards stress-alleviation and reduction in the possibility of fracture. Wen et al. experimented with the hollow Si nanotube anodes and found improved rate capacity and cycle life.²⁵

In this study, we computationally quantify the stress evolution during lithiation in Si_{0.5}Ge_{0.5} alloy nanopillar and find a 17% reduction in the maximum stress compared to that in pure Si. We also investigate the stress evolution in a Si-Ge core-shell nanopillar. We find that the Si-Ge core-shell nanopillar does not show a significant reduction in the maximum stress at full lithiation. Another configuration considered in this study is the nanotube which is hollow from inside thereby providing additional surface for stress relaxation. We model the coupled Li-diffusion and stress-evolution problems in the nanotubes for lithiation from both the inside and outside boundaries. Due to the capillary pressure, the internal surface of the nanotube may not actually come into contact with the electrolyte. Hence, we also consider a case when lithiation occurs only from the outer boundary. We optimize the ratio of inner to outer radii of the nanotube and find $R_{in}/R_{out} = 0.4$ leads to the highest reduction in the maximum stress (by ~16%). We believe

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that the design insights presented in the current study will lead to an optimum trade-off for LIB anodes based on Si and Ge.

Methodology

We adopt the chemo-mechanical model considering coupled stress-diffusion model during lithiation in Si nanopillars devised by Hui Yang et al.⁶ The Si nanopillar anodes are assumed to be completely wetted by the electrolyte of the Li-ion battery. Hence, the outer surface of the nanopillars is always lithiated, even before the start of the electrochemical cycling. During the charging of the battery, the lithium ions get transported into the cross-section of the nanopillar. Hence, a two-dimensional model is deployed (as in Ref. 6) to simulate the lithiation process in the nanopillar.

Following Ref. 6, the Li-diffusion is modelled using Fick's second law:

$$\frac{\partial c}{\partial t} = \nabla \cdot (D \nabla c) \quad [1]$$

where, c is the normalized Li concentration ($0 \leq c \leq 1$) in the nanopillar and D is the Li diffusivity. The diffusivity (D) depends critically on the lithium concentration (c)⁸ and hydrostatic stress.¹² It has been shown that Li transport in Si can be anisotropic due to orientation dependent reaction within the lithiating medium.²⁴

$$D = D_c(c) \cdot D_0(\theta) \cdot D_s(\sigma_h) \quad [2]$$

Based on these observations, a multiplicative representation is hypothesized in Ref. 6 for the effective diffusivity. In the above equation, the first term, $D_c(c)$, incorporates the dependence of lithium diffusivity on the normalized Li concentration ($0 \leq c \leq 1$). From the experimental observations, it is known that the lithium diffusivity in the amorphous lithiated medium is few orders of magnitude higher than in the crystalline unlithiated region.^{26–30} This dependence is captured by $D_c(c) = [1/(1 - c) + \alpha \cdot c]$ following Ref. 8. As can be seen from the expression, $D_c(c)$ blows up at $c = 1$, approximating the high diffusivity in the lithiated amorphous region. For numerical purposes, we restrict the $D_c(c)$ in the lithiated amorphous region to a value 1000 times that of the crystalline region. In situ experiments on lithiation of Si nanopillars¹⁸ also reveal that the alloying leads to the formation of amorphous Li_xSi phase and the interface thickness between the lithiated and unlithiated phases is approximately 1 nm (Fig. S1, available online at stacks.iop.org/JES/167/013542/mmedia). This is captured by introducing a tuneable parameter, α , in the expression of $D_c(c)$. From a sensitivity study on Si nanopillar, we find that $\alpha = 0.1$ creates an interface thickness of 1 nm which matches with the experimental value in Fig. S1. Thus $\alpha = 0.1$ is used in all the simulations performed in this work.

The second term in Eq. 2, $D_0(\theta)$, incorporates anisotropic lithium reactive-diffusion fluxes in different electrode material considered in this work. For instance, the lithium transport in Si (100) nanopillars is maximum along $\theta = n\pi/2$ and minimum along $\theta = (2n + 1)\pi/4$ (where n is an integer).⁶ In contrast, the transport of lithium in Ge is isotropic as discussed in Ref. 12. The anisotropic reactive-diffusion profile on (100) plane for Si, Ge and $\text{Si}_{0.5}\text{Ge}_{0.5}$ alloy are shown in Fig. S3. As can be seen from the figure, the θ -dependent lithium diffusivity in Si shows a flower-like profile due to the aforementioned anisotropy, while a circular profile can be seen for Ge due to isotropy. A mixture rule obtained via density functional simulations is used for lithium diffusivity in $\text{Si}_{0.5}\text{Ge}_{0.5}$ alloy following Ref. 31, and thus $D_0(\theta)$ shows a profile that is in between pure Si and pure Ge.

The last term in Eq. 2, $D_s(\sigma_h)$, describes the dependence of diffusivity on the hydrostatic stress (σ_h) and is expressed by $D_s(\sigma_h) = e^{\frac{\sigma_h \Omega}{kT}}$, where Ω is the activation volume of Li diffusion, k is the Boltzmann constant, and T is the temperature.¹² This form of the equation implies that under the action of positive hydrostatic stress the lattice stretches volumetrically leading to an increase in diffusivity. An opposite behaviour can be envisaged under negative hydrostatic stress.

The chemo-mechanical simulations are performed for the lithiation of the bulk, similar to Ref. 6. The outer surface of the nanopillars, being in contact with the electrolyte, is always uniformly lithiated. This condition is maintained by enforcing the following boundary condition:

$$c = 1 \text{ on } \Gamma_{c1} \quad [3]$$

where (Γ_{c1}) is the external surface of the nanopillar. The same condition is enforced for the outer surface of a nanotube. However, the inner surface of a nanotube may or may not be accessible to Li ions for intercalation depending on the capillary pressure. Hence, we consider two different boundary conditions for the inner surface (Γ_{c2}) of the nanotube as follows:

$$c = \begin{cases} 0 & \text{for no lithiation of } \Gamma_{c2} \\ 1 & \text{for lithiation of } \Gamma_{c2} \end{cases} \quad [4]$$

Before the start of electrochemical charge cycle, bulk Si is unlithiated, hence the initial condition $c(x, t = 0) = 0$ is considered to represent the same. The lithium diffusivities in Si and $\text{Si}_{0.5}\text{Ge}_{0.5}$ alloy show four-fold symmetry (Fig. S3), which can be leveraged to reduce the simulation domain to a quarter circle as shown in Fig. 1. A zero-flux condition on surfaces Γ_{d1} and Γ_{d2} is maintained to represent the situation if the full circular domain is considered.

The insertion of the lithium ions into the interstitial sites of the crystal during lithiation results in volume expansion of the material.

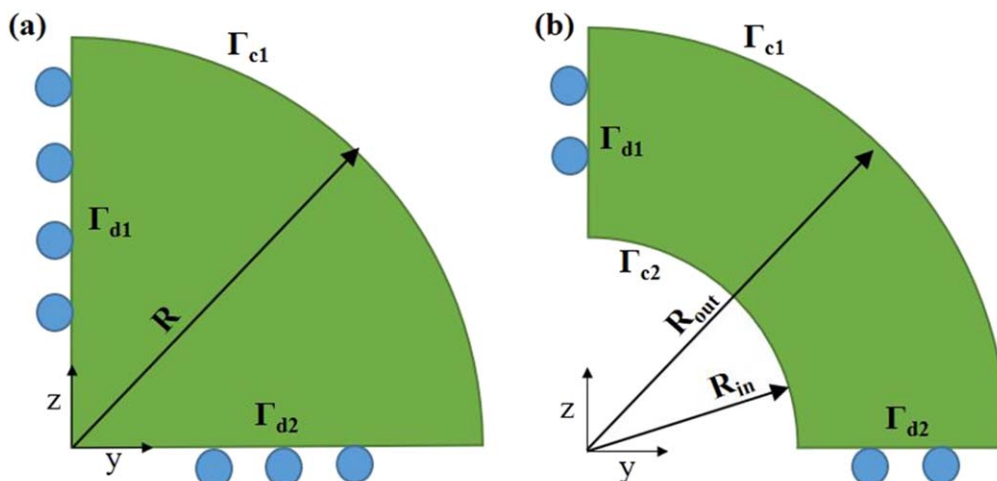


Figure 1. Two-dimensional quarter cross-sectional domain for (100)-oriented (a) nanopillar (b) nanotubes.

Table I. Young's modulus, Poisson's ratio and expansion coefficient for different materials.

	Young's modulus (GPa)		Poisson's ratio		expansion coefficient
	$c = 0$	$c = 1$	$c = 0$	$c = 1$	
Si	160	40	0.24	0.22	0.6
Ge	120	40	0.22	0.17	0.52
Si _{0.5} Ge _{0.5} alloy	140	40	0.23	0.195	0.56

From experimental observations, an isotropic volumetric expansion strain due to lithiation is considered with expansion coefficient, β of 0.6 and 0.52 for Si and Ge, respectively.^{5–8} We assume an average value of $\beta = 0.56$ for the Si_{0.5}Ge_{0.5} alloy.

Anisotropic lithiation leads to a non-uniform volumetric expansion, particularly in the circumferential direction, resulting in more localized and higher peak stress in the material. The stresses are calculated from the isotropic elasto-plastic model of Hui Yang et al.⁶ presented in detail in the supplementary information. The parameters of the plastic model, Young's modulus and Poisson's ratio are adopted from the literature and are shown in Table I.^{32–35} The properties at any concentration, $0 < c < 1$, are evaluated by linearly interpolating from the corresponding properties at the unlithiated ($c = 0$) and fully lithiated ($c = 1$) states. For more details, refer to the supplementary information and Table SI.

It is assumed, as in Ref. 6, that the nanopillar/nanotube maintains a state of static equilibrium at all times during lithiation and is enforced by satisfying

$$\nabla \cdot \sigma = 0 \quad [5]$$

in the 2D domain. The outer (and inner) surface of the nanopillar (and nanotube) is considered to be traction-free

$$\sigma \cdot n = 0 \text{ on } \Gamma_{c1} \text{ (and } \Gamma_{c2}) \quad [6]$$

based on the fact that the electrolyte applies negligible pressure on the nanopillar/nanotube and assuming that the expanding nanopillar/nanotube never comes in contact with its neighbouring nanopillars or cell wall. Furthermore, it is assumed in all the simulations that the nanopillar/nanotube is initially at rest, $u(x, t = 0) = 0$ and stress-free $\sigma(x, t = 0) = 0$.

We simulate only the quarter domain of the nanopillar/nanotubes due to the fourfold symmetry expected in the response. Hence, the displacement boundary condition

$u_x = 0$ on Γ_{d1} and $u_y = 0$ on Γ_{d2} is applied to simulate the deformation behaviour of the nanopillars and nanotubes during lithiation.

The model validation is performed with the previous study of Hui Yang et al. (Ref. 6) for Si nanopillar electrodes. The stress and concentration profiles at different degrees of lithiation are plotted in the supplementary information (Fig. S5). We find that the stress profiles from our model compare well with that of Hui Yang et al.

Results and Discussion

We study the lithiation in the nanopillars and nanotubes for different materials such as pure Si, pure Ge and Si_{0.5}Ge_{0.5} alloy. In addition, we consider a material configuration with an inner core of Si and an outer shell of Ge, commonly described as the Si–Ge core-shell geometry. The lithiation process of these materials is first simulated for a nanopillar. Further, we investigate the nanotube configuration that provides additional free surface for stress relaxation during lithiation. In nanotubes, at first, we consider lithiation only from the outer boundary, and we note a significant reduction in stresses for a Si nanotube when compared to a nanopillar. Subsequently, we optimize the ratio of R_{in}/R_{out} to minimize the Hoop (circumferential) stress in the nanotube. Hoop stress component is dominant under non-uniform volume expansion and can also

cause initiation and growth of radial cracks. Thus, this particular stress component is considered for comparison and design of nanopillar-electrodes with the least probability of failure. For the optimum geometry of the nanotube, we further consider lithiation from both the outer and the inner surfaces.

Nanopillars.—We analyse the Hoop stress evolution for nanopillars made of Si, Ge, Si_{0.5}Ge_{0.5} alloy and Si–Ge core-shell, each having outer radii of $R = 10$ nm. Some typical stress and the corresponding Li concentration profiles are shown in Fig. 2. These profiles are shown on the deformed geometry, which are drawn to scale. The lithiation front starts to move from the outer boundary (when the y-intercept of the Li front, $y_{Li-front} = R$) towards the centre of the nanopillar (when the y-intercept of the Li front, $y_{Li-front} = 0$). We show the stress and Li concentration profiles at two positions; when the y-intercept of Li-front, $y_{Li-front} = R/2$ (Fig. 2a) and $y_{Li-front} = R/5$ (Fig. 2b). In the Si nanopillar (Figs. 2a, 2i), we see a sharp Li front which propagates anisotropically into the cylinder. The extent of penetration of the Li front is greater along the y and z directions due to higher Li diffusion along these directions. This leads to a shape change from the initially circular to a diamond-shaped geometry as the Li front proceeds. The anisotropic expansion leads to an accumulation of stress at the corner points which show maximum Hoop stress of 1.88 GPa. This behaviour can be attributed to the elasto-plastic constitutive model considered in this work. The use of this model is justifiable since constrained expansion can lead to elevated stresses causing lattice shearing and micro-cracking. The elasto-plastic model can simplistically represent these stress relaxing mechanisms.

For Si, the larger volumetric expansion at regions of higher lithiation, and the surrounding constraints, lead to compressive stresses, and results in plastic deformation of the lithiated domain. Since, these regions are only free on the outer surface, the isochoric plastic deformation is accommodated by further outward bulging along the outward radial direction through these regions. This additional radial elongation due to plastic deformation on the outer surface leads to circumferential stretching of the surrounding region to maintain strain compatibility. This stretching develops large circumferential tensile stresses at corners with least rate of lithiation. At a higher degree of lithiation, i.e. at a higher penetration depth of the Li front (Figs. 2b,i), the anisotropy further grows leading to a flower-shaped geometry. The large anisotropy causes the Hoop stress to increase to as high as 2.24 GPa at the corner points suggesting that fracture of the material at these points is possible. Electrochemical lithiation of (100)-oriented single-crystal nanopillars, fabricated via photolithography, has shown a similar anisotropic lithiation, shape change, crack initiation and fracture at corner points.²² The anisotropic expansion in Si nanopillars has also been simulated computationally in the literature.^{6,8} Furthermore, the inner core of the material is still under compressive stresses, which means that even if a crack initiates at the corner points, it will not propagate up to the centre, but will get deflected to form circumferential cracks as shown in Ref. 22.

The next structure shown in (Figs. 2a,ii) is the Si–Ge core-shell nanopillar. The ratio of core to shell volume fraction is 1. The initial lithiation occurs in the outer Ge shell of the nanopillar. As Ge has isotropic diffusion we see that the anisotropy in deformation is less compared to that in pure Si (Figs. 2a,i). Further, a reduced inhomogeneity in circumferential component of strain reduces the circumferential constraint to volume expansion in the core-shell than the pure Si nanopillar. Thus, the lower maximum Hoop stress in the core-shell structure (1.75 GPa) is lower when compared to that in pure Si (1.88 GPa) at $y_{Li-front} = R/2$. As Li intercalation proceeds into the Si core, the anisotropy of the Li diffusion increases leading to a change in shape to a flowery structure similar to pure Si. The inhomogeneity in volume expansion increases significantly, resulting in increased circumferential constraint to volume expansion causing Hoop stress at the corner points to substantially increase to 2.23 GPa (Figs. 2b,ii), much closer to the maximum Hoop stress

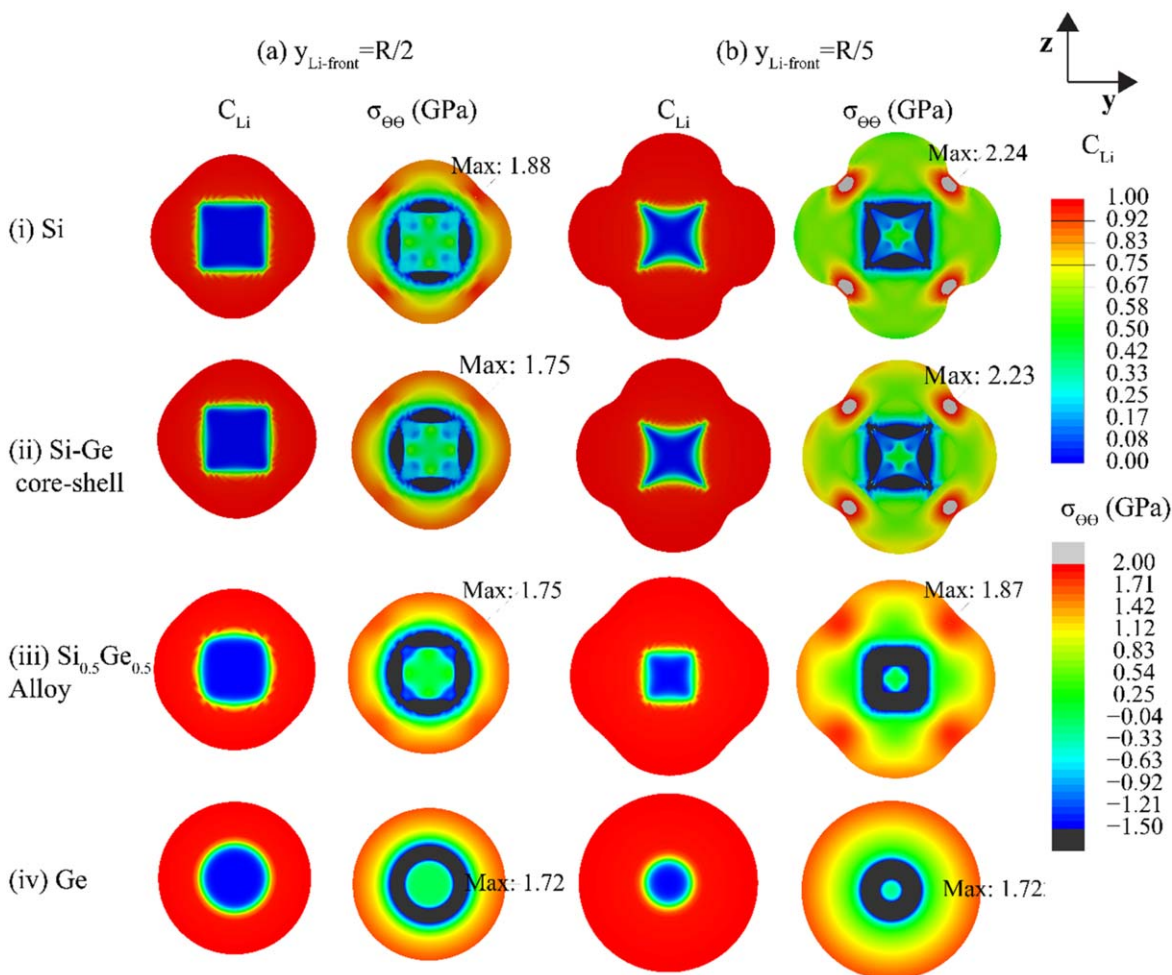


Figure 2. Li concentration (C_{Li}) and Hoop stress profiles ($\sigma_{\theta\theta}$) along the cross section of (100)-oriented nanopillars (of initial radii $R = 10$ nm) at different levels of lithiation. (a) $y_{Li-front} = R/2$. (b) $y_{Li-front} = R/5$. Four different material and structural configurations are considered: (i) Si, (ii) Si-Ge core-shell (iii) $Si_{0.5}Ge_{0.5}$ alloy (iv) Ge. While cases (i)–(iii) have four symmetrically located points with maximum Hoop stress, case (iv) experiences uniform maximum Hoop stress along the periphery.

observed in the case of Si (2.24 GPa, in Fig. 2b,i). The (ii) case thus shows that the core-shell structure exhibits lower Hoop stress only when the lithiation is contained within the Ge shell. As soon as the Li front moves into the Si core, we find that the stresses increase to a value comparable to the pure Si case.

The next structure that is analysed is the $Si_{0.5}Ge_{0.5}$ alloy (Figs. 2a,iii). The diffusivity of the alloy is less anisotropic than Si as discussed in the methodology section and can be seen from Fig. S3. Correspondingly, the distortion is less and we see a near circular shape in (Figs. 2a,iii). Due to reduced anisotropy in diffusivity, inhomogeneity in volume expansion is lower than pure Si or core-shell structure leading to lower circumferential constraints and maximum Hoop stress. From (Figs. 2b,iii), we see a much lower stress (1.87 GPa) in this case as compared to that in the Si nanopillar (2.24 GPa). The stress reduction in $Si_{0.5}Ge_{0.5}$ alloy suggests that the material can prevent fracture during reversible cycling of the anode. Thus, alloying Ge with Si seems to be a good option in order to design more robust anode material with high capacity.

The last case considered in the nanopillar geometry is that of pure Ge (Fig. 2iv). We see a complete isotropic propagation of the lithium front at all stages of lithiation. The complete isotropic lithiation prevents stress concentration at any point and significantly reduces the chances of fracture in the material. It has been observed in previous studies that pure Ge nanopillars do not fracture during lithiation.¹² The stresses observed in this case are the lowest among

all materials (1.72 GPa). Though it is conclusive from the analysis that Ge nanopillars are the safest from failure consideration, its higher density and cost make it undesirable as the anode material. This puts a design limitation on the use of a full Ge anode. However, alloying with Si can reduce the cost and the weight of the anode material without much increase in the stresses. Thus, alloying Ge with Si seems to be one of the solutions to the problem of fracture of Si anodes.

Nanotubes.—The free internal surface of the nanotube lowers the restraint on the volumetrically expanding lithiated domain as well as isochoric plastic deformation. This may reduce the stress levels in the nanotubes when compared to nanopillars. Hence, nanotubes with different outer to inner radii but constant volume as that of the nanopillar is considered in this study. For the boundary conditions, the outer surface of the nanotube is always taken to be lithiated, i.e. $c = 1$. However, the inner surface of the nanotube could be accessible to the Li ions or restricted for intercalation due to the high capillary pressure in the nanotube. Hence, we consider two cases with different boundary conditions for the inner boundary: one with an unlithiated inner wall or zero flux condition and the other with lithiation ($c = 1$) from inside as well.

Unlithiated inner surface.—In this section, we study the stresses during lithiation in nanotubes with unlithiated inner surface represented by zero-flux boundary condition. The nanotube considered is

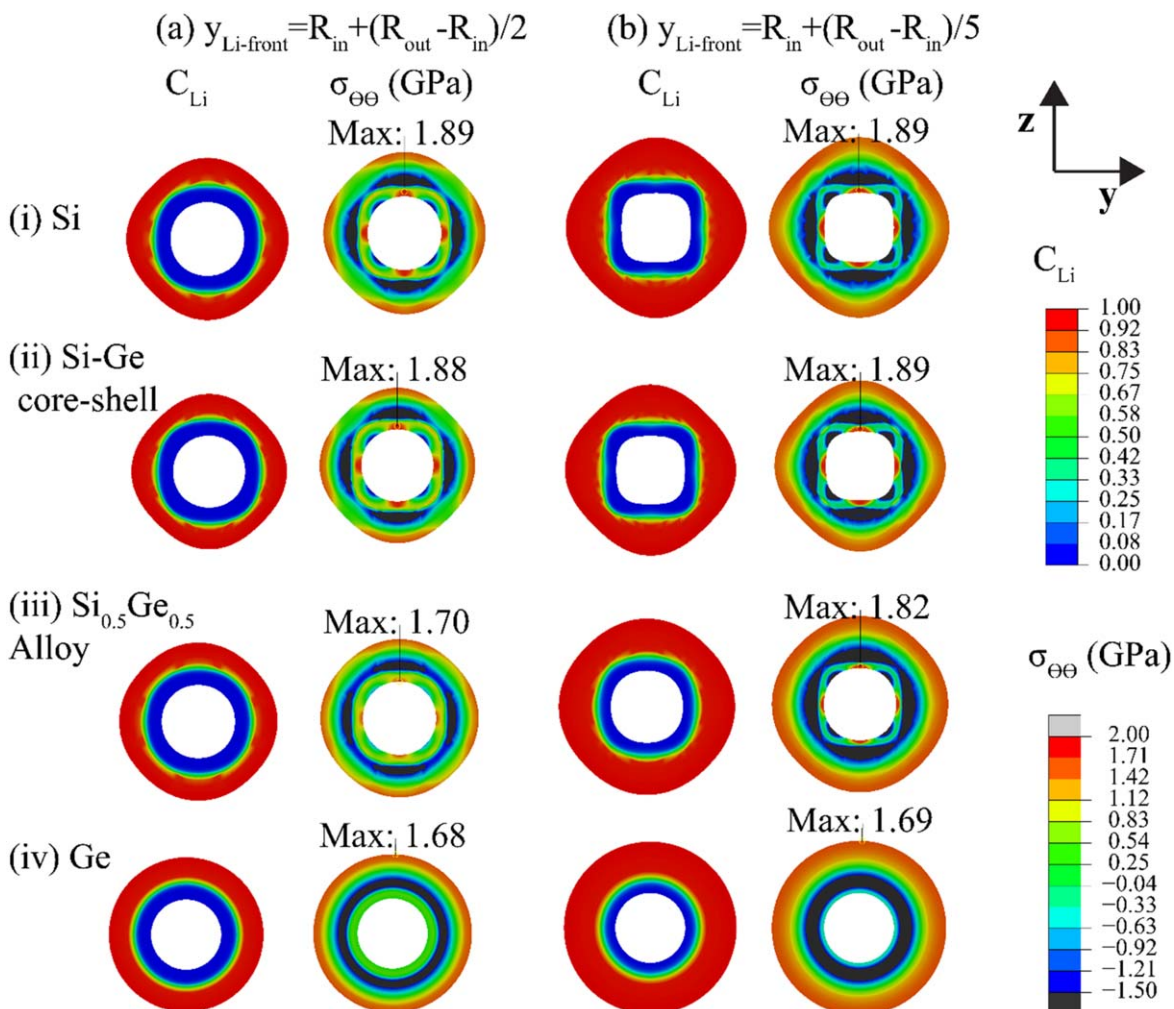


Figure 3. Li concentration (C_{Li}) and Hoop stress profiles ($\sigma_{\theta\theta}$) along the cross section of (100)-oriented nanotubes (of initial outer radii, $R_{out} = 12.5$ nm and inner radii $R_{in} = 7.5$ nm) at different penetrations of Li front. (a) y-intercept of the Li front, $y_{Li-front} = R_{in} + (R_{out} - R_{in})/2$. (b) y-intercept of the Li front, $y_{Li-front} = R_{in} + (R_{out} - R_{in})/5$. Four different material and structural configurations are considered: (i) Si, (ii) Si-Ge core-shell (iii) $Si_{0.5}Ge_{0.5}$ alloy (iv) Ge. While cases (i)-(iii) have four symmetrically located points with maximum Hoop stress, case (iv) experiences uniform maximum Hoop stress along the periphery.

of dimension $R_{out} = 12.5$ nm, $R_{in} = 7.5$ nm and has the same volume as that of the nanopillar in the previous section. Lithiation is assumed to start from the outer surface and proceed to the inner surface. The Li concentration and Hoop stress profiles at two different levels of lithiation are shown in Fig. 3. We observe that in this case, the point of maximum stress occurs at the interior of the cylinder rather than at the outside for Si (Fig. 3i), Si-Ge core-shell (Fig. 3ii) and $Si_{0.5}Ge_{0.5}$ alloy (Fig. 3iii). However, for pure Ge nanotube (Fig. 3iv), the maximum stresses are still at the exterior of the hollow cylinder due to isotropic lithiation. Furthermore, the maximum stresses in the nanotubes at the near-final stage of lithiation (Fig. 3b) are less than that in the nanopillars (Fig. 2b). The reason for the stress reduction is the traction free inner surface that allows expansion with lesser elastic energy penalty. This is also evident from the lower geometric distortion in the nanopillars when compared to nanotubes. The results suggest that hollow cylindrical geometry of anodes can significantly reduce the chances of failure even when lithiation is strongly anisotropic. Amongst all the nanopillar materials considered, $Si_{0.5}Ge_{0.5}$ alloy and Ge show lower stresses than pure Si and Si-Ge core-shell structure.

Optimal geometry of Si-nanotubes (effect of R_{in}/R_{out}).—As seen in the previous section, there is a significant reduction in Hoop stress for the Si nanotube when compared to Si nanopillar. In this section, we evaluate the optimal geometry of the Si nanotube, i.e. the initial

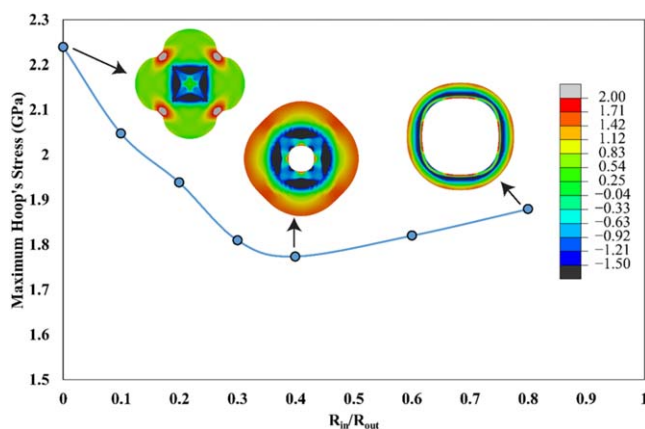


Figure 4. Maximum Hoop stress along the cross-section of (100)-oriented Si nanotubes with different values of R_{in}/R_{out} . The corresponding stress profiles are shown for $R_{in}/R_{out} = 0$ (nanopillar), 0.4 and 0.8.

ratio of inner to outer radii of the nanotube (R_{in}/R_{out}) that generates the least Hoop stress at full lithiation. While the ratio of radii is varied, it is ensured that the total volume remains the same for all the geometries considered. We show the maximum Hoop stress when

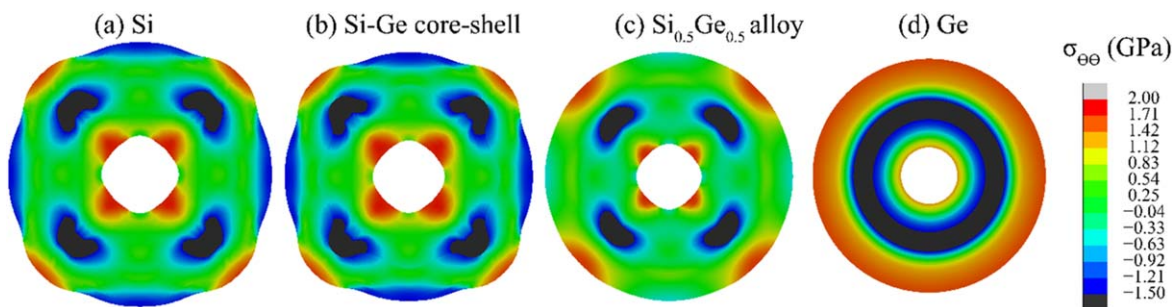


Figure 5. Hoop stress profiles ($\sigma_{\theta\theta}$) along the cross-section of (100)-oriented nanotubes for different materials at full lithiation. Four material configurations are considered: (i) Si, (ii) Si-Ge core-shell (iii) $\text{Si}_{0.5}\text{Ge}_{0.5}$ alloy (iv) Ge.

Table II. Maximum Hoop stresses in nanopillars and nanotubes at different degree of lithiation.

	Maximum Hoop stress in nanopillar (GPa) $y_{\text{Li-front}} = R/5$	Maximum Hoop stress in nanotube (No lithiation from inside) (GPa) $y_{\text{Li-front}} = R_{\text{in}} + (R_{\text{out}} - R_{\text{in}})/5$	Maximum Hoop stress in nanotube (Lithiation from both sides) (GPa) 100% lithiation ⁶
Si	2.24	1.89	1.91
Si-Ge core-shell	2.23	1.89	1.93
$\text{Si}_{0.5}\text{Ge}_{0.5}$ alloy	1.87	1.82	1.83
Ge	1.72	1.69	1.70

the y-intercept of the Li-front, $y_{\text{Li-front}} = R_{\text{in}} + (R_{\text{out}} - R_{\text{in}})/5$ for different ratios of $R_{\text{in}}/R_{\text{out}}$ in Fig. 4, where $R_{\text{in}}/R_{\text{out}} = 0$ corresponds to the nanopillar described in subsection *Nanopillars* and $R_{\text{in}}/R_{\text{out}} \rightarrow 1$ represents a very thin nanotube. We restrict ourselves within $R_{\text{in}}/R_{\text{out}} = 0.8$ since it is difficult to manufacture very thin nanotube and to maintain its structural integrity. We see that, as we increase the ratio of inner to outer radii, there is an initial decrease in the maximum Hoop stress up to $R_{\text{in}}/R_{\text{out}} = 0.4$ due to the creation of free surface for volume expansion. Beyond that, the maximum Hoop stress starts to increase, due to the interaction of stress fields developed at the inner and outer surfaces. Hence, we can conclude that Si-nanotube with $R_{\text{in}}/R_{\text{out}} = 0.4$ is the structurally optimal anode geometry.

Lithiation from both the inner and the outer surfaces.—In this section, we study the Hoop stress in nanotubes while considering the lithiation from both inner and outer surfaces. We note that the nanotube with inner to outer radius ratio of 0.4 shows the minimum Hoop stress for the Si nanotube. In this section that particular geometry is considered to evaluate the evolution of stress if Li-intercalation also occurs from the inner surface. The stress profiles at 100% lithiation for pure Si, Si-Ge core shell, Si-Ge alloy and pure Ge are shown in Fig. 5. It can be seen that when lithiation occurs from both directions, distortion of the nanotube is significantly lower which reduces the stresses inside the material. The maximum Hoop stress in Si, Si-Ge core-shell, $\text{Si}_{0.5}\text{Ge}_{0.5}$ alloy and Ge are 1.91, 1.93, 1.83 and 1.7 GPa respectively, as shown in Table II, which are lower than the respective nanopillars. We see that $\text{Si}_{0.5}\text{Ge}_{0.5}$ alloy and Ge have the lowest stresses. Hence, we can conclude from this analysis that the nanotube geometry of $\text{Si}_{0.5}\text{Ge}_{0.5}$ alloy is possibly the best option in terms of balancing between the resistance to failure and the specific capacitance.

Conclusions

Large volume expansion, fracture during repeated cycling and low-cycle life are practical challenges with Si nanopillar anodes that need to be overcome to foster their implementation in Li-ion batteries. In this study, we computationally investigate two approaches to alleviate the stresses in Si nanopillar anodes. These are alloying Si with Ge to reduce the anisotropy of lithiation and by creating nanotubes that can reduce the constraint on volume expansion and isochoric plastic deformation. We adopt a well-established and

experimentally-verified coupled stress-diffusion model from the literature. We use the model to evaluate lithiation behaviour and stress evolution in Si, Ge, $\text{Si}_{0.5}\text{Ge}_{0.5}$ alloy, and Si-Ge core-shell nanopillars and nanotubes. We find that alloying Si with Ge reduces the Hoop stresses by around 17% at near-full lithiation. The Si-core-Ge-shell structure does not show a significant reduction in stresses. We find 16% lower stresses in Si nanotubes as compared to Si nanopillars due to the availability of additional inner surface enabling stress relaxation. We further optimize the nanotube geometry by varying the ratio of inner and outer radii of the nanotube to minimize the stresses. We find $R_{\text{in}}/R_{\text{out}} = 0.4$ to be the critical radius ratio yielding minimum stresses. Hence, alloying with Ge and hollowing are observed to be effective strategies to alleviate the fracture in Si nanopillar anodes.

Acknowledgments

Authors are grateful to Indian Space Research Organization (ISRO) for supporting this work via Grant No. STC/CHE/2014098. We acknowledge Sudhanshu Tandon of IIT Kanpur, for undertaking the preliminary study during his M. Tech. thesis at IIT Kanpur.³¹

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