Effect of silicon configurations on the mechanical integrity of silicon-carbon
nanotube heterostructured anode for lithium ion battery: A computational study

Sameer S. Damle ^a, Siladitya Pal ^b,

Spandan Maiti ^{a,c,d} and Prashant N. Kumta ^{a,c,d,e *}

^a Department of Chemical Engineering, University of Pittsburgh, PA 15261, USA

^b Department of Mechanical and Industrial Engineering, Indian Institute of
Technology Roorkee, Roorkee, Uttarakhand, 247667, India

^c Department of Bioengineering, University of Pittsburgh, PA 15261, USA

^d Center for Complex Engineered Multifunctional Materials, University of
Pittsburgh, PA 15261

^e Department of Mechanical Engineering and Materials Science, University of
Pittsburgh, PA, 15261

*Corresponding address:

815 C Benedum Hall,

3700 O'Hara Street,

Pittsburgh PA 15261

Tel. [\(412\)-648-0223](tel:(412)648-0223)

Fax: [\(412\)-624-3699](tel:(412)624-3699)

E-mail: pkumta@pitt.edu

1. Introduction

In the past decade, lithium ion batteries have emerged as the most dominant energy storage device among other battery technologies such as Ni-Cd, Ni-MH, lead acid, etc. Current state of the art Li ion batteries have graphitic anode providing an electrochemical capacity of 372 mAh g^{-1} [1]. Improvement in battery technology is constantly pursued as the demand for energy storage devices is expected to rise in future. Silicon is projected as the most promising anode for Li ion batteries replacing graphite due to its high theoretical gravimetric capacity of 4200 mAh g^{-1} . However, mechanical degradation and eventual failure of Si due to the lithium alloying induced stresses during electrochemical cycling leads to the loss of capacity, thus limiting its cycle life and commercialization [2, 3].

In order to address the issue of mechanical failure of silicon as the anode material, size of the active material has been identified as a major factor. Experimental as well as modeling studies have revealed that the use of nano-sized amorphous Silicon (*a*-Si) anode configurations in the form of nanoparticles [4], hollow nanospheres [5], nanowires [6], nanotubes [7], or nanofilm patterns [8] significantly improve the anode capacity retention over multiple electrochemical cycles. The critical sizes below which mechanical failure can be averted during electrochemical cycling have been identified for these configurations [9-13]. However, *a*-Si suffers from other issues such as poor electronic conductivity and charge transport, significant first cycle irreversible loss, inferior performance at higher charge rates, and low columbic efficiency. On the other hand, multiwall

carbon nanotubes (MWCNTs) are known to have very good mechanical strength along with excellent electrical and thermal properties [14-16]. In addition, they exhibit moderate capacity of $\sim 300 \text{ mAhg}^{-1}$ following Li intercalation [17]. Thus, core-shell heterostructures comprised of carbon nanotube (CNT) core and nanostructured Si shell that combines the merits of both these anode elements have emerged as a promising candidate for Si based anode for Li-ion batteries.

Many researchers have recently reported synthesis of a Si-CNT core-shell heterostructure consisting of a thin continuous Si coating on the CNT. Hu et al. [18] deposited Si coating on CNT sponge structure by CVD. Electrochemical cycling of the heterostructure in a voltage range of 0.05 to 1 V showed an impressive first cycle discharge capacity of 3200 mAhg^{-1} with 14% irreversible loss. After 50 cycles, however, the anode capacity faded to 1900 mAhg^{-1} . Formation of nanopores in the Si coating due to the high stresses encountered during electrochemical cycling was determined to be responsible for the capacity fade. Fu et al. [19] observed formation of axial cracks in the Si coating in the Si-CNT herterostructure post electrochemical cycling. In-situ TEM investigation by Wang et al. [20] on a heterostructure comprising of a thin ($\sim 13 \text{ nm}$) Si coating adhered to a carbon nano-fiber showed cracking of the Si coating during electrochemical cycling. They concluded that accumulation of damage in the Si coating over prolonged electrochemical cycling to be the mechanism for eventual capacity fade of the anode structure. A similar observation was reported by Sun et al. [21], where they observed the formation of axial cracks along the length of

the continuous Si coating on CNT during in-situ electrochemical cycling of the heterostructure. It should be emphasized here that such axial cracks might not cause complete loss of capacity as long as the active material remains adhered to the CNT. For complete capacity fade, substantial loss of electronic contact between current collector and the active material mediated by disintegration of the active component is required.

Experimentalists have tested different strategies to limit the mechanical failure of the Si-CNT heterostructure thus improving its capacity retention, such as: providing sufficient inter-wire spacing [22, 23], improving adhesion at the Si-CNT interface [24], coating the Si film on CNT with a thin carbon layer [19][25], and employing a binder free approach by directly scribing the active material onto current collector [26]. Another approach that has been tested to improve the capacity retention of Si-CNT heterostructured anode is by tailoring the geometry of silicon shell to limit the Li alloying induced mechanical degradation. Gohier et al. [27] decorated vertically aligned thin CNTs of 5 nm diameter with 10 nm sized Si droplets. Providing sufficient free space for expansion of Si droplets resulted in a high reversible capacity of 3000 mAhg^{-1} at 1.3 C *C-rate* with 90% capacity retention after 37 cycles. Work done in the Kumta group by Wang et al. [28, 29] has demonstrated the electrochemical performance of the hybrid Si-CNT heterostructure anode by synthesizing ~ 40 nm diameter droplets of Si tethered to MWCNT by CVD process. The heterostructure anode showed a steady capacity of $\sim 2000 \text{ mAhg}^{-1}$ for 22 cycles. Building on the work of Wang et al. [28, 29], Epur

et al. [30] varied the morphology of *a*-Si coated on the CNT by changing the flow conditions in the CVD process. The synthesis yielded two different Si geometries in the Si-CNT heterostructure based on the flow conditions: continuous Si film on CNT, and Si droplets deposited on CNT. The heterostructure with continuous Si film showed an initial capacity of $\sim 3200 \text{ mAhg}^{-1}$ with 10% first cycle irreversible loss. After 20 cycles the capacity dropped to $\sim 1950 \text{ mAhg}^{-1}$. In case of the heterostructure with Si droplet configuration, an initial capacity of $\sim 2700 \text{ mAhg}^{-1}$ with 10% first cycle irreversible loss was observed. However, the capacity fade rate was considerably less and a capacity of $\sim 2340 \text{ mAhg}^{-1}$ was retained after 20 cycles. Thus, the electrochemical cycling results consistently demonstrated that the droplet configuration outperformed the film configuration. It can be inferred from the above-mentioned experimental observations that the geometrical features of Si can alter the anode cyclic performance significantly, and thus can be a promising route to design anode configurations with improved cyclic performance. Realization of this feature will however require fundamental insight into the configuration dependent mechanical performance of Si-CNT heterostructures. Motivated by this objective, herein we report the effect of the geometry of the active material in the Si-CNT heterostructures on its mechanical integrity during a single electrochemical cycle. We have resorted to a thermodynamically consistent theoretical framework and its computational counterpart recently developed by us [31-33]. Our methodology considers alloying induced stress and consequent mechanical failure of the electrode material. In the course of this paper, we systematically varied the geometry of the

Si film coating on CNT from a continuous Si film to a Si particle in the shape of $1/8^{\text{th}}$ of a nano-ring adhered to CNT. Mechanical integrity of the different configurations was analyzed by studying mechanical stress state as well as plastic flow within the active material. Possible nucleation and growth of voids in the plastic solid leading to the mechanical failure of silicon was of particular interest. We demonstrate that the mechanical constraints arising from the adhesion of Si shell to the CNT core, as well as the configuration of the active material itself, is responsible for the mechanical failure of the anode configuration. Providing sufficient free space for Si expansion and thus reducing the mechanical constraints significantly reduces the stresses, thus improving its mechanical integrity during electrochemical cycling. We relate our simulation results to the experimental observations found in the literature whenever possible.

The paper is organized as follows: In section 2 we briefly describe the basic assumptions and detail the equations of the previously developed theoretical framework. In section 3, we present the computational methods for the simulation study. Section 4 contains the description of the heterostructure configurations under consideration and the relevant materials properties as well as boundary conditions utilized in the simulation. Results obtained from the simulation studies and a brief discussion on it is presented in Sections 5 and 6, respectively. The conclusions and future directions from the work presented in this research article are summarized in the last section.

2. Theoretical framework

In this section we briefly describe the theoretical framework used to model transport of lithium in silicon and attendant mechanical stress field in the silicon domain. The governing equations of the model are detailed in Table 1. For the definition of each variable, please see the list of symbols provided at the end of the article. The details of the framework can be found in our previously published reports [31-33].

For our simulations, we assumed that the *a*-Si shell contributes primarily towards the overall electrochemical capacity of the anode configuration owing to its order of magnitude higher capacity ($\sim 4200 \text{ mAhg}^{-1}$) compared to that of CNT ($\sim 300 \text{ mAhg}^{-1}$). Accordingly, we did not consider any Li transport in the CNT core. Electrochemical cycling of the anode heterostructure was carried out under galvanostatic conditions similar to that performed in experiments [30]. The electrochemical reaction was considered at all surfaces of the active material that were exposed to the electrolyte. Faradaic reaction kinetics at the active material/electrolyte interface was modeled using the classical Butler-Volmer approach (Equation 2, Table 2). Lithium alloying of *a*-Si was modeled by considering Li concentration dependent diffusivity of Li into the *a*-Si [21, 34-36]. During electrochemical cycling, Si undergoes the well-known colossal volumetric expansion ($\sim 300\%$) [37]. Experimental observations suggest that the Li-Si alloy undergoes severe elasto-plastic deformation when the effective stress exceeds

the yield strength [38, 39]. Both of these phenomena were taken into account through a multiplicative decomposition of the total deformation gradient $\mathbf{F}$ into an elastic part ($\mathbf{F}_e$), plastic part ($\mathbf{F}_p$) and a concentration dependent component ($\mathbf{F}_\theta$), as described by Equations 4 & 5 in Table 1. The transport equation for the lithium is described by Equation 7, where the effect of mechanical stress has been incorporated through the last term in the bracket. The expression for a “pressure-like” term p is given by Equation 8 in Table 1. We modeled the elastoplastic behavior of the electrode suitably defining the (1) yield condition, (2) flow rule and (3) hardening behavior. In the present study, we considered J₂ plasticity theory with linear strain hardening and associated flow rule (Equation 9, Table 1). Lithium alloying of Si also leads to its elastic softening [40] and was included in our modeling framework by a linear reduction of elastic modulus dependent on the lithium volume fraction (Equation 11, Table 1). CNT was assumed to undergo only elastic deformation. We considered that the interface between the CNT and *a*-Si was not perfectly bonded and used a cohesive zone modeling technique [32, 41-46] to allow for possible opening, sliding and consequent delamination at the Si/CNT interface. The traction-separation law used to describe the failure behavior of the interface is given by Equation 12 in Table 1.

3. Computational methods based on finite element technique

The lithium transport and mechanical equilibrium equations as described in the last section (see Table 1) were solved using a custom finite element based

computational framework. The mechanical response of the heterostructured anode configurations was simulated for one complete electrochemical cycle. First, the concentration of lithium $c(\mathbf{X}, t)$ in the active material was determined for a given electrode cycling conditions followed by calculation of the resulting displacement $\mathbf{u}(\mathbf{X}, t)$ of the anode. Variational forms of the coupled equilibrium and transport equations were obtained to perform finite element semi-discretization in space [31]. A backward Euler implicit time stepping algorithm was employed to solve the resulting temporal ordinary differential equations numerically. For a given global iteration step, a backward Euler scheme was used to update the stresses and the plastic parameter (internal variable) at finite element gauss points in the intermediate configuration. Using a trial deformation gradient, the stress state at the intermediate configuration was obtained to determine whether it lies in plastic or elastic range. In case of plastic response, we integrated the flow rule from the previous time step to the current step using exponential map and the increment of the plastic parameter. We also constructed a residual for the Green-Lagrange strain tensor. To find the increment of the plastic parameter and Green-Lagrange strain tensor, linearization of the residual strain vector and yield function were performed with respect to the plastic parameter and Green-Lagrange strain tensor. Using a Newton-Raphson (N-R) iterative scheme, the increments of plastic parameter and Green-Lagrange strain tensor were updated. Furthermore, consistent tangent moduli in the intermediated configuration were also derived and pulled back to the reference configuration to construct the global stiffness matrix as required for the N-R

scheme. The calculated stress components were post-processed to enumerate hydrostatic stress σ_m , effective stress σ_e (also called von Mises stress) and the stress triaxiality ($T = \sigma_m / \sigma_e$) at different normalized cycle time (τ). Normalized cycle time $\tau = 0.0$ corresponds to the start of lithium alloying, $\tau = 0.5$ indicates end of lithium alloying, while $\tau = 1.0$ indicates the end of a full alloy-based delithiation (de-alloying) i.e. completion of one electrochemical cycle. Visualization of the results were performed using the software ParaView [47].

4. Model geometry and simulation parameters

Epur et al. [30] from our group previously reported electrochemical performance of Si-CNT heterostructure consisting of nano-crystalline / amorphous continuous Si film of 50 nm thickness deposited on multi-walled CNTs. Accordingly, we considered a single multi-walled CNT (inner diameter of 10 nm and outer diameter of 80 nm) with a continuous Si coating of thickness 50 nm for the modeling purpose. We chose a finite sized straight segment of length 400 nm for this configuration, as shown in Fig. 1 (a). However, the experimental heterostructures are very long in the axial direction. To include the effect of “infinite” length in our finite sized model, top and bottom edges of the computational domain were constrained with generalized plane-strain boundary conditions.

To study the effect of geometry of the active component, we varied the Si domain systematically while keeping the dimensions of the CNT constant. The

continuous film discussed above is labeled as Configuration I for the following text. For Configuration II, the span of the Si film coating in the axial direction was reduced creating nano-rings of Si having a thickness of 50 nm in both radial and axial directions. We assumed that the adjacent nano-rings were separated sufficiently so that they do not interact with each other mechanically. Accordingly, for the simulation purpose, we considered only one nano-ring of Si tethered to the CNT (Fig. 1 (b)). We note that the generalized plane-strain boundary condition was applied only on CNT for this case; the Si domain was free to move in the axial direction. In the third configuration (labeled as Configuration III), continuity of the active material in the circumferential direction was reduced further: We considered a particle of Si in the shape of $1/8^{\text{th}}$ of the nano-ring adhered to the CNT (see Fig. 1 (c)). The dimensions of the active material in the radial and axial directions were chosen as 50 nm so that it approximates a droplet. As before, the ends of the carbon nanotube were provided with generalized plane-strain boundary condition.

Exploiting the advantage of the axisymmetric geometry of the anode configurations, we considered only $1/8^{\text{th}}$ of the actual geometry for the FE simulations of the SI-CNT heterostructure with continuous Si coating and Si nano-ring to reduce the computational effort. Assuming the length of the CNT oriented along the z-axis and the origin (0,0,0) located midway along the length of the CNT, a $1/8^{\text{th}}$ section of the geometry between the X, Y and Z planes passing through the origin was taken for simulation in case of the Configuration I

and II (see Fig. 1 for orientation of axes). Symmetry boundary conditions were employed on the XY, YZ and XZ planes. In case of the 1/8th of the Si nano-ring adhered to CNT, 1/4th section of the geometry between the X and Z planes passing through the origin and having symmetry boundary conditions on the XZ and XY plane was utilized for FE simulation. The domains were meshed with 8 noded hexahedral elements using the CUBIT meshing software [48], resulting in 8959, 9568 and 6996 elements for Configuration I, II and III, respectively. The interface between Si and the CNT was modeled with 289, 130, and 132 8-noded cohesive elements of zero thickness for Configuration I, II and III, respectively [31, 32].

During the simulation of one electrochemical cycle of the Si-CNT heterostructure, the active material (α -Si) was cycled (alloyed and de-alloyed) at C/4 charge rate under galvanostatic conditions up to the theoretical electrochemical capacity of 4200 mAhg⁻¹. The partial molar volume of Li in Si (η) was considered to be $4.5 \times 10^{-6} \text{ m}^3 \text{ mol}^{-1}$ [31, 32] (see Equation (5)). We took the Li concentration dependent diffusivity of Li during lithium alloying/de-alloying with silicon as [21, 34-36]

$$D(\mathbf{X}, t) = D_0(1 / (1 - c(\mathbf{X}, t)) - 4c(\mathbf{X}, t))$$

where D_0 is the diffusivity constant. To avoid any numerical instability during the finite element simulations, we limited the maximum Li diffusivity as

$\max(D(\mathbf{X}, t)) = 10^3 D_0$ i.e. $10^{-15} \text{ m}^2 \text{ s}^{-1}$, which is comparable to the experimentally calculated average value of $0.51 \times 10^{-15} \text{ m}^2 \text{ s}^{-1}$ [49].

Experiments have shown that lithiated Li-Si alloy has significantly lower fracture strength as compared to the pristine Si [50, 51]. Accordingly, for our simulations, we assumed an average fracture strength (σ_c^{Si}) of 1.6 GPa [50] for Si. Since CNTs are known to be stiffer in the axial direction as compared to the radial direction, it was assumed to have transversely isotropic materials properties [52]. As the CNTs are known to have very high mechanical strength, our study focuses on the mechanical response of the Si. Compressible Neo-Hookean constitutive model was used for all the materials to simulate the large deformation mechanical response. The materials and interfacial properties used for the simulations are reported in Table 2.

5. Results

In this section we present a detailed parametric study of the effect of Si configuration on the mechanical response of heterostructured anodes during an entire electrochemical cycle. We first examine the evolution of Li concentration and mechanical stress field generated in the active material during the entire electrochemical cycle. We find that the magnitude of peak effective stress (σ_e) is high enough to cause plastic flow of silicon. Accordingly, we next present the evolution of plasticity in the different Si configurations considered in this study with the electrochemical cycling. One of the prominent mechanisms of ductile

failure of materials is the nucleation, growth and coalescence of voids in the plastic region. We thus finally study the possibility of void nucleation and growth in the active silicon component during electrochemical cycling that might give rise to mechanical failure.

5.1 Electrochemical cycling of the heterostructure and volume expansion of silicon

Evolution of Li concentration and the attendant volumetric expansion for the different Si configurations of the active material during lithium alloying half-cycle ($\tau = 0$ to 0.5) are presented in Fig. 2 (a-c). Fig. 2 (a) shows the evolution of the normalized lithium concentration ($c_{Li} / c_{Li\max}$) at different normalized cycle times (τ) along the longitudinal (LONG) section (XZ plane) of the Si film coating (Configuration I). The Li concentration at the outer regions of silicon that are exposed to the electrolyte builds faster as compared to the inside and the resulting front of Li moves inwards expanding the silicon domain as the lithium alloying progresses. It can be observed from Fig. 2 (a) that the Si film expands primarily in the radial direction (~83.6%), accompanied by a small expansion in the axial direction (~2.4%). In the case of Configuration II, the lithium alloying front in the Si nano-ring propagates inwards from the top, bottom and the circumferential boundaries that are exposed to the electrolyte. Si can be seen to expand in the radial as well as axial direction (Fig. 2 (b)). Displacements calculated from the FE simulations indicate that Si expands about ~41% in both the radial as well as axial directions. In the third configuration, Li transport occurs

in the radial, axial and circumferential directions as it has five surfaces exposed to the electrolyte. In this case, the ratio of the surface area exposed to the electrolyte to the active material volume is the highest among the three different heterostructured configurations considered. Therefore, the Li concentration profile in the active material geometry is more uniform as compared to the first two configurations (Fig. 2 (c)). Reducing the continuous Si film coating to 1/8th of the Si nano-ring allows the Si expansion to occur in the radial, axial as well as the circumferential direction during the alloying half cycle. Our simulations show that Si expands ~39% in the radial and axial direction, and ~37 % in the circumferential direction, indicative of the uniform expansion occurring from Li alloying.

Along with the geometry of the Si configuration, the dimensions of the active material are also expected to affect the Li concentration profile in the Si. The reader is advised to refer to supplementary information (SI) where the effect of Si configuration dimensions on the Li concentration profiles and the attendant stresses in Si is explored.

5.2. Stress analysis of different silicon configurations in Si-CNT heterostructures

Fig. 3 (a-j) shows the contours of the radial stress (σ_{rr}), axial stress (σ_{zz}), circumferential stress ($\sigma_{\theta\theta}$), effective stress (σ_e) and the plastic strain (ε_p) in the longitudinal section of the Si film coating in the continuous Si-CNT heterostructure at the end of alloying ($\tau = 0.5$) and de-alloying ($\tau = 1.0$). The

scale bar for normal stress components shows a lower limit of compressive stress of magnitude 1.0 *GPa* and the upper limit is capped at 1.75 *GPa* tensile stress, which is slightly greater than the average fracture strength of Si ($\sigma_c^{Si} = 1.6$ *GPa*) [50]. From Fig. 3 (a) and (f), it can be seen that the magnitude of σ_{rr} is negligible at the end of alloying as well as de-alloying. As discussed in section 5.1, during electrochemical cycling, the Si film coating can expand freely in the radial direction and thus no stress is generated in this direction. However, as the axial deformation is constrained due to continuity of the Si domain in that direction, large compressive axial stress is generated during alloying of lithium (Fig. 3 (b)). Distribution of effective stress at the end of cycling (Fig. 3 (d)) reveals that the yield stress of the material (1.5 *GPa*) is exceeded in the Si coating. This phenomenon causes Si to undergo inelastic deformation leading to accumulation of plastic strain (Fig. 3 (e)). During de-alloying, as the Li is extracted out from the Li_xSi alloy, presence of the plastic regions leads to tensile stresses in the axial direction in the active film. The tensile axial stress observed at the end of de-alloying (Fig. 3 (g)) is greater than its fracture strength σ_c^{Si} . This fact putatively validates and also inexplicably serves to explain the experimental observation of axial cracks in the Si nanofilm adhered to the carbon nanotube post electrochemical cycling [19]. In addition, there is further accumulation of considerable plastic strain in the Si coating (Fig. 3 (j)) during de-alloying. Observe that plastic strain is highest (and in excess of 0.5) at the interfacial region as well as near the free edge of Si film. Presence of substantial plastic flow in the Si nano-films has also been reported by [38, 39]. These are also the

potential locations for void nucleation and growth that will be discussed in the next section. The circumferential stress at the end of alloying shows the presence of compressive stress near the Si-CNT interface (~ 0.9 GPa). However, during de-alloying the inelastic deformation of Si leads to generation of tensile circumferential stress of magnitude ~ 1.5 GPa near the Si-CNT interface (Fig. 3 (h)). This magnitude is comparable to the fracture strength of *a*-Si σ_c^{Si} signifying circumferential cracking in the XZ plane may also appear near the interface at the end of de-alloying half cycle. The results could substantiate the observed capacity fade reported by Epur et al. [30] as per discussed in the next section.

Stress and plastic strain contours at the longitudinal section of Si nano-ring in the second heterostructured configuration at the end of alloying ($\tau = 0.5$) and dealloying half cycle ($\tau = 1$) are shown in Fig. 4 (a-j). As observed from Fig. 4 (a) and (f), the radial stresses occurring at any location in the Si nano-ring are much lesser than σ_c^{Si} . During Li alloying, the adhesion of Si nano-ring to the CNT presents mechanical constraints to the axial expansion of Si only in the vicinity of the Si-CNT interface. As a result, the fully lithiated Si nano-ring shows presence of compressive stress near the Si-CNT interface (Fig. 4 (b)). Interestingly, the axial stresses show a significant reduction (Fig. 4 (g)) compared to the continuous nanofilm configuration presented (Fig. 3 (g)). Again, this reduction is a direct consequence of release of the axial constraint on the active material by choosing the nano-ring configuration. However, contours of circumferential stress shown in Fig. 4 (h) indicate that near the center of the nano-ring, the Si still has

significant circumferential stress (1.45 GPa) that is comparable to σ_c^{Si} . Plastic region in the Si nano-ring at the end of the electrochemical cycle (Fig. 4 (j)) is also reduced as compared to that shown in Fig. 3 (j). The maximum value of plastic strain is observed near the Si-CNT interface, albeit much reduced in magnitude compared to the last configuration. Corresponding to the maxima of plastic strain, the maximum value of effective stress are obtained near the Si-CNT interface (Fig. 4 (i)) at the end of the de-alloying cycle.

For Configuration III, the mechanical constraints on Si are further reduced in the circumferential direction as compared to the Si nano-ring. Accordingly, the active material expands in radial, axial, as well as circumferential directions. Stress contours in Fig. 5 show a significant reduction of all three components of stresses (radial, axial and circumferential) as compared to that observed in the continuous Si film coating (Fig. 3) as well as the Si nano-ring configuration (Fig. 4). Again, similar to the nano-ring configuration, the axial stresses observed at the end of de-alloying half cycle near the Si-CNT interface are compressive (Fig. 5 (b)). However, it is important to note that the effective stress (Fig. 5 (i)) and the residual plastic strain (Fig. 5 (j)) accumulated in the active material at the end of electrochemical cycling ($\tau = 1$) are considerably less (less than ~ 0.2 everywhere except two points at the interface) than that observed in both the previous Si morphologies (continuous Si film coating and Si nano-ring).

5.3 Evolution of effective stress, hydrostatic stress and stress triaxility

Plastic regions in the silicon domains serve as potential locations for void nucleation and growth induced material degradation and failure. Voids may nucleate when the linear combination of effective stress and tensile hydrostatic stress exceeds the local void nucleation strength [53]. Once nucleated, the voids may grow under the influence of high stress triaxiality [54-56]. To understand the feasibility of void nucleation and growth in the Si-CNT heterostructured anode, we studied the evolution of the combination of the effective and hydrostatic stress ($\sigma_e + \sigma_m$) and the stress triaxiality ($T = \sigma_m / \sigma_e$) during electrochemical cycling of the anode. In Fig. 6 (a-c), we plot $\sigma_e + \sigma_m$ and T at different normalized radial thicknesses ($\bar{r}$) in the continuous Si coating for the first Si-CNT heterostructure configuration considered. Normalized radial thickness of $\bar{r} = 1$ corresponds to the outer surface of Si exposed to the electrolyte, while $\bar{r} = 0$ corresponds to the inner Si-CNT interface. For better representation of the stress triaxiality data, we have capped the lower limit of T at 0 (i.e. when hydrostatic stress is negative) and the upper limit at 1.5. As the de-alloying progresses, $\sigma_e + \sigma_m$ can be seen to increase steadily at $\bar{r} = 1$. After $\tau = 0.7$, $\sigma_e + \sigma_m$ exceeds 2 GPa (higher than $\sigma_c^{Si} = 1.6$ GPa) indicating conditions favorable for void nucleation. The stress triaxiality remains low beyond this time point signifying that voids may not grow even if they nucleate. However, conditions favorable to the nucleation as well as growth of voids can be found to exist in at $\bar{r} = 0.5$ (Fig. 6 (b)) and at $\bar{r} = 0$ (Fig. 6 (c)) towards the end of Li de-alloying.

In Fig. 7 (a-c), we plot the evolution of $\sigma_e + \sigma_m$ and T at three different normalized radial thicknesses along a central line in the Si nano-ring. From Fig. 7 (a), it can be observed that the stress triaxiality T never exceeds 0.5. Similar situation can be observed in Fig. 7 (c)). Nonetheless, Fig. 7 (b) shows that at $\tau = 0.97$, the value of $\sigma_e + \sigma_m$ can reach 1.7 GPa with concomitant very high stress triaxiality (≥ 1.5). Thus, at the completion of the electrochemical cycle, the Si nano-ring may show void growth induced mechanical degradation around $\bar{r} = 0.5$.

Similar to Fig. 7, data is plotted in Fig. 8 (a-c) for the $1/8^{\text{th}}$ of the Si nano-ring. At $\bar{r} = 1.0$, although the combination of effective and hydrostatic stress ($\sigma_e + \sigma_m$) exceeds the fracture strength of Si, the stress triaxiality T is not sufficient to cause void growth (Fig. 8 (a)). In case of $\bar{r} = 0.5$ and $\bar{r} = 0$, it can be observed that $\sigma_e + \sigma_m$ does not exceed the fracture strength (Fig. 8 (b) and (c)), even though the stress triaxiality is favorable for void growth at these locations. Thus, void nucleation is unlikely to occur in the active material in this Si-CNT heterostructure configuration indicating the likely uncanny stability of this configuration during electrochemical cycling as reported in the experimental work of Epur et al., [30] further discussed in detail in the next section.

6. Discussion

In this paper, we have studied mechanical response of different Si morphologies in Si-CNT heterostructure during a complete electrochemical cycle by utilizing a novel multiphysics modeling framework previously developed by us [31-33]. We demonstrated that mechanical constraints from the bonding between carbon nanotube and silicon domain have a profound effect on the stress state in the active component. In the Si-CNT heterostructured configuration with continuous Si coating, the mechanical constraints imposed by the adhesion of Si film to CNT limits the expansion of Si in axial direction. Thus, the lithium alloying induced volumetric expansion was accommodated only along the radial direction (Fig. 2 (a)). Similar observation has been reported by in situ TEM studies by Wang et al. [20]. In the case of the Si nano-ring adhered to CNT, the dimensions of the continuous Si film coating was reduced in the axial direction, which alleviated the mechanical constraints on the Si in the axial direction. Adhesion of the Si nano-ring to CNT at the inner surface of Si nano-ring presents a certain amount of mechanical constraint. However, expansion of Si in the axial direction at the Si-CNT interface was allowed, the extent of which would depend on the adhesion properties of the interface. Away from the Si-CNT interface, the active material can expand in radial as well as axial direction as it can be seen from Fig. 2 (b). For the last configuration with $1/8^{\text{th}}$ of the Si nano-ring adhered to the CNT, the mechanical constraint on the active material are the least as Si can expand in radial, axial, as well as the circumferential direction during electrochemical cycling (Fig. 2 (c)).

The stress contours shown in Fig. 3 reveal that there is significant axial and circumferential stress in the continuous Si film coating at the end of the electrochemical cycle. Similar observations have been made by Wang et al. [35] for the stresses observed at the end of the electrochemical cycle in a thin layer of Si coated on carbon nano-fibers. Such high axial tensile stress observed at the end of de-alloying can cause axial fracture in the Si coating. These axial cracks can expose additional area of Si to the electrolyte and the formation of solid-electrolyte interphase (SEI), irreversibly consuming lithium and resulting in poor coulombic efficiencies. However, axial cracking of silicon thin film may alone not cause electrochemical capacity fade as long as the Si film maintains a current collecting pathway. Thus additional mechanisms must be in effect to explain the substantial loss of capacity for Si-CNT heterostructures after repeated electrochemical cycling. We determined that very high diffusion induced stress in silicon may result in its substantial plastic flow, which may activate ductile failure mechanisms and eventual disintegration of the active component. The ductile failure can be mediated by nucleation, growth and coalescence of voids from the structural pores present in lithiated amorphous silicon. This phenomenon may bring gradual mechanical failure of the active component over many electrochemical cycles. Fracture of silicon results in volumetric loss in active material and thus reduction in electrochemical capacity. This observation may explain the gradual disintegration of silicon and attendant capacity fade over multiple electrochemical cycles as observed in many experiments [19, 25, 30]. It has been experimentally observed that amorphous silicon can undergo

substantial plastic flow during electrochemical cycling [38, 39]. Formation of voids in lithiated silicon during electrochemical cycling has been experimentally observed [18, 57, 58]. Choi et al. [57] have experimentally demonstrated that “nanopores” may form during extraction of lithium from silicon nanowires. During tensile testing of lithiated Si nanowires, Kushima et al. [50] have also observed void formation in the Si nanowire under tensile stress. Lu et al. [24] have noticed that the Si coating becomes rough and porous on the electrochemical cycling of the Si coating-Ni-CNT heterostructure.

Argon et al. [53] have suggested that voids may nucleate under the influence of combined effective stress σ_e and tensile hydrostatic stress σ_m . We determined that this combination, i.e., $\sigma_e + \sigma_m$ exceeds 2 GPa in continuous Si thin films coated on CNT towards the final stage of Li de-alloying, see Fig. 6. The average fracture strength of silicon which is being electrochemical cycled is observed to be in the range of 1.6 GPa [50]. Thus, the magnitude of combined stress $\sigma_e + \sigma_m$ may be sufficient to nucleate voids from the migration of Li atoms. Post nucleation, voids grow under the influence of stress triaxiality [55, 56]. Observe the occurrence of high stress triaxiality (~ 0.5) near the interface and the middle of the silicon domain in the same figure at the end of the electrochemical cycle. In the case of the Si nano-ring adhered to the CNT, the continuity of the Si coating in Si-CNT heterostructure configuration is reduced in the axial direction. This change is reflected in the reduced axial stress observed in the Si nano-ring (Fig. 4 (a)). However, plot of combination of effective and hydrostatic stress in Fig. 7

(b) shows that the magnitude of $\sigma_e + \sigma_m$ can exceed 1.6 GPa with attendant high stress triaxiality at $\bar{r} = 0.5$. Thus, void nucleation and growth may occur for this configuration in the mid-depth region of the active component.

For the Si-CNT heterostructure containing a particle in the shape of 1/8th of the Si nano-ring adhered to CNT, representative of the Si nano droplet configuration on CNT obtained experimentally [28-30], the mechanical constraints are further reduced by allowing the active material to expand in the circumferential direction. Even though the surface area per volume of the active material is highest in this configuration, which is expected to give a relatively higher first cycle irreversible loss due to the large surface area based SEI layer formation, this configuration shows the least magnitude of stress (Fig. 5) and plastic flow. Also note that void nucleation and growth condition does not occur anywhere within the domain, signifying possible long-term mechanical failure resistance of this configuration (Fig. 8).

We compare the heterostructured configuration consisting of 1/8th of the Si nano-ring adhered to CNT, to that synthesized previously in our laboratory, the details of which can be found in [28-30]. The synthesized Si-CNT heterostructure consists of multi-walled CNT decorated by ~60 nm diameter droplets of nano-crystalline / amorphous Si. The droplets are separated from each other by a defined, sufficiently spaced distance. This allows lithium alloying induced expansion of Si without interference and coalescence with the adjacent droplets.

The diameter of the droplets is less than the critical diameter of Si particles (~150 nm) predicted by Liu et al. [9] below which fracture of Si particles during electrochemical cycling is averted. Furthermore, there is a noticeable geometrical similarity between the droplet configuration synthesized by Epur et al. [30] and the 1/8th of the Si nano-ring configuration considered by us here in this study. The active material volume of an individual Si droplet is ~11.4% lower than that of 1/8th of Si nano-ring considered by us (Fig. 1 (c)). Also, the Si droplet geometry and the 1/8th of Si nano-ring have a similar surface area/volume ratio of ~0.1 and ~0.107 m⁻¹, respectively. Thus, the Si droplet configuration is expected to be mechanically stable. The electrochemical cycling results shown by Epur et al. [30] show that the heterostructure with Si droplet configuration gives an initial capacity of ~2700 mAhg⁻¹ with 10% first cycle irreversible loss. The capacity fade rate was ~0.25% per cycle and a capacity ~2340 mAhg⁻¹ was retained after 20 cycles. The continuous Si film showed an initial capacity of ~3200 mAhg⁻¹ and a capacity with 10 % first cycle irreversible loss. However, a capacity of only ~1950 mAhg⁻¹ was retained after 20 electrochemical cycles, thus showing a higher capacity fade rate of 1.7% per cycle (see Fig. 6 (a) in the reference [30]). These results show that Si droplet configuration outperforms the Si continuous film configuration, in agreement with our findings.

7. Conclusions

Different Si configurations in Si-CNT heterostructured anode have been studied for its mechanical integrity during electrochemical cycling by utilizing a

multiphysics framework employed in a finite element setting. It was observed that reducing the mechanical constraints on the active material reduces the ensuing stresses and the material inelastic flow; a conclusion that is not only limited to Si based nanostructured anodes. The Si-CNT heterostructured anodes for Li ion battery with continuous Si film coating configuration is prone to the formation of nano-voids which can cause active material disintegration during electrochemical cycling. Heterostructure with $1/8^{\text{th}}$ of the Si nano-ring, with the least mechanical constraint on the active component, was found to exhibit the least amount of stress, as well as plastic deformation of Si compared to other morphologies considered in this work. In addition, conditions for void nucleation were most unfavorable in this configuration. We conclude that heterostructures with Si droplets adhered to CNT is thus expected to be mechanically stable during the operation of a Li-ion battery. The present computational study provides a mechanistic understanding of mechanical failure and attendant capacity fade of carbon nanotube based heterostructured anodes during electrochemical cycling. This knowledge we envisage can be further applied to other anode geometries for the design of mechanical failure resistant electrode configurations.

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Nomenclature

A	Surface area of Si in contact with electrolyte (m^2)
c	Concentration of Li in the reference configuration (molm^{-3})
c_{max}	Maximum Li intercalation concentration in anode material (molm^{-3})
c_e	Concentration of electrolyte (molm^{-3})
c_s	Concentration of Li ions on the surface of the active material (molm^{-3})
C	Capacity of the electrode material (mAhg^{-1})
$C - rate$	Charge rate
D	Diffusivity of Li atom in the anode material ($\text{m}^2 \text{s}^{-1}$)
DI	Delamination index
E	Young's modulus (Pa)
f	Yield function
F	Faraday's constant (Ahmol^{-1})
$\mathbf{F}$	Deformation gradient
$\mathbf{F}_e$	Elastic component of the deformation gradient
$\mathbf{F}_p$	Plastic component of the deformation gradient
$\mathbf{F}_q$	Expansion component of the deformation gradient
H	Hardening Modulus (Pa)
i_0	Exchange current density (A m^{-2})

$\mathbf{I}$	Identity tensor
G_c	Fracture toughness of the material/interface (J m^{-2})
J_{Li}	Li atom flux ($\text{mol m}^{-2} \text{s}^{-1}$)
J_θ	Jacobian associated with expansion component of the deformation gradient
k	Kinetic rate constant ($\text{m s}^{-1})(\text{mol m}^3)^{-0.5}$)
$Li_{fraction}$	Fraction of lithium concentration in Li_xSi alloy
m	Mass of the active material (Si) in the electrode configuration (kg)
$\mathbf{M}_e$	Mandel stress tensor
n	Duration of the lithium alloying/de-alloying half cycle (hr)
p	Hydrostatic pressure (Pa)
$\mathbf{P}$	First Piola-Kirchhoff stress tensor
R	Universal gas constant ($\text{J mol}^{-1} \text{K}^{-1}$)
$\mathbf{S}$	Second Piola-Kirchhoff stress tensor
T	Stress triaxiality
t_e	Effective traction
$\mathbf{t}_c$	Traction at the cohesive surface
$\mathbf{u}$	Displacement field
$\mathbf{X}$	Position vector of material point in reference configuration
α_a, α_c	Anodic and cathodic transfer coefficient
δ	Displacement jump vector

δ_e, δ_c	Effective and characteristic opening displacement jump
ν	Poisson's ratio
$\dot{\lambda}$	Plastic rate parameter
ε_p	Plastic strain
η	Partial volume of Li in Si ($\text{m}^3 \text{mol}^{-1}$)
σ_c	Maximum cohesive normal traction (Pa)
σ_e	Effective stress (Pa)
σ_m	Hydrostatic stress (Pa)
σ_y	Yield strength of the material (Pa)
ω	Rate of change of elastic modulus of <i>a</i> -Si with Li fraction in the Li_xSi alloy ($\text{Pa Li}_{fraction}^{-1}$)
Ψ	Free energy functional

Figure Captions

Fig. 1: (Color online) Schematics of Si-CNT heterostructure anode geometries studied. (a) Continuous Si film coating on CNT (b) Si nano-ring adhered to CNT and (c) $1/8^{\text{th}}$ of Si nano-ring adhered to CNT. Dimensions of the anode heterostructure components are specified in nm.

Fig. 2: (Color online) Evolution of normalized Li concentration ($c_{Li} / c_{Li\max}$) in Si during lithium alloying half cycle along the longitudinal (LONG) section (XZ plane) of a **(a)** continuous Si thin film on CNT, **(b)** Si nano-ring tethered around CNT and **(c)** $1/8^{\text{th}}$ of Si nano-ring tethered to CNT at different normalized cycle times (τ).

Fig. 3: (Color online) Radial stress, axial stress, circumferential stress, von Mises stress and plastic strain contours in the longitudinal section (XZ plane) of continuous Si coating in first Si-CNT heterostructure configuration at the end of lithium alloying (a-e) and at end of de-alloying (f-j).

Fig. 4: (Color online) Radial stress, axial stress, circumferential stress, von Mises stress and plastic strain contours in the longitudinal section (XZ plane) of the Si nano-ring in second Si-CNT heterostructure configuration at the end of lithium alloying (a-e) and at end of de-alloying (f-j).

Fig. 5: (Color online) Radial stress, axial stress, circumferential stress, von Mises stress and plastic strain contours in the longitudinal section (XZ plane) of the 1/8th of the Si nano-ring in third Si-CNT heterostructure configuration at the end of lithium alloying (a-e) and at end of de-alloying (f-j).

Fig. 6: Evolution of combination of effective and hydrostatic stress ($\sigma_e + \sigma_m$) and stress triaxiality (T) in the continuous Si coating in the first Si-CNT heterostructure at the normalized radial thickness of (a) $\bar{r} = 1$, (b) $\bar{r} = 0.5$ and (c) $\bar{r} = 0$.

Fig. 7: (Color online) Evolution of combination of effective and hydrostatic stress ($\sigma_e + \sigma_m$) and stress triaxiality (T) in the Si nano-ring in the second Si-CNT heterostructure at the normalized radial thickness of (a) $\bar{r} = 1$, (b) $\bar{r} = 0.5$ and (c) $\bar{r} = 0$.

Fig. 8: (Color online) Evolution of combination of effective and hydrostatic stress ($\sigma_e + \sigma_m$) and stress triaxiality (T) in 1/8th of the Si nano-ring in the third Si-CNT heterostructure at the normalized radial thickness of (a) $\bar{r} = 1$, (b) $\bar{r} = 0.5$ and (c) $\bar{r} = 0$.

Table 1: Constitutive equations of the theoretical framework

<i>Surface reaction rate / Li flux at a-Si surface</i>	
$J_{Li} = C m / F A n = i / F$	(1)
<i>Charge transfer kinetics (Butler-Volmer equation)</i>	
$i = i_0 \left[\exp \left(\frac{\alpha_a F}{RT} \eta_s \right) - \exp \left(\frac{\alpha_c F}{RT} \eta_s \right) \right]$	(2)
$i_0 = F k (C_e)^{\alpha_a} (C_{max} - C_s)^{\alpha_a} (C_s)^{\alpha_c}$ (Exchange current density)	(3)
<i>Electrode deformation</i>	
$\mathbf{F} = \mathbf{F}_e \mathbf{F}_p \mathbf{F}_\theta$ (Multiplicative decomposition of deformation gradient)	(4)
$\mathbf{F}_\theta = (1 + \eta c)^{1/3} \mathbf{I}$	(5)
$\nabla_X \cdot \mathbf{P} = 0$ with $\mathbf{P} = \mathbf{F} \mathbf{S}$ (linear momentum balance)	(6)
<i>Coupled transport inside bulk anode</i>	
$\partial_t c = D \nabla \left[\nabla c + \frac{c}{RT} \nabla \left(\frac{\partial \Psi_1}{\partial c} \right) - \frac{\eta c}{RT} \nabla p \right]$	(7)
$p = \frac{1}{3} \text{tr} \left[J_\theta^{2/3} \mathbf{M}_e \mathbf{F}_\theta^{-1} \right]$	(8)
<i>The flow rule of material is defined as</i>	
$\dot{\mathbf{F}}_p \mathbf{F}_p^{-1} = \dot{\lambda} \frac{\partial f}{\partial \mathbf{M}_e}$	(9)
<i>Yield function for isotropic linearly hardening material</i>	
	(10)

$f(\mathbf{M}_e, \bar{\varepsilon}_p) = \sqrt{\frac{3}{2} \mathbf{M}_e^d : \mathbf{M}_e^d} - [\sigma_y + H \bar{\varepsilon}_p] = 0$	
<i>Elastic softening of silicon due to lithium alloying</i>	
$E_0^{Si}(Li_{fraction}) = E_0^{Si} - \omega \times Li_{fraction} \quad [40]$	(11)
<i>Traction at the Si/CNT or Si/Si interface</i>	
$\mathbf{t}_c = \frac{t_e}{\delta_e} \hat{\mathbf{t}}, \quad \hat{\mathbf{t}} = [\beta^2 \boldsymbol{\delta} + (1 - \beta^2)(\boldsymbol{\delta} \cdot \mathbf{n})\mathbf{n}] \quad [45]$	(12)

Table 2: Material properties employed for the simulations reported in this article.

Young's modulus of a-Si (E_0^{Si})	90 GPa [40]
Rate of change of elastic modulus of a-Si with Li fraction (ω)	71.25 GPa/ $Li_{fraction}$
Poisson's ratio of a-Si (ν_0^{Si})	0.28
Yield strength of a-Si (σ_y^{Si})	1.5 GPa [9]
Hardening modulus of Si (H^{Si})	1 GPa
Average fracture strength of a-Si during electrochemical cycling (σ_c^{Si})	1.6 GPa [50, 51]
Young's modulus of multiwalled CNT (transverse isotropic material properties)	$E_r^{CNT} = 10$ GPa [52] $E_t^{CNT} = 200$ GPa [14]
Si-CNT interface fracture strength (σ_c^{Si-CNT})	0.5 GPa
Si-CNT interface toughness (G_c^{Si-CNT})	5 J/m ²
Diffusivity of Li in Si (D_o)	10 ⁻¹⁸ m ² /s [21]

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