Supporting Information


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Supporting Materials

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1. Carbon nanotube sponge

Figure S1 shows the surface morphology of a Si-CNT sponge at a relative low magnification. The distribution of CNTs appears quite uniform at the centimeter scale. The CNTs are micrometers in length and are entangled with each other, thus forming a mechanically stable film. The pore volume in the sponge is over 90%, as determined by a simple compression test.
Figure S1 SEM image of a CNT sponge film in plan view, the flat surface reveals uniformly distributed CNTs entangled with each other, thus forming a 3D porous film.

2. Si-CNT coaxial sponge

Figures S2-S4 show more details of Si-CNT coaxial sponge films. Due to the porous structure of the CNT sponges, the CVD deposition of Si is rather uniform throughout the entire film which is 2×2×1 mm in size. Although the images shown are taken from the interior of the samples after sectioning with a razorblade, the samples are essentially uniform and there is no observable difference between the interior and the surface.

Figure S2 SEM image of a Si-CNT coaxial sponge after sectioning through the middle. The CNT surfaces are conformally coated with Si. The coating is uniform throughout the entire structure due to the porous nature of the sponge and the easy paths the structure provides for the convection of Si-containing Ar gas.
Figure S3 Close-up view of an area in Figure S2. The circle highlights the cross section of a Si-CNT coaxial structure, with the CNT core being clearly seen.

Figure S4 TEM image of an area in Figure S2 showing uniform Si coating around the CNTs. Si was removed in certain areas by sonication during the TEM sample preparation process.

3. Morphology of Si-CNT sponge after cycling with an operating range of 0.05-1 V
Figures S5-S6 show SEM images of Si-CNT sponges after charge-discharge cycling between 0.05 and 1 V. The solid Si-CNT shell-core structure has become highly porous after 50 cycles.

**Figure S5** A typical SEM image of a Si-CNT sponge after 50 charge-discharge cycles with an operating range of 0.05-1.00 V.

**Figure S6** SEM image of a different area of a Si-CNT sponge after 50 charge-discharge cycles with an operating range of 0.05-1.00 V. The highlight area shows nanopore formation all the way down to the CNT surface.
4. Morphology of Si-CNT sponge after cycling with an operating range of 0.17-0.6V

Figures S7-8 show SEM images of a Si-CNT sponge after 50 charge-discharge cycles between 0.05 and 0.6 V. The narrower operating voltage range compared with the range of 0.05-1.00 V in Figures S5-S6 significantly reduced the development of nano pores in the Si shell.

**Figure S7** SEM image of a Si-CNT sponge after 50 charge-discharge cycles with an operating voltage range of 0.17 V-0.6 V.

**Figure S8** Close-up view of a Si-CNT sponge after 50 charge-discharge cycles between 0.17 and 0.6V.
5. Morphology of Si-CNT sponge after cycling with an operating voltage range of 0.17-1V

Figure S9 shows a SEM image of a Si-CNT sponge after 50 charge-discharge cycles between 0.175 and 1.0 V. The surface of the Si-CNT shell-core structure is less porous than that for the 0.05-1.0V case (Figures S5-S6) but more porous than that for the 0.17V-0.6V case (Figures S7-S8).

![Figure S9 SEM image of a Si-CNT sponge after 50 charge-discharge cycles with an operating voltage range of 0.17 V-1V.](image)

6. Inelastic deformation of Li/Si shell during charge/discharge

The formation of nano-voids in the Si shell of Si-CNT structures and LiSi NWs[1] upon cycling suggests that LiSi can undergo large inelastic deformations. In its amorphous phase, even pure silicon exhibits significant plasticity at the microscopic scale.[2] Very recently, Sethuraman et al.[3] measured the evolution of stress in silicon thin films during electrochemical lithiation and delithiation and showed that the flow stress of lithiated Si decreases as Li concentration increases. The finding suggests that parameters which depend on stress singularities such as the mode I fracture toughness $K_{IC}$ are not very relevant for nanostructured Li/Si electrodes. Instead, plastic (or viscoplastic) flow is an important process that cannot be neglected. Here, we will first show that inelastic flow of LiSi is inevitable in a Si-CNT coaxial structure during cycling. We will then calculate the stress states in the Li/Si shell with a simple plasticity model. Because tensile stresses during discharging act as the main driving force for nano-pore nucleation and growth, quantitative understanding of how stresses evolve is the first step in the design of robust CNT-Si core-shell anodes.
Consider the CNT-Si core-shell structure with CNT radius $a$ and Si shell thickness $b-a$ illustrated in Fig. 4a. We assume that the Si shell is well-bonded to the CNT core, as suggested by the fact that Si shell cannot be sonicated off the core in our experiments. At the slow charging speed of C/5 used in the experiments, Li concentration is quite uniform in the Li/Si shell and therefore diffusion-induced stress (DIS) contributions due to Li concentration inhomogeneity, which is inversely related to charging rate, $^4$ can be neglected. Consequently, stresses in the Li/Si shell are entirely due to the constraint effect of the CNT core which can be regarded as rigid because its elastic stiffness is $\sim$10 times that of Si.$^5$ This treatment of the CNT core as a rigid rod allows us to focus on the dominant physical processes that govern the behavior at hand. A resulting simplification is that conditions of plane strain prevail due to the large length-to-diameter ratio of the core-shell structure. The infinitesimal deformation formulation is used to allow the derivation of close-form solutions, although the actual deformation is finite.

6.1 Elastic Regime

We first calculate the stresses for a fully elastic case without plasticity. If the shell is stress-free initially with a homogeneous lithium concentration of $c_0$, the elastic stress-strain relation when the shell is charged/discharged to concentration $c$ is

$$
\varepsilon = \frac{1+\nu}{E} \sigma - \frac{\nu}{E} \sigma_r r (\sigma) I + \frac{1}{3} \Omega \Delta c I, ~ (1)
$$

where $\Delta c = c - c_0$ is the lithium concentration change ($\Delta c > 0$ for charging and $\Delta c < 0$ for discharging). $\varepsilon$ is the small strain tensor measured relative to the initial state, $\sigma$ is the Cauchy stress. $E = E(c)$ is the concentration-dependent Young’s modulus and $\nu = \nu(c)$ is the Poisson’s ratio. $\Omega$ is the partial atomic volume of Li in Li/Si.

The equilibrium condition is

$$
\frac{d\sigma_r}{dr} + \frac{\sigma_r - \sigma_\theta}{r} = 0 \text{ for } a < r < b, ~ (2)
$$
with
\[ \sigma_r = 0 \text{ at } r = b. \] (3)

Equation (3) implies traction-free boundary condition at the outer shell surface. To justify this simplification, a few comments are in order about the role of surface tension on the cylindrical surface at \( r = b \). This surface tension makes a contribution to the bulk stress in the shell, the magnitude of which being \( \sigma^t \sim -\gamma / b \), where \( \gamma \) is the surface energy of Li/Si per unit area. If \( b = 35 \text{ nm} \) and \( \gamma \sim 1 \text{ J/m}^2 \), \( \sigma^t \sim -30 \text{ MPa} \). As we will show next, stresses due to shell expansion can easily reach as high as \( \sim 1 \text{ GPa} \) during battery operation. Compared with such stress levels, \( \sigma^t \) is highly insignificant and is therefore neglected in our analyses here. On the other hand, SEI, a by-product which usually forms on the surface of the LiSi shell during battery operation, can pose a mechanical constraint. To the best of our knowledge, accurate data on the mechanical properties of SEI is not currently available. Here, we assume the surface of the shell is traction-free (3) and focus on the inelasticity and void nucleation inside the shell, leaving the effects of SEI as an open question for to be analyzed in the future.

Symmetry dictates that the displacements in a cylindrical coordinate system are of the form
\[ u_r = u(r), \quad u_\theta = 0, \quad u_z = 0 \] (4)

The corresponding strains are
\[ \varepsilon_r = \frac{du_r}{dr}, \quad \varepsilon_\theta = \frac{u_r}{r}, \quad \varepsilon_z = 0. \] (5)

Since the CNT core is rigid,
\[ u_r = 0, \text{ at } r = a. \] (6)
The solution to equations (1)-(6) are

\[ \sigma_r = \sigma_s \left( \frac{a^2}{r^2} - \frac{a^2}{b^2} \right), \quad \sigma_\theta = -\sigma_s \left( \frac{a^2}{r^2} + \frac{a^2}{b^2} \right), \quad \sigma_z = -\sigma_s \left( 1 + \frac{a^2}{b^2} \right), \]  

(7)

where the elastic scaling factor is

\[ \sigma_s = K \Omega \Delta \varepsilon \left( \frac{a^2}{b^2} + \frac{1}{1 - 2\nu} \right)^{-1}. \]  

(8)

In the above expression, \( K \) is the bulk modulus of Li/Si. The von Mises effective stress is therefore

\[ \sigma_e = |\sigma_s| \sqrt{1 + 3 \frac{a^2}{r^2}}. \]  

(9)

For a typical relevant structure, \( a = 5 \text{ nm} \) and \( b = 35 \text{ nm} \), the elastic solution in equation (7) (normalized by \( \sigma_s \)) for a charging process are shown in Figure 4. For Li\( _\xi \)Si (\( \xi \) Li atoms per Li atom), \( \Omega = 14.3 \text{ Å}^3 \) \[^6\] \( E = E(\xi) = (18.90\xi + 90.13) / (1 + \xi) \) GPa and \( \nu = \nu(\xi) = (0.24\xi + 0.28) / (1 + \xi) \).\[^7\] If the initial charging state is \( c_0 = 0 \) (pure Si), \( \sigma_s \) is as high as \(~1\ GPa\) as the shell is elastically charged to \( \text{Li}_{0.05}\text{Si} \). However, the plastic flow stress measured in Li/Si thin films is only around 1 to 1.7 GPa.\[^3\] Since the charging limit of Li/Si is \( \xi_{\text{max}} = 4.4 \), the stresses in the Li/Si shell are well above the yield strength under normal operational conditions. Therefore, inelasticity dominates the response of Li/Si in Si-CNT coaxial structures and must be accounted for.
Figure S1: Normalized stresses based on an elastic solution for a Si-CNT core-shell structure with $a=5$ nm and $b=35$ nm.

6.2 Plasticity in Li/Si shell

Accounting for both elastic and plastic strain contributions, the strain rate in Li/Si is

$$\dot{\varepsilon} = \dot{\varepsilon}_E + \dot{\varepsilon}_p + \frac{1}{3} \Omega \dot{c} I,$$ (10)

where $\dot{\varepsilon}_E = \frac{1 + \nu}{E} \sigma - \frac{\nu}{E} tr(\sigma) I$ is the elastic strain rate and $\dot{\varepsilon}_p$ is the plastic strain rate. The flow-rule of Li/Si is assumed to be associated with a well-defined yield surface of $Q(\sigma, c) = \frac{1}{2} \sigma^{dev} : \sigma^{dev} - \frac{1}{3} \sigma_0^2 = 0$, where $\sigma_0$ is the yield strength and $\sigma^{dev} = \sigma - (tr \sigma / 3) I$ is the deviatoric stress. To focus on the most relevant physics, strain hardening/softening is
neglected, therefore, $\sigma_0$ is independent of strain but depends on the lithium concentration, i.e. $\sigma_0 = \sigma_0(e)$. The associated flow-rule leads to

$$\dot{\varepsilon}_p = \dot{\lambda} \frac{\partial Q}{\partial \sigma},$$ (11)

where $\dot{\lambda}$ is a proportionality factor that can be determined through the consistency condition of

$$\frac{\partial Q}{\partial \sigma} : \dot{\sigma} + \frac{\partial Q}{\partial c} \dot{c} = 0. \quad (12)$$

Equations (11) and (12) give

$$\dot{\varepsilon}_p = \frac{3}{2} \frac{1}{\sigma_0^2} \left( \sigma^{\text{dev}} \otimes \sigma^{\text{dev}} \right) : \dot{\varepsilon} + \frac{1}{2G} \frac{\partial \sigma_0}{\partial c} \dot{c} \sigma^{\text{dev}}. \quad (13)$$

Equation (13) can be simplified by the following arguments. Firstly, except for very early stages of plastic flow, the elastic strain rate is much smaller than the total strain rate, i.e. $\|\dot{\varepsilon}_E\| \ll \|\dot{\varepsilon}\|$. Secondly, the fact that the change of $\sigma_0$ with Li concentration satisfies the condition of

$$\frac{1}{2G} \frac{\partial \sigma_0}{\partial c} \ll \Omega \quad [3]$$

leads to

$$\frac{1}{2G} \frac{\partial \sigma_0}{\partial c} \|\sigma^{\text{dev}}\| \ll \frac{1}{3} \Omega \dot{c}.$$ 

Therefore, neglecting the small terms in (13) leads to the perfect plasticity approximation of

$$\dot{\varepsilon} = \frac{3}{2} \frac{1}{\sigma_0^2} \left( \sigma^{\text{dev}} \otimes \sigma^{\text{dev}} \right) : \dot{\varepsilon} + \frac{1}{3} \Omega \dot{c} \mathbf{I}. \quad (14)$$

Taking the trace of (14) leads to
\[ \frac{d}{dt} \left( \frac{du_r}{dr} + \frac{u_r}{r} \right) = \Omega \dot{c}. \]  

(15)

With the help of the boundary condition in (6), equation (15) can be integrated to yield

\[ u_r = \frac{\Omega \Delta c}{2} r - \frac{a^2 \Omega \Delta c}{2r}. \]  

(16)

This result and equation (5) give

\[ \varepsilon_r = \frac{\Omega \Delta c}{2} + \frac{a^2 \Omega \Delta c}{2r^2}, \]
\[ \varepsilon_\theta = \frac{\Omega \Delta c}{2} - \frac{a^2 \Omega \Delta c}{2r^2}, \]  

and

\[ \varepsilon_z = 0. \]  

Equation (14) and (17) combine to yield

\[ \sigma_r^{dev} = \frac{1}{3} + \frac{a^2}{r^2} \sigma_0 \text{sgn} (\Delta c), \]
\[ \sigma_\theta^{dev} = \frac{1}{3} - \frac{a^2}{r^2} \sigma_0 \text{sgn} (\Delta c), \]
\[ \sigma_z^{dev} = \frac{2}{3} \frac{1}{\sqrt{1 + \frac{a^4}{r^4}}} \sigma_0 \text{sgn} (\Delta c), \]  

(18)

where \( \text{sgn}(\Delta c) \) denotes the sign of \( \Delta c \). The hydrostatic stress \( \sigma_m = tr \sigma / 3 \) can be obtained through (2) and (3) as

\[ \sigma_m = -\sigma_r^{dev} + \frac{\sigma_0}{\sqrt{3}} \sinh^{-1} \left[ \sqrt{\frac{a^2}{r^2}} \right] \text{sgn}(\Delta c) - \frac{\sigma_0}{\sqrt{3}} \sinh^{-1} \left[ \sqrt{\frac{a^2}{b^2}} \right] \text{sgn}(\Delta c). \]  

(19)
Finally, the stress distribution in the Li/Si shell accounting for inelastic flow is

\[
\sigma_r = \left( \frac{\sigma_0}{\sqrt{3}} \sinh^{-1} \left[ \sqrt{3} \frac{a^2}{r^2} \right] \right) - \left( \frac{\sigma_0}{\sqrt{3}} \sinh^{-1} \left[ \sqrt{3} \frac{a^2}{b^2} \right] \right) \pm \sigma_c \Delta c,
\]

\[
\sigma_\theta = \left[ \frac{2 a^2}{r^2} - \sigma_0 \sinh^{-1} \left[ \sqrt{3} \frac{a^2}{r^2} \right] - \sigma_0 \sinh^{-1} \left[ \sqrt{3} \frac{a^2}{b^2} \right] \right] \pm \sigma_c \Delta c,
\]

\[
\sigma_z = \left[ \frac{1 + a^2}{r^2} - \sigma_0 \sinh^{-1} \left[ \sqrt{3} \frac{a^2}{r^2} \right] - \sigma_0 \sinh^{-1} \left[ \sqrt{3} \frac{a^2}{b^2} \right] \right] \pm \sigma_c \Delta c.
\]

Equation (17) shows that material in the Si shell is squeezed out radially during lithiation. Since the shell is constrained by the CNT core and cannot lengthen in the axial direction, the shell’s aspect ratio (or length-to-radius ratio) decreases during charging. On the other hand, the stresses during delithiation are predominantly tensile (cf. Figure 4b in the main text), acting as the driving force for nano-pore nucleation and growth.