# Electronic supplementary information

# Carbon coating may expedite the fracture of carbon-coated silicon core-shell nanoparticles during lithiation

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**Analogous simulation of lithiation-induced expansion as thermal expansion**

For simplicity, in our simulation of lithiation, the NPs were treated as two-dimensional (plane strain) circular solids. The volume expansion of Si due to lithiation was assumed proportional to the $Li^+$ concentration which can be equated as the "temperature" in a thermal expansion problem due to the similarity between the governing equations of a diffusion problem and a thermal conduction problem.[1] Thus, the stress in Si@C NP due to lithiation can be equivalently calculated as the "thermal" stress as long as the thermal expansion coefficient is taken as a value correlated to the strain of unconstrained Si at full lithiation. In our analogous simulation, the thermal expansion coefficient of Si was taken as 0.4 per unit degree of "temperature" increment, simulating Si with 0.4 strain at full lithiation. Such analogous thermal expansion problem can be readily solved by commercial FEA package. To simulate the effect of phase transition from Si to $Li_xSi$, the mechanical properties (Young's modulus, Poisson's ratio and yield

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strength) of Si were set to be linearly proportional to the Li$^+$ concentration (i.e. "temperature") with the properties of the pristine Si (i.e., "temperature" = 0 degree) and the fully lithiated Si (i.e., "temperature" = 1 degree) being taken as the values shown in Table 1. The lithiation of carbon was not taken into account due to its negligible volume expansion compared to the Si.[2,3] Two-dimensional 8-node plane-strain thermally coupled quadrilateral, biquadratic displacement-bilinear temperature element with reduced integration (CPE8RT in ABAQUS, Dassault Systèmes, France) was adopted.

It was reported that the interface between the lithiated Si and the unlithiated Si is sharp.[4-7] The gradient of Li$^+$ concentration between the lithiated Si shell and the unlithiated Si core is ignored in our simulation. To simulate the process of lithiation in Si core, the Si core was discretized into $N$ thin annuluses with uniform thickness, as shown in Fig. S1a. Unit temperature increment was applied on the annuluses one after another from outside to inside, simulating the procedure of lithiation in the Si core. Convergence of the results was examined by taking $N$ = 5, 10, 20, 40, 80. Fig. S1b shows the dependence of the maximum tensile stress, $\sigma_{max}$, in the carbon coating on the number of the annuluses during lithiation. For a Si@C NP with diameter of Si core being 100 nm and thickness of carbon coating being 5 nm, the convergent result of the maximum tensile stress is obtained as $N > 40$ (Fig. S1b). Therefore, $N$ = 50 is taken in the simulation.
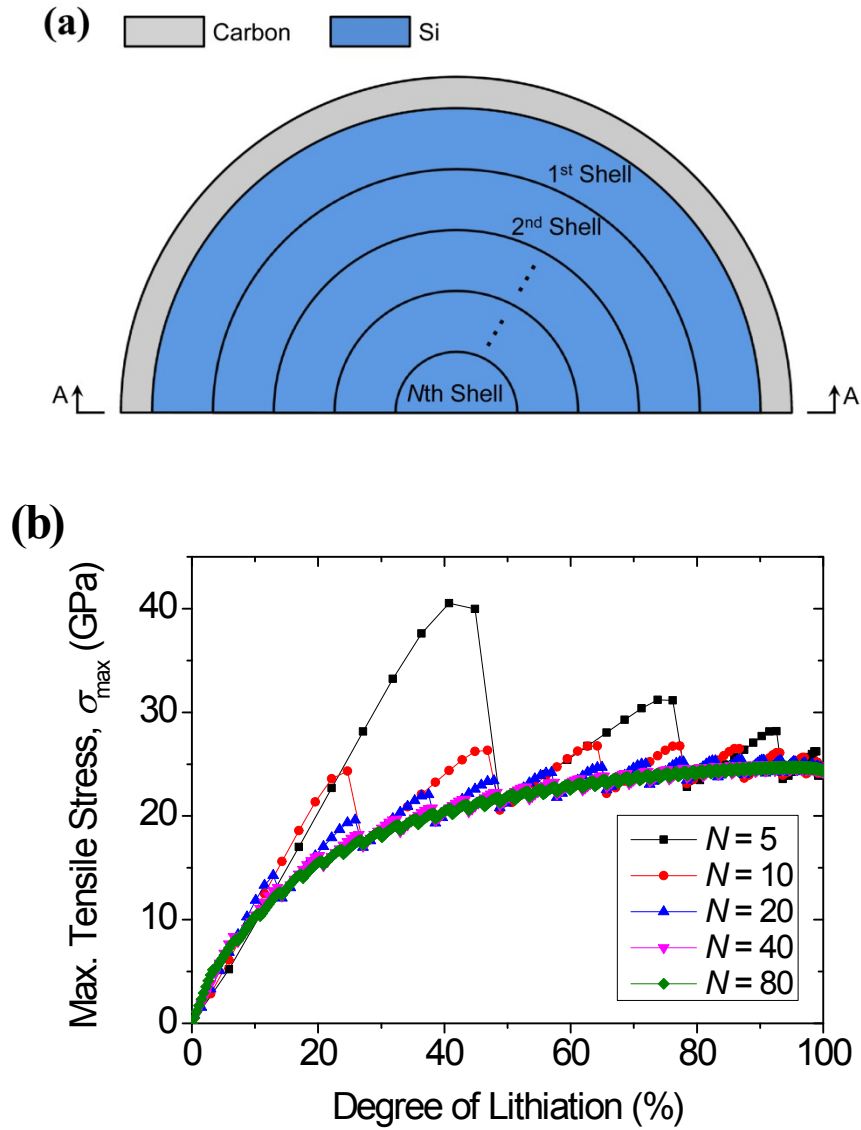
**Fig. S1 (a) Schematic showing the discretization scheme of the Si core for simulating the lithiation process. For symmetry, only half of the model is shown. (b) Calculated maximum tensile stress ($\sigma_{max}$) in the carbon coating of Si@C NP when $N$ is taken as different values. Here, the diameter of Si core is 100 nm and the thickness of carbon coating is 5 nm.**

**Material's inhomogeneity effect on the energy release rate**

The material's inhomogeneity effect was further studied by comparing the near tip $J$-integrals, $J_{tip}$, in a cracked Si@C NP and an uncoated Si NP, as shown in Fig. S2. The diameter of the uncoated Si NP is taken as 110 nm (the same as the diameter of Si@C NP considered above) with a preexisting crack being 5 nm, which is equal to the thickness of carbon coating in Si@C NP. It can be seen that even though the crack length (5 nm) is same for both cases, the energy release rate $J_{tip}$ in Si@C NP increases much more rapidly than that in the uncoated Si NP. This is due to the inhomogeneity effect on the $J$-integral around the crack tip in Si@C NP and the $J$-integral increases when the crack propagates from the hard/stiff carbon coating into the soft/compliant Si core in the Si@C NP.
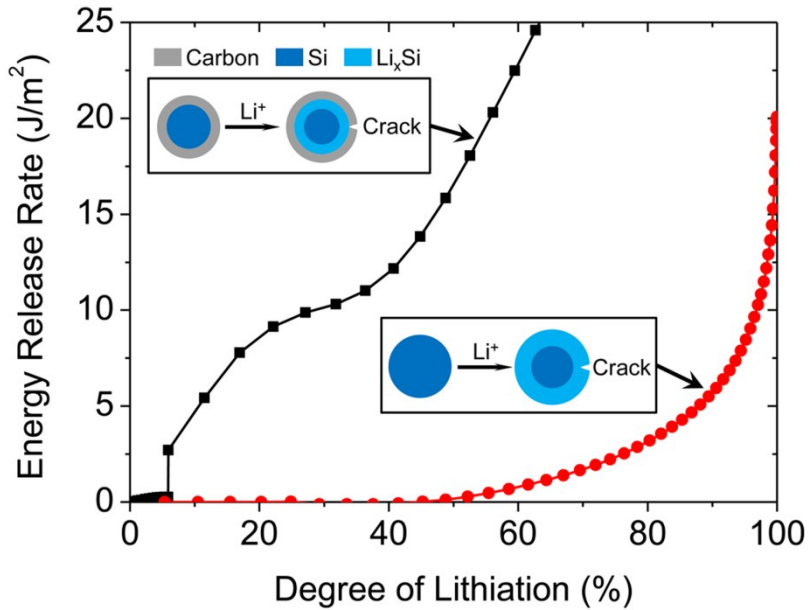


**Fig. S2 Comparison of the near tip energy release rates ($J_{tip}$) as functions of degree of lithiation in a cracked Si@C NP and an uncoated Si NP.**

**Calculation of energy release rate in cracked NPs**

Fig. S3a shows the schematic of the paths ($\Gamma_n$) used to evaluate the energy release rate (*J*-integral) near the tip of a crack terminating at the carbon/Si interface. We used the crack tip element in ABAQUS (Dassault Systèmes, France). The elements in the region around the crack tip, with a $r^{-1}$ strain singularity ($r$ is the distance from the crack tip), were meshed with quad-dominated shape. The paths are numbered in sequence from the crack tip outwards to the far field. In the simulation, the energy release rate was found to be path-dependent and decrease from the inner path to the outer one, as shown in Fig. S3b. Actually, it was reported in literature that the *J*-integral near the crack tip is greater than the far-field *J*-integral when the crack approaches the interface from a higher strength material to a lower strength material due to the inhomogeneity of the two materials.[8] The energy release rate of all the paths increase rapidly and soon exceed the fracture energy of Li$_x$Si indicating the potential propagation of crack from carbon coating into the lithiated Si core. It can be seen that *J*-integral converges to a steady value after $\Gamma_5$ and the convergent *J*-value, $J_{\Gamma 5}$, is taken as the effective crack tip energy release rate, as shown in Fig. 5b.
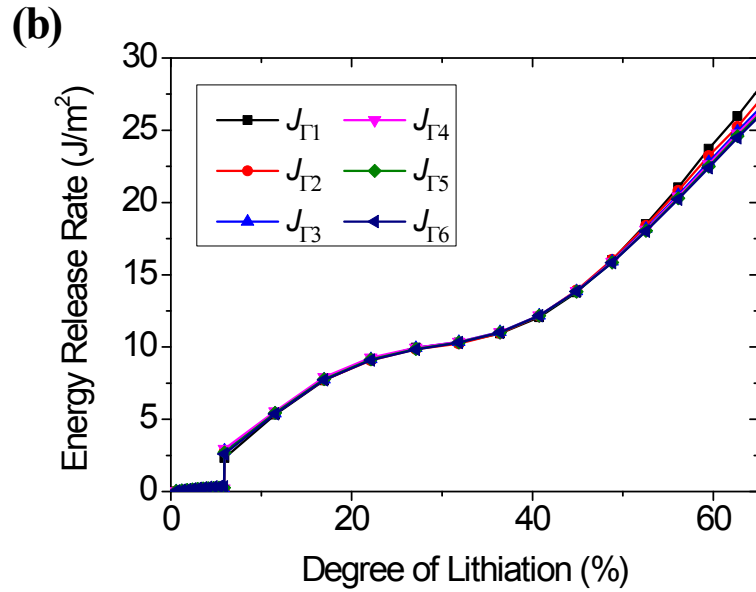
**(a)**

**(b)**
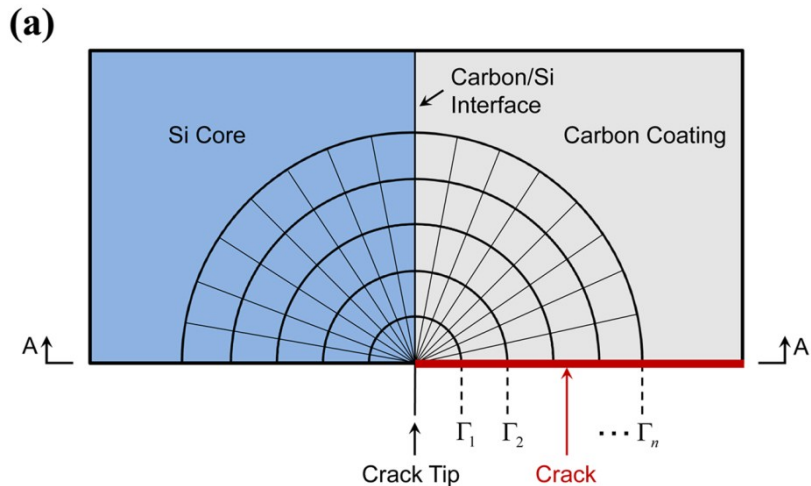


Fig. S3 (a) Schematic showing the *J*-integral paths near the crack tip of the Si@C NP. For symmetry, only half of the model is shown. (b) Calculated path-dependent energy release rate (*J*-integral) as a function of the degree of lithiation for Si@C NP.

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