

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

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### Abstract

Previous studies on silicon (Si) indicate the lithiation-induced fracture of crystalline Si nanoparticles can be greatly inhibited if their diameter is reduced to below a critical length scale around 150 nm. In this paper, *in situ* lithiation of individual carbon-coated Si nanoparticles (Si@C NPs) is conducted and shows that Si@C NPs will fracture during lithiation even though the diameter is much smaller than 150 nm, implying a deleterious effect of the carbon coating on the integrity of the Si@C NPs during lithiation. To shed light on this effect, finite element analysis is carried out and reveals that the carbon coating, if fractured during lithiation, will induce cracks terminating at the C/Si interface. Such cracks, upon further lithiation, can immediately propagate into the Si core due to the elevated driving force caused by material inhomogeneity between the coating and core. To prevent the fracture of the carbon coating so as to protect the Si core, a design guideline is proposed by controlling the ratio between the diameter of Si core and the thickness of carbon coating. The results in this paper should be of practical value to the design and application of Si-based core-shell structured anode materials for lithium ion batteries.

### **Finite Element Analysis**



## In Situ TEM Observation



Figure 1. (a) Schematic of the setup of *in situ* lithiation test; (b, c) TEM images of the Si@C NPs under different magnifications; (d) high resolution TEM image showing the amorphous carbon coating and the crystalline Si core as confirmed by the selected area electron diffraction pattern in (e).

#### Degree of Lithiation (%)

Figure 4. (a) Schematic of FEA model of Si@C NP for evaluating the stress developed in the carbon coating during lithiation; (b) Variation of the maximum tensile stress ( $\sigma_{max}$ ) in the carbon coating of Si@C NP with lithiation. Fracture of the carbon coating takes place at ~6% lithiation.  $\sigma_{\max}^{FL}$  here denotes the maximum tensile stress in the carbon coating at the full lithiation moment.



Figure 5. (a) Meshed finite element model for calculating the energy release rate (J-integral) near the tip of a crack terminating at the carbon/lithiated Si interface and (b) calculated J-integral as a function of the degree of lithiation. The energy release rate increases rapidly after the cracking of the carbon coating and easily exceeds the fracture energy of Li<sub>x</sub>Si due to material inhomogeneity, leading to the penetration of crack into the core and the fracture of the whole Si@C NP.

## **Optimal Design of Si**(*a*)**C NP**

#### 150 -

• Larger *D* and smaller *t* result



**Figure 2.** Temporal evolution of the morphology of Si@C NP during *in situ* lithiation. It was reported that bare crystalline Si NP with diameter smaller than 150 nm will not fracture during lithi-



in higher  $\sigma_{\max}^{\text{FL}}$ , indicating that Si@C NPs with larger D and smaller t tend to fracture during lithiation. Fracture strength of a-carbon  $6 \text{ GPa} < \sigma_{\rm f} < 12 \text{ GPa}$ 

**Figure 6.** Maximum tensile stress at full lithiation in the carbon coating of Si@C NPs with different core diameters D and coating thicknesses t. Here,  $\sigma_{\text{max}}^{\text{FL}}$  is normalized by  $E_{\text{C}} = 300$  GPa.

## Conclusion

- In situ lithiation shows that the Si@C NPs fractured with Si core diameters smaller than 150 nm, which has been viewed as the maximum allowable size of bare crystalline Si nanoparticles immune to lithiation-induced fracture.
- FE simulation results indicated that excessive tensile stress will be readily developed in the carbon coating, leading to the fracture of the carbon coating. The resulting crack in the carbon coating will experience an elevated driving force for growth due to the unfavorable material inhomogeneity be-

#### ation. However, the Si@C NP, with Si core diameter of only ~60 nm, was found to fracture.



Figure 3. Dependence of fracture of Si@C NP on the diameter of Si core and thickness of carbon coating.

• Si@C NPs with larger D and smaller t tend to fracture during lithiation.

• If D/t > 7.0, fracture occurs.

• If D/t < 3.5, no fracture is observed.

• Critical ratio 3.5 < D/t < 7.0, below

### which no fracture occurs.

Thickness of Carbon Coating, *t* (nm)

tween the carbon coating and the lithiated Si, leading to the fracture of Si@C NP.

• A design guideline for Si@C NP is proposed by optimizing the ratio between the Si core diameter and the carbon coating thickness to avoid the cracking of carbon coating so as to maintain the integrity of Si@C NP during electrochemical cycling

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