

# Mechanistic Model of Lithiation and Delithiation in Silicon

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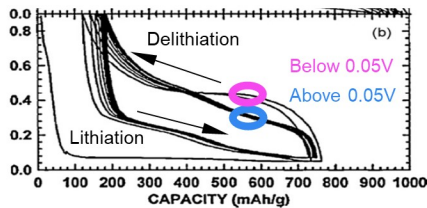
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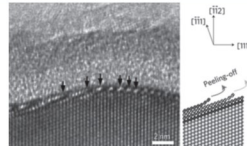
**Introduction.** Silicon has been an attractive alternative to graphite as an anode material in lithium-ion batteries. Here we report a new mechanistic model of silicon anodes considering multi-step phase transformations, crystallization and amorphization. The asymmetric voltage hysteresis of silicon is reproduced, the abrupt appearance of the crystalline Li-Si phase in lithiation and its gradual disappearance in de-lithiation are retrieved.

## 1. Unique behaviors



## Heterogeneous amorphization

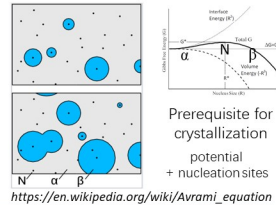
$$E_{(b2),0} = \frac{\Delta G_{(2b),0}}{(3.75-x)e} = \frac{\Delta G_{(2),0} + \Delta G}{(3.75-x)e} = E_{(2),0} + E^*$$



Liu X H, Wang J W, et al. Nature nanotechnology, 2012

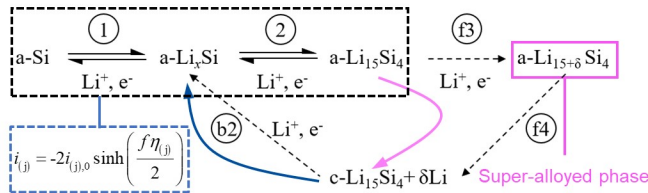
## Homogeneous crystallization

$$\frac{dx_3}{dt} = k_{cry} \left( \frac{x_3}{\Delta x_3} - x_4 \right) x_4$$

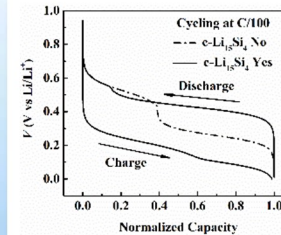


[https://en.wikipedia.org/wiki/Avrami\\_equation](https://en.wikipedia.org/wiki/Avrami_equation)

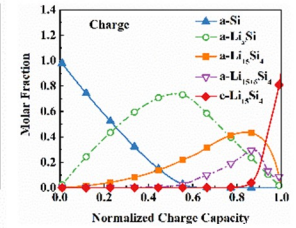
## 2. Reaction pathways



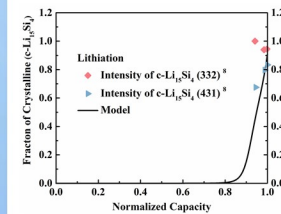
## 3. Simulation results



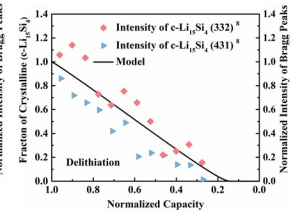
Voltage curves



Variations of Li-Si phases



Growth of c-Li<sub>15</sub>Si<sub>4</sub> in lithiation



Amorphization of c-Li<sub>15</sub>Si<sub>4</sub> in delithiation

**Conclusions.** A mechanistic model is developed for silicon anodes. The processes of phase transformations, crystallization and amorphization underlying the electrode behaviors are resolved in the model. Comparisons show a good agreement between the model and experimental results.