

4D_Li+ battery: Fading

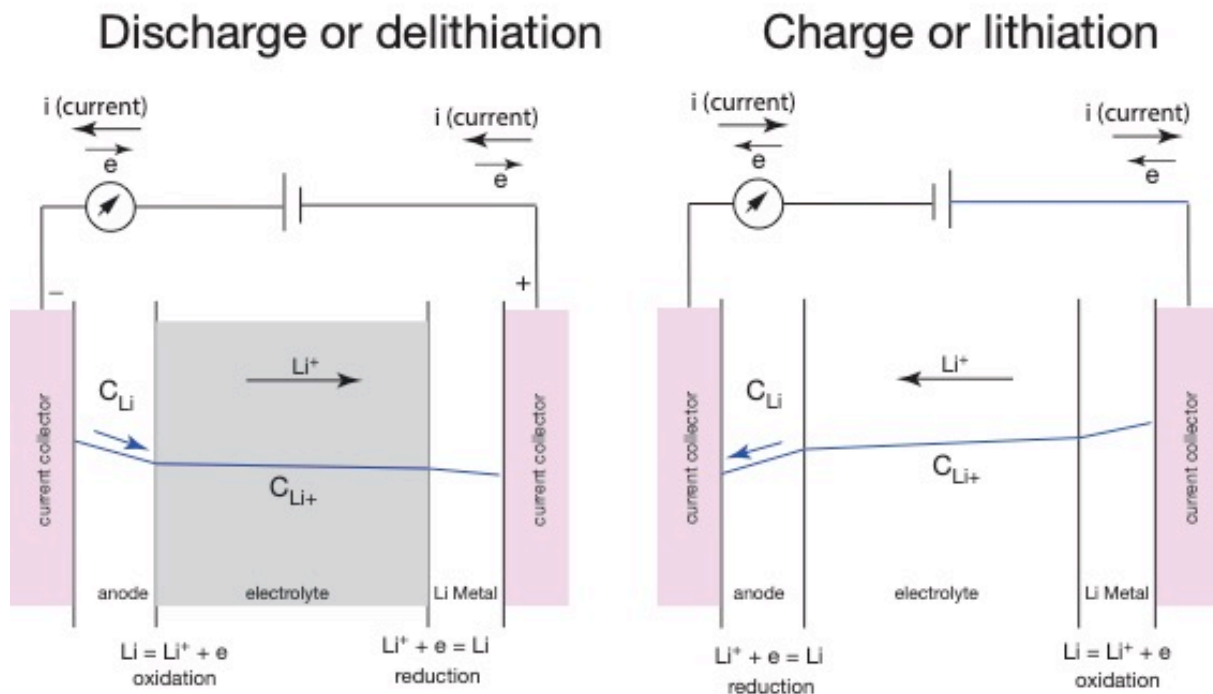
Fading is related to a decline in the charge capacity $\frac{mAh}{g}$ in the anode with:

- number of cycles

Experimental Method

Experiments are carried out by forcing a current through the "cell", and measuring the voltage with respect to Li metal at the other anode. These experiments are called "half cells", where the main electrode is the actual anode material (for example graphite) and the other electrode is Li metal.

Half Cell (anode/Li metal)



The Half-Cell is not a battery: it is a configuration to evaluate the capacity of the anode against Lithium metal (which serves as the reference).

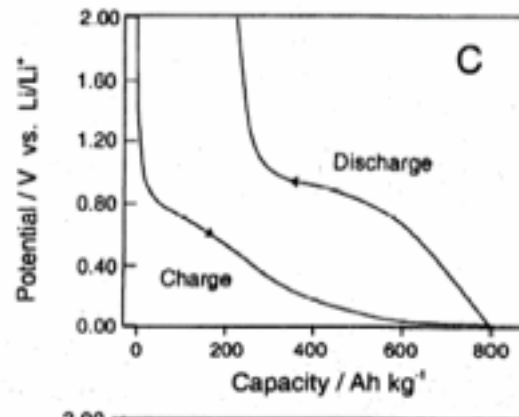
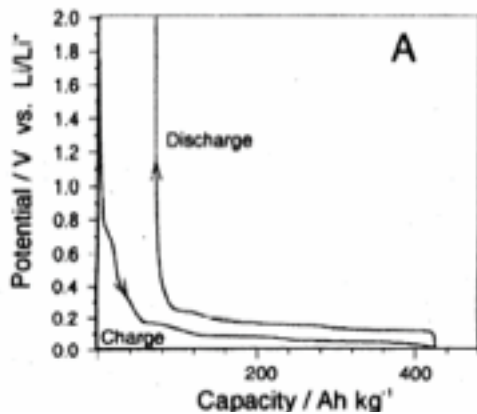
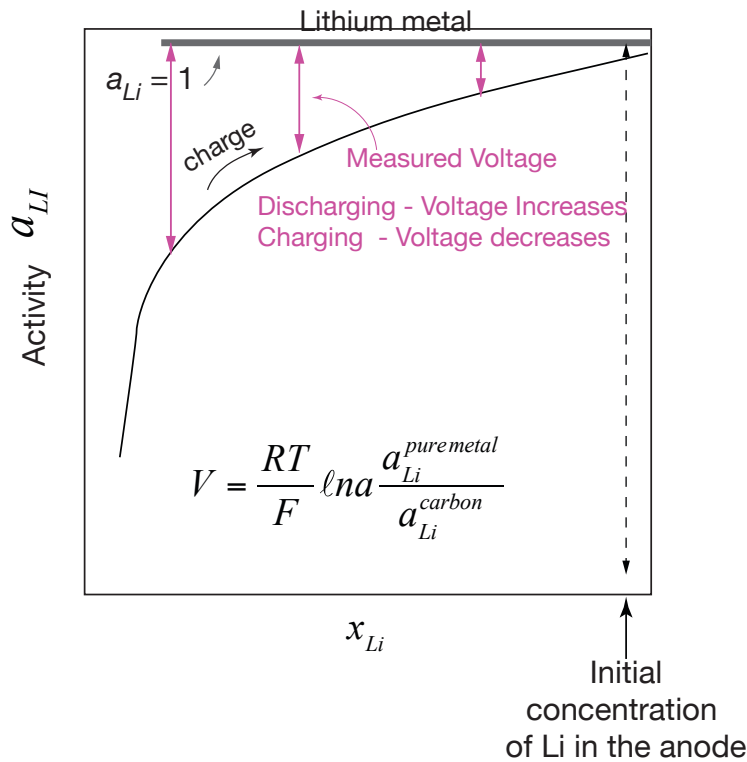
In a half cell, the Li^+ current is driven by an external power source. If the current drains the lithium from the anode then it is equivalent to discharge. If the current feeds Li into the anode then it is like charging.

Let us consider how the voltage will change as the anode is charged and discharged. We must consider the activity plot.

Discharge or delithiation - Li is drawn out of the anode towards the Li metal electrode

Charge or lithiation - Li metal is inserted into the anode transported from the Li metal electrode.

Half Cell: Used to measure the anode performance (graphite/silicon)



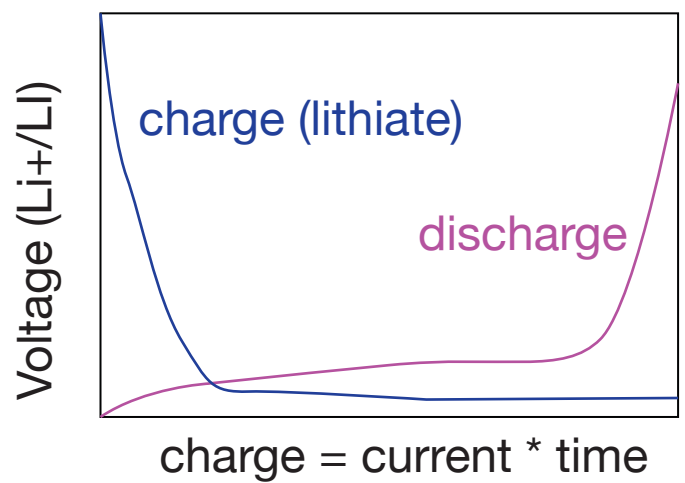
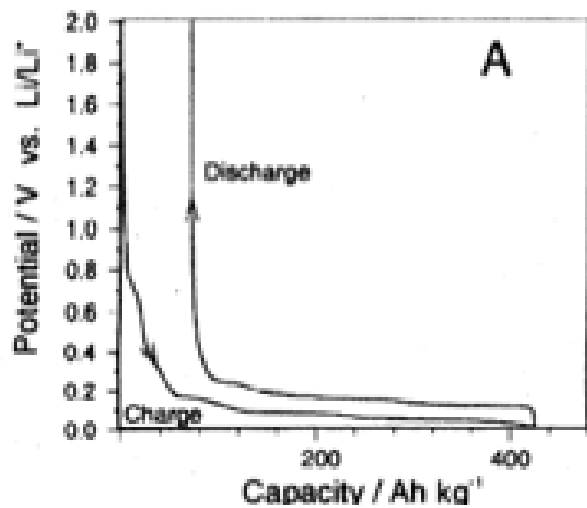
The above figure shows the results from two different types of carbon (processed differently)

The full cycle consists of (see the figure on the left above)

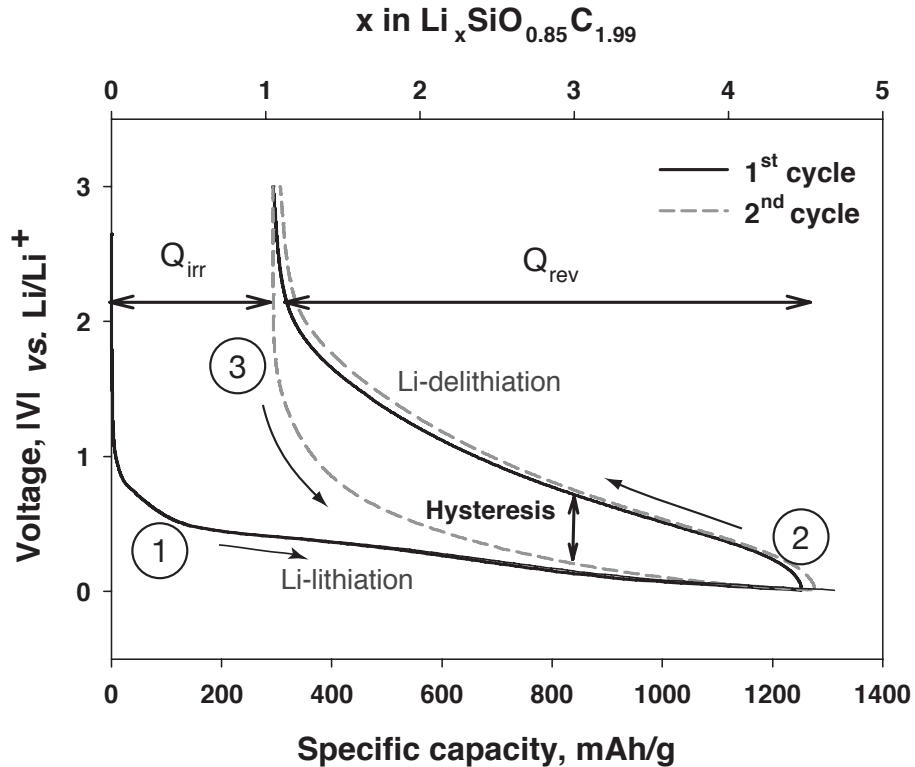
(i) Discharging a fully anode which holds +400 mAh/g until it is essentially depleted. This reaction is therefore carried out from the right to the left.

(ii) Re-lithiating the anode by forcing the current in the opposite direction, until the charge reaches its saturation value.

Lest there be confusion, another way of showing the above result (an equivalent result, not exact) is as follows:



The process is perhaps better illustrated from the following result obtained in our own laboratory:



Step 1: start with a virgin anode made from a carbonaceous material. The voltage drops to near zero (with respect to Li metal) when fully lithiated.

Step 2: Switch the applied current to delithiate. The voltage rises to the Nernst potential when the anode is empty.

Step 3: Recharge the anode until the voltage drops to near zero, that is the activity of lithium in the anode is the same as in pure lithium metal (the opposite electrode).

Note (i) the first cycles loss, and (ii) the hysteretic loss of energy: more work is done to insert the lithium into the anode than to draw it out from the anode. This deficit is dissipated as heat which requires cooling to operate the battery.

Measure Of Performance

$$\frac{mAh}{g}$$

How much capacity in does the graphite (for example) anode can deliver as a function of:

- The current rate (how fast the anode is discharged) - so called the C rate expressed as a number per hour. High rate reduces the available capacity
- Coulombic efficiency: what percent of the charged Coulombs can be available during discharge. First cycle loss is a huge concern.
- Fading: Declining capacity with cycles.

The charge and discharge data for two different carbon materials is shown on the right.

Element	Lithiated Phase	capacity, mAh/g	capacity, mAh/ml	Volume change, %
C	LiC ₆	372	833	12
Al	Li ₉ Al ₁₄	2235	6035	238
Si	Li ₂₁ Si ₅	4010	9340	297
Sn	Li ₁₇ Sn ₄	959	7000	257
Bi	Li ₃ Bi	385	3773	115

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Important Note: The linear expansion is one third of the volumetric expansion (approximately)

Strictly speaking the linear expansion (ϵ_1) should be derived from the volumetric expansion in the following way:

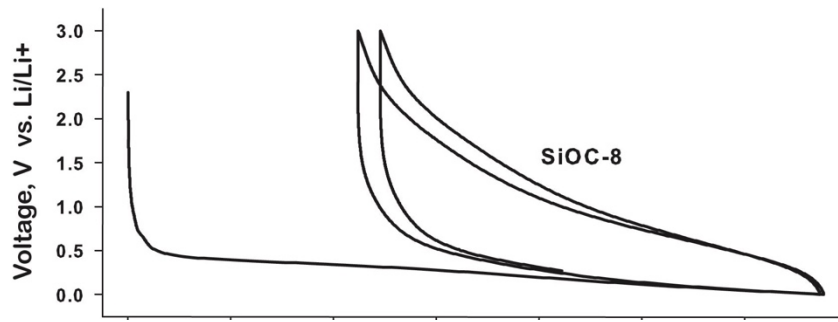
$$\epsilon_1 = \ln\left(\frac{L}{L_o}\right) = \ln\left(\frac{L_o + \Delta L}{L_o}\right) = \ln\left(1 + \frac{\Delta L}{L_o}\right) \approx \frac{\Delta L}{L_o} \quad \text{if } \frac{\Delta L}{L_o} \ll 1 \quad \text{(that is for small strain approximation)}$$

The volumetric strain $\epsilon_a = 3\epsilon_1$ since

$$\epsilon_a = \ln\left(\frac{V}{V_o}\right) = \ln\left(\frac{L_1}{L} \frac{L_2}{L} \frac{L_3}{L}\right) = \ln\left(\frac{L_1}{L}\right)^3 = 3\ln\left(\frac{L_1}{L}\right) = 3\epsilon_1$$

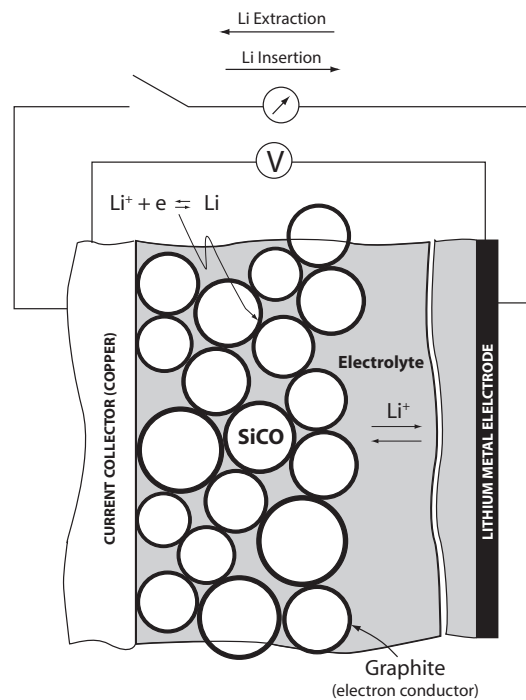
Fading

The capacity often decreases with cycles as shown below for two cycles in a carbonaceous material- this is called FADING



Fading often arises from fragmentation of the anode material which reduces the capacity of the anode from cycle to cycle. The main reason for fragmentation (fracture) is volumetric expansion and contraction associated with lithiation and delithiation which produces a tensile stress in the anode.

The anode consists of particles of the active anode materials which are coated with a conducting agent as shown below:



Analysis for the Mechanism of Fragmentation of the Anode Particles

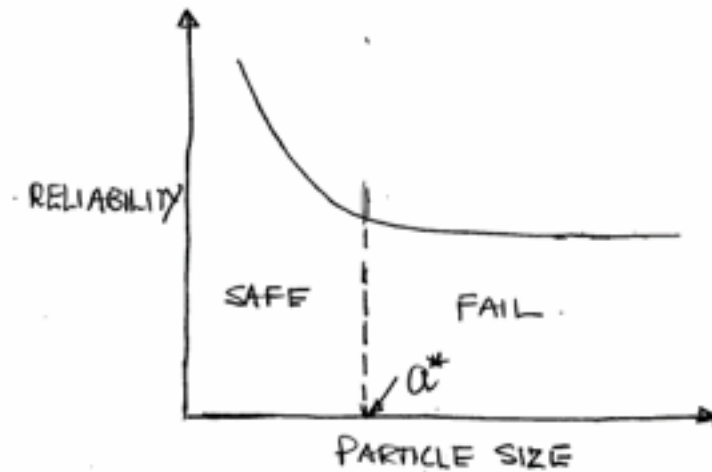
As in the table just above, the volume expansion *We recall the topic of fracture at small length scale, where we argued that when the length scale of the specimen becomes very small (or the same order as the flaw size) then the fracture strength can approach the "ideal value" which is expected to be about 15% of the elastic modulus. That is, fracture will occur if the strain is greater than 15%.*

This concept essentially rules out Si as a viable material. But even for the case of carbon the length scale of the anode architecture has to be below the threshold in order to invoke the concept of "ideal fracture" discussed earlier in the course.

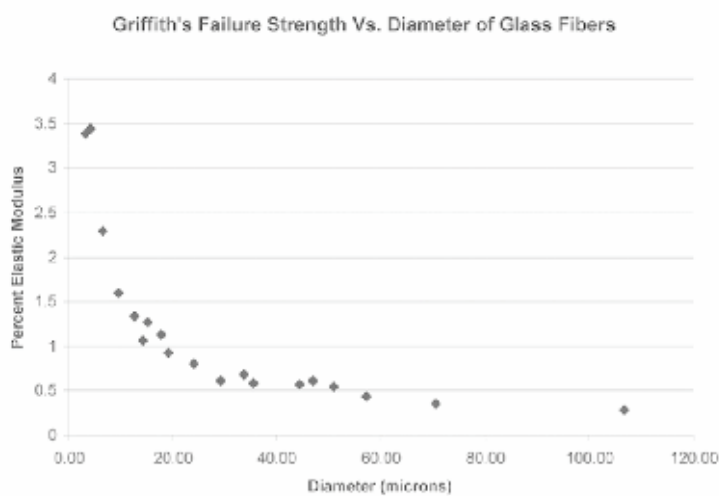
The carbon is in the form of small particles (recall the multilayer structure that was discussed in the context of HW 11).

The mechanism of lithium charge and discharge is that the Li^+ arrive at the surface of the particles where they react to give up (or absorb - depending on the charge or the discharge cycle) an electron. The electron is carried to the current collector from the conducting agent which coats the carbon particles. The conducting coating is actually carbon black. The caveat is that the carbon which stored Li has poor electronic conductivity, and therefore, requires a conducting agent, which is like itself.

Consider the stress distribution in the particles when lithium moves in and out of the carbon particles. As shown on the right the intercalation of Li induces a compressive stress in the surface of the particles, while the delithiation from the surface produces a tensile stress in the surface layer.. this tensile stress can cause the particle to fracture, leading to fading.



Recall the change in the fracture strength of glass fibers with their strength.

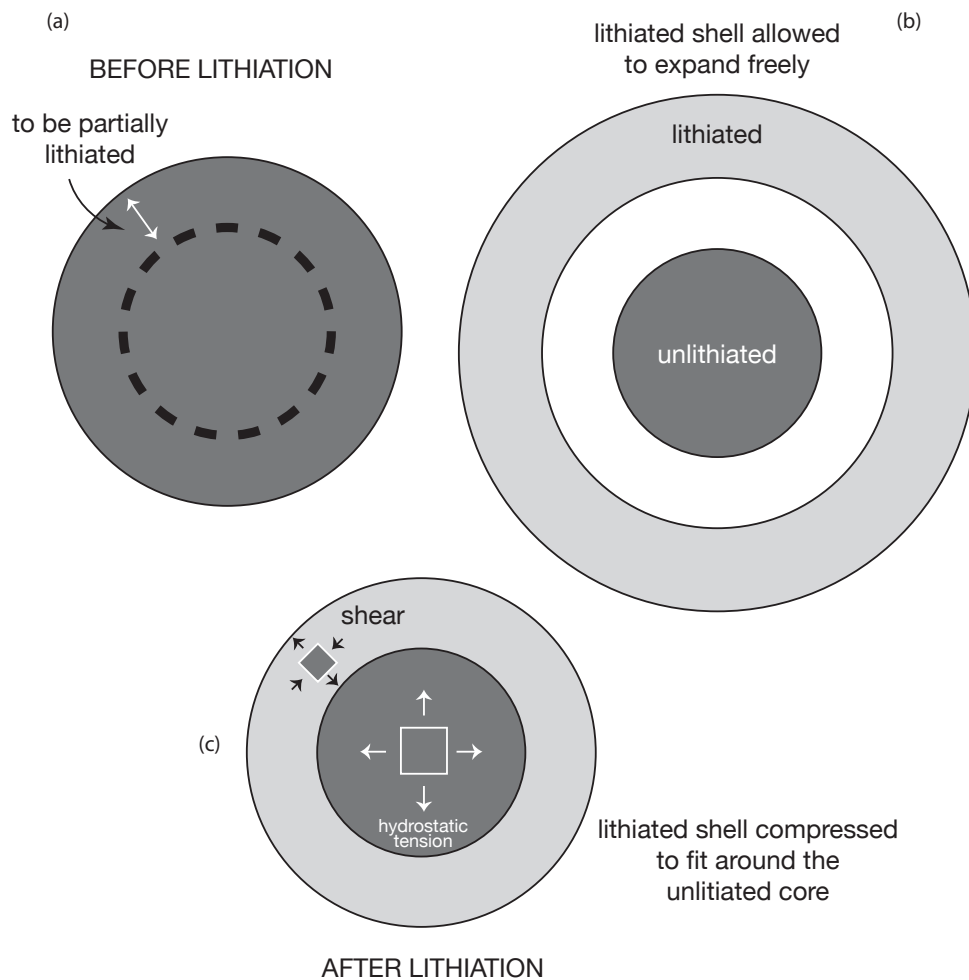


Here we accept that results from the topic of "Fracture at Small Length Scales".

Generation of Tensile Stress upon Volume Expansion and Contraction

As discussed above the theoretical limit stress for fracture is approximately 15% of the Young's modulus, that is, the particle will fracture when the elastic strain reaches 15% regardless of the size of the particles.

Here we address how tensile elastic strain is induced during lithiation (and delithiation). Note, as explained below, that elastic strains arise during the lithiation process, when the particles are only partly lithiated.



The generation of stress follows the following steps as explained above

- (i) An entirely unlithiated particle is shown in (a). The dotted line shows the boundary (to be) between lithiated and unlithiated portion of the particle.
- (ii) Lithium is allowed to enter up to the dotted line. The shell therefore expands since there is a volume change (in silicon this volume increase is 300%). In a gedanken experiment we separate the shell from the unlithiated core, so it is now free to expand. It is therefore bigger than the core.

(iii) The shell is now compressed to fit around the core. This step produces and compressive stress in the shell, and correspondingly a tensile strain within the core. This strain, which is hydrostatic, will be of the order of the volume expansion which is 300% (linear strain of about 100%), which is far greater than the theoretical fracture strength.

THE ABOVE DEPICTION IF FOR LITHIATION. WITH TIME (IF THE STRESS CAN SOMEHOW BE RELAXED - IT CAN BY SHEAR FLOW) THEN THE WHOLE PARTICLE WOULD HAVE UNIFORMLY EXPANDED.

Now consider delithiation of a fully lithiated particle, by the same method as above. Show that now the core will be placed in hydrostatic compression and the shell will encounter tensile stress.

CAVEATS:

(i) Volumetric expansion in lithiated graphite is approximately 12%, that is about 4% linear strain which is below the theoretical fracture strain limit.

(ii) A great deal of effort has been spent to accommodate the expansion in silicon by creating a porous space around it. But these efforts belie the theoretical upper bound in strength according to which fracture will prevail no matter what if the volume expansion is 300%

(iii) Fully intercalated silicon can have up to 7 Li atoms for each Si atom, that each silicon atom is surrounded by seven lithium atoms. Lithium atoms are very mobile (since lithium has a melting point of 180.5 °C) and therefore can flow in a viscous way to relax incompatible stresses. This time dependent relaxation can obviate fracture. Full analysis of this mechanism is only now being realized and has not yet been published.