that we have considered for the anode, a key
difference being that while anode is a Li atom
conductor the electrolyte must be a Li-ion
conductor. The essential attribute of the
electrolyte is that it should not conduct either Li
atoms or electrons.

(e)   The transport of Li across the battery is a
      dissipative process which generates heat. Thus
      thermal management is often a significant aspect of
      integrated battery design.

6. Volume Expansion Related to Lithium Insertion

6.1 Introduction

Insertion of Li atoms into the active anode material
often produces an increase in the volume of the host
material. Formally speaking, as discussed in the chapter on
Materials Science, this quantity is called the partial
molar volume of the Li: it is equal to the change in volume
of the solid solution of the lithium and the host, per mole
of Li added to the solution.

The increase in volume is important because a gradient
in the lithium concentration in particle of the anode
material would produce a gradient in the expansion, or
contraction, which will result in elastic stresses. These
stresses can cause the particle to fracture, and,
eventually, the cell to fail.

For engineering analysis the volume expansion upon lithium insertion is specified at the saturation values of lithium insertion into the anode, which are given in Table 1. These expansions can be very large, about 10% for graphite, but many times more for silicon. In this section we address the question of how failure arising from expansion and contraction is related to the particle size and the other material parameters of the active anode materials.
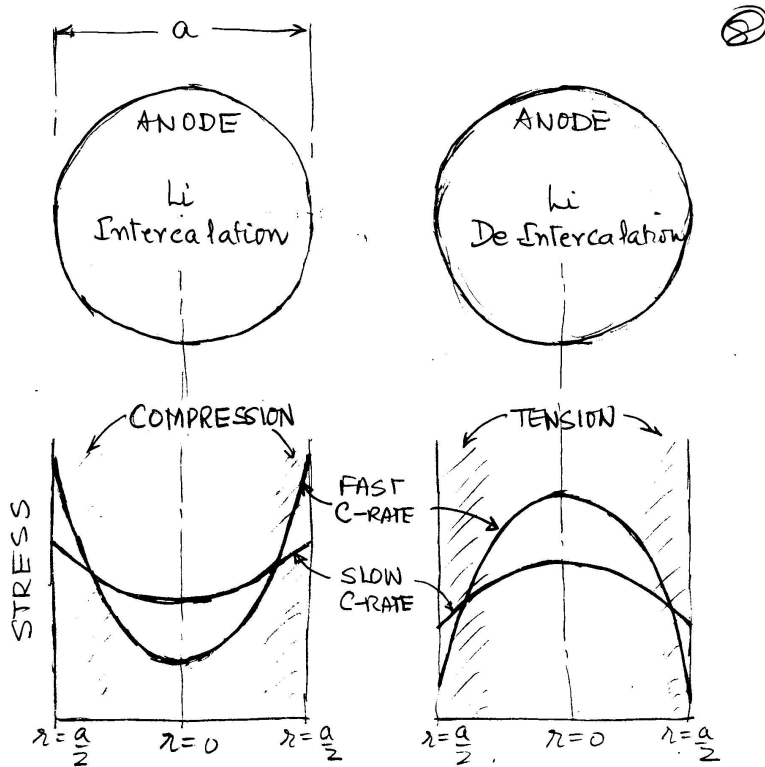

Figure 9: Concentration gradients of Li in the anode particles create compressive and tensile stresses in the anode particles because of the volume change.

The origin of stress in the particle is the gradient in the concentration of Li from the surface into the interior of the anode particles. Examples of these profiles during intercalation and de-intercalation are shown in Fig.

8. The stress swings from compressive to tensile during the charging and the discharging sweeps of the cycle.

The magnitude of the stresses will depend on (a) the amount of lithium inserted in the anode, (b) the rate at which it is inserted, and (c) the diffusivity of Li in the anode material. A higher rate of charge and discharge of Li, and a slower diffusivity of Li will lead to higher stresses, and thus a higher probability of failure. It is for this reason that one of the criteria of battery performance is the highest C-rate it can withstand at failure. C-rate is the inverse of the time taken to discharge the battery. The time is expressed in units of hours. For example a C-rate of 1C means that the battery is discharged in 1 h, 10C, in 0.1 h, and so on. The highest C-rate capability of anode materials is closely related to the volume expansion and contraction from Li insertion. A low value of volume expansion translates into tolerance for a higher C-rate. Remember that C-rate capacity is directly linked to the power density of the battery.

6.2 Approximate Analysis

The exact analysis for correlating the C-rate, diffusivity and particle—size, to failure—probability is complex. However, by the following approximate analysis one can find a parametric correlation between the volume expansion, the particle size and the probability of failure. The approach is to make an upper bound estimate of the strain energy that can be stored in the particle as a result of volume expansion and contraction. The particle

size dependence of failure is then derived by asking how much work is required to fracture the particle.
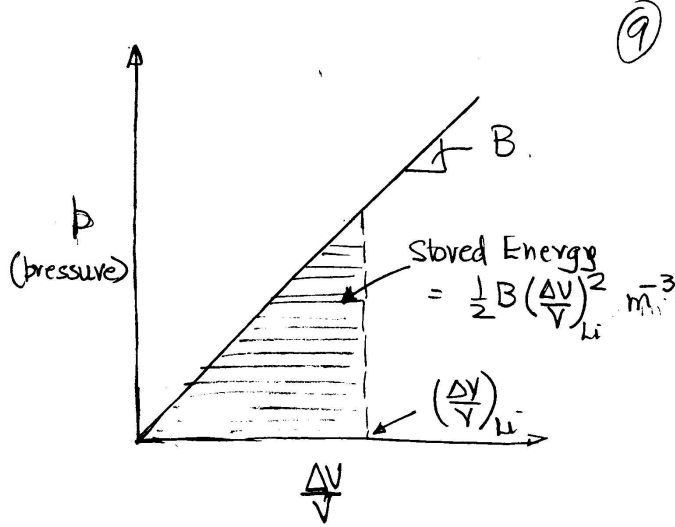

Figure 9: The upper bound of the energy stored in the particle is related to the bulk modulus and the volume change when Li intercalates into the anode.

We calculate the maximum strain energy that can be stored in the particle by enclosing the particle within rigid boundary, not allowing the particle to contract when lithium is removed from it. The constraint will give rise to a negative pressure on the particle, which will change linearly with the volume change, as shown in Fig. 9, with the slope being equal to the bulk modulus, B of the material. If the volume strain in the particle upon de—intercalation is $\left(\dfrac{\Delta V}{V}\right)_{Li}$ then the total strain energy in the particle, U_E, would be equal to the strain energy stored per unit volume, as shown in Fig. 9, multiplied by the volume of the particle:

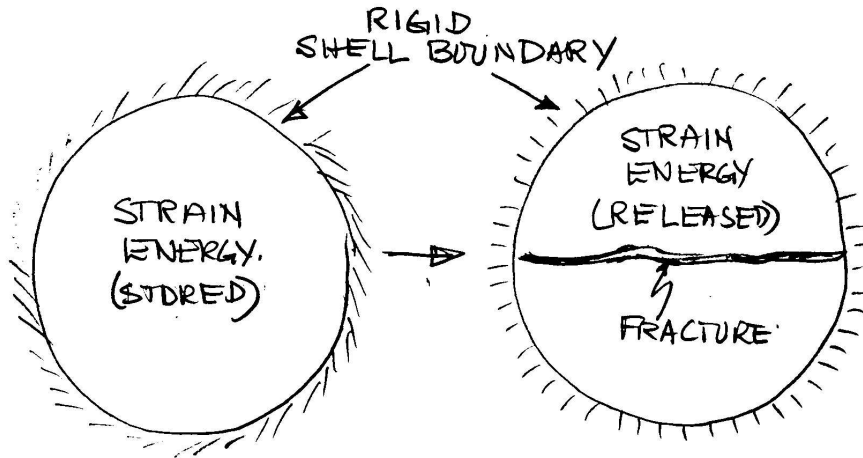$$U_E = \frac{1}{2} B \left(\frac{\Delta V}{V}\right)^2_{Li} . \frac{\pi}{6} a^3 \qquad (23)$$

Figure 10: The model considers the anode particle to be constrained by a rigid boundary, and then, the strain energy so created to cause the particle to fracture.

Let us now consider the work of fracture, which will break the particle into two halves, as shown in Fig. 10, thereby releasing the strain energy. The work of fracture is given by the fracture energy, γ_F, which is the work done to extend the fracture surface by one unit area. Therefore the work that must be done to fracture the particle, U_F, would be given by the work required per unit area multiplied by the new surface created by the fracture:

$$U_F = 2\gamma_F \frac{\pi}{4} a^2 \tag{24}$$

The factor of two in front arises because fracture creates two surfaces facing each other.

The FAIL/SAFE criterion is that obtained by comparing Eqns (23) and (24): the safe condition being that $U_F \geq U_E$.

This condition leads to an expression for a critical particle size, a^*:

$$a^* = \frac{6\gamma_F}{B(\Delta V / V)^2_{Li}} \tag{25}$$

where the "safe" condition obtains when, $a < a^*$.

The sketch in Fig. 11 illustrates the very important role of particle size in the reliability of Li ion batteries. Volume expansion failure as discussed here is often the cause of poor reliability.
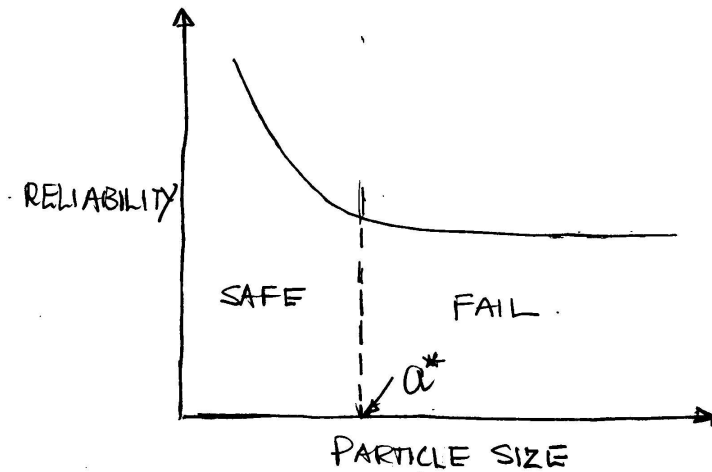

Figure 11: The reliability of the anode depends strongly on the particle size of the active material.

The condition derived in Eq. (25) gives guidelines for how the failure probability depends on the volume expansion. The critical particle size decreases as the second power of the volume expansion. The fracture energy and the bulk modulus also play a role, but are relatively less important when the anodes are made from brittle ceramics, which have

a low fracture energy (typically 5 to 10 Jm^{-2}),and a high bulk modulus (in the 70 to 150 GPa). The condition we have derived here, however, is severe since we assume the upper bound in the strain energy. In reality the stress induced in the particle depends on the C-rate, as discussed above; Eq. (25) does not address this issue.

Let us insert nominal values into the right hand side of Eq. (25). If γ_F=5 Jm^{-2}, B = 100 GPa, and $(\Delta V / V)_{Li} = 0.1$, then $a^* = 30$ nm. The actual values for the transition from "safe" to "fail" behavior is likely to occur when the particle size becomes about 100 nm.