Lithium Ion (Li+) Batteries

1. Introduction

A lithium ion battery, in its simplest description, consists of two electrodes separated by an electrolyte. The difference in the “chemical energy level” of Li atoms between the electrodes makes the battery function. The electrolyte has the special property of being able to conduct Li–ions but not Li atoms, and of being insulating with respect to electron transport. The electrode materials (the active materials) are selected in such a way that the native energy level of Li is higher in one electrode – the anode – than in the other electrode – the cathode. The architecture of the battery can be imagined like a sandwich with the electrolyte in the middle, and with electrical leads that carry a current of electrons from the electrodes to the outside electrical circuit.

The essential performance of the battery is measured (i) by its energy density, i.e. the Joules of energy that it can deliver per unit weight and/or per unit volume of the active materials, and (ii) by its power density, that is, the Watts per unit weight. The other parameters relate to the gradual loss of performance with cycling, life, and safety. A discussion of these latter issues is outside the scope of this book. We are concerned here with how the two performance parameters are related to the selection and the nanoscale design of the active materials.

At a fundamental level the energy density and the power density require an understanding of the thermodynamics and the kinetics of material properties, and how they work together in the battery. Thermodynamics gives the basis for the “open circuit voltage” or OCV that is measured at the electrode terminals when the current flowing through the battery is essentially zero. Kinetics, on the other hand is related to the rate of transport of Li, Li-ions and electrons through the circuit when the battery is “running”. Experimentally, the battery performance is characterized by measuring the current flowing through, and the concomitant voltage across the electrodes. These measurements can be carried out in different ways: by discharging and charging the battery at different rates (electrical current) and measuring the voltage, or applying a voltage and measuring the current.

This chapter begins with a brief description of the architecture of lithium ion batteries (LIB) and examples of electrode materials from which they can be constructed. The micro and nanostructure of the electrodes are discussed later in the chapter: it is there that we shall pull together fundamental science and nanoscale design to predict performance.

The sections following the description of the architecture deal first with thermodynamics of electrochemical systems, and next with their kinetics. While these sections contain numerical examples their relevance to the problem becomes apparent only when we apply them specifically to the nanoscale design of lithium ion batteries, in the later sections.

A description of the electrochemistry of LIBs requires terms and definitions that are peculiar to this field. OCV—the open circuit voltage—is already an example of this nomenclature. For the sake of reference these terms are listed at the end of the chapter. While numerical examples are given throughout, the student is strongly recommended to attempt the end—of-chapter problems to gain a visceral understanding of the subject matter.

2. The Architecture and Materials Selection for LIBs

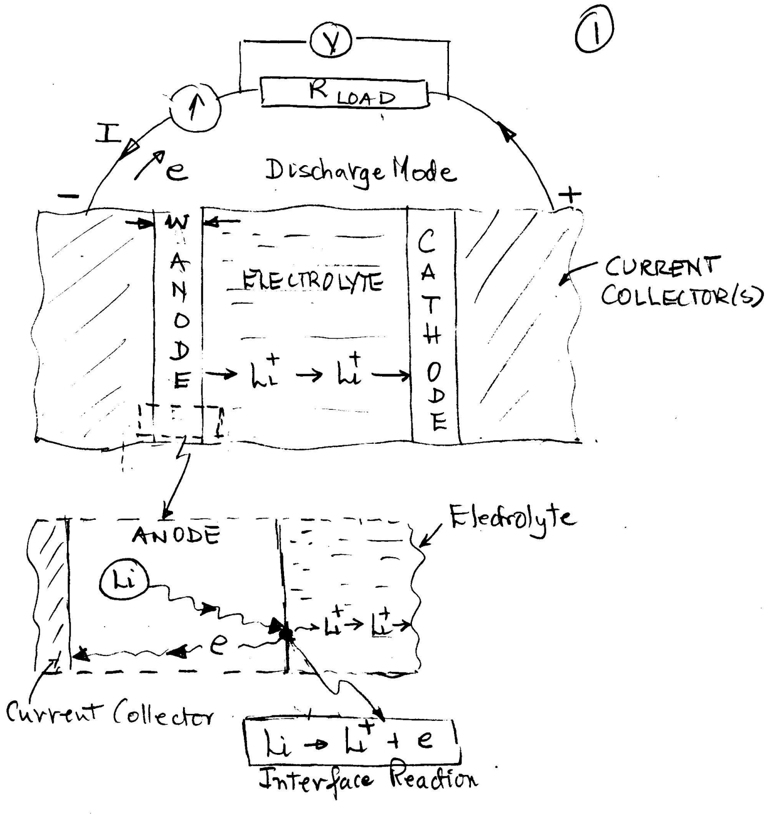


Figure 1: The basic architecture, reaction and transport processes in a lithium ion battery.

The schematic in Fig. 1 shows the general architecture of a LIB. It consists of a current collector, which serves as the gateway for the transfer of electrons from the electrodes to the outside circuit. The electrodes store lithium, chemically, but at two different energy levels. The battery converts this difference in energies into electrical work by the reactions written into Fig. 1. Let us consider the reaction at the anode carefully. The Li atom in the anode is converted into Li^+ where it touches the electrolyte, by releasing an electron. For this reaction to occur successfully the electron must be transported away from this anode/electrolyte interface to the current collector, while the Li^+ must be able to diffuse away into the electrolyte towards the cathode. The viability of this reaction therefore places the following requirements on the design and selection of materials for the anode, the electrolyte and the electrode:

(a) The anode must be able to transport electrons, as well as be able to store lithium at a high potential (and the cathode at a low potential). The caveat is that the active anodes materials are sometimes conducting with respect electrons (graphite for example) and sometimes not (such as lithium titanate). The same dichotomy holds for the cathode materials. When the active material is not electronically conducting then the anode must be a nanocomposite made by combining a “conducting agent” with non-conducting active material.

(b) The electrolyte must be able to rapidly transport Li^+, but should not conduct electrons. Furthermore it must have negligible solubility for neutral Li atoms, otherwise Li will simply diffuse as neutral species from the anode to the cathode, negating the battery function.

(c) The current collector material should be chosen so that it does not dissolve lithium atoms into itself, thus draining the electrodes of their lithium content. (Remember that the amount of energy that can be stored in the battery is essentially equal to how many lithium atoms can be stored in the anode and in the cathode.) Since the current collectors are clearly electron conductors, and not Li^+ conductors, they can dissolve only neutral Li atoms. Copper is the material of choice at the anode. At the cathode, where the chemical potential of lithium is much lower, there is greater choice since any metal which holds lithium at a chemical potential that is significantly higher than the intrinsic potential in the cathode, will do. As such aluminum is often the choice for the current collector on the cathode side. Aluminum is cheaper than copper.

The amount of power that can be delivered to the external load, R_L, is limited by internal losses within the battery. One measure of this internal loss is the effective internal resistance of the battery, R_I, If a current I flows through the battery then it leads to a voltage drop that subtracts from the OCV, so that the voltage available to the external circuit, V, is now given by:

$$V = V_{OCV} - R_I I \qquad (1)$$

(In addition to resistive losses there can also be internal back potentials, produced by electrical polarization at the electrodes that reduce the available voltage. A discussion of these effects can be found in books dedicated to electrochemistry.)

It is immediately evident from Eq. (1) that the amount of power available from a battery depends critically on the internal resistance since the power loss within the battery is equal to $R_I I^2$.

The internal resistance of the battery, R_I can arise from the transport of Li^+ through the electrolyte, the transport of Li atoms through the electrodes, and the transport of electrons through the electrodes and the current collectors. All of them contribute additively in some measure to the total internal resistance. Nearly always the electronic resistance is negligible. The diffusive transport of Li^+ through the electrolyte and the diffusion of Li atoms through the electrodes are often the rate controlling phenomena. Liquid electrolytes such as LFP_6 are fast conductors of Li^+; in these instances the diffusion of Li through the electrodes becomes important. When solid–state electrolytes are used then they, as well as the electrodes contribute to the internal resistance. For the sake of fundamental discussion it suffices to consider how the nanostructure of the electrode can affect the internal resistance. In this chapter we discuss how the nanostructure of the anode is related to this internal resistance. These derivations however have generality and equally valid to the properties of the cathode and the solid state electrolyte. The essential problem we pose for ourselves is how the internal resistance depends on the structure and the materials selection of the anode, the first relating to the nanocomposite nature of the electrode, and the second to the diffusive transport of Li atoms in the active material.

Examples of active materials for the anode and the cathode are given in Table 1. Note that the performance of the electrode materials is given in terms of mAh/g. This number is directly related to the amount of Li atoms the electrode material can hold. One mole of Li atoms corresponds to 1 mol of electron charge since Li and has a charge number of one. To convert mAh into Coulombs we divide by 1,000, to convert mA to A, and multiply by 3600 to convert h into s. Therefore 1 mAh is equal to 3.6 Coulombs. One Faraday, or F, is equal to the number of Coulombs of charge held by one mole of electrons. It is equal to the charge on one electron, 1.6×10^{-19} C, times the Avogadro's number, 6.02×10^{23}, which gives that F=96,500 C mol^{-1}. Therefore 1 mAh is equivalent to $(3.6/96500)=3.6 \times 10^{-5}$ moles of Li. Therefore if the active electrode materials holds 1 mAh/g that is equivalent to 3.6×10^{-5} mol of Li per g of the electrode material.

The storage capacities for several anode and cathode materials are given in Table 1. The selection of a material depends not only on the capacity but also upon its durability, on whether or not it is electronically conducting (being conducting is preferred of course), upon how fast Li atoms can diffuse through the material since that affects how quickly the battery can deliver energy, i.e. its power density, and lastly and most importantly cost competitiveness. One of the issues affecting durability is the volume expansion and contraction in the material associated with intercalation and de–intercalation of lithium. These repetitive expansions and contraction cycles cause fracture and thus failure of the cell; we shall discuss this point later since the nanoscale design of the electrode structure can help to reduce the risk of this type of failure.

Table 1: Storage capacity of various anode and cathode materials.

Materials	Specific capacity, mAhg^{-1}
Anode Materials	
Lithium Titanate	140
Hard carbon	527
Sphere graphite	364
MCMB (special carbon)	340
Silicon	3200
Tin	638
Tin Oxide	850
Cathode Materials	
LiCoO2	170
LiNi0.8Co0.15Al0.05O2	160
LiFePO4	160
LiCo0.3Ni0.7O2	165
LiMn0.67Ni0.33O2	250

Finally we discuss the effect of the thickness of the electrodes, shown by *w* in Fig. 1 on the energy density of the battery as a whole. The battery has a sandwich architecture in order to reduce the distance Li atoms and ions have to travel in between the electrodes to deliver energy. The shorter this distance the quicker they can move from one side to the other and the faster the energy can be delivered. In other words a shorter travel distance means a higher *power density*; thus, from this point of view, the electrodes shown be thin, giving the battery a sheet like appearance. The *energy density*, on the other hand, is a volumetric quantity being related simply to how much lithium can be stored in the active materials. Therefore, a high energy density requires the electrodes to be thick; the reason is that the total weight of the battery includes an overhead, over and above the weight of the active electrode materials. The electrolyte, the current collectors and other packaging constitute nearly two thirds of the battery weight. If a given volume of the anode material is distributed into several sheet electrodes, the collateral weight associated with the "overhead" goes up, and the overall energy density of the battery suffers.

Thus, the dichotomy between power density and energy density arises because the energy density is simply proportional to the total volume of the electrode material: it is independent of the thickness of the electrodes. But, the power density is higher if the electrodes are thinner. The use of thinner electrodes means that the overhead on the weight, from collateral components becomes greater raising the weight of the battery without increasing its storage capacity.

It is for this reason that batteries are often engineered by normalizing its energy and power capacities with respect to the interface area of the electrodes. The thicker the electrodes the higher the energy density per unit area of the electrodes. The power density depends on the how much current the battery can deliver per unit area of the electrodes. The current depends on how fast the Li atoms can diffuse across the electrodes. Thus thinner electrodes can deliver a higher current, imparting a higher power density to the battery. The thickness must be optimized in order to find a balance between the energy density and the power density. The design of the nanostructure to enhance the diffusivity of Li atoms can directly improve the power density, without sacrificing the power density. We shall return to this point later in the chapter.

The next two sections discuss the fundamentals of the thermodynamics and kinetics that will form the foundation for the nanoscale design and engineering of the lithium ion batteries, later on. Remember to differentiate between thermodynamics and kinetic phenomena: thermodynamics is related to the “energy levels” of different states of a system. For example the potential energy of the water level which is raised higher by a dam is a thermodynamic quantity that is related to the height (the state) of the dam. Kinetics explains the rate at which energy can be extracted between two different levels of a given species. Again in the water dam analogy, the rate at which water can flow over the height of the dam delivering energy to a turbine is a kinetics issue. Kinetics always involves irreversible processes, in other words energy loss that cannot be recovered. In the dam analogy the viscous flow of water dissipates energy that cannot be delivered to the turbine. The magnitude of these irreversible losses depends on how fast the energy is extracted, that is they are rate dependent. In the case of the lithium ion battery, it is immediately evident from Eq. (1) that the energy loss, $R_L I^2$, increases with the current, that is, the faster the battery is drained the greater is the loss, and the lower is the power density that the battery can deliver.

Therefore, a fundamental study of LIBs can be separated into thermodynamics and kinetics. The first is related to intrinsic properties of materials, and therefore influences material selection. Kinetics, on the other hand requires an understanding of now the nanostructure anode, viewed as a composite material, can be optimized in order to maximize performance.

3. Electrochemical Thermodynamics

3.1 Gibbs Free Energy

In the Materials Science chapter we described the thermodynamic properties of chemical systems in terms of their Gibbs Free Energy. A given *state* of the system had a specific free energy. If two states had the same free energy then they were in equilibrium with one another. A difference in the free energy implied that reactions would occur such that their free energies would tend to converge. Thus the difference between the free energy provided the thermodynamic driving force for these reactions.

Gibbs Free Energy has units of work, usually normalized with respect to one mole of the chemical compound, and, therefore, expressed as kJ mol^{-1}. This work can also be expressed as electrical work. In electrostatics work is described by the act of moving an electron between two potentials. The potential is given the units of volts.

The work done is then equal to the charge on an electron multiplied by the voltage difference. This product of charge, when expressed in Coulombs and the voltage difference when expressed in volts, has the units of Joules. Indeed this description of energy leads to a new unit of energy which we call eV, which is equal to the work done to move one electron charge across a difference in potential equal to 1 V. Since the charge on one electron is 1.6 x 10^{-19} C, one eV is equal to 1.6 x 10^{-19} J per electron. The work done to move one mole of electrons across a potential difference of one volt is equal to one Faraday unit of charge multiplied by one, which is equal to 96.5 kJ mol^{-1}. In this way equivalence between electrostatics and chemical thermodynamics is established. To summarize:

$$V \equiv \frac{\Delta G}{nF} \qquad (2)$$

where V is the volts—difference equivalent of difference in the chemical free energy, ΔG in units of J mol^{-1}. F is a Faraday, equal to 96,500 Coulombs, and n is the charge number. The ionization of Li into (Li^++e), for example means that n=1. Ionization of oxygen involves two electrons, so that n=2, and so on.

Let us apply equation (2) to determine the decomposition potential for the electrolysis of water. Water can be decomposed into hydrogen and oxygen if a voltage greater than 1.25 V is applied across two platinum electrodes. This voltage is related to the chemical free energy for forming water from its constituents, which can be read from thermodynamic tables (see Chapter on Materials Science):

$$H_2O = H_2 + \tfrac{1}{2}O_2 \qquad \Delta G = +240\ \text{kJ mol}^{-1} \qquad (3)$$

The above reaction can be expressed as the *sum* of the following electrochemical reactions:

$$H_2O = 2H^+ + O^{2-}$$
$$2H^+ + 2e = H_2$$
$$O^{2-} - 2e = O_2 \qquad (4)$$

Note that the electrochemical reactions involve two electron charges, therefore n = 2. Substituting the values for ΔG, and n, into equation to we obtain the number for the decomposition voltage of 1.25 V, its handbook value.

3.2 The Electrochemical Potential of Electrons

The chemical potential, is, as its name implies, the electrical equivalent of eV. For example, as discussed in the chapter on Physics, the Fermi level of electrons in a metal is the equivalent of the chemical potential: it is the potential at which the electron interacts with electrons in another system. For example, if two metals with different Fermi levels are brought into contact then the electrons in the metal with the higher Fermi level will flow into the metal with the lower potential. If a potential difference is applied across a bar of a metal, then the chemical potential of the electrons at one end become higher relative to the other end, providing the driving force for the electrons to flow from one side to the other. Let us see how this simple picture of a gradient in potential leads us to the well known Ohm’s law, which states that the electrical field (the gradient of the potential) is proportional to the current density via the specific conductivity of the metal.

We begin by expanding the definition of chemical potential to include the influence of an applied voltage, which leads to the definition of the *electrochemical potential*:

$$\tilde{\eta}_e = \mu_e^o + eV \qquad (5)$$

where $\tilde{\eta}_e$ is the electrochemical potential of the electrons, μ_e^o is the standard, or reference potential, e is the charge on an electron in Coulombs, and V is the voltage. The standard potential of the electrons is none other that the Fermi level we had discussed in the chapter on Physics.

Let us reflect for a moment on the salient features of Eq. (5): (a) The definition of the electrochemical potential is specific to a given species, in this instance the electrons, (b) The chemical potential for the electrons is also specific to the state of electrons in a certain system of species. For example copper would have a different chemical potential than tungsten. If tungsten is alloyed into copper then the chemical potential of the electrons in the copper alloy would change, because the chemistry of the system has changed. (c) In a given system the voltage can vary spatially, as in the Ohm’s Law experiment. Just as a gradient of chemical potential of a species can give rise to a diffusion flux of that species in a chemical system as discussed in materials science, so can a gradient in the electrochemical potential. Indeed the equation for diffusion flux discussed in Materials Science applies equally well to gradients of electrochemical potential, which leads immediately to:

$$j_e = -\frac{D_e c_e}{k_B T}\frac{d\eta_e}{dx} \qquad (6)$$

Here, j_e is the flux of the electrons, with units of number of electrons flowing through a unit cross section per unit time, D_e is the "true" diffusivity of the electron species having the units of $\mathrm{m^2 s^{-1}}$ and c_e is the concentration of electrons in units of species per unit volume. It is left to the student to show that Eq. (6) reduces to the classical Ohm's law, which specifies a linear relationship between the current density and the electrical field:

$$i_e = \sigma_e \frac{dV}{dx} \qquad (7)$$

where,

$$\sigma_e = \frac{D_e c_e e^2}{k_B T} \qquad (8)$$

Here i_e is the current density in Amperes $\mathrm{m^{-2}}$, and σ_e is the specific conductivity in units of $(\mathrm{Ohm\ m})^{-1}$.

In an Ohm's Law experiment the electrodes to measure the conductivity of a metal, say copper, must made from the same metal, say tungsten. Therefore the standard chemical potential of the electrons at the two ends of the copper specimen are equal and the only driving force for the transport of electrons derives from the applied potential gradient. In this experiment the electrodes are *non–blocking*, that is, the electrons can flow freely from the specimen to the outer electrodes.

3.3 The Nernst Potential in Electrochemical Cells

The situation becomes immediately much more complicated if the system is such that in addition to electrons, the charge can also be transported by an ionic species. Consider an idealized lithium ion battery, as sketched in Fig. 1. The heart of the system consists of an electrolyte and two electrodes on either side. The electrolyte is non–conducting to electrons but highly conducting to Li^+. The two sides of the electrolyte are in contact with reservoirs of Li atoms that hold Li at different chemical potentials – in the anode this potential is high, in the cathode it is low. To simplify the discussion we assume that the cathode and the anode are electron conductors. Furthermore, Li *atoms* are assumed to be highly mobile in both electrodes.

The electrodes are connected to metal conductors that are impermeable to Li. These conductors are connected to an outside electrical circuit which can be used to draw electrical work from the battery. Let us now consider the salient features of this battery system, and draw a distinction between the Ohms law experiment and the battery.

The cathode and the anode are blocking to Li$^+$ since the electrodes cannot transport lithium–ions. However, if the Li atoms were to give up an electron at the anode then Li$^+$ could be injected into the electrolyte. Conversely, aat the cathode, the absorption of an electron would convert a Li$^+$ into lithium metal atoms which could then diffuse into the cathode. These events are described by the following equations:

$Li - e = Li^+$ (at the anode; Fig. 1) (9)

$Li^+ + e = Li$ (at the cathode; Fig. 1) (10)

(The terminology of anode and cathode is consistently defined by the oxidation and reduction reactions. Oxidation is a process of removing an electron from a species: it occurs at the anode. Reduction, on the other hand, is the addition of an electron to a species, which takes place at the cathode.)

We can show that the difference between the *chemical potential* of Li atoms between the anode and the cathode is converted into a voltage difference at the two electrodes, which can be measured with a voltmeter (a voltmeter, by definition has a infinitely high resistance so that it does not draw a current). This is called the open–circuit voltage, OCV. The electrochemical potentials for the lithium atoms at the electrodes, differentiated by subscripts *C* and *A* for the cathode and the anode, can be immediately written as:

$$\tilde{\eta}_{Li}^{C} = \mu_{Li}^{0} + k_B T \ell n \; a_{Li}^{C} \qquad (11)$$

and,

$$\tilde{\eta}_{Li}^{A} = \mu_{Li}^{0} + k_B T \ell n \; a_{Li}^{A} \qquad (12)$$

Note the absence of the *eV* term on the right hand side because Li atoms are neutral species whose potential is unaffected by electrostatic fields. In the above μ_{Li}^{0} is the standard state for Li atoms, assumed here to be pure lithium metal with an activity of unity, while a_{Li}^{C} and a_{Li}^{A} are the activities of Li at the cathode and the anode. Please refer to the Materials Science chapter for a discussion of *activity*.

The electrochemical potentials of Li at the two electrodes may be related to one another by enforcing equilibrium between the lithium atoms, the lithium ions and the electrons, by enforcing Eqns (9) and (10), which leads to the following relationships:

$$\tilde{\eta}_{Li}^{A} - \tilde{\eta}_{e}^{A} = \tilde{\eta}_{Li+}^{A} \qquad (13)$$

$$\tilde{\eta}_{Li+}^{C} + \tilde{\eta}_{e}^{C} = \tilde{\eta}_{Li}^{C} \qquad (14)$$

In the open circuit condition, the high mobility of the ions in the electrolyte will cause their electrochemical potentials to become equal.
Inserting Eqs(5), (11) and (12), into (13) and (14) and setting $\tilde{\eta}_{Li+}^{C} = \tilde{\eta}_{Li+}^{A}$ gives the following important result:

$$V_C - V_A = \frac{k_B T}{e} \ell n \frac{a_{Li}^A}{a_{Li}^C} \qquad \text{sd(11)}$$

Equation (11) is known as the Nernst Equation, which is usually written as:

$$\Delta V = \frac{RT}{nF} \ell n \frac{a_i^A}{a_i^C} \qquad (12)$$

The quantity *n* is the charge number on the ions (named *i* in the above equation), which was equal to one for the lithium ions, *F* is the Faraday constant equal to the charge on one mole of electrons, which compensates for the gas constant, *R*, being equal to the Boltzmann's constant times the Avogadro's number.

Let us consider, briefly, the meaning of activity in the context of lithium ion batteries. As noted in Eqs (11 & 12) it is a powerful way of expressing the chemical potential of a species in a system. The chemical potential of a species is the measure of how the Gibbs Free Energy of the system changes when one mole of species is added to the system. Thus the total free energy of the system is equal to sum of the products of the molar concentration times the chemical potential of all species in the system. The activity, therefore, gives us a measure of the chemical state of a given species in a system. Often, when dealing with practical problems, we are interested in how the thermodynamic analysis can be related to the molar concentration of a given species. For example, we would like to know how the activity of lithium in a graphite anode is related to molar concentration of lithium in it. Therefore we write that:

$$a_i = \gamma_i x_i \tag{13}$$

where $a, \gamma,$ and x are the activity, the activity coefficient, and the molar concentration of the species i. The highest value of the activity is equal to one, corresponding to the chemical potential of the standard state, which is always taken to be the state of that species when it is pure element or molecule. For example for the Li ion batteries $a_{Li} = 1$ corresponds to pure lithium metal at the temperature of the battery.

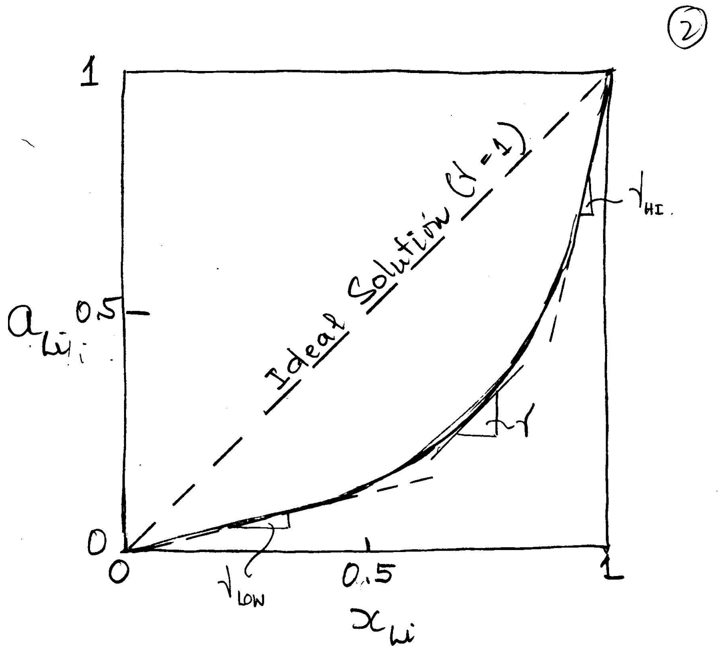


Figure 2: The change in activity with the molar concentration for the full range.

The activity therefore has a range from 0 to 1, as the molar concentration changes from 0 to 1. The shape of this relationship in lithium ion batteries is given in Fig. 2 (the dashed line illustrates the case of an "ideal solution" where the activity coefficient is equal to unity). The activity coefficient is the slope of this curve at any point – it varies with the concentration, but in a certain range, at low molar concentrations or high molar concentration the slope can be approximately constant, meaning that the activity coefficient has a constant value within a certain limited range.

3.4 Relationship between the Electrochemical Potential, the Activity and the Open–Circuit–Voltage (OCV) in LIBs

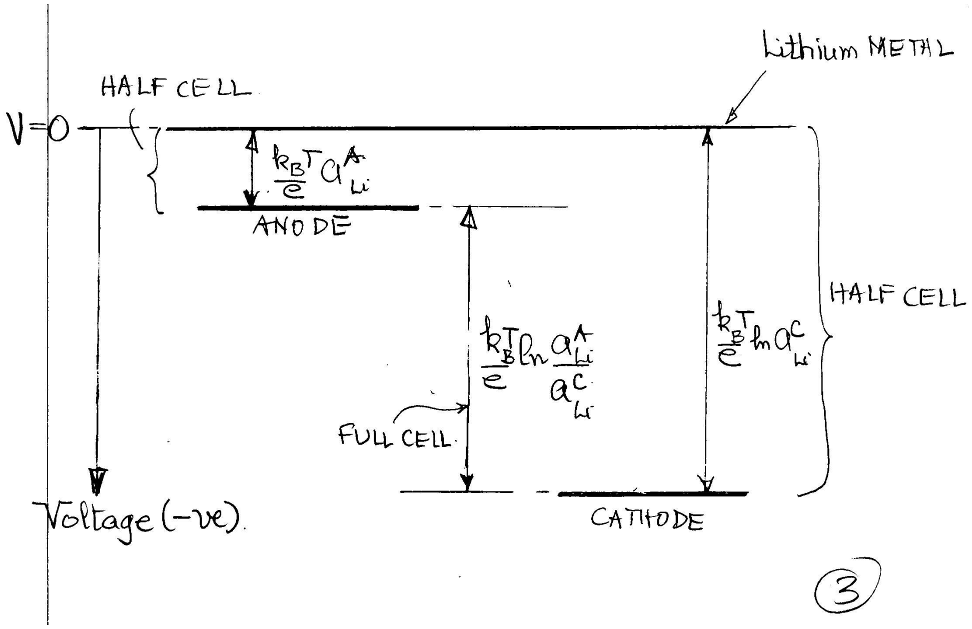


Figure 3: A schematic of energy levels of Li in the anode and the cathode, and their electrical equivalent.

As prescribed by Eq. (11) the OCV of a lithium ion battery depends on the ratio of the activities of lithium in the anode and the cathode. Let us draw an "energy level" diagram for the battery using pure lithium metal as the reference electrode. The potentials with respect to lithium metal can then be shown as in Fig. 3, where ΔV_A is the voltage of the anode and ΔV_C is the voltage at the cathode. The OCV for the battery is then given by $(\Delta V_A - \Delta V_B)$, which is equal to the right hand side of Eq. (11). Since the OCV is related to the activities of Li in the anode and the cathode, and since the activities vary with molar concentration of Li, as sketched in Fig. 2, it immediately follows that the maximum voltage available from the battery will likely change as the charge stored in the battery changes.

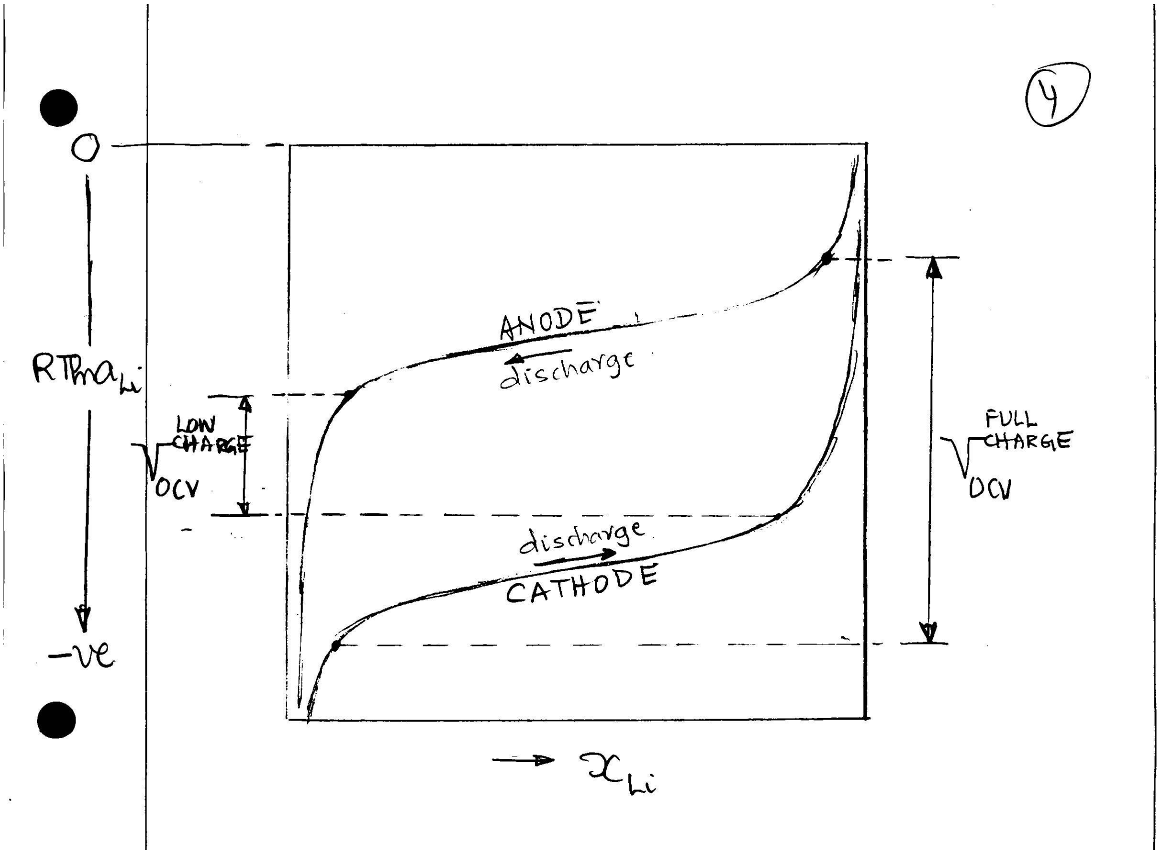


Figure 4: The change in the OCV of the battery at full charge and at low charge is related to the shape of the curves for the logarithm of the activity vs Li concentration.

Let us think about this issue by considering curves for the *logarithm of the activity* in the anode and the cathode, as a function of the molar concentration of Li in these two materials. The activity must have the limits of 0 when $x_{Li} = 0$, and 1 when $x_{Li} = 1$. Thus the logarithm of the activity must approach $-\infty$ at one extreme and 0 at the other. Consider now how the OCV will change as Li is transferred from the anode to the cathode, i.e. as the battery gradually discharges. When the battery is full the Li concentration is high in the anode and low in the cathode, giving an OCV of V_{full}. When the battery is nearly discharged the OCV will be given by V_{low}, as shown graphically in Fig. 4. This exercise makes clear that the chemical selection and design of the anode and cathode materials must pay attention to how the activity of lithium in them varies with lithium content. The maximum power that can be delivered by the battery is related to the OCV, and, therefore, how this power level changes with the charge level of the battery depends on how the activity varies with concentration.

Before leaving this section we refer again to Fig. 3 to give definitions to a “half—cell” and the “full-cell”, terms that are commonly used in the battery and fuel cell communities. A half—cell is a battery made by using lithium metal as one of the electrodes; there can be an anode half cell and a cathode half cell. The OCV of these half—cells would be ΔV_A, and ΔV_C. Often half—cells are used to evaluate anode materials, or cathode materials, before attempting to insert them into a full battery. The meaning of a full—cell is self—evident.

4. Electrochemical Kinetics

4.1 The Diffusion Equations

Whereas thermodynamics tells the direction in which a reaction would occur (higher chemical potential to a lower one), and also, provides the driving force for the reaction (equal to the difference between the chemical potentials), the rate at which that reaction occurs is described by kinetics. In the present problem the situation is rather simple since only the Li atoms and ions are the mobile species (actually the electrons are also traveling but they are nearly always much more mobile than the atoms or the ions, so they rarely limit the overall kinetics).

Nearly always the reaction pathway consists of several steps. For example consider the transport of Li from the anode to the cathode in Fig. 1. The first step in the reaction occurs at the anode/electrolyte interface, $\mathrm{Li} = \mathrm{Li}^{+} + e$. In order for this reaction to continue, the Li^{+} must move across the electrolyte towards the cathode, and, at the same time the electron must move through the anode to the current collector. (Note that the anode has been assumed to be an electron conductor – this is not always the case, and we shall discuss this point later.) At the same time the Li, that is removed from the anode at the electrolyte interface, must be replenished with Li atoms from the farther interior of the anode. Once the lithium ion arrives at the electrolyte/cathode interface the same reactions that occurred at the anode must occur there too, but in the opposite way. Thus there are many things that need to happen for the battery to continue delivering current to the external circuit. For the purpose of discussion we shall consider only the reaction at the anode/electrolyte interface. The reaction at the cathode interface has the same basic science issues: the knowledge and understanding of the anode reaction can be directly transferred to the cathode.

The first step in simplifying a kinetics problem is to identify the slowest step in the reaction. Electronic transport is rarely, if ever, the rate controlling step in the battery. Modern, commercially available electrolytes, such $LiFP_6$, being a liquid polymer, are wonderfully fast conductors of Li^+ and rarely limit the overall transport process (note that this not necessarily true for solid state electrolytes). Thus the rate controlling step in the delivery of current is the diffusion of Li from within the anode to the anode/electrolyte interface. This conclusion is easily reached if one appreciates that diffusion of atoms in the solid state is always much slower than diffusion in a liquid medium. Let us now consider the fundamental aspects of the diffusion of lithium within the anode.

A little further thought to the above discussion will reveal to the reader that the power density of the battery is directly linked to the diffusivity of lithium atoms in the anode material. The electron current that the battery can deliver is indeed directly proportional to how fast Li can diffuse from within the anode to the anode/electrolyte interface. The power density is equal to the voltage times the current. Therefore, we move to understand how diffusivity and the physical length scale of the battery is related to the power density.

Let us begin by combining equations (6), (12) and (13), applying them to the diffusion of Li in the anode by using the appropriate subscripts and superscripts in notation:

$$j_{Li}^{a} = -\frac{D_{Li}^{a} c_{Li}}{k_B T}\frac{d\eta_{Li}^{A}}{dx} = D_{Li}^{A} c_{Li}\frac{d\ell n(\gamma_{Li} x_{Li})}{dx} \tag{14}$$

Here c_{Li} is the concentration, that is the number of Li atoms per unit volume of the anode material, while x_{Li} is the molar concentration (which is dimensionless). In order to simplify the analysis we assume that the activity coefficient γ_{Li} is a constant; then Eq. (14) reduces to:

$$j_{Li}^{a} = D_{Li}^{A}\frac{dc_{Li}}{dx} \tag{15}$$

where we have used the proportional relationship between the mole fraction (x_{Li}) and the volumetric concentration of Li atoms in the anode material (c_{Li}).

Note that the diffusion coefficient for Li in Eq. (15) will vary with the concentration of lithium if γ_{Li} , the activity, varies with composition. However, the diffusion coefficient in Eq. (14) is more fundamental, since it does not depend on the concentration. These diffusion coefficients, therefore, are given different names, the one in Eq. (14) is called the tracer diffusion coefficient while the one in (15) is called the chemical diffusion coefficient.

4.2 Relating Diffusion and Length Scale to Power Density

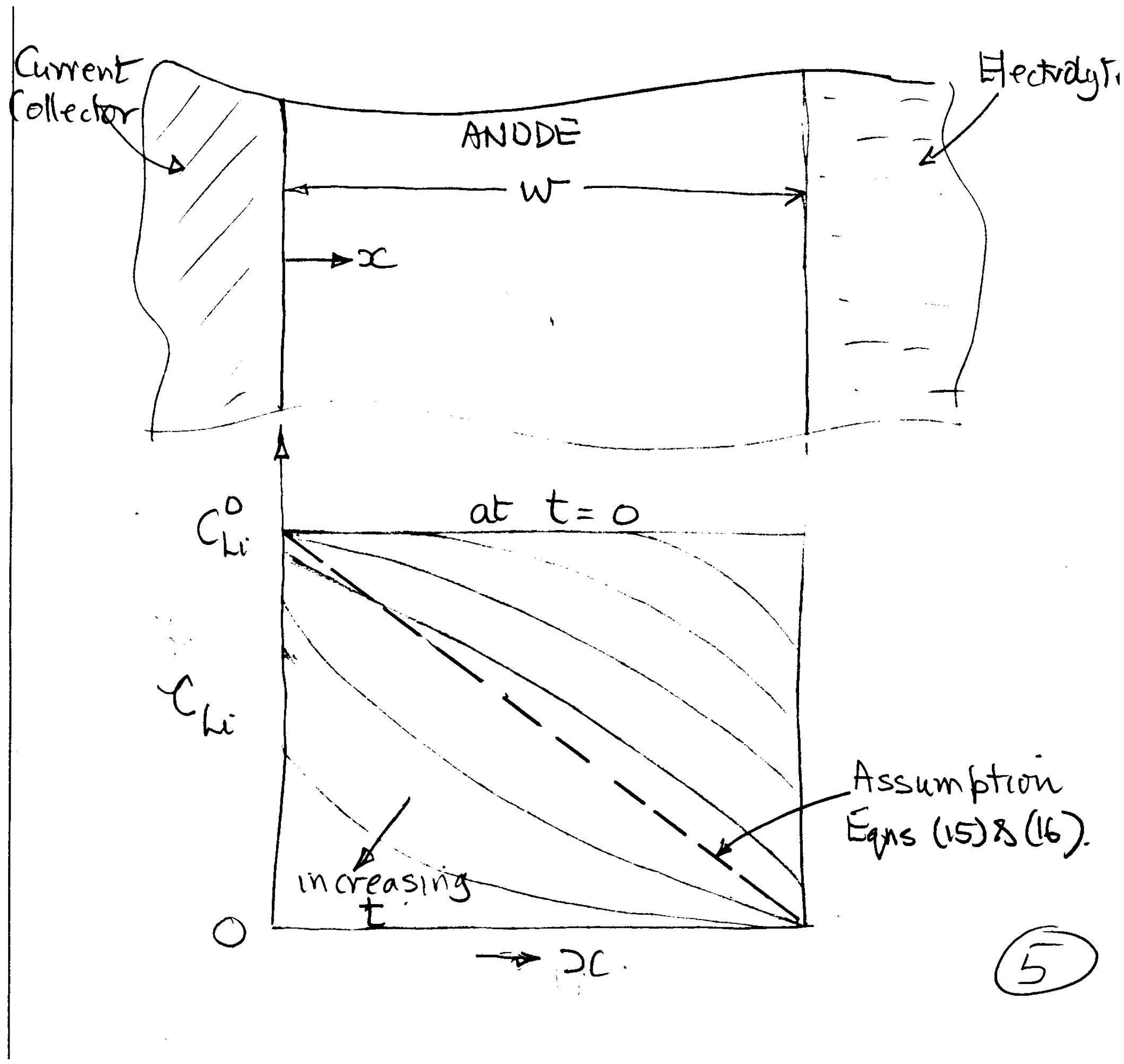


Figure 5: The concentration profile of Li in the anode, as a function of time.

The power density is the product of the battery voltage multiplied by the current that can be drawn from it. The current is proportional to the rate at which Li can be delivered to the anode/electrolyte interface. Diffusion is driven by the gradient of the Li concentration within the anode. The time dependent profile of Li concentration across the width of the anode is shown schematically in Fig. 5. At the start the concentration of lithium will be uniform. As time progresses, and Li is drained from the anode, the concentration of Li would assume a gradient. The Li atoms will diffuse down this gradient towards the anode/electrolyte interface. Gradually the anode will be depleted of the Li atoms. Clearly the voltage (see Fig. 4) as well as the current density, which is proportional to the amount of Li delivered per second at the anode/electrolyte interface will change will time. Such a complex analysis is outside the scope of this book; nevertheless, a scaling relationship between the geometry of the anode and its performance can be obtained through an approximate analysis.

The objective of this analysis is to draw an approximate relationship between the power density, the energy density, and the geometry of the anode. We will show that whereas the energy density is a handbook number related to the theoretical capacity of the material, the power density depends on the coefficient of diffusion and length scale of the battery design. The power density can be limited by Li diffusion at the anode or the cathode, whichever is slower. In this problem the anode is assumed to be the limiting electrode. Note that energy density is expressed as mAh/g, while the power density is usually written as W/g (or kW/kg).

This analysis assumes that the anode, as shown in Fig. 1, is an efficient electron conductor.

Let us consider the power density in 1 kg of the anode material. If the density of the anode is ρ_A kg m^{-3}, then its volume is $(1/\rho_A)$ m^3, and the surface area of the electrode is $(1/w\rho_A)$ where w is the width of the anode. It follows that the current available from the battery, I will be given by:

$$I = \frac{1}{w\rho_A} . J_{Li} \qquad (16)$$

where J_{Li} is given by Eq. (15). It is now necessary to obtain an average value for $\frac{dc_{Li}}{dx}$. A reasonable assumption would be equate this gradient to the volumetric concentration of lithium in the anode, c_{Li}, divided by the width of the anode, w. If the energy density, is expressed in mAh/g, then we have that:

$$\frac{dc_{Li}}{dx} = \frac{10^{-3} * 3600 * (\text{mAh/g}) * 10^3 \rho_A}{w} \ \text{C(oulombs) m}^{-4} \qquad (17)$$

The first factor of 10^{-3} converts mA to A, 3600 converts h into seconds, the next 10^3 converts the concentration from per g into per kg, and multiplying it by ρ_A converts the gravimetric concentration into volumetric concentration.

Substituting Eq. (17) into (15), and inserting J_{Li} into Eq. (16) we obtain the current that can be drawn from the battery. If the nominal voltage of the battery is *V*, then the power density, *PD*, given by the product of the voltage and the current, will be equal to:

$$PD = 3.6\frac{D_{Li}^{A}}{w^{2}}(\mathrm{mAh/g})V \quad (\mathrm{kW/kg}) \qquad (18)$$

The most noteworthy feature of Eq. (18) is that the *PD* is inversely proportional to the second power of the width of the anode. An anode which is a factor of two thinner can potentially yield four time higher *PD*.

For anodes made from graphite the nominal available capacity is approximately 100 mAh/g (the theoretical value is 350 mAh/g). The nominal voltage for a LIB is 2.5 V, and the diffusion coefficient for Li in graphite is approximately 10^{-13} $\mathrm{m^2 s^{-1}}$ at ambient temperature. Substituting these numbers into Eq. (18) we obtain *PD* to be equal to 0.9 kW/kg if w=10 μm and 90 kW/kg if w=1 μm. (One Horse—Power is equal to 0.746 kW). If the electrodes were just a few nm thick the *PD* will be extraordinarily high.

As was discussed in Introduction thin electrodes place a penalty on the overall weight of the battery. The overhead weight of the collateral components (the electrolyte, current collectors etc.) depends on the surface area of the electrodes. If the electrodes are thinner then they have a smaller volume per unit area of the electrode surface, and therefore, the total amount of charge that can be stored, per unit area of the electrode, will be less. Thus *PD* and energy density (mAh/g) place competing demands on the design of the battery.

In the next section we discuss the design of the electrodes in order to increase the power density, without sacrificing its energy density, by using nanoscale particles of the active anode material. Sometimes the anode materials are not electron conductors (e.g. lithium titanate), as has been assumed so far. These are the topics that are addressed in the next section.

5. Nanocomposite Electrodes

There are two fundamental considerations in the engineering design of LIBs: the energy density and the power density. The first is a "bulk" parameter and is prescribed when the current drawn from the battery is very small, so that diffusional limitations are relatively less important. The energy density, however, depends critically on the nanostructure of the electrodes, and it is this topic that we shall consider in detail. Whether or not the anode material is electronically conducting is also an important consideration. If it is not then a "conducting agent" must be used to transport the electrons from the anode/electrolyte interface to the current collector. We begin with a brief discussion of the energy density.

5.1 The Energy Density

The energy density is measured gravimetrically with units of mAh/g, or volumetrically as mAh/cm^3. Here we shall consider the gravimetric numbers.

As a reference point the energy density of 87 Octane gasoline is 45,000 kJ/kg, or 45,000 J/g. Let us estimate the weight of the active anode material that would be required to carry this amount of energy. Assuming the energy density to be 100 mAh/g, and a nominal operating voltage of 2.5 V, leads to an energy density of 2.5*100*3.6 J/g, which is equal to 900 J/g. Adding to this the collateral weight from other components in the battery reduces the effective energy density to approximately 450 J/g. Therefore, 100 kg of battery weight would be required to store the amount of energy stored in one kg of gasoline. One gallon of gasoline weighs 2.7 kg, which would be equivalent to 270 kg of battery weight.

The difference between gasoline and battery is that the battery can be charged to restore its stored energy. Furthermore the electrical engine is three to five times more efficient than the internal combustion engine. Therefore, 270 kg of battery (the equivalent of one gallon of gasoline) can give a driving range of up to 200 miles. The analysis highlights the importance of new materials that have a higher energy capacity. We shall continue to discover and invent new materials towards this goal over the next several decades.

5.2 Power Density

The *PD*, as given by Eq. (18), depends not only on the energy density (mAh/g) but also on the diffusivity of lithium in the active anode material, as well as on the length scale of the microstructure. The equation refers to Fig. 1, where the length scale, *w*, is defined as the width of the anode material layer, deposited on the current collector. Again, keep in mind that, in this instance, the anode is assumed to be a good electron conductor: that is not always the case. Thus, the objective of the nano/microscale design, and the materials selection of the anode must be (a) to find materials that have a high diffusivity for Li, (b) to reduce the length scale, w, as much as possible, and (c) to design the structure in such a way that electrons can be conducted from the surface of the active material to the current collector.

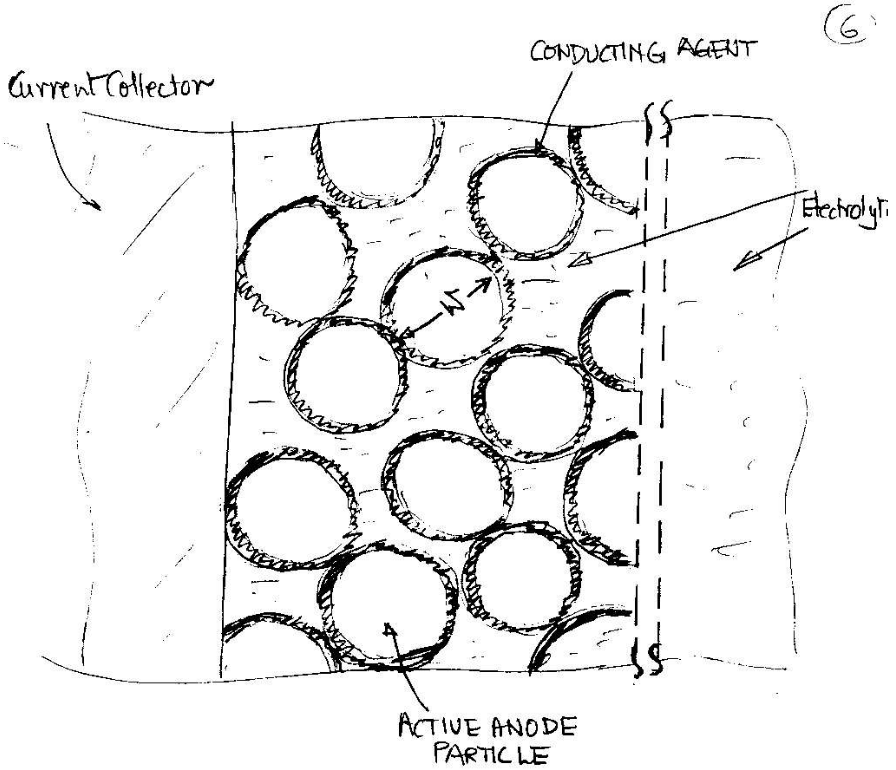


Figure 6: A nanocomposite design of the anode which, simultaneously, achieves both energy density and power density.

The above requirements lead us to consider the anode not as a momolithic material, but as a composite structure made from different materials. In order to meet requirement (c) it is necessary to add a “conducting agent” to the composite. An excellent choice for the conducting agent is carbon since it is conductive both to electrons, and to Li atoms. There are many forms of carbon that can be used, although graphite, because of its cost competitiveness, is often chosen.

Let us consider a nanocomposite having the structure sketched in Fig. 6. The active anode material is in the form of (nano)particles. The particles are coated with a thin layer of the conducting agent (carbon). The carbon coated particles form a percolating network to transfer electrons from the particles to the current collector. In order for each particle to contribute its share of Li storage to the battery it would be essential for the electrolyte to make contact with the particle. In this way the reaction, $\mathrm{Li} = \mathrm{Li}^{+} + \mathrm{e}$, can occur on the surface of the particle, the Li^{+} being transported away towards the cathode via the electrolyte, and the electron towards the current collector through the conducting agent.

The *PD* for the anode can still be estimated from Eq. (18), where, now, w is equivalent to the diameter of the particles of the anode material. Remember that power density as high as 90 kW/kg was possible if $w = 1000\ \mathrm{nm}$, using graphite as a baseline material.

To estimate an approximate value for the power density from the energy density, consider a 100 hp gasoline engine (keep in mind that a dc electrical motor can deliver high torque at low speeds much more efficiently than can a gasoline engine). This translates in an engine having the power of 100*0.746 = 75 kW. Therefore a power density of 90 kW/kg for a lithium ion battery would be more than sufficient to achieve the performance of a gasoline engine.

However, there are caveats, which are discussed in Section 5.4.

5.3 Electrode Balance

The anode and the cathode act in tandem to define the performance of the battery as a whole. For optimum design the energy stored in the anode must be balanced with the energy stored in the cathode. The energy density of the battery is therefore a composite of the energy densities of the anode and the cathode materials. Here we calculate the total energy density, Q^*, as a function of the energy densities of the anode, Q_A, and that of the cathode, Q_C.

If the weight of the anode and the cathode active materials is m_A and m_C, then for idea matching:

$$Q_C m_C = Q_A m_A \tag{19}$$

and,

$$Q^* = \frac{Q_A m_A}{m_A + m_C} \tag{20}$$

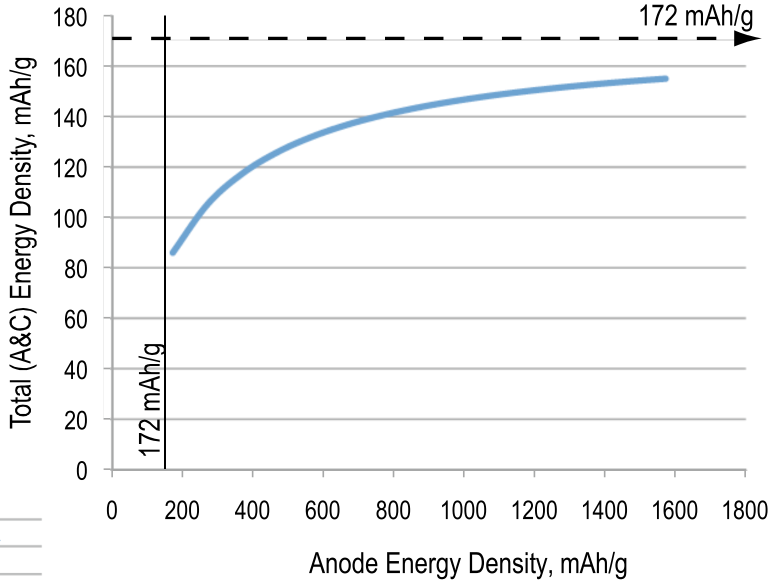
Dividing the numerator and the denominator by m_A we have:

$$Q^* = \frac{Q_A}{1 + \frac{m_C}{mA}} \tag{21}$$

Now substituting from Eq. (19) into (21), we obtain:

$$Q^* = \frac{Q_A}{1+\dfrac{Q_A}{Q_C}}, \qquad \text{or,} \qquad Q^* = \frac{Q_C}{1+\dfrac{Q_C}{Q_A}} \tag{22}$$

Note that Eq. (22) has the appropriate limits: if one electrode has a very large capacity then the overall capacity becomes equal to the capacity of the other electrode. For example if $Q_A \to \infty$ then $Q^* \to Q_C$. Plot for Q^* as a function of Q_A, when $Q_C = 172 \text{ mAh/g}$ is shown in Fig. 7. It illustrates the point that increasing the capacity of just one of the electrodes has diminishing returns unless the capacity of the other electrode is also, simultaneously increased.



Cathode=172 mAh/g

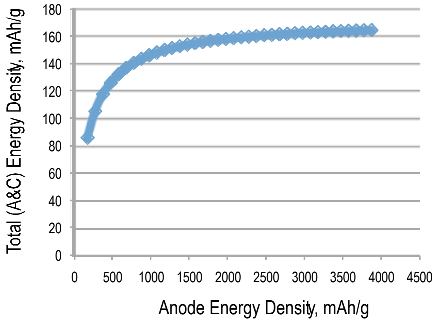


Figure 7: Relationship between the total energy density and the anode energy density, when the cathode has a fixed value of 172 mAh/g, as estimated by Eq. 22.

5.4 Caveats

The scenario analyzed in this chapter has many assumptions and simplifications, since our objective was not to show how a lithium ion battery should be engineered, but rather to the fundamental parameters that come into play in the selection of the materials and the design of anodes (and cathodes) in the form of nanocomposites. While these concept have considerable generality, there are many more issues that enter into the design and the performance of the battery as a whole. These issues arise because the transport of lithium from the anode current collector to the cathode current collector occurs through several steps, with slowest step controlling the overall rate of charge transfer. As the design changes this critical step can migrate. For example, in the case of nanocomposite sketched in Fig. 6, there would be a limit to the total thickness of the anode. As the thickness of the anode increases so will the resistance for transporting the Li^+ through the electrolyte. At some point the diffusivity of Li^+ rather than the diffusivity of Li in the anode material would become rate controlling. The following points summarize this and other issues that enter in the overall design and materials selection for the lithium ion battery:

(a) Often the anode material and the electrolyte can react at the interface forming an layer that inhibits the transfer of Li and electrons. This layer is called the SEI, or the solid–electrolyte–

interface. The role of SEI become increasingly important as the particles of the active material become smaller, since the surface to volume ratio of the particles is proportional to the inverse of the particle size. Thus, rather than the diffusion of Li within the volume of the particle, the reaction may become limited by the interface as the particles become small.

(b) You will recall that the reason for making the anode as a composite (Fig. 6) was that the power density of the anode became limited by the thickness of the anode when it was made from a monolithic material (Fig. 1). However, there is a limit to how thick the composite can be made since the interpenetrating channels of the electrolyte also carry a resistance to the transport of Li^+. Although the ions can diffuse quickly in liquid electrolytes, long and thin channels can become rate controlling of the composite electrode becomes increasingly thick.

(c) The analysis of the anode presented here can be applied equally well to the design and analysis of the cathode electrode. Either the anode or the cathode can become the rate controlling step in the overall transport of lithium.

(d) In some instances it is better to use a solid state electrolyte since it is more durable and stable for long term applications. The design of a solid state electrolyte is likely to encounter the same issues 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.

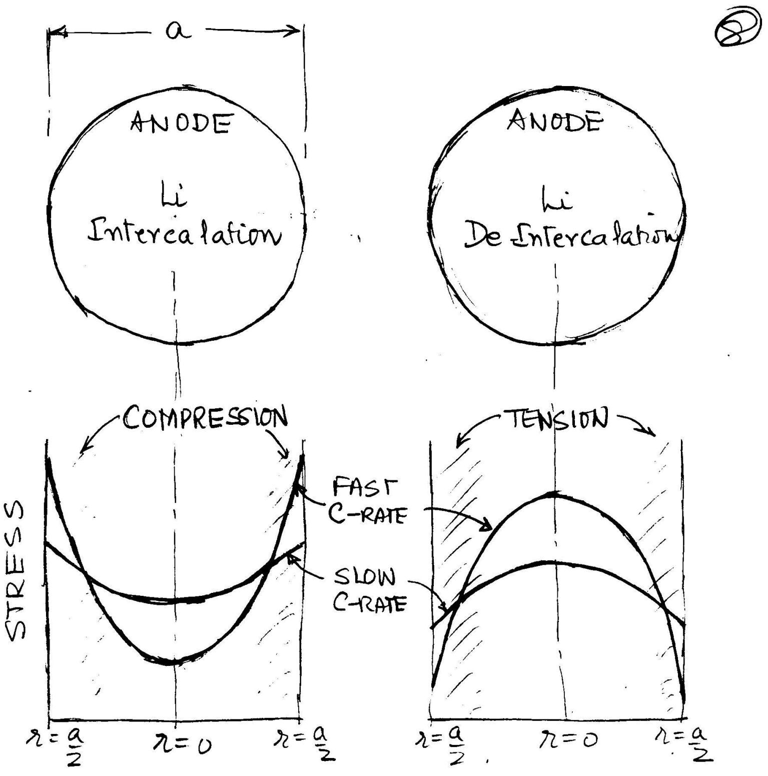


Figure 9: Concentration gradients of Li in the anode particles create compressive and tensile stresses in the anode particles because of the volume change.

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.

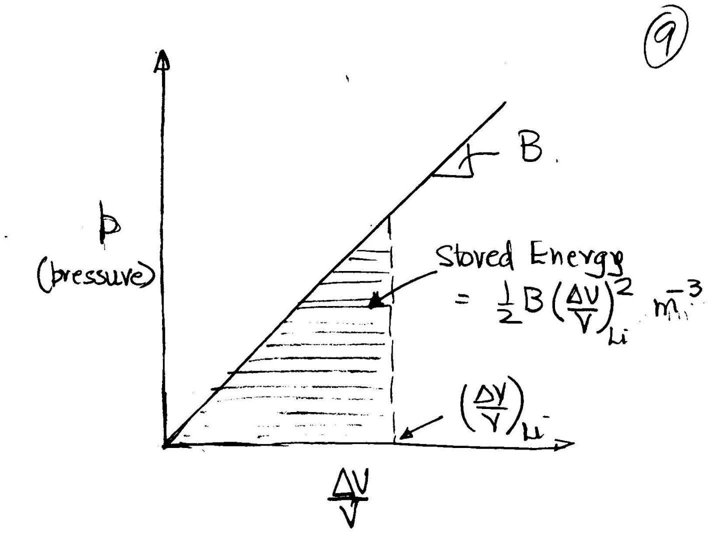


Figure 9: The upper bound of the energy stored in the particle is related to the bulk modulus and the volume change when Li intercalates into the anode.

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 $\left(\frac{\Delta V}{V}\right)_{Li}$ 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:

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

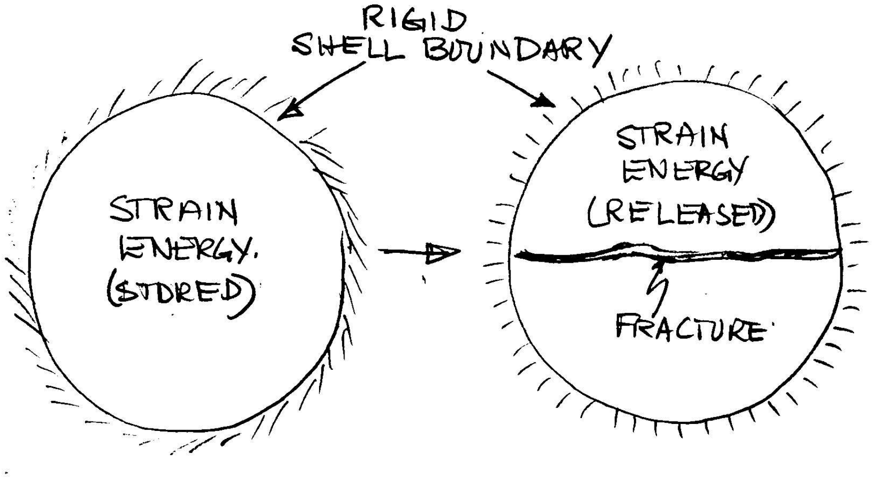


Figure 10: The model considers the anode particle to be constrained by a rigid boundary, and then, the strain energy so created to cause the particle to fracture.

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^*:

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

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.

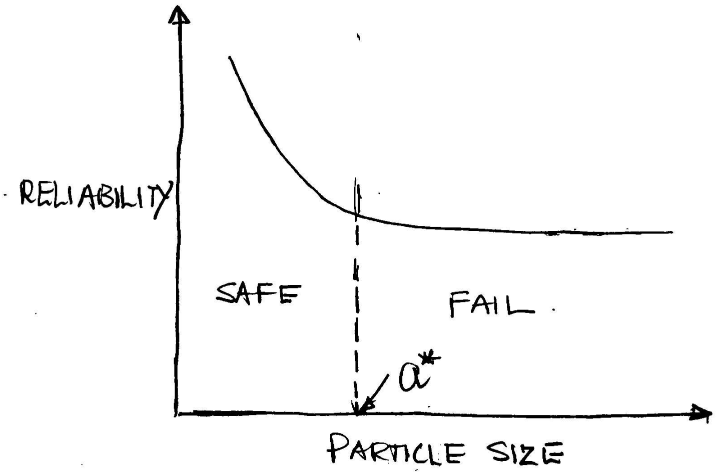


Figure 11: The reliability of the anode depends strongly on the particle size of the active material.

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 $a^* = 30\ \mathrm{nm}$. The actual values for the transition from “safe” to “fail” behavior is likely to occur when the particle size becomes about 100 nm.