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:

$$j^{a}_{Li} = -\frac{D^{a}_{Li} c_{Li}}{k_B T} \frac{d\eta^{A}_{Li}}{dx} = D^{A}_{Li} c_{Li} \frac{d\ell n(\gamma_{Li} x_{Li})}{dx} \qquad (14)$$

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:

$$j^{a}_{Li} = D^{A}_{Li} \frac{dc_{Li}}{dx} \qquad (15)$$

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

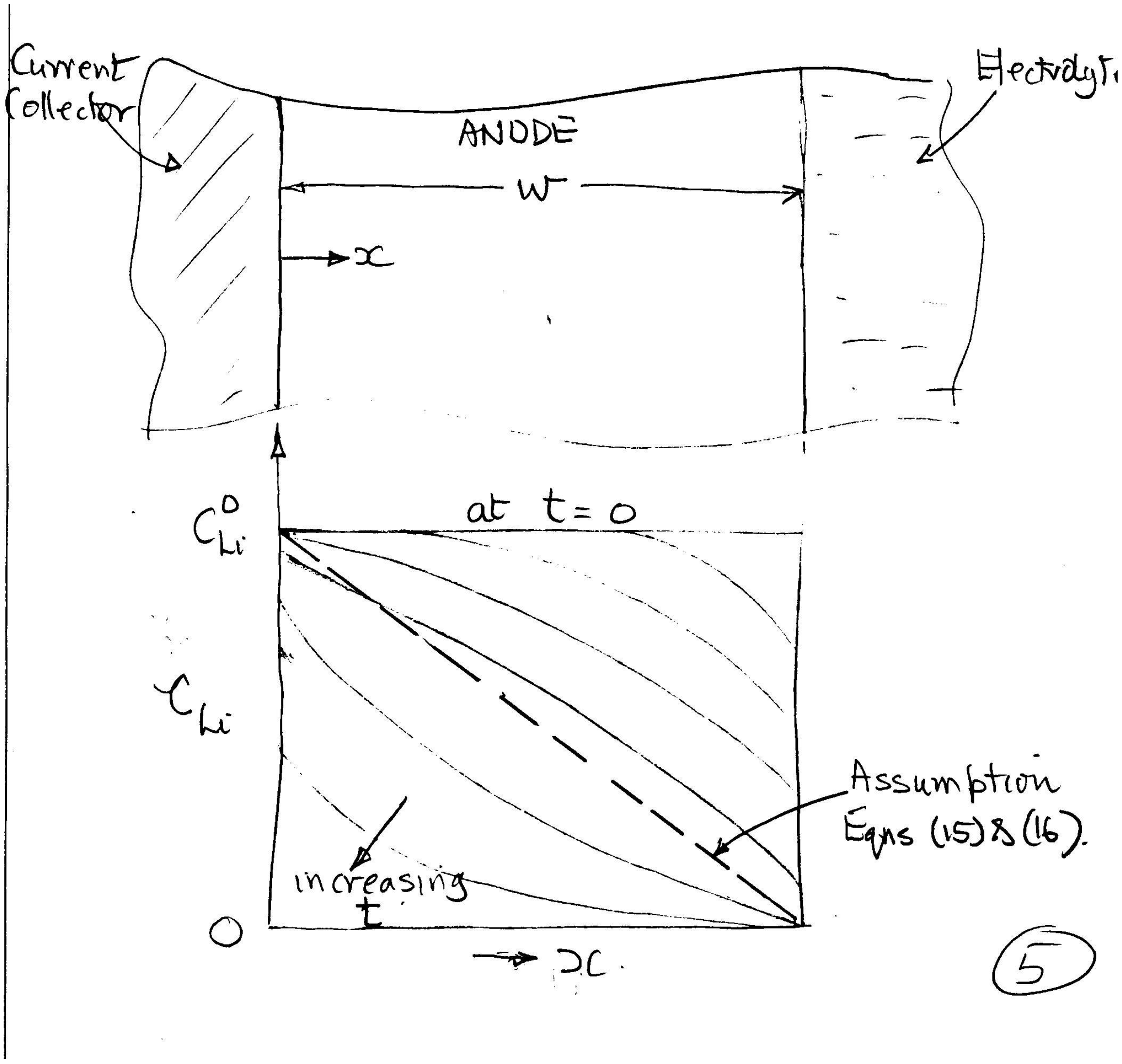

Figure 5: The concentration profile of Li in the anode, as a function of time.

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:

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

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:

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

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} $\mathrm{m^2s^{-1}}$ 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