

DEPARTMENT OF MATHEMATICAL SCIENCES

MATHEMATICAL MODELLING

Chemical analysis of lithium batteries

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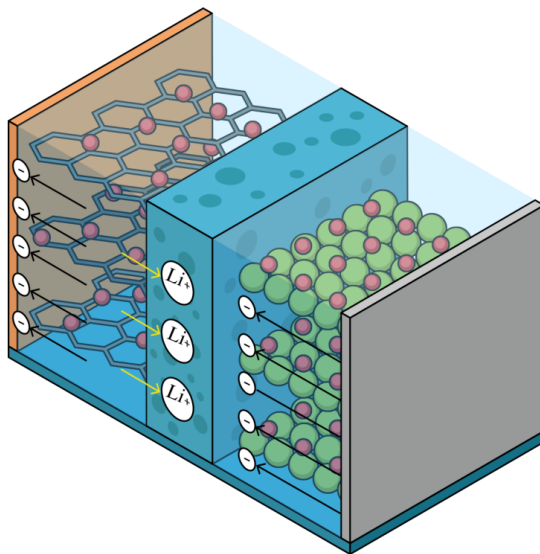
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Autumn 2023

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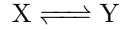
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Introduction

The conversion of chemical energy into electrical power through redox reactions constitutes the core mechanism within a battery. For rechargeable batteries, this process reverses, enabling the storage of electrical energy in a chemical state. Lithium-ion batteries have an exceptionally high energy density, harboring a significant amount of energy within a small space. In this project we aim to model and understand the behaviour of such Lithium-ion batteries, with a particular emphasis on equilibrium conditions and short time effects. Though we will also explore more general results regarding the chemical and electrical effects in a battery.

Part 1: Chemical reaction equilibrium

Consider a general system with a constituent that can take two forms, namely X and Y:



We denote by n_X and n_Y the number of X and Y respectively. The Gibbs free energy, denoted by G , is an extensive value of the system state and it naturally tends towards a minimum, in which case we say that the system has reached an equilibrium. Note that the system has reached an equilibrium if and only if the differential $dG = 0$. The differential for G is given by:

$$dG = -SdT + VdP + \mu_X dn_X + \mu_Y dn_Y$$

where $\mu_X = \frac{\partial G}{\partial n_X}$, $\mu_Y = \frac{\partial G}{\partial n_Y}$ are the chemical potentials of X and Y respectively.

1.1 Chemical potentials constraint in a simple reaction under a state equilibrium

Given the system described above, suppose that the pressure and the temperature is constant, and that the total number of constituents is preserved, i.e. that $n := n_X + n_Y$ is constant as well. We may then describe the chemical potentials of X and Y when the system has reached an equilibrium. We get the following relations:

$$\begin{aligned} dG &= \mu_X dn_X + \mu_Y dn_Y \\ dn &= dn_X + dn_Y \end{aligned}$$

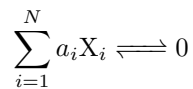
At equilibrium we have that $dG = 0$, and with a constant n we get that $dn = 0$. From this it follows that $dn_X = -dn_Y$, so we have $0 = dG = \mu_X dn_X + \mu_Y dn_Y = (\mu_X - \mu_Y)dn_X$, which finally yields:

$$\mu_X = \mu_Y \tag{1}$$

Though we note that even if the system has not reached an equilibrium we see that $dG = (\mu_X - \mu_Y)dn_X$ holds regardless.

1.2 Chemical potentials constraint in a general reaction at equilibrium

Consider now the general reaction of the form:



By stoichiometry we have that a_i of constituent X_i moves to the right in the equation, only when a_j of constituent X_j moves to the right as well, where a negative coefficient is interpreted as moving to the left instead. Thus we must have that the ratio of the movement of constituent X_i and X_j is given by:

$$\frac{dn_{X_i}}{dn_{X_j}} = \frac{a_i}{a_j} \iff \frac{1}{a_i} dn_{X_i} = \frac{1}{a_j} dn_{X_j} \tag{2}$$

We may now use this constraint to find an expression for the Gibbs free energy of the reaction under equilibrium, assuming as before that we have constant pressure and temperature. Now in this reaction, the Gibbs free energy is given by:

$$dG = \sum_{i=1}^N \mu_{X_i} dn_{X_i}$$

From the constraint given by (2), and the fact that $dG = 0$ at equilibrium it follows that:

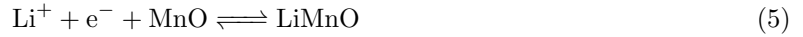
$$dG = \sum_{i=1}^N \mu_{X_i} dn_{X_i} = \frac{1}{a_j} dn_{X_j} \sum_{i=1}^N a_i \mu_{X_i} = 0$$

which holds for any $1 \leq j \leq N$. Hence we find that we must have:

$$\sum_{i=1}^N a_i \mu_{X_i} = 0 \quad (3)$$

1.3 The open circuit voltage

In the battery we have the following redox reactions at the negative and positive electrode respectively:



At equilibrium we have from eq. (3) that:

$$\mu_{\text{Li}^+}^{ne} + \mu_{\text{e}^-}^{ne} + \mu_{\text{C}_6}^{ne} = \mu_{\text{LiC}_6}^{ne} \quad \text{and} \quad \mu_{\text{Li}^+}^{pe} + \mu_{\text{e}^-}^{pe} + \mu_{\text{MnO}}^{pe} = \mu_{\text{LiMnO}}^{pe}$$

Thus we find that the difference of potential for the electrons between the negative and positive electrode is given by:

$$\delta W = \mu_{\text{e}^-}^{ne} - \mu_{\text{e}^-}^{pe} = (\mu_{\text{LiC}_6}^{ne} - \mu_{\text{Li}^+}^{ne} - \mu_{\text{C}_6}^{ne}) - (\mu_{\text{LiMnO}}^{pe} - \mu_{\text{Li}^+}^{pe} - \mu_{\text{MnO}}^{pe})$$

We assume the ion potentials of Li^+ to be equal at both electrodes, i.e. $\mu_{\text{Li}^+}^{ne} = \mu_{\text{Li}^+}^{pe}$, as the Li^+ ions are assumed to freely flow through the electrolyte. This yields the equation:

$$\delta W = (\mu_{\text{LiC}_6}^{ne} - \mu_{\text{C}_6}^{ne}) - (\mu_{\text{LiMnO}}^{pe} - \mu_{\text{MnO}}^{pe}) \quad (6)$$

The quantity δW can also be directly related to the difference between the electrical potentials at the positive electrode (ϕ^{pe}) and at the negative electrode (ϕ^{ne}):

$$\delta W = F(\phi^{pe} - \phi^{ne}) \quad (7)$$

Where F is the Faraday constant. Furthermore the open circuit voltage is given by the difference of the electrical potentials:

$$\text{OCV} = \phi^{pe} - \phi^{ne} \quad (8)$$

Combining eq. (8), eq. (6) and eq. (7) yields:

$$\text{OCV} = \frac{\delta W}{F} = \frac{(\mu_{\text{LiC}_6}^{ne} - \mu_{\text{C}_6}^{ne}) - (\mu_{\text{LiMnO}}^{pe} - \mu_{\text{MnO}}^{pe})}{F} \quad (9)$$

Part 2: Chemical reactions kinetics

We will again consider a general equation of the form:



The reaction rate depends on the concentrations c , the temperature T , and the activation energy E_a . We assume that the constituents in the form X go through an unstable state of higher energy before reaching the new stable state where they take the form of the constitute Y. To reach the unstable equilibrium state, the element X needs an extra amount of energy, which we denote by E_a^f , where f stands for forward. Then, as the constituents are in the unstable equilibrium, it will release energy as it reaches the new stable state where it takes the form Y, we denote this energy by E_a^b , where b stands for backward.

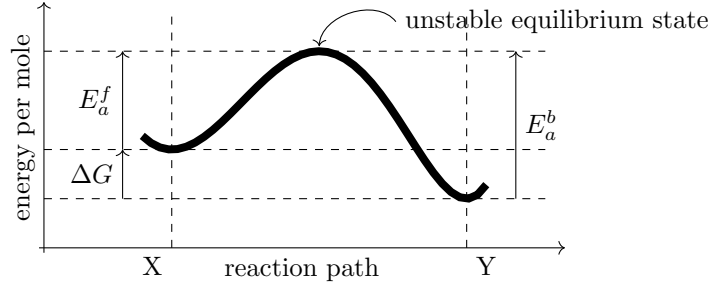


Figure 1: Reaction path and activation energy

Hence the total released energy is $E_f^b - E_a^b$ which must be negative for the reaction to be spontaneous. Using the Boltzmann distribution, we know that the probability that the element X reaches an energy larger or equal to E_a^f is proportional to $e^{-\frac{E_a^f}{RT}}$. Assuming a constant volume, we define the concentration of each species c_{X_i} as the numbers of moles per volume. Then by the law of mass action with an Arrhenius type of dependence on the activation energies:

$$\frac{dc_Y}{dt} = -\frac{dc_X}{dt} = k_f c_X e^{-\frac{E_a^f}{RT}} - k_b c_Y e^{-\frac{E_a^b}{RT}} \quad (11)$$

where k_f and k_b are some constants.

For the general reaction of the form



we get the expressions

$$\frac{1}{b_i} \frac{dc_{Y_i}}{dt} = -\frac{1}{a_i} \frac{dc_{X_i}}{dt} = k_f e^{-\frac{E_a^f}{RT}} \prod_{i=1}^{N_X} c_{X_i}^{a_i} - k_b e^{-\frac{E_a^b}{RT}} \prod_{i=1}^{N_Y} c_{Y_i}^{b_i} := r \quad (13)$$

2.1 Interpretation of the differential equations

Equation (11) describes the concentration change of reactants in a reversible reaction eq. (10). It is comprised of two components, namely: $k_f c_X e^{-\frac{E_a^f}{RT}}$ for the forward reaction and $k_b c_Y e^{-\frac{E_a^b}{RT}}$ for the backwards reaction.

An interpretation of the $k_f e^{-\frac{E_a^f}{RT}}$ ($k_b c_Y e^{-\frac{E_a^b}{RT}}$) term alone, is that it is the likelihood that a molecule of constituent X (Y) overcomes the activation barrier and thus becomes the other constituent through the reaction.

If the activation energy decreases, then $k_f e^{-\frac{E_a^f}{RT}}$ ($k_b c_Y e^{-\frac{E_a^b}{RT}}$) increases, and vice versa. This means that as the activation energy decreases, the probability that a given molecule of constituent X (Y) becomes the other constituent in the reaction increases. Now assuming ideal conditions, so that the probability that one constituent goes through the reaction is independent of whether any other constituent goes through the reaction, we find that the total change in the concentration is given by eq. (11).

The extended form of eq. (11), i.e. eq. (13) is essentially exactly analogous to the base case. Here, r is the net participation of the reaction based on the same probabilities we discussed in the above paragraph.

2.2 Equilibrium equations

At equilibrium we have that the change in concentration is 0, hence from eq. (13) we must have:

$$k_f e^{-\frac{E_a^f}{RT}} \prod_{i=1}^{N_X} c_{X_i}^{a_i} = k_b e^{-\frac{E_a^b}{RT}} \prod_{i=1}^{N_Y} c_{Y_i}^{b_i} \quad (14)$$

Assuming that we have a dilute solution, we may write:

$$\mu_{X_i} = \mu_{X_i}^0 + RT \ln(c_{X_i}/c_0) \quad (15)$$

where $\mu_{X_i}^0$ is the standard potential. And of course the analogous expression for Y_i also holds. We then have that eq. (14) becomes:

$$\begin{aligned} k_f e^{-\frac{E_a^f}{RT}} \prod_{i=1}^{N_X} c_0^{a_i} e^{a_i(\mu_{X_i} - \mu_{X_i}^0)/RT} &= k_b e^{-\frac{E_a^b}{RT}} \prod_{i=1}^{N_Y} c_0^{b_i} e^{b_i(\mu_{Y_i} - \mu_{Y_i}^0)/RT} \\ k_f e^{-\frac{E_a^f}{RT}} c_0^{\sum_{i=1}^{N_X} a_i} e^{\frac{1}{RT} \sum_{i=1}^{N_X} a_i(\mu_{X_i} - \mu_{X_i}^0)} &= k_b e^{-\frac{E_a^b}{RT}} c_0^{\sum_{i=1}^{N_Y} b_i} e^{\frac{1}{RT} \sum_{i=1}^{N_Y} b_i(\mu_{Y_i} - \mu_{Y_i}^0)} \end{aligned}$$

By eq. (3) we know that $\sum_{i=1}^{N_X} a_i \mu_{X_i} = \sum_{i=1}^{N_Y} b_i \mu_{Y_i}$, hence we may further write:

$$k_f e^{-\frac{E_a^f}{RT}} c_0^{\sum_{i=1}^{N_X} a_i} e^{-\frac{1}{RT} \sum_{i=1}^{N_X} a_i \mu_{X_i}^0} = k_b e^{-\frac{E_a^b}{RT}} c_0^{\sum_{i=1}^{N_Y} b_i} e^{-\frac{1}{RT} \sum_{i=1}^{N_Y} b_i \mu_{Y_i}^0}$$

Hence the compatibility condition for eq. (3), eq. (14) and eq. (15) to hold simultaneously is:

$$\frac{k_f}{k_b} e^{-\frac{E_a^f - E_a^b}{RT}} c_0^{\left(\sum_{i=1}^{N_X} a_i - \sum_{i=1}^{N_Y} b_i\right)} e^{-\frac{1}{RT} \left(\sum_{i=1}^{N_X} a_i \mu_{X_i}^0 - \sum_{i=1}^{N_Y} b_i \mu_{Y_i}^0\right)} = 1 \quad (16)$$

Part 3: Influence of the electrical potential on the chemical reaction equilibrium and kinetics

We consider now a reaction that involves a charged species. In particular we will look at:



3.1 Deriving the open circuit potential at equilibrium

We start by considering the case where eq. (17) is at equilibrium. The equilibrium condition was given by eq. (3) as:

$$\sum_{i=1}^N a_i \tilde{\mu}_{X_i} = 0 \quad (18)$$

Where $\mu_{X_i} = \mu_{X_i} + zFU$ is the electro-chemical potential. We want to express the electro-chemical potentials in terms of the chemical potential and electrical potential, in accordance to reaction (17). We further want to simplify the chemical potential using eq. (15) (assuming we are in ideal conditions)

$$\tilde{\mu}_{\text{Li}} = \mu_{\text{Li}}^0 + RT \ln a_{\text{Li}} \quad \tilde{\mu}_{\text{Li}^+} = \mu_{\text{Li}^+}^0 + RT \ln a_{\text{Li}^+} + FU_{\text{elyte}} \quad \tilde{\mu}_{\text{e}^-} = -FU_{\text{elde}}$$

where $a_{\text{Li}} \stackrel{\text{def}}{=} \frac{c_{\text{Li}}}{c_0}$, $a_{\text{Li}^+} \stackrel{\text{def}}{=} \frac{c_{\text{Li}^+}}{c_0}$ are the activities of Li and Li^+ respectively. Putting all this into eq. (3) i.e.:

$$\tilde{\mu}_{\text{Li}} = \tilde{\mu}_{\text{Li}^+} + \tilde{\mu}_{\text{e}^-}$$

yields:

$$\mu_{\text{Li}}^0 + RT \ln a_{\text{Li}} = \mu_{\text{Li}^+}^0 + RT \ln a_{\text{Li}^+} + F(U_{\text{elyte}} - U_{\text{elde}})$$

Thus, we find the following expression for the open circuit potential:

$$U_{eq} = U_{elde} - U_{elyte} = \frac{\mu_{\text{Li}^+}^0 - \mu_{\text{Li}}^0}{F} + \frac{RT}{F} \ln \left(\frac{a_{\text{Li}^+}}{a_{\text{Li}}} \right)$$

Now using $a_{\text{Li}^+}/a_{\text{Li}} = c_{\text{Li}^+}/c_{\text{Li}}$, we conclude that:

$$U_{eq} = \frac{\mu_{\text{Li}^+}^0 - \mu_{\text{Li}}^0}{F} + \frac{RT}{F} \ln \left(\frac{c_{\text{Li}^+}}{c_{\text{Li}}} \right) \quad (19)$$

3.2 Kinetic equations

At equilibrium, $\frac{dc_Y}{dt} = \frac{dc_X}{dt} = 0$. We can then write:

$$k_f c_{\text{Li}} e^{-\frac{E_a^f}{RT}} = k_b c_{\text{Li}^+} e^{-\frac{E_a^b}{RT}} \implies \frac{k_f}{k_b} = \frac{c_{\text{Li}^+} e^{-\frac{E_a^b}{RT}}}{c_{\text{Li}} e^{-\frac{E_a^f}{RT}}} \implies \ln \left(\frac{k_f}{k_b} \right) = \ln \left(\frac{c_{\text{Li}^+}}{c_{\text{Li}}} \right) + \frac{E_a^f - E_a^b}{RT}$$

We also have that:

$$F\delta U = (E_{a,0}^f - E_{a,0}^b) - (E_a^f - E_a^b) = \Delta G_0 - \Delta G \quad (20)$$

If we let $k_b = k_f$ and substitute using eq. (20) we get the following:

$$0 = \ln(1) = \ln \left(\frac{c_{\text{Li}^+}}{c_{\text{Li}}} \right) + \frac{\Delta G_0 - F\delta U}{RT}$$

Solving for δU and using that $\delta U = U_{eq}$ at equilibrium, we get:

$$U_{eq} = \frac{RT}{F} \ln \left(\frac{c_{\text{Li}^+}}{c_{\text{Li}}} \right) + \frac{\Delta G_0}{F} \quad (21)$$

3.3 Consistency of the equilibrium potential

We have now calculated two expressions for U_{eq} , namely eq. (19) and eq. (21)

Assuming that the two expressions are consistent we get:

$$\frac{RT}{F} \ln \left(\frac{c_{\text{Li}^+}}{c_{\text{Li}}} \right) + \frac{\Delta G_0}{F} = \frac{RT}{F} \ln \left(\frac{c_{\text{Li}^+}}{c_{\text{Li}}} \right) + \frac{\mu_{\text{Li}^+}^0 - \mu_{\text{Li}}^0}{F}$$

Hence for the equations to be consistent, we must have:

$$\Delta G_0 = \mu_{\text{Li}^+}^0 - \mu_{\text{Li}}^0 \quad (22)$$

Which may be considered as a compatibility condition.

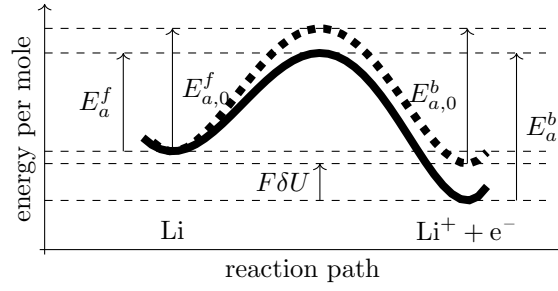


Figure 2: Reaction path and activation energy at some reference potential (dashed line and zero subscript for the activation energies) and after increasing the electrical potential with δU (plain line).

3.4 Relation between volumetric current and the surface over potential

The surface over-potential (unit in Ampere) is given by:

$$\eta = \phi_{elde} - \phi_{elyte} - U_{eq} = \delta U - U_{eq}$$

We have earlier found an expression for U_{eq} , which gives:

$$\eta = \delta U - \left(\frac{RT}{F} \ln \left(\frac{c_{Li^+}}{c_{Li}} \right) + \frac{\Delta G_0}{F} \right)$$

Solving for δU :

$$\delta U = \eta + \frac{RT}{F} \ln \left(\frac{c_{Li^+}}{c_{Li}} \right) + \frac{\Delta G_0}{F}$$

It is also given that:

$$E_a^f = E_{a,0}^f - \beta F \delta U \quad \text{and} \quad E_a^b = E_{a,0}^b + (1 - \beta) F \delta U$$

as well as:

$$i = -F \frac{dc_{e^-}}{dt}$$

It is evident from the reaction equation that $\frac{dc_{e^-}}{dt} = \frac{dc_{Li^+}}{dt}$, and we can hence express i by eq. (11). Taking all this into consideration, we get:

$$i = Fk \left(c_{Li^+} e^{-\frac{E_{a,0}^f + F(1-\beta) \left(\eta + \frac{RT}{F} \ln \left(\frac{c_{Li^+}}{c_{Li}} \right) + \frac{\Delta G_0}{F} \right)}{RT}} - c_{Li} e^{-\frac{E_{a,0}^b - F\beta \left(\eta + \frac{RT}{F} \ln \left(\frac{c_{Li^+}}{c_{Li}} \right) + \frac{\Delta G_0}{F} \right)}{RT}} \right)$$

Inserting $\Delta G_0 = E_{a,0}^f - E_{a,0}^b$ and simplifying:

$$\begin{aligned} i &= Fk \left(c_{Li^+} e^{-\frac{E_{a,0}^b}{RT}} \left(\frac{c_{Li^+}}{c_{Li}} \right)^{-(1-\beta)} e^{\frac{-F(1-\beta)\eta}{RT}} e^{\frac{(1-\beta)(E_{a,0}^b - E_{a,0}^f)}{RT}} - c_{Li} e^{-\frac{E_{a,0}^f}{RT}} \left(\frac{c_{Li^+}}{c_{Li}} \right)^\beta e^{\frac{\beta F\eta}{RT}} e^{-\frac{-\beta(E_{a,0}^b - E_{a,0}^f)}{RT}} \right) \\ &= Fk \left(c_{Li^+}^\beta c_{Li}^{1-\beta} e^{-\frac{\beta E_{a,0}^b}{RT}} e^{-\frac{(1-\beta)F\eta}{RT}} - c_{Li}^{1-\beta} c_{Li^+}^\beta e^{-\frac{\beta E_{a,0}^b}{RT}} e^{-\frac{(1-\beta)E_{a,0}^f}{RT}} e^{\frac{\beta F\eta}{RT}} \right) \end{aligned}$$

Taking out the common factor yields:

$$i = Fk \left(c_{Li^+} e^{-\frac{E_{a,0}^b}{RT}} \right)^\beta \left(c_{Li} e^{-\frac{E_{a,0}^f}{RT}} \right)^{1-\beta} \left(e^{-\frac{(1-\beta)F\eta}{RT}} - e^{\frac{\beta F\eta}{RT}} \right) = i_0 \left(e^{-\frac{(1-\beta)F\eta}{RT}} - e^{\frac{\beta F\eta}{RT}} \right) \quad (23)$$

Where

$$i_0 = Fk \left(c_{Li+} e^{-\frac{E_{a,0}^b}{RT}} \right)^\beta \left(c_{Li} e^{-\frac{E_{a,0}^f}{RT}} \right)^{1-\beta} \quad (24)$$

Part 4: Charge conservation equation

Let ρ denote the charge density, and let \mathbf{j} denote the current density.

4.1 Deriving the charge conservation equation

The total charge in a time dependent volume $\Sigma(t)$ at time t is given by

$$\varphi_{\Sigma(t)}(t) = \int_{\Sigma(t)} \rho(\mathbf{x}, t) dV$$

Let $\partial\Sigma(t) = \Gamma(t)$ denote the boundary of the volume Σ , we then have by Reynolds transport theorem that:

$$\frac{d}{dt} \int_{\Sigma(t)} \rho(\mathbf{x}, t) dV \Big|_{t=t_0} = \int_{\Sigma(t_0)} \frac{\partial}{\partial t} \rho(\mathbf{x}, t) dV + \int_{\Gamma(t_0)} \mathbf{j}(\mathbf{x}, t) \cdot \hat{\mathbf{n}} dS$$

Since charge is conserved we must have $\frac{d}{dt} \varphi_{\Sigma(t)}(t) = 0$, and so by the divergence theorem we get:

$$0 = \int_{\Sigma(t_0)} \frac{\partial}{\partial t} \rho(\mathbf{x}, t) dV + \int_{\Sigma(t_0)} \nabla \cdot \mathbf{j}(\mathbf{x}, t) dV = \int_{\Sigma(t_0)} \left(\frac{\partial}{\partial t} \rho(\mathbf{x}, t) + \nabla \cdot \mathbf{j}(\mathbf{x}, t) \right) dV$$

Note that $\Sigma(t)$ was chosen arbitrarily, hence we must have:

$$\frac{\partial}{\partial t} \rho(\mathbf{x}, t) + \nabla \cdot \mathbf{j}(\mathbf{x}, t) = 0 \quad (25)$$

4.2 Wire example

We assume that we have charge neutrality, so $\rho = 0$. Consider a cylindrical wire of length L , radius S and a given imposed uniform electrical potentials ϕ_L and ϕ_R at the the left and right extremity respectively, and suppose there is no flux out of the wire. Furthermore, we shall presume that Ohm's law holds, so we may write $\mathbf{j} = \sigma \mathbf{E}$, where $E = -\nabla \phi$ for some electrical potential.

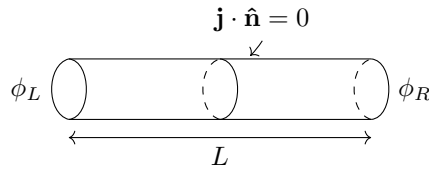


Figure 3: Illustration of a cylindrical wire with the applied boundary conditions

These presumptions yield the following boundary value problem:

$$\begin{cases} \nabla^2 \phi = 0 \\ \phi(r, \theta, 0) = \phi_L, \forall r, \theta \\ \phi(r, \theta, L) = \phi_R, \forall r, \theta \\ \partial_r \phi(S, \theta, z) = 0, \forall \theta, z \end{cases}$$

Where we have written ϕ in cylindrical coordinates. Note however that by symmetry we should expect ϕ to be independent of θ , and we should also expect $\partial_z^2 \phi = 0$ because the strength of the electrical field E

should be constant in the z -direction. Hence we may restate the boundary value problem in the following way:

$$\begin{cases} \frac{1}{r}\partial_r(r\partial_r\phi) = 0 \\ \partial_z^2\phi = 0 \\ \phi(r, 0) = \phi_L, \forall r \\ \phi(r, L) = \phi_R, \forall r \\ \partial_r\phi(S, z) = 0, \forall z \end{cases} \quad (26)$$

Integrating twice then readily yields:

$$\phi(r, \theta) = c_1(z) \ln r + c_2(z)$$

Thus $\partial_r\phi(S, z) = c_1(z)/S = 0$, so $c_1(z) = 0$. Hence ϕ is actually only a function of z . And since $\partial_z^2\phi = 0$, we must have $\phi(z) = a + bz$ for constants a, b . Using the boundary condition, we then see that:

$$\phi(z) = \phi_L + \frac{\phi_R - \phi_L}{L}z$$

We may then calculate $\mathbf{j} = -\sigma\nabla\phi$ to be given by $\mathbf{j} = \sigma(\frac{\phi_L - \phi_R}{L})\hat{\mathbf{z}}$. Furthermore we may deduce that the current I is given by:

$$I = \int_{S_R} \mathbf{j} \cdot \hat{\mathbf{z}} dS = A\sigma \left(\frac{\phi_L - \phi_R}{L} \right)$$

where S_R is the surface of the right extremity.

Hence we may write:

$$U = RI \quad (27)$$

where $U = \phi_L - \phi_R$, and $R = \frac{L}{\sigma A}$.

Part 5: Activation phase setup

We consider a one-dimensional system with two electrodes and an electrolyte. We impose a current I for $t > 0$, and we consider the activation phase, when t is so small that a negligible amount of ions have had time to move in the electrolyte, and the electrodes are homogeneous, i.e. ion concentrations are constant in space. We simplify eq. (23) by assuming $\beta = \frac{1}{2}$. Then our assumptions tell us that for each electrode, we have an equation on the following form for the current

$$I = V \cdot i = V \cdot i_0 \cdot \left(e^{-\frac{F\eta}{2RT}} - e^{\frac{F\eta}{2RT}} \right) = I_0 \cdot \sinh \left(\frac{F\eta}{2RT} \right) \quad (28)$$

where V is the volume of the electrode, and $I_0 = -2 \cdot V \cdot i_0$

5.1 Relation between potential drop and the current

We assume there is a constant resistance density R_{ne} , R_{pe} , and R_{elyte} in the negative electrode, positive electrode, and the electrolyte respectively. This gives a voltage drop over each of the components by using $\delta V_i = R_i I$ giving

$$\phi_- - \phi_n = R_{ne}I \quad \phi_{e,n} - \phi_{e,p} = R_{elyte}I \quad \phi_p - \phi_+ = R_{pe}I$$

The equations for the voltage differences at the transitions between the electrodes and electrolyte can be found by

$$\phi_n - \phi_{e,n} = \eta_n + U_{eq,n} \quad \phi_p - \phi_{e,p} = \eta_p + U_{eq,p}$$

η_n and η_p are the surface over-potentials at the corresponding electrodes.

And using eq. (28) for each of the transitions between electrode and electrolyte, we have

$$\eta_n = \phi_n - \phi_{e,n} - U_{eq,n} = \frac{2RT}{F} \cdot \sinh^{-1} \left(\frac{I}{I_{0,n}} \right) \quad \eta_p = \phi_p - \phi_{e,p} - U_{eq,p} = \frac{2RT}{F} \cdot \sinh^{-1} \left(\frac{I}{I_{0,p}} \right)$$

Where $I_{0,\cdot}$ are the constants for each electrode related to $i_{0,\cdot}$ as above.

Then by using:

$$U = \phi_+ - \phi_- = (\phi_+ - \phi_p) + (\phi_p - \phi_{e,p}) + (\phi_{e,p} - \phi_{e,n}) + (\phi_{e,n} - \phi_n) + (\phi_n - \phi_-)$$

We get the equation $U = f(I)$ on the form:

$$U = -I(R_{ne} + R_{elyte} + R_{pe}) + \frac{2RT}{F} \left(\sinh^{-1} \left(\frac{I}{I_{0,p}} \right) - \sinh^{-1} \left(\frac{I}{I_{0,n}} \right) \right) + (U_{eq,p} - U_{eq,n}) \quad (29)$$

For a simple case we can assume that $i = I$ (since it is 1D) and that $V = 1$. We then get the following:

$$U = -I \cdot (R_{ne} + R_{elyte} + R_{pe}) + \frac{2RT}{F} \left[\sinh^{-1} \left(\frac{I e^{\frac{E_{a,0}^{f,n} + E_{a,0}^{b,n}}{2RT}}}{2Fk_n \sqrt{c_{Li}^n c_{Li^+}^n}} \right) - \sinh^{-1} \left(\frac{I e^{\frac{E_{a,0}^{f,p} + E_{a,0}^{b,p}}{2RT}}}{2Fk_p \sqrt{c_{Li}^p c_{Li^+}^p}} \right) \right] \quad (30)$$

$$+ \frac{RT}{F} \ln \left(\frac{c_{Li^+}^p c_{Li}^n}{c_{Li}^p c_{Li^+}^n} \right) + \frac{1}{F} \left[E_{a,0}^{f,p} - E_{a,0}^{b,p} - (E_{a,0}^{f,n} - E_{a,0}^{b,n}) \right]$$

Where the super-/subscripts of p and n denote those values for the reaction at the positive and negative electrode respectively.

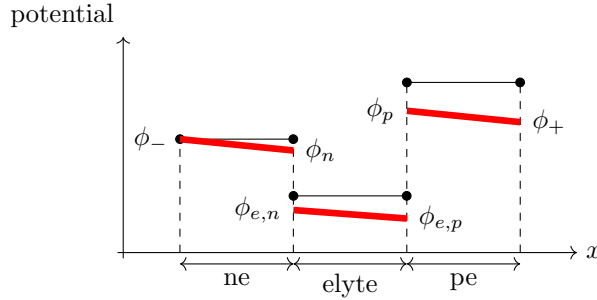


Figure 4: Illustration of the activation phase. The black lines is with no current at $t < 0$. The red lines is with current equal to $I > 0$ and at $t \geq 0$. The current inside the battery is going from left to right from states of lower to higher electrical potential.

Part 6: Ion transport in the electrolyte

A liquid electrolyte contains several ions, at least two of opposite charge in order to have charge neutrality. The ions will move in the solution due to the combined effect of two driving forces, the migration and diffusion forces. The migration force corresponds to the electrical force which drives positively charged particles in the direction of decreasing electrical potential. The diffusion force results from repulsive microscopic forces. For a given ion indexed by i , we denote by N_i the flux in $mol\ m^{-2}s^{-1}$. The flux is given by:

$$N_i = -z_i u_i F c_i \nabla \phi - D_i \nabla c_i \quad (31)$$

For the given ion indexed by i , z_i denotes the charge number, u_i denotes the mobility (in $m^2\ mol\ J^{-1}s^{-1}$), c_i denotes the concentration, D_i denotes the diffusion coefficient. In the electrolyte, all the ions, which by definition correspond to the charged particles, contribute to the electrical current. The current density ($A\ m^{-2}$) in an electrolyte is indeed given by the sum of the ion fluxes multiplied with the Faraday constant:

$$j = F \sum_{i=1}^M z_i N_i \quad (32)$$

where M denotes the number of different ions in the electrolyte.

6.1 The migration term of the flux equation

We will now derive the migration term $-z_i u_i F c_i \nabla \phi$ in eq. (31) using classical electrodynamics. The force on a charged particle with charge q is given by $f_E = qE = -q \nabla \phi$, however considering only this we find that the particle velocity grows ad infinitum, which of course is nonphysical. Hence there must be some friction force, which physically may be explained as the particles colliding with each other, which ought to depend on the velocity of the particles, and also the particle charge. This friction force may therefore be expressed as $f_{friction} = -|q_i| \tau_i v_i$ where the minus sign and absolute value follow from the fact that the friction should act in the opposite direction of the velocity. As $t \rightarrow \infty$ the ions reach a critical speed at which $\frac{\partial v_i}{\partial t} = 0$, and we will in the following derivation assume that this speed has been reached. We then have:

$$\begin{aligned} f_E + f_{friction} &= m_i \dot{v}_i = 0 \\ q_i \nabla \phi + |q_i| \tau_i v_i &= 0 \end{aligned}$$

Writing $q_i = z_i e$, where e is the elementary charge, we get the following expression for the particle velocity:

$$v_i = -\frac{z_i \nabla \phi}{|z_i| \tau_i}$$

Finally the flux is given by $N_i = c_i v_i$, hence we find that the particle flux for each ion is given by:

$$N_i = -z_i c_i \nabla \phi \frac{1}{|z_i| \tau_i} \quad (33)$$

Note that we may now easily relate the coefficient τ_i with the mobility u_i by comparing eq. (31) with eq. (33), which yields:

$$\tau_i = \frac{1}{F |z_i| u_i} \quad (34)$$

Now considering the case where $D_i = 0$, i.e. when we neglect the diffusion term, we may find an expression for the conductivity of the electrolyte. In this case we may simply use the relation $j = \sigma E = -\sigma \nabla \phi$, and compare it with eq. (32), which yields:

$$\sigma = F^2 \sum_{i=1}^M z_i^2 u_i c_i \quad (35)$$

6.2 The governing equations

The governing equations in the electrolyte system are given by mass conservation (for each ion) and charge conservation. Let us consider the simplest case of a binary electrolyte, that is an electrolyte with only two ions of opposite charge. A typical binary electrolyte for a lithium battery consists of a solution with lithium ion Li^+ and hexafluorophosphate ion PF_6^- .

Similarly as for part 4, if we replace ρ with c we may deduce that the mass preservation equation (or equivalently the particle preservation equation) is given by:

$$\frac{\partial c_i}{\partial t} + \nabla \cdot (c_i v_i) = 0 \quad \implies \quad \frac{\partial c_i}{\partial t} = -\nabla \cdot N_i \quad (36)$$

We will denote the positive ion by $i = +$, and the negative ion by $i = -$. Now by noting that $z_+ = 1$ and $z_- = -1$ we get by eq. (36) and eq. (31) the following governing equations:

$$\frac{\partial c_+}{\partial t} = u_+ F \nabla \cdot (c_+ \nabla \phi) + D_+ \Delta c_+ \quad (37)$$

$$\frac{\partial c_-}{\partial t} = -u_- F \nabla \cdot (c_- \nabla \phi) + D_- \Delta c_- \quad (38)$$

We have yet to use charge conservation, i.e. eq. (25), which together with eq. (32) yields:

$$0 = \nabla \cdot j = F (\nabla \cdot N_+ - \nabla \cdot N_-) = -F \left(\frac{\partial c_+}{\partial t} - \frac{\partial c_-}{\partial t} \right)$$

Thus we must also have

$$\frac{\partial}{\partial t}(c_+ - c_-) = 0$$

However, noting that the electrolyte initially was empty of ions, i.e. $c_+ = c_- = 0$ initially, it follows that we actually have the slightly stronger condition

$$c_+ - c_- = 0 \tag{39}$$

Part 7: Modeling equations for the whole battery

We consider a 3D battery with two electrodes and an electrolyte. We impose a constant current at the external side of the positive electrode, and a constant potential at the external face of the negative electrode. The unknowns in each domain are the electrical potential and the concentration of lithium.

7.1 The governing equations for the entire battery

The governing equations in each of the domains (P, N and E) follow an analogous derivation to how we found eq. (37) and eq. (39), i.e. preservation of charge and mass, which yields

$$\frac{\partial c_\alpha}{\partial t} = u_\alpha F \nabla \cdot (c_\alpha \nabla \phi_\alpha) + D_\alpha \Delta c_\alpha, \quad \alpha \in \{ne, elyte, pe\}$$

When modelling the battery, we will assume that the initial concentrations are known, that the potential at the far left part of the negative electrode is known, and that the current density at the far right part of the positive electrode is known.

Note that this last condition may be written more explicitly by noting that from eq. (35) we have $j_{pe} = -\sigma \nabla \phi_{pe} = -F^2 u_{pe} c_{pe} \nabla \phi_{pe}$.

We will assume that the flux is continuous, i.e. at the boundaries Γ_- and Γ_+ , we have that the normal component of the fluxes for Li^+ at each side of the boundaries are equal. We denote the flux of Li^+ in each component by N_α . The value of N_α is given by eq. (31), and is a function of both c_α and ϕ_α .

We also have by the same argument as for eq. (28), the Butler-Volmer equation, that the difference in potential on either side of Γ_- and Γ_+ are given analogously to eq. (28).

Hence we get the following initial, interface and boundary conditions:

$$\left\{ \begin{array}{ll} (u_+ + u_-) F \nabla \cdot (c_{elyte} \nabla \phi_{elyte}) + (D_+ - D_-) \Delta c_{elyte} = 0 & \\ c_\alpha = c_{\alpha,0} & \text{at } t = 0, \alpha \in \{elyte, pe, ne\} \\ \phi_\alpha = \phi_{\alpha,0} & \text{at } t = 0, \alpha \in \{elyte, pe, ne\} \\ \phi_{ne} = \phi_0 & \text{at } \Gamma_0 \\ \nabla \phi_\alpha \cdot \hat{n} = 0 & \text{at } \partial\Omega \\ c_{pe} \nabla \phi_{pe} = -\frac{j_0}{F^2 u_{pe}} & \text{at } \Gamma_1 \\ N_{ne} \cdot \hat{n}_{ne} = -N_{elyte} \cdot \hat{n}_{elyte,n} & \text{at } \Gamma_- \\ \phi_{ne} - \phi_{elyte} = U_{eq,ne} + \frac{2RT}{F} \sinh^{-1} \left(\frac{F \frac{\partial c_{ne}}{\partial t}}{i_{0,ne}} \right) & \text{at } \Gamma_- \\ N_{pe} \cdot \hat{n}_{pe} = -N_{elyte} \cdot \hat{n}_{elyte,p} & \text{at } \Gamma_+ \\ \phi_{pe} - \phi_{elyte} = U_{eq,pe} + \frac{2RT}{F} \sinh^{-1} \left(\frac{F \frac{\partial c_{pe}}{\partial t}}{i_{0,pe}} \right) & \text{at } \Gamma_+ \end{array} \right.$$

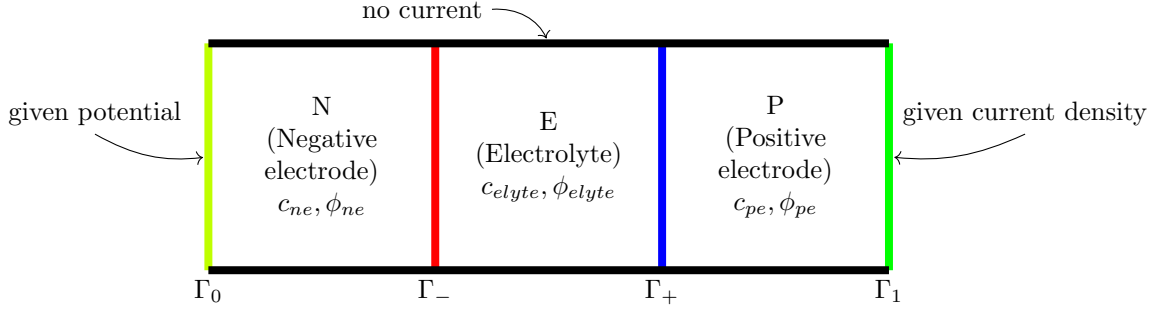


Figure 5: Battery model in 2D

7.2 Modeling the battery

We want to derive the equations for the short-time solution in 1D, that is $t = \varepsilon \bar{t}$ for $\varepsilon \ll 1$ and $\bar{t} \approx 1$. We use an asymptotic assumption to linearize the equations:

$$c_\alpha(\bar{t}, x) = c_\alpha^0(x) + \varepsilon c_\alpha^1(\bar{t}, x)$$

$$\phi_\alpha(\bar{t}, x) = \phi_\alpha^0(x) + \varepsilon \phi_\alpha^1(\bar{t}, x)$$

for $\alpha \in \{ne, elyte, pe\}$.

Inserting this assumption in the governing equations gives:

$$\begin{aligned} \frac{\partial(c_\alpha^0(x) + \varepsilon c_\alpha^1(\bar{t}, x))}{\partial t} &= u_\alpha F \frac{\partial}{\partial x} \left((c_\alpha^0(x) + \varepsilon c_\alpha^1(\bar{t}, x)) \frac{\partial}{\partial x} (\phi_\alpha^0(x) + \varepsilon \phi_\alpha^1(\bar{t}, x)) \right) \\ &\quad + D_\alpha \frac{\partial^2}{\partial x^2} (c_\alpha^0(x) + \varepsilon c_\alpha^1(\bar{t}, x)) \end{aligned}$$

We can simplify the left hand side by $t = \varepsilon \bar{t}$ for $\alpha \in \{ne, elyte, pe\}$:

$$\begin{aligned} \frac{\partial c_\alpha^0(x)}{\partial t} &= 0 \\ \varepsilon \frac{\partial c_\alpha^1(\bar{t}, x)}{\partial t} &= \frac{\partial c_\alpha^1(\bar{t}, x)}{\partial \bar{t}} \end{aligned}$$

Linearize the equations using perturbation theory. Arrange the terms based on what power of ε they contain. For terms not containing ε :

$$\frac{\partial c_\alpha^1}{\partial \bar{t}} = u_\alpha F \frac{\partial}{\partial x} \left[c_\alpha^0 \frac{\partial}{\partial x} \phi_\alpha^0 \right] + D_\alpha \frac{\partial^2}{\partial x^2} c_\alpha^0$$

For terms containing ε :

$$0 = \varepsilon u_\alpha F \frac{\partial}{\partial x} \left[c_\alpha^0 \frac{\partial}{\partial x} \phi_\alpha^1 + c_\alpha^1 \frac{\partial}{\partial x} \phi_\alpha^0 \right] + \varepsilon D_\alpha \frac{\partial^2}{\partial x^2} c_\alpha^1$$

We will neglect the ε^2 -terms, since we are only using a first order approximation as our asymptotic assumption.

With these equations, along with our initial and boundary conditions, we can now proceed to solve them numerically.

7.3 Scaling the equations

Before any numerical solution can be coded, we want to write our equations in dimensionless form.

We have the natural scalings:

$$x \rightarrow Lx \quad c \rightarrow \bar{c}c \quad \phi \rightarrow \phi_0\phi \quad t \rightarrow Tt \quad (40)$$

where L is the total length of the battery, i.e. $L = L_p + L_{\text{elyte}} + L_n$, where L_α is the length of the section α . \bar{c} is the average concentration of Lithium. This can be computed by finding the total number of Li^+ as the integral over the entire volume, and dividing by the total volume. i.e. $\bar{c} = \frac{1}{L} \int_0^L c(x, 0) dx$. And ϕ_0 is the constant imposed potential at the negative electrode.

We are modelling two different effects, so there are two natural timescales to consider. The time scale for diffusion in the electrolyte: $T = \frac{L^2}{D_{\text{elyte}}}$, and the time scale for mobility. To find the time scale for mobility, we will consider the time it takes for a molecule to move across the entire length of the battery in some ideal condition. We assume the potential drop across the entire battery to be linear, and also assume the mobility of Lithium to be equal in all 3 sections. Then the critical velocity of the ions become $v = \frac{Fu\phi_0}{L}$. Thus this time scale becomes $T = \frac{L}{v} = \frac{L^2}{Fu\phi_0}$, where we let u be the mobility of Li^+ in the electrolyte. I.e. $T = \frac{L^2}{Fu_{\text{elyte}}\phi_0}$.

Using the time scale for diffusion, our equations with dimensionless unknowns become:

$$\begin{aligned} \frac{\bar{c}}{T} \frac{\partial c_\alpha^1}{\partial \bar{t}} &= \frac{u_\alpha F \bar{c} \phi_0}{L^2} \frac{\partial}{\partial x} \left[c_\alpha^0 \frac{\partial}{\partial x} \phi_\alpha^0 \right] + \frac{D_\alpha \bar{c}}{L^2} \frac{\partial^2}{\partial x^2} c_\alpha^0 \\ 0 &= \frac{u_\alpha F \bar{c} \phi_0}{L^2} \frac{\partial}{\partial x} \left[c_\alpha^0 \frac{\partial}{\partial x} \phi_\alpha^1 + c_\alpha^1 \frac{\partial}{\partial x} \phi_\alpha^0 \right] + \frac{D_\alpha \bar{c}}{L^2} \frac{\partial^2}{\partial x^2} c_\alpha^1 \end{aligned}$$

Simplifying yields:

$$\begin{aligned} \frac{\partial c_\alpha^1}{\partial \bar{t}} &= \frac{u_\alpha F \phi_0}{D_{\text{elyte}}} \frac{\partial}{\partial x} \left[c_\alpha^0 \frac{\partial}{\partial x} \phi_\alpha^0 \right] + \frac{D_\alpha}{D_{\text{elyte}}} \frac{\partial^2}{\partial x^2} c_\alpha^0 \\ 0 &= u_\alpha F \phi_0 \frac{\partial}{\partial x} \left[c_\alpha^0 \frac{\partial}{\partial x} \phi_\alpha^1 + c_\alpha^1 \frac{\partial}{\partial x} \phi_\alpha^0 \right] + D_\alpha \frac{\partial^2}{\partial x^2} c_\alpha^1 \end{aligned}$$

We define the coefficients $\gamma \stackrel{\text{def}}{=} \frac{u_\alpha F \phi_0}{D_{\text{elyte}}}$, $\delta \stackrel{\text{def}}{=} \frac{D_\alpha}{D_{\text{elyte}}}$, $\zeta = u_\alpha F \phi_0$, and get the final equations which can be solved numerically:

$$\frac{\partial c_\alpha^1}{\partial \bar{t}} = \gamma \frac{\partial}{\partial x} \left[c_\alpha^0 \frac{\partial}{\partial x} \phi_\alpha^0 \right] + \delta \frac{\partial^2}{\partial x^2} c_\alpha^0 \quad (41)$$

$$0 = \zeta \frac{\partial}{\partial x} \left[c_\alpha^0 \frac{\partial}{\partial x} \phi_\alpha^1 + c_\alpha^1 \frac{\partial}{\partial x} \phi_\alpha^0 \right] + D_\alpha \frac{\partial^2}{\partial x^2} c_\alpha^1 \quad (42)$$

Summary

In this project we have worked with a simple model of a Lithium-ion battery. We have looked at chemical potential measurements, equilibrium states, and reaction kinetics to explain the relationship between electrical and chemical properties in the Lithium-ion batteries. We looked at the system as a whole and created governing equations for our Lithium-ion battery by using these relations. We lastly made an asymptotic linear approximation of the governing equations for the one dimensional case, and scaled it to be dimensionless, yielding a system which may be solved numerically.

Bibliography

Raynaud, X.M. (2023). *Mathematical modeling of lithium battery*. URL: <https://www.math.ntnu.no/emner/TMA4195/2023h/public/project.pdf> (visited on 21st Nov. 2023).